

A Thesis Entitled

"THE SYNTHESIS AND PROPERTIES OF SOME HIGHER MEMBERED
FUSED ALICYCLIC RING SYSTEMS"

Submitted by D.H.S. Horn, (M.Sc. B.A.)
in fulfilment of the requirements
for admittance to the degree of

DOCTOR OF PHILOSOPHY

of the

UNIVERSITY OF CAPE TOWN

1948

The copyright of this thesis vests in the author. No quotation from it or information derived from it is to be published without full acknowledgement of the source. The thesis is to be used for private study or non-commercial research purposes only.

Published by the University of Cape Town (UCT) in terms of the non-exclusive license granted to UCT by the author.

SUMMARY.

Because of the theoretical interest in the ring system consisting of twofused fully unsaturated seven-membered rings (Wilson Baker, Tilden lecture J., 1945, 258), for which the trivial name "heptalene" is suggested, attempts have been made to synthesise this hydrocarbon to study its chemical and physical properties.

The application of the Demjanov ring expansion reaction to the synthesis of seven-membered ring systems has been explored and it has been found that 2-aminomethyl-1,2,3,4-tetrahydro-naphthalene undergoes the normal reaction with nitrous acid to yield derivatives of benz-cyclo-heptane. However, further attempts to apply this reaction to the synthesis of bicyclo-[0.5.5] -dodecane derivatives was abandoned because of the difficulty of preparing the required amine intermediates.

The use of an intramolecular Grignard condensation for the synthesis of alicyclic ring systems has also been investigated. This approach was not followed up as difficulty was experienced in the formation of the aryl Grignard intermediates.

The Buchner ring expansion of benzenoid rings to derivatives of ethyl cyclo-heptatriene carboxylate by means of ethyl diazoacetic ester has been found convenient for the synthesis of partially unsaturated [0.5.5] -bicyclo-dodecane derivatives. Thus ethyl [0.5.5] -bicyclo-dodecatriene carboxylate has been prepared by the action of ethyl diazoacetic ester on benz-cyclo-heptane. It has also been found possible to extend this reaction to the synthesis of the more unsaturated [0.5.5] -

/bicyclo....

bicyclo-dodecatetraene carboxylic acid by treating 3-acetoxy-1:2-benz-cyclo-heptane with ethyl diazoacetic ester and hydrolysing and dehydrating the hydroxy-acid so formed.

However, attempts to dehydrogenate these [0.5.5] - bicyclo-dodecane systems to heptalene derivatives could not be accomplished. Instead rearrangement products such as dimethyl naphthalene and ethyl azulene were produced, clearly indicating that the heptalene structure cannot be produced with the same facility as azulenes.

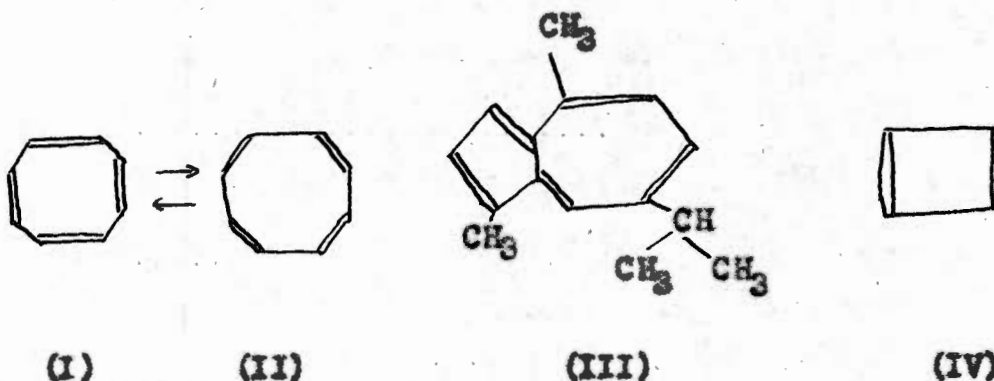
Attempts to reach the heptalene structure by dibromination of methyl [0.5.5] -bicyclo-dodecatetraene carboxylate and the mild dehydrobromination with diethyl aniline failed to yield the required product, once again demonstrating that the heptalene system has not the stability which is expected for a fully conjugated planar structure.

C O N T E N T S .

	<u>Page.</u>
Introduction	1
Approaches to the Synthesis of Cyclic Polycyclics	13
The Synthesis and Dehydrogenation of [0.5.5]- <u>Bicyclo-</u> dodecane Derivatives and Related Compounds.	
(A) The Study of the Demjanov Reaction for the Synthesis of [0.5.5]- <u>Bicyclo-</u> dodecane Ring Systems	32
(B) The Attempted Synthesis of Ring Systems using an Intramolecular Grignard Reaction ..	39
(C) The Synthesis and Dehydrogenation of Heptatriene Ring Systems prepared by the Expansion of Benzenoid Compounds with Ethyl Diazosacetate	43
Attempted Synthesis of Heptalene using Dehydro- bromination Reactions	63
Experimental	71
Appendix (Absorption Spectra Data)	134
Acknowledgements	152

INTRODUCTION.

The preparation, in recent years of such compounds as cyclo-octatetraene (I) and guaiscezulene, (III) in sufficient quantity for a precise study of their chemical and



physical properties, has stimulated a renewed interest in the structure and stability of unsaturated cyclic hydrocarbons, for it has offered fresh opportunities for the quantitative testing of the new concepts of molecular structure.

The work to be described in this thesis arose out of the need for the knowledge of the stability of many other interesting polyene ring systems.

Before proceeding to a more detailed account of the aim of the work, a brief critical survey of the field of conjugated cyclic polyenes may be of value to set it in its natural perspective.

Of the simple monocyclic systems, apart from

benzene, cyclo-octatetraene is the only one which has been thoroughly studied. The synthesis of cyclo-butadiene (IV), the first member of this series was attempted by Willstätter and Schmaedel (Ber., 1906, 38, 1992). Their failure to prepare it using relatively mild reaction conditions, seems to indicate that if this hydrocarbon is capable of existence, it is highly unstable. Since such a structure requires the valency angles of the carbon atoms to be considerably distorted from the value of 125° ; the angle between a double and a single bond about a carbon atom, it is not unreasonable to expect the molecule to be subject to some considerable geometric strain. In the highly stable benzene on the other hand the angles approach this ideal value.

The synthesis and properties of cyclo-octatetraene, the next member of this series, was first described by Willstätter (Ber., 1911, 44, 3423, Ber., 1913, 46, 517). However, in recent years, the authenticity of Willstätter's hydrocarbon has been challenged by several chemists who have drawn attention to the similarity in properties of his hydrocarbon and styrene. The independent syntheses of cyclo-octatetraene by Reppe (Report on cyclo-polyolefines, B.I.O.S. Final Report 137 item 22) and Cope and Overberger (J. Amer. Chem. Soc., 1947, 69, 976.) have on the other hand proved the structure of Willstätter's hydrocarbon to be indeed cyclo-octatetraene. It has also been shown by Reppe "that all the double bonds of cyclo-octatetraene are open to all the

reactions of the ethylenic chemistry," and that the molecule does not exhibit any of the properties peculiar to resonating aromatic systems.

Although early measurements of the resonance energy of cyclo-octatetraene (c.f. Maccoll, Nature, 1946, 157, 695.) suggested a value of 28 Kcal. - cal. per g. mol. (c.f. 41 Kcal. - cal. per g. mol. for benzene): a value to be associated with at least a partially resonating structure, more recent measurements of the heats of combustion, formation and isomerization to styrene (Rossini *et alia*, J. Amer. Chem. Soc., 1947, 69, 2068), have shown conclusively, that cyclo-octatetraene has a resonance energy 34 Kcal. - cal. per g. mol. less than that of styrene. This low value for the resonance energy which is indicative of a purely aliphatic structure, is in closer agreement with the chemical evidence.

Four structures can be postulated for the cyclo-octatetraene molecule, see fig. 1.



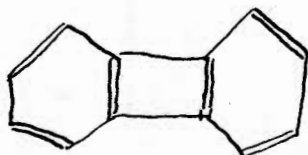
fig. 1.

The "crown" form - all trans configuration; the "tub" or "boat" form - all cis; the "chair" form - half cis, half trans, and the "plane" form. Of these configurations, the "plane" form is the most unlikely, for it presumes a high 4/resonance...

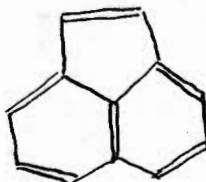
resonance energy for the molecule. Thus Penny (Proc. Roy. Soc., 1934, A 146, 223) and Wheland (J. Chem. Phys., 1935, 3, 230) who have studied the quantum mechanics of the planar non-strained ring of eight - CH - groups by the valence bond method have predicted that such a molecule would have a resonance energy of at least 48 Kcal. - cal. per g. mol.

For cyclo-octatetraene to have a planar structure, the valency angles must assume the value of 135° , which is considerably greater than the normal value of 125° , and it is possible therefore, that the molecule is forced to assume a strainless multiplanar configuration with a consequent limiting of the resonance between the two Kekule-like structures, and a reduction in the value of the resonance energy.

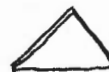
Nevertheless it seems doubtful that the low stability of cyclo-octatetraene can be explained on grounds of strain alone, because a number of extraordinarily stable compounds are known which would be expected to be considerably strained. In diphenylene (VII), for example, the bonds attached to the benzenoid rings are strained through an angle of 30° . Acenaphthene (VIII) and cyclo-propene (IX) (Demjanov and Dojarenko, Ber., 1923, 56, 2200, and Schlatter J. Amer. Chem. Soc., 1941, 63, 1733-7) are other examples.



(VII)



(VIII)



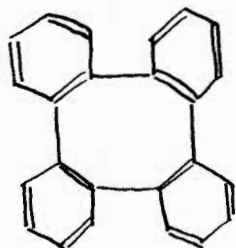
(IX)

From a study of the Raman Spectrum of cyclo-octatetraene, Lippincott and Lord (J. Amer. Chem. Soc., 1946 68, 1868) have concluded that the molecule cannot have two different geometrical forms, analagous to the "chair" and "boat" space isomers of cyclo-hexane, and that the structure is more likely to be that of a puckered eight membered ring with alternate single and double bonds, i.e. with the "crown" configuration. This view is supported by Hassel and co-workers (Nature, 1947, 160, 128) who have made an electron diffraction study of cyclo-octatetraene.

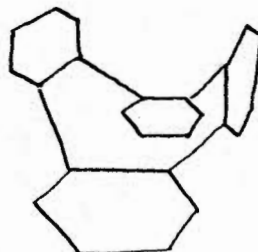
However, more recent studies of the Raman Spectra have led Thompson (see Kaufmann, Fankucher and Mark, Nature, 1948, 161, 165) to favour the "tub" form, and this view is supported by Kaufmann and co-workers (loc. cit.) who have made a study of the x-Ray diffraction of crystalline cyclo-octatetraene (melting point - 7°C). They have shown that the lengths of the double bonds are 1.34 Å, while those of the single bonds are 1.54 Å and that the c-c-c bond angle is 125°. These values, which indicate little or no resonance energy, are thus in agreement with the chemical data.

It is interesting to note that tetraphenylene (1,2,3,4,5,6,7,8-tetrabenz- Δ ^{1,3,5,7}-cyclo-octatetraene, V) prepared by Rapsen and Shuttleworth and co-workers (J. 1943, 326; J. 1944, 71.), has been shown by Karle and Brockway (J. Amer. Chem. Soc., 1944, 66, 1974) from an electron diffraction examination, to have a multiphase structure, the centres of the benzene rings lying at the corners of a regular

tetrahedron as shown (VI), that is, with the cyclo-octatetraene ring in the "tub" configuration.

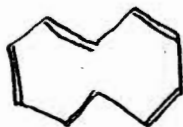


(V)

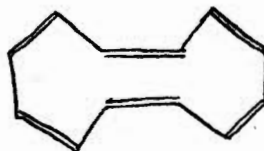


(VI)

As yet, higher homologues of cyclo-octatetraene have not been investigated. Reppe (Modern Plastics, 1946, 23, No. 6, 218 -25th Kuzo report 1941) has claimed to have prepared cyclo-decapentatriene (X) and cyclo-dodecahexatriene (XI) but the evidence in support of these structures has since been questioned (B.I.O.S., report No. 352, 1944).



(X)

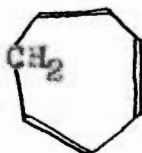


(XI)

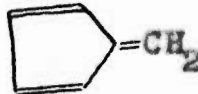
Besides the simple monocyclic conjugated polyenes containing rings with even numbers of carbon atoms, compounds like fulvenes (XIV), e.g. (XV) are



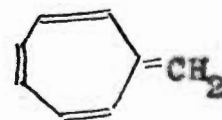
(XII)



(XIII)



(XIV)



(XV)

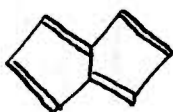
possible, and because they are more completely conjugated than the corresponding cyclo-pentadiene (XII) and cyclo-

heptatriene (XIII) respectively, might be expected to be fairly stable. However, the resonance energy of such compounds cannot be expected to approach that of aromatic systems because this type of structure does not permit a resonance between two Kekule individuals. Fulvene is the only member of this series which has been prepared. Although it is chemically reactive, it may be prepared by fairly severe reaction conditions and it can be concluded therefore to possess at least a moderate resonance energy. The next member of this series (XV), which would be expected to have less geometric strain than fulvene, might be, on that account, rather more stable.

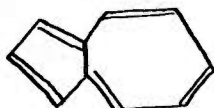
In the bicyclic series, apart from such structures as benzfulvene, two types of combinations which permit complete conjugation are possible. The first includes those made up of two rings, both containing even numbers of carbon atoms, and the second, those made up of two rings, both containing odd numbers of carbon atoms.

Apart from the highly stable naphthalene, other structures of the first type, such as benz-cyclo-octatetraene, have not as yet been synthesized and are not likely to have a very high resonance energy unless the rings are large enough to be able to assume a strainless planar configuration. In the second type on the other hand, there are several systems which could be expected to have aromatic stability. The simplest is bicyclo-octatetraene (XVI), for which the name

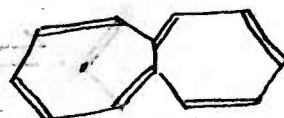
"pentalene" has been suggested in Fatterson and Capell's "The Ring Index" (1940, p110). However the surprising failure by Barrett and Linstead (J., 1936, 612.) to prepare it by dehydrogenation of the corresponding [0:3:3] - bicyclo-octane, led them to conclude that pentalene does not possess



(XVI)



(XVII)



(XVIII)

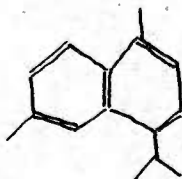
aromatic stability. It is difficult to suggest adequate reasons for this, and W. Baker (J., 1945, 258.) has drawn attention to three limiting factors.

Firstly, in pentalene there would be only four free electrons per ring as compared with six in a benzenoid one. Secondly, pentalene is structurally similar to fulvene which is rather unstable. Thirdly, on the basis of the classical strain theory the carbon valency angles would have to assume a value of 108° , the internal angle of a regular pentagon, compared with the natural value of 125° . However as pointed out by Baker, the precise measurement of the heats of hydrogenation of the unsaturated five and six membered rings has thrown some doubt on the validity of this simple strain theory.

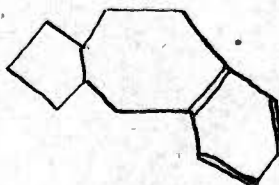
By contrast the structure of azulene (XVII), containing a five membered ring fused to a seven membered ring has aromatic stability. Baker (loc. cit.) draws attention to two points in this connection. "First, the azulene molecule may be in part less strained than that of pentalene because

the internal angles of a regular heptagon are 128.6° which is very close to 125° , and secondly the seven membered ring contains three pairs of doubly bound carbon atoms and, therefore, has six "free" electrons. It follows that, if these two points are valid, then the system consisting of two fused seven-membered rings containing six double bonds (XVIII) should show aromatic stability, but as yet compounds of this type are unknown." The study of this system of two fused seven membered rings, for which the name "heptalene" is suggested, is therefore of considerable theoretical interest, for a knowledge of its stability would throw new light on the factors which determine aromatic stability.

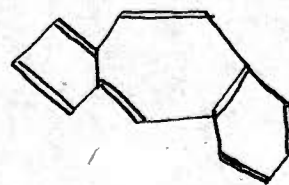
The azulene structure is as yet unique in being a completely nonbenzenoid hydrocarbon with a considerable resonance energy and aromatic characteristics. Nevertheless the azulene structure is less stable than the isomeric naphthalene. Thus guaiac-azulene (III) has been shown by Perrettet, Taub, and Briner (Helv. Chim. Acta, 1940, 23, 1260) to have a heat of combustion of 29.5 kcal. per g. -mol. higher than that of the isomeric cadalene (XIX) and the resonance energy of azulene



(XIX)



(XX)



(XXI)

10/has then....

has then been calculated as 45 kg.-cals. per g.-mol. as compared with 75 kg.-cals. per g.-mol for naphthalene.

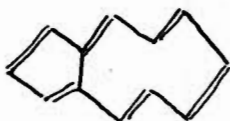
The simple unsubstituted azulene is rather less stable than its alkylated homologues such as guaiacazulene and it is difficult to offer adequate explanations for this. However it is possible that the resonance which results from the hyperconjugation of say two or more methyl groups with the azulene nucleus may be sufficient to stabilize the molecule as a whole, and reduce the heat of hydrogenation to a value more compatible with aromatic characteristics, (c.f. J.W. Baker and M.L. Hamming, J., 1942, 191).

The surprising failure of Cook, McGinnis, and Mitchell (J., 1944, 280) to prepare a benz-azulene (XXI) by the normal methods of dehydrogenation of the corresponding saturated benz-azulene structure (XX), shows again that the stability of the azulene system is very sensitive to small effects introduced by substituents, and that it may be weakened by fusion to a benzenoid ring. This is not unexpected if the benzenoid ring tends to exist as an independent resonating system, only partially conjugated with the rest of the azulene molecule, or if the fused benzene ring introduces geometrical strains into the azulene structure. The synthesis and study of the three isomeric benz-azulenes is

ll/thus.....

thus of special importance.

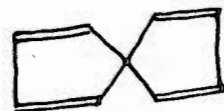
Other bicyclic systems such as bicyclo-[0.3.7] - dodecahexene (XXII) are possible, but more difficult of



(XXII)

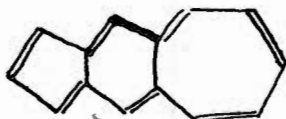


(XXIII)

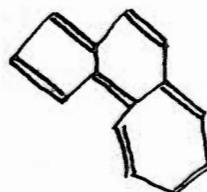


(XXIV)

synthesis. The spiro-compound (XXIV) is of interest although the structure does not permit full conjugation. However the dehydrogenation of the spiro-4:4 nonene (XXIII) (Zelinsky and Elagina, Compt. rend. Acad. Sci. U.R.S.S., 1946, 52, 227) yielded *o*-ethyl toluene.



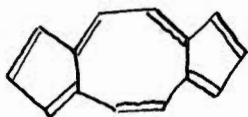
(XXV)



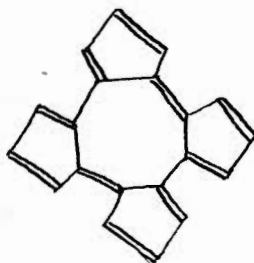
(XXVI)

The interposition of a six-membered ring between the five- and the seven-membered rings of the azulene structure, as in (XXV) and (XXVI), is of interest, for it may show up the extent to which stresses and strains are counterbalanced in the azulene structure.

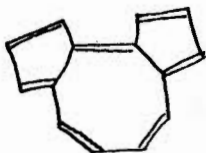
12/ (XXVII)....



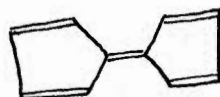
(XXVII)



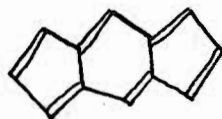
(XXVIII)



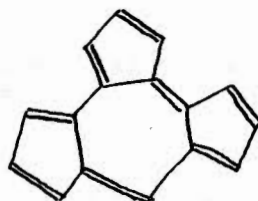
(XXIX)



(XXX)

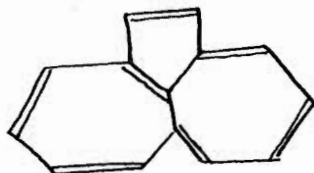


(XXXI)



(XXXII)

Besides combinations of benzene rings fused to bicyclic systems already mentioned, there are numerous other possible combinations such as (XXVII-XXXIII), which have not been synthesised and may have interesting properties.



(XXXIII)

APPROACHES TO THE SYNTHESIS OF CYCLIC POLYOLEFINES

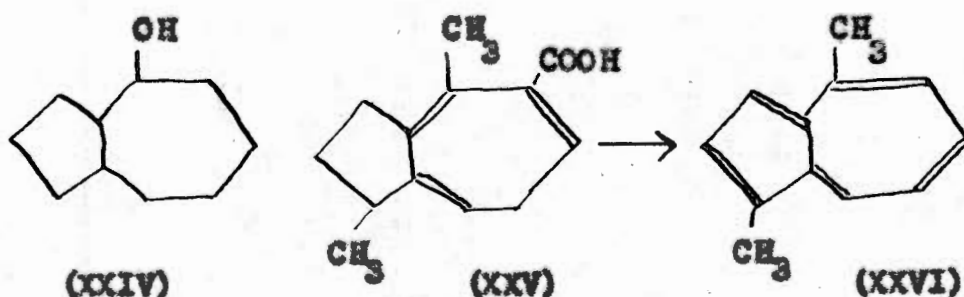
The main object of the work described in this thesis was the synthesis and study of the stability of heptalene derivatives, the theoretical importance of which has already been mentioned in the preceding section. It was hoped at the same time to open up general methods for the synthesis of polyene ring systems.

Although benzenoid compounds, azulene and cyclo-octatetraene have all been obtained directly by the polymerization of three or more molecules of acetylene, in general, derivatives of these compounds can only be prepared by dehydrogenation of the more or less saturated ring skeletons built up by fairly long stage syntheses. The synthesis of these alicyclic systems does not as a rule present any serious difficulties, but the final removal of hydrogen, because of the drastic reaction conditions involved, has often proved the stumbling block in the synthesis of a cyclic polyene.

Thus it is necessary, where the required cyclic olefine is likely to have a low resonance energy, to choose those methods of synthesis which lead to relatively unsaturated ring systems and which therefore need but little dehydrogenation to yield the required fully conjugated structure. Where the required product has aromatic stability this is less important, because the dehydrogenation of the

fully saturated structures can invariably be accomplished without difficulty.

Nevertheless, the more saturated the structure, the more difficult it is to remove the hydrogen and the more severe the reaction conditions must be to bring about complete dehydrogenation. Thus decahydro- and octahydro-naphthalenes yield naphthalene only on being heated with palladium charcoal catalyst in the vapour phase at 350° (Linstead and co-workers, *J.*, 1937, 1146), while tetralin yields naphthalene easily in the liquid phase. This rule has also been found to hold in the azulene series. Thus [0.3.5]-bi-cyclo-decanol (XXIV) yields azulene only on

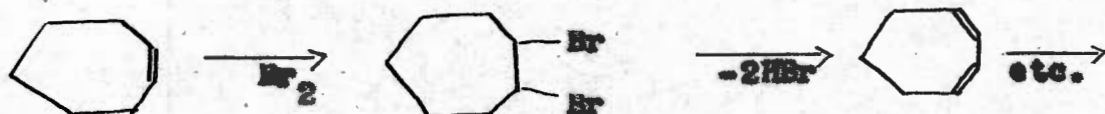


continuous dehydrogenation for 16 hours in the vapour phase over a palladium charcoal catalyst (Plattner & St. Pflau, *Helv. Chim. Acta*, 1937, 20, 224), whereas the acid (XXV) yields 1:4-dimethyl azulene (XXVI) on rapid distillation from a palladium charcoal catalyst (Plattner and Wyss, *Helv. Chim. Acta*, 1940, 23, 907).

When the required cyclic polyene does not possess aromatic stability, the normal methods of dehydrogenation cannot be used, because they either bring about rearrangements or complete decomposition of the alicyclic material.

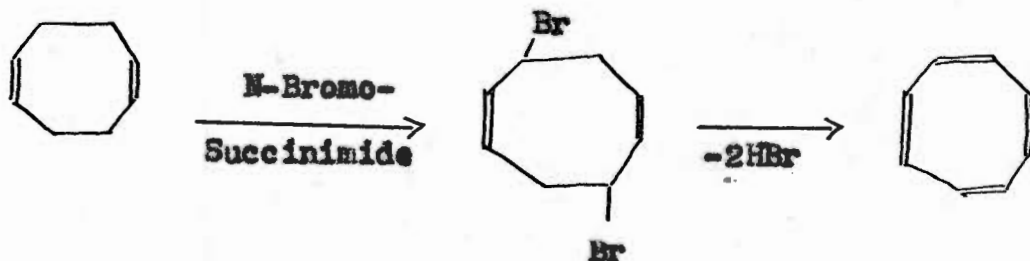
Thus the catalytic dehydrogenation of cyclo-octene over chromium oxide catalyst at 425°C by Goldwasser and Taylor (J. Amer. Chem. Soc., 1939, 61, 1260) yielded styrene while dehydrogenation of cyclo-octane (Ruzicka and Seidel, Ital. Chim. Acta, 1936, 19, 424) yielded xylene at 440°C. However, the dehydrogenation of these rather unstable systems, may be accomplished chemically from the more saturated forms, either by the addition of bromine to the partially unsaturated ring system, and removal of the elements of hydrogen bromide, or by replacement of a hydrogen atom in an active methylene group adjacent to a double bond, with a bromine atom, by treating the cyclic olefins with *N*-bromo-succinimide, and the process completed by the elimination of the elements of hydrogen bromide. These processes are repeated until the fully unsaturated system is reached.

The former method has been used with success by Willstätter and co-workers in the synthesis of cyclo-octatetraene (Willstätter and Wasser, Ber., 1911, 44, 3423; Willstätter and Heidelberg, Ber., 1913, 46, 517) and cyclo-heptatriene (Willstätter, Ann., 1901, 317, 307).



The latter method, which makes use of *N*-bromo-succinimide has been developed by Ziegler and co-workers

(Ann., 1942, 551, 80-119). It has already found numerous applications and has been applied with success to the synthesis of cyclo-octatetraene by Cope and Overberger (private communication) as follows:-



However this simple method may not prove to be of general application, because it has been found by Ziegler (loc. cit.) that only mono-olefines or unconjugated diolefines are successfully brominated. It nevertheless offers an easy route to the simple more unstable cyclic polyenes, and it may be possible to use it in the synthesis of such compounds as pentalene, where other methods of dehydrogenation have proved unsuccessful.

The methods used for the synthesis of alicyclic intermediates fall into two types, those dependent upon ring closure of open chain compounds, and those which make use of ring expansions and contractions. The first method, which can employ almost every type of reaction involving the formation of the carbon-carbon bond, has been used with considerable success in the synthesis of rings containing up to six carbon atoms. However, for the synthesis of rings containing more than six atoms only a few of these reactions

are suitable, and very few give good yields of compounds with rings consisting of 7 to 12 carbon atoms, although larger rings are easily produced (Ziegler and Weber, Ann., 1934, 512, 164; Kuzicka and co-workers, Helv. Chim. Acta, 1926, 6, 499). For the synthesis of rings intermediate in size between the six-membered rings and the very large ones, the second method employing ring expansions is the more satisfactory, not only because the yields are better, but also because the starting materials are generally more easily prepared than the straight chain compounds required for ring closure reactions.

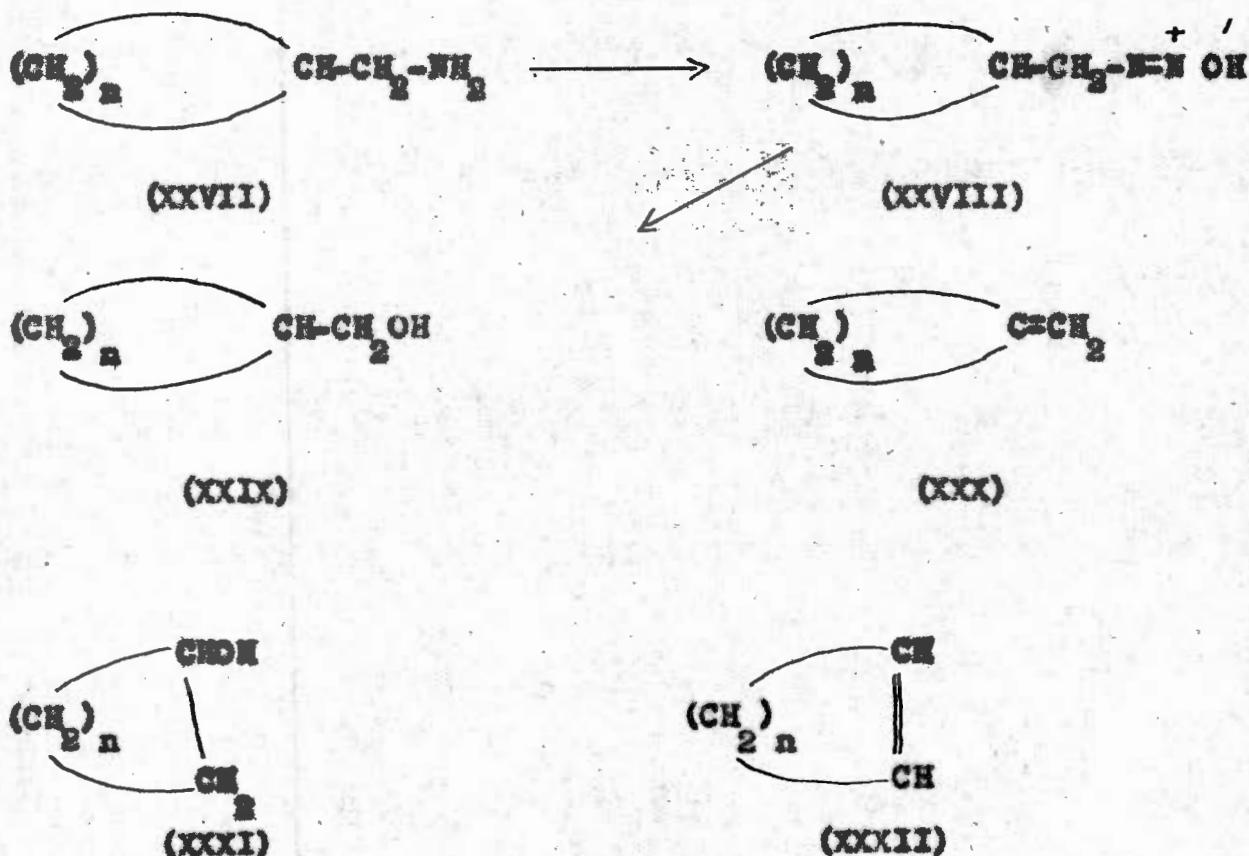
Thus in the synthesis of azulene intermediates, ring closure reactions have been used principally in building up the five-membered ring in this system. In general, a (0.3.4)-bicyclo-nonane is first synthesised, and the required (0.3.5)-bicyclo-decane system reached by expansion of the six-membered ring.

These methods of ring expansion are of particular interest, as they offer the most ready route to heptalene derivatives and will therefore be considered in some detail.

THE DEMJANOV REARRANGEMENT

A reaction which has been particularly successful in the preparation of seven-membered ring systems, is the ring widening reaction first observed by Demjanov and Luschnikow, (J. Russ. Phys. Chem. Soc., 1903, 25, 26; A., 1903, 24, (1) 403). The reaction is brought about by the

action of nitrous acid on a cyclic-alkyl-methylamine in which migration of ring-bound valencies then takes place, so that besides the expected primary alcohol, (XXIX), the next member of the cyclic-polymethylene homologous series (XXXI) is also produced, together with smaller quantities of the corresponding olefines (XXX) and (XXXII), as shown below.

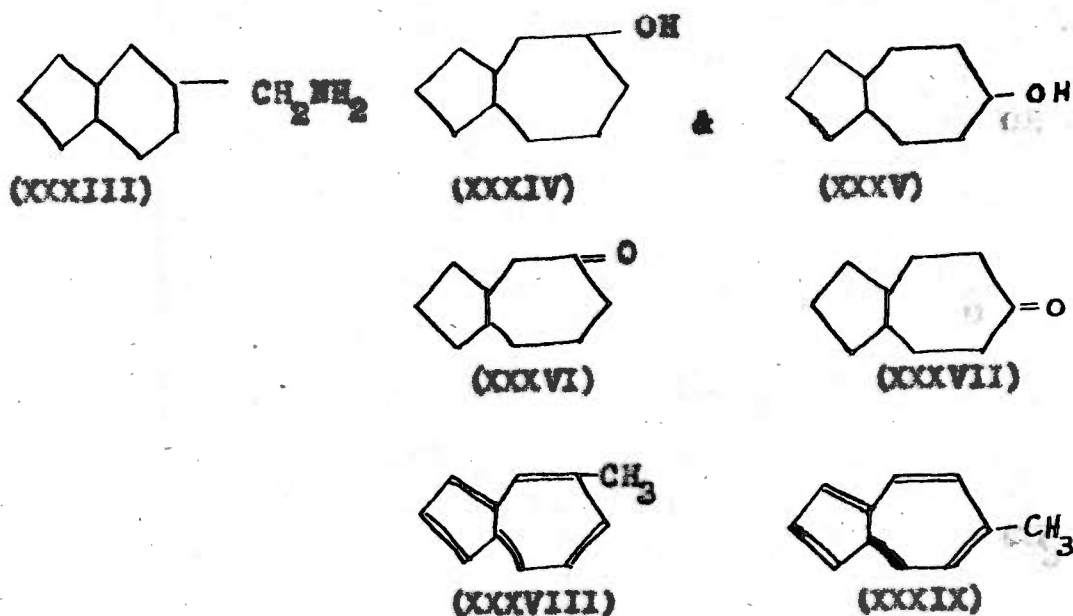


The expansion of cyclic-hexyl-methylamines to seven-membered cyclic compounds was first explored by Demjanov (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 166; *A.*, 1904, 36, (1) 410) and later thoroughly investigated by Ruzicka and Brugger, (*Ital. Chim. Acta*, 1926, 2, 399), who found that the main

19/products...

products from the reaction of cyclo-hexyl-methylamine were cyclo-heptanol and cyclo-heptene.

The reaction has also been applied to the ring expansion of 1.1.3-trimethyl-cyclo-hexyl-5-methylamine in the synthesis of seven-membered cyclic alcohols and ketones by Barbier (Halv. Chim. Acta. 1940, 23, 519). In this instance, however, all the theoretically possible products were obtained and characterized. The reaction has also been employed in the synthesis of methyl-azulene by Arnold (Ber., 1943, 76B, 777-88) as follows:-



The main reaction product was a mixture of two alcohols (XXXIV) and (XXXV), which were not separated. They were oxidized to the corresponding ketones (XXXVI) and (XXXVII) and the mixture separated by fractional crystallisation of the semicarbazones. The ketones were then separately

treated with methyl magnesium iodide and the alcohols produced dehydrogenated to the two isomeric methyl azulenes (XXXVIII) and (XXXIX).

As a method of synthesis, the ring expansion reaction suffers from two disadvantages. Firstly the reaction product is a mixture of at least four substances; two hydrocarbons, a primary and the required secondary alcohol. Although the hydrocarbons may be isolated from the higher boiling alcohols by fractionation, the two hydrocarbons themselves, are not easily separated. The alcohols on the other hand are readily separated by taking advantage of the fact that only the primary alcohol reacts with phthalic anhydride to form a mono-ester. This can be removed from the mixture by virtue of its solubility in dilute alkali. Thus the pure material isolated from the crude reaction product rarely exceeds 50% of the mixture. Secondly, none of the routes that have been investigated have led to satisfactory yields of the required cyclic hexyl-methylamines.

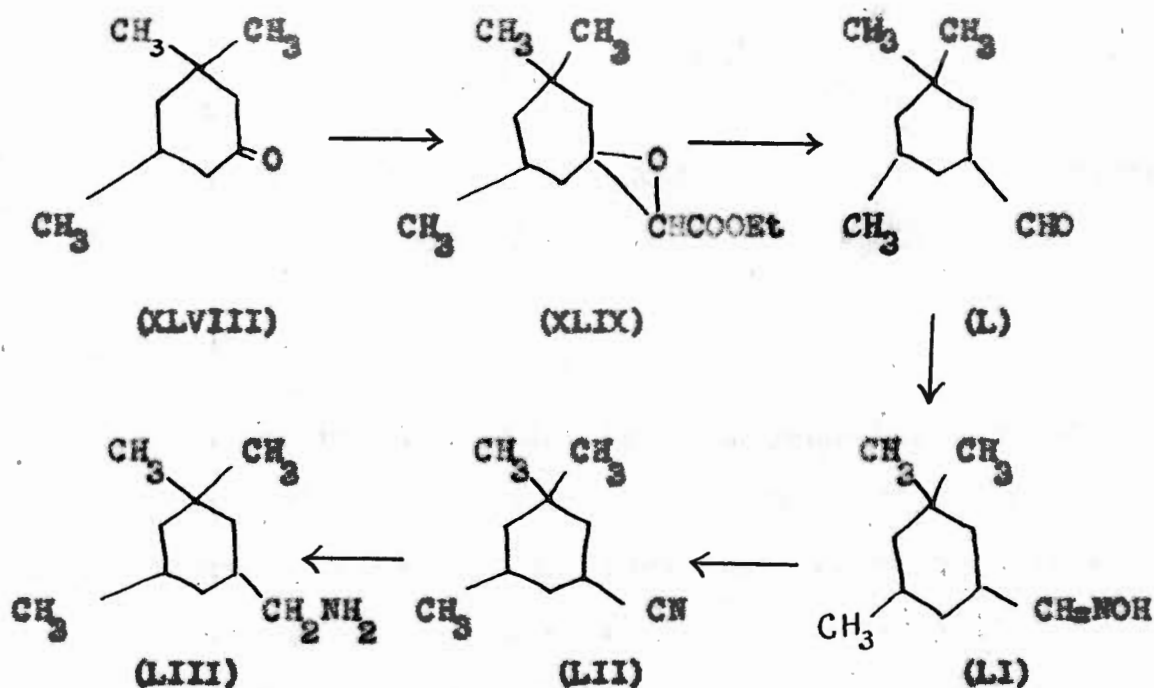
The four most important methods which have been used to synthesise these substances are as follows:-

(a) The Method of Demianov (1904, loc. cit.)

Cyclo-hexane-carboxylic acid (XL) was converted to its amide by way of the acid chloride and the amide dehydrated to the nitrile, which was then reduced to the required cyclo-hexyl-methylamine (XLIII) with sodium and

21/alcohol...

alcoholic solution to yield the glycidic ester (XLIX) which on hydrolysis and distillation decomposed into the cyclohexenyl-aldehyde (L). The aldehyde was then converted to the oxime (LI). This was dehydrated to the nitrile (LII) which was finally reduced to the required amine (LIII). No yields are given.

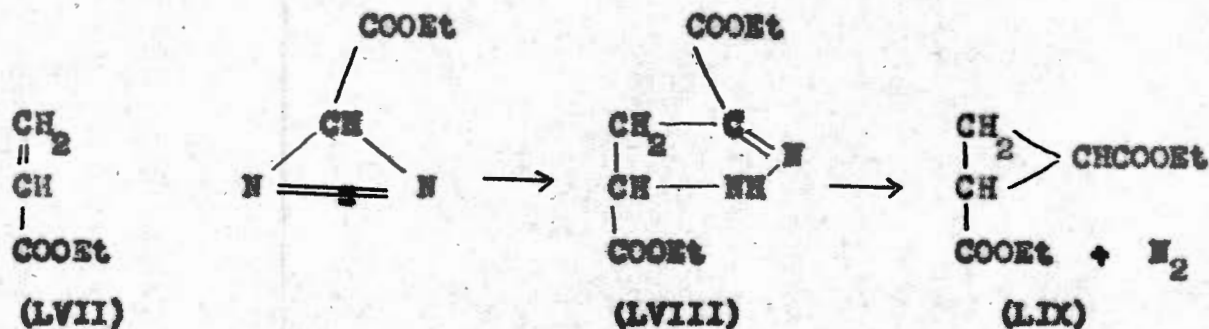


(d) The Method of Arnold.

The chloromethyl-compound (LV) was treated with potassium cyanide to yield the nitrile (LVI) which was hydrolysed to the corresponding ethyl indenyl-acetate (LVII). This was hydrogenated to the hexahydroform (LVIII) and converted to the required amine (LIX) by means of sodium azide and sulphuric acid. The overall yield is not given.

bonds. However the addition products formed with cyclic olefins do not rearrange. Thus cyclo-hexene (fr. Ebel, Brunner & Mangel, Halv. Chim. Acta. 1929, 12, 19.) and camphene (Buchner and Wegand, Ber., 1913, 46, 759) react readily enough, but are very stable and do not undergo ring enlargement.

The probable course of these addition reactions of diazoacetic esters to olefins is indicated by the fact that they combine with $\alpha\beta$ -unsaturated carboxylic esters to form pyrazoline carboxylic esters. Thus ethyl diazo-acetate with acrylic ester (LVII) (Buchner and co-workers, Ann., 1892, 273, 214.) reacts as follows:-



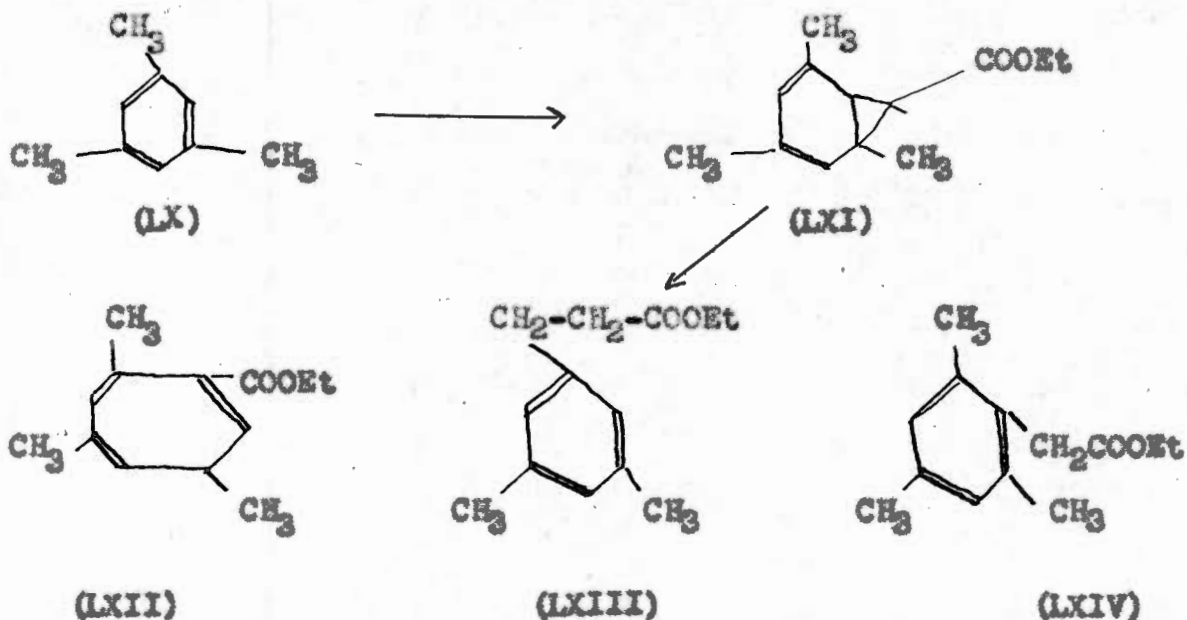
The pyrazoline ester (LVIII) formed in this reaction eliminates nitrogen to yield a cyclo-propane derivative (LIX) (Buchner loc. cit. 229). The reaction can be effected without isolation of the intermediate pyrazoline, by heating the reaction mixture after the completion of the addition reaction.

The reaction with aromatic nuclei investigated mainly by Buchner and co-workers, probably follows the same course, although the isolation of a pyrazoline intermediate has not been reported. In the case of more highly alkylated aromatic

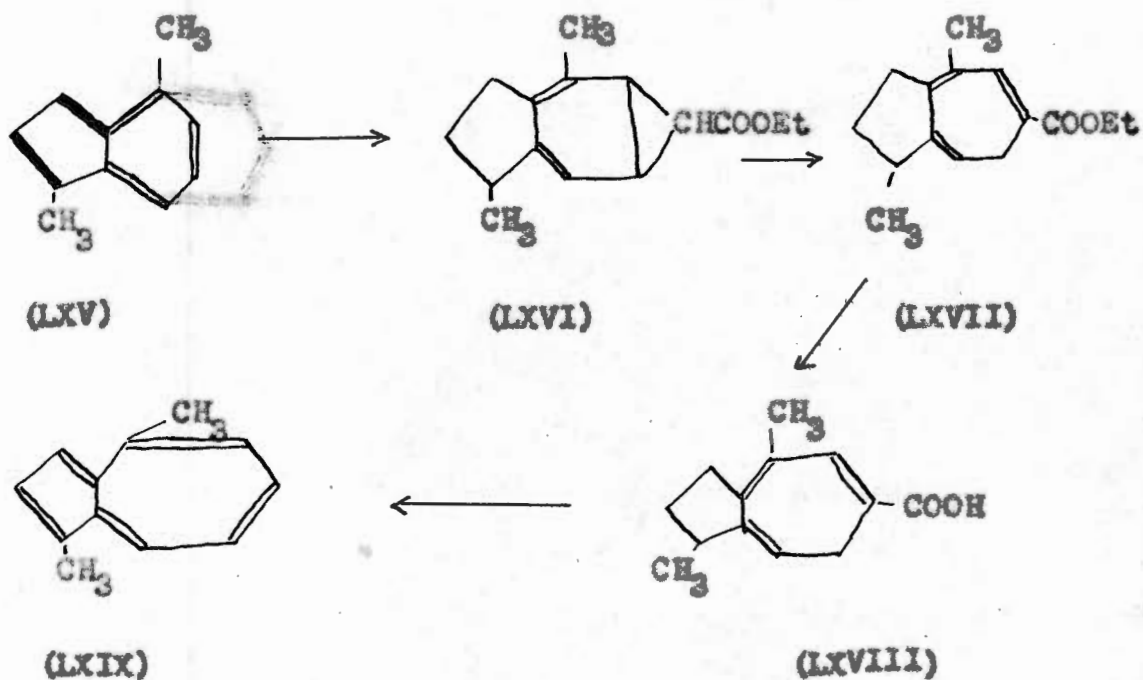
nuclei, the bicyclic norcaradiene system, if formed, is unstable, and besides derivatives of cyclo-heptatriene, phenyl acetic acids and 2-phenylpropionic acids are formed; the latter rearrangement taking place only when the initial aromatic hydrocarbon contains one or more alkyl groups. Examples of this are encountered in the cases of p-xylene (Buchner and Schulze, Ann., 377, 259) and durene (Smith and Townay, J. Amer. Chem. Soc., 1934, 56, 2167).

In all cases studied by Buchner and co-workers, the addition proceeded in such a way that a norcaradiene containing a quaternary carbon atom was not formed. When mesitylene was used, a case in which a quaternary carbon atom could not be avoided in the primary addition, no bicyclic system could be isolated (Buchner and Schottenhammer, Ber., 1920, 53B, 365). Instead the product consisted chiefly of ethyl 2:4:6-trimethyl-cyclo-heptatriene carboxylate (LXII) together with smaller quantities of ethyl 3:5-dimethyl hydro-cinnamate (LXIII) and ethyl mesityl acetate (LXIV).

The readiness of the bicyclic condensation products to undergo rearrangement to heptatriene derivatives offers a ready method for the synthesis of seven-membered ring systems, and thus the reaction has been effectively used by numerous workers in the synthesis of azulene and its homologues.



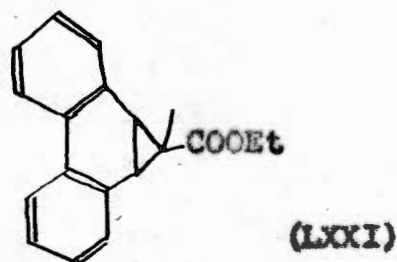
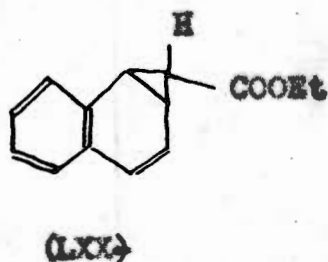
Thus, for example, 1:4-dimethyl azulene was obtained by Plattner and Wyss (*Helv. Chim. Acta*, 1940, 23, 907) by treating 1:4-dimethyl indane.



(LXV) with ethyl diazoacetate and the resulting condensation product, thought to have the structure (LXVI), rearranged to

the cyclo-heptatriene isomer (LXVII) by heat. On hydrolysis the corresponding acid (LXVIII) was obtained. The distillation of this acid from a palladium charcoal catalyst, yielded 1:4-dimethyl azulene (LXIX) by simultaneous dehydrogenation and decarboxylation. Plattner and Reniger (Helv. Chim. Acta., 1942, 25, 1077) have found that it is possible, however, to preserve the carboxy group, by dehydrogenation of the corresponding ester.

Ethyl diazoacetate also condenses with naphthalene and phenanthrene to yield ethyl benznorcaradiene carboxylate (LXX) (Buchner and Hediger, Ber., 1903, 36, 3502) and ethyl dibenz-norcaradiene carboxylate (LXXI) (Drake and Sweeny, J. Org. Chem., 1946, II, 67), respectively.



However, in both these instances the ring systems are extraordinarily stable and incapable of rearrangement to the corresponding cyclo-heptatriene derivatives. Buchner has suggested that the stability of (LXX) is traceable to the presence of the benzene ring.

In the condensation of diazoacetic esters with aromatic rings, the ethyl ester has been found to give higher yields of condensation product than methyl

diazoacetate (Braren and Buchner, Ber., 1901, 34, 982). Also the reaction proceeds more easily with alkylated aromatic nuclei. The reaction must be carried out at a minimum temperature of 130°C . for below this condensation does not proceed. However, in some instances the reaction may be brought about at lower temperatures by the use of copper powder as a catalyst (Ebel, Brunner and Mengel, Helv. Chim. Acta, 1929, 12, 19).

In order to obtain good yields of condensation product it is essential to add the ethyl diazoacetate to a large excess of the hydro-carbon so as to avoid the polymerization of a large measure of the diazoacetic ester before condensation is effected. This is a serious disadvantage, especially where only a relatively small quantity of hydrocarbon is available because the unchanged material has to be recycled many times to get a reasonable conversion.

The temperature at which the reaction is carried out, often influences the nature of the condensation product produced. Thus benzene reacts with diazoacetic ester at $130-135^{\circ}\text{C}$. to yield mainly ethyl norcaradiene carboxylate, while above 135°C . the yield of this material is increasingly small with increasing temperature, and at 140°C . ethyl cyclo-heptatriene carboxylate is the sole product of the reaction. A careful control of temperature is thus necessary, if the norcaradiene compounds are required.

As the condensations lead to a multiplicity of products, mainly isomers and diazoacetic ester polymers (Darapsky, Bar., 1910, 43, 1121; Buchner, Bar., 1885, 34, 345; Silbered, J., 32, 179), and because these products are invariably oily substances which do not form crystalline derivatives, the task of elucidating the structure of these substances is often difficult and tedious. Buchner found that in most cases crystalline products could only be obtained through the amides, often crystalline compounds, which are at best prepared by contact with aqueous ammonia in a sealed tube for between three weeks to six months. The preparation of the amide via the acid chloride, though quicker, invariably led to an oily mixture which could not be crystallised.

Because of this difficulty of isolating pure products from the condensations of diazoacetic ester with hydrocarbons, it has become common practice, in the synthesis of azulenes, to proceed with the synthesis without rigorous purification. The process of dehydrogenation with palladium charcoal catalyst chases most of the nitrogenous impurities, and the azulenes themselves are readily purified by taking advantage of their solubility in 85% phosphoric acid, and their ability to form crystalline addition products with

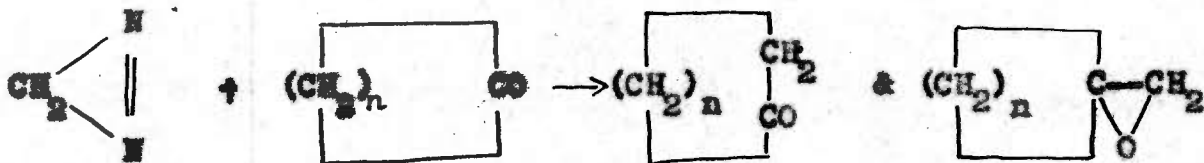
SO₂picric...

picric acid, trinitrobenzene and trinitrotoluene.

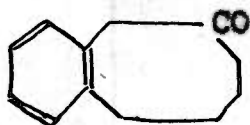
The disadvantage of the reaction is the low yields obtained; 1% in some azulene syntheses, (Arnold, Bar., 1943, 76B, 777), and the large number of isomers produced. It has however, the great advantage, as mentioned previously, of yielding a product which is relatively unsaturated and therefore needs only mild dehydrogenation to give the required fully conjugated azulene structure.

RING EXPANSION OF CYCLIC KETONES

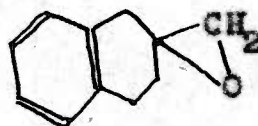
The ring expansion of cyclic ketones with diazomethane is a reaction which can be used for the preparation of seven-membered ring systems as follows:-



Unfortunately the normal course of the reaction is disturbed when the ring is attached to a benzenoid nucleus. Thus α -tetralone yields benz-cyclo-octenone (LXXII), (Thompson, J. Amer. Chem. Soc., 1944, 66, 156), while β -tetralone yields the epoxycompound (LXXIII) (Mosettig and Burger, J. Amer. Chem. Soc., 1931, 53, 2295.)



(LXXII)



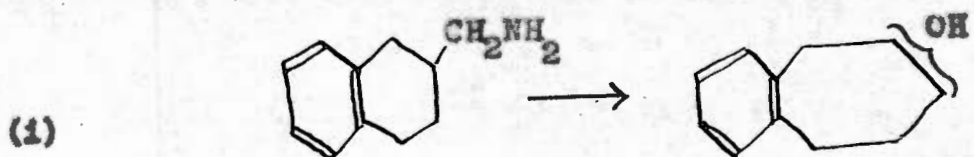
(LXXIII)

This method was deemed less adaptable to the synthesis of heptalene than the two methods already discussed and is not therefore considered in detail.

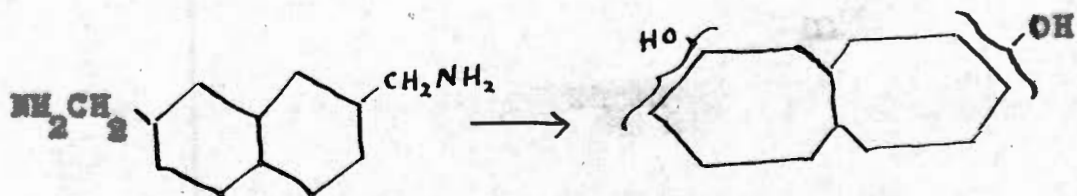
THE SYNTHESIS AND DEHYDROGENATION OF [0.5.5] -BICYCLO-
DODECANE DERIVATIVES AND RELATED COMPOUNDS.

(A) The Study of the Demjanov Reaction for the Synthesis of
[0.5.5]-Bicyclo-dodecane Ring Systems.

The reaction first explored with a view to the synthesis of heptalene was the Demjanov reaction, as it was considered possible to synthesise readily the [0.5.5] -bicyclo-dodecane intermediate by either two separate consecutive expansions of two fused six-membered rings, as shown:-



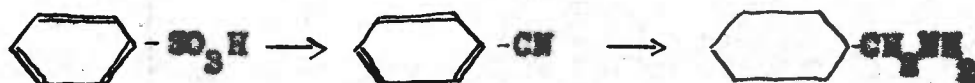
or by two simultaneous expansions of two fused six-membered rings.



Since the heptalene system was expected on theoretical grounds, as mentioned in the introduction, to have aromatic stability comparable with that of azulene,

it was thought that the heptalene structure could be reached by the dehydrogenation of the corresponding saturated hydrocarbon, using methods similar to those employed in the synthesis of azulene.

It was also considered possible to avoid the lengthy preparations of the required cyclo-hexyl-methyl-amines discussed in the preceding section by taking advantage of the following series of reactions:-



First the sulphonation of the benzenoid nucleus, then the substitution of a nitrile grouping for the sulphonic acid group by the distillation with a metallic cyanide, and finally, the simultaneous reduction of the benzene ring and the cyanide group to the required cyclo-hexyl-methyl-amine.

This series of reactions was first explored with 2-naphthalene sulphonic acid as the starting material. The conversion of this sulphonate into 2-naphthenitrile was accomplished by the distillation of the potassium salt with potassium ferricyanide. Although fairly good yields (45-50%) could be obtained when the reaction was carried out in small quantities, the yield was considerably smaller when it was carried out on a larger scale, using one or two moles of cyanide.

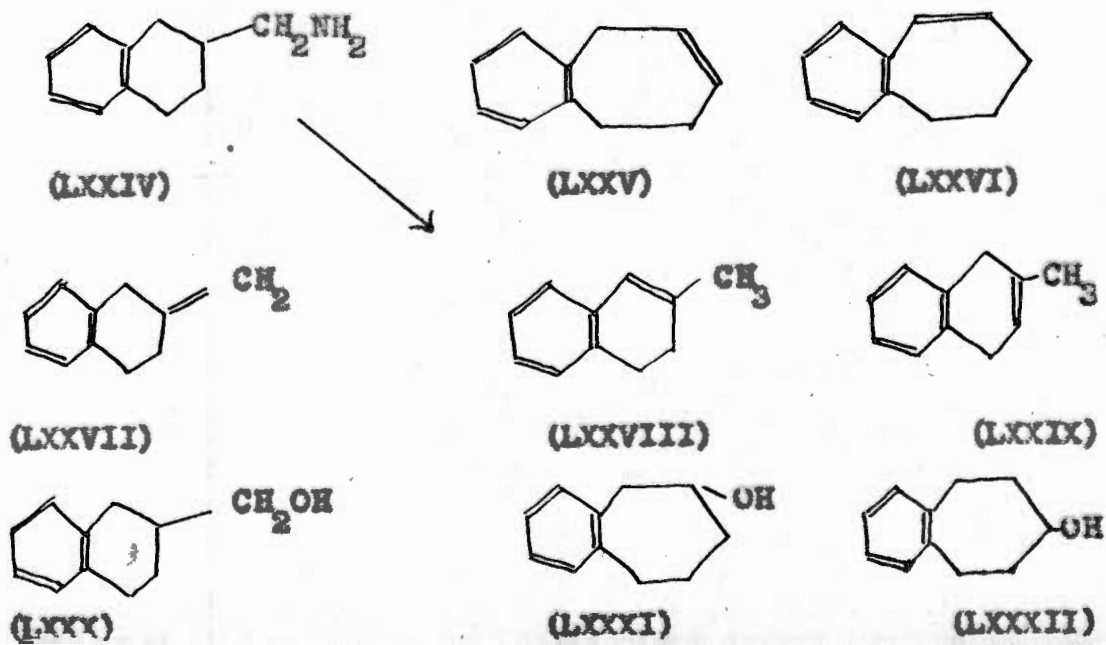
The required 1,2,3,4,-tetrahydro-2-naphthyl methylamine was then obtained by the reduction of the aryl

nitrile with sodium and alcohol in roughly 50% yield. Thus although this method of synthesis involves fewer manipulations than those discussed in the introduction, the overall yield is probably not much improved.

The beta-substituted naphthalene was chosen for this study rather than the alpha-isomer because it was considered that the course of the Demjanov rearrangement reaction was less likely to be disturbed by the benzenoid ring in this instance for the active methylamine group is separated from the benzene ring by a methylene group.

Although the expansion of a six-membered ring fused to a saturated five-membered ring has been carried out, the effect on the reaction of replacing the five ring with a six-membered one has not been investigated.

The 1,2,3,4-tetrahydro-2-naphthyl methylamine (LXXIV) was treated with nitrous acid and yielded the usual complex product with a wide

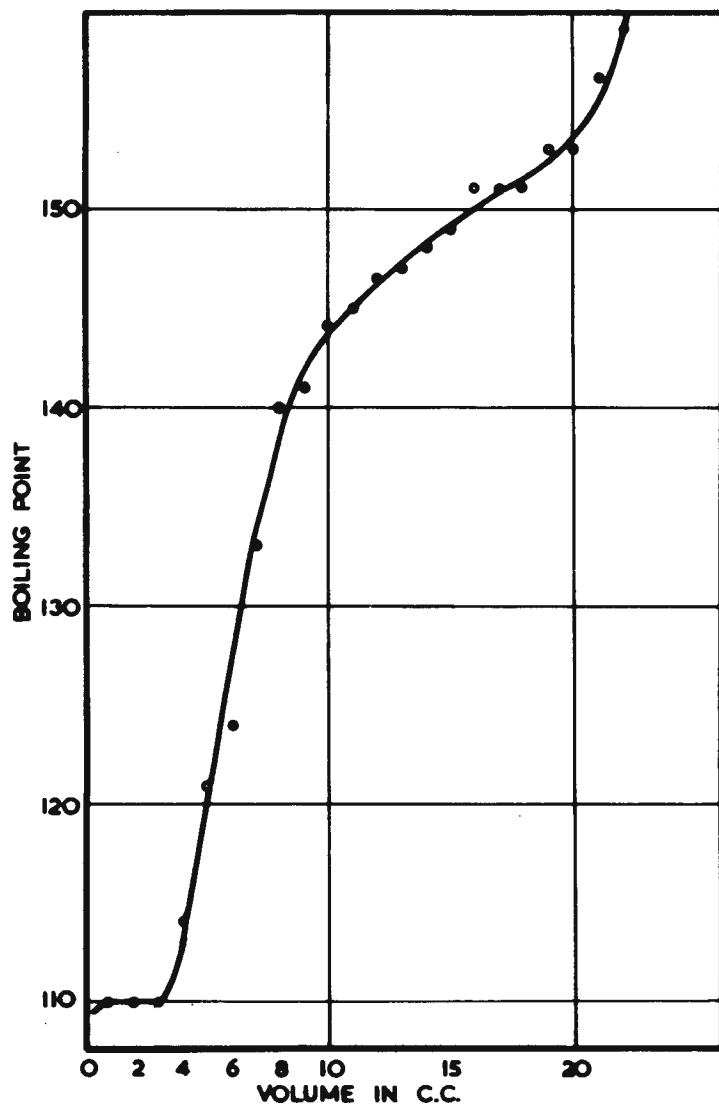


boiling range, see graph I. The products which are theoretically possible are as shown above. Both the rearrangement products of (LXXVII) are possible but (LXXVIII) is more likely to be present than (LXXIX) because of the readiness with which 1:4-dihydronaphthalenes isomerise to the 1:2-isomers (Straus and Lemmel, Ber., 1913, 46, 236).

The reaction mixture was roughly divided into a low boiling olefin fraction and the higher boiling alcohol fraction. The olefin fraction was oxidized with alkaline potassium permanganate in order to isolate acids which would give a clue to the constitution of this product. However, the only acids that could be isolated pure were phthalic acid and homophthalic acid.

The alcohol fraction was easily separated into a primary and a secondary alcohol, in the ratio of 1/2.8, by partial esterification with phthalic anhydride. The phthalyl ester of the primary alcohol on hydrolysis yielded a pure alcohol b.p., 152-4°C./15m.m. which on oxidation with chromic oxide in acetic acid yielded four main products.

(1) a very small quantity of an acid m.p. 85°C. which could not be properly crystallized because of its high solubility in all organic solvents. It is thought to be 1,2,3,4-tetrahydro-2-naphthoic acid. When it was mixed with an authentic sample of 1,2,3,4-tetrahydro-2-naphthoic acid m.p. 94-5°C., prepared according to the instructions of



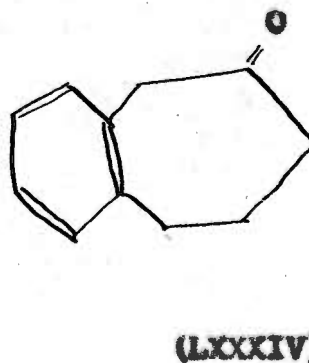
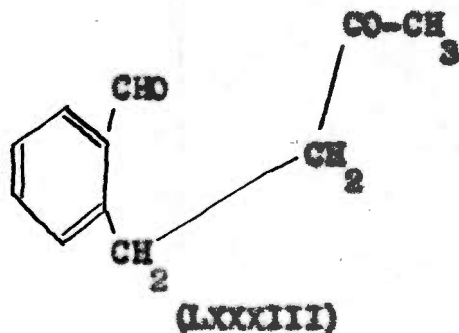
REACTION PRODUCT FROM THE DEMJANOV REACTION

Graph I

Baeyer (Ann., 1891, 266, 198) the mixture melted at 89-92°C.

(ii) a small fraction which did not form a semi-carbazone, doubtless the unchanged alcohol.

(iii) a compound which formed a very insoluble di-semicarbazone m.p. 218-220°C., for which the formula (LXXXIII) is suggested as the most likely.



It is possible that such a compound could be formed in the partial oxidation of (LXXVIII).

Although it was not found possible with the quantity of material available to rigorously characterize the oxidation products there seems little doubt that the primary alcohol which forms the mono-phthalyl ester is the 1,2,3,4-tetrahydro-2-naphthyl carbinol (LXXX).

The alcohol fraction which failed to form an ester with phthalic anhydride was oxidized with chromic oxide and yielded an acid which could not be characterized, and a ketone m.p. 41-2°C., (phenylhydrazone 91-2°C. and semicarbazone 185-8°C.). This ketone is considered to be 1,2-benz-cyclohepten-4-one (LXXXIV) because the melting point of its

semicarbazone is lower than that of 1:2-benz-cyclo-hepten-3-one, which is given by Kipping and Hunter (J. 1901, 79, 606) as 206-7°C. and is depressed on admixture with an authentic specimen of the semicarbazone of 1:2-benz-cyclo-hepten-3-one. Also the phenyl-hydrazone melts higher than that of 1:2-benz-cyclo-hepten-5-one, given by Kubota and Isemura (Bull. Soc. Japan, 1931, 6, 103-6) as 85°C.

Ketone	The Ketone	Semicarbazone	phenyl-hydrazone	smell
-3-one	liquid	206-7°C	-	Odourless
-4-one	41-2°C	185-8°C	91-2°C	"
+5-one	41-2°C	-	85°C	peppermint

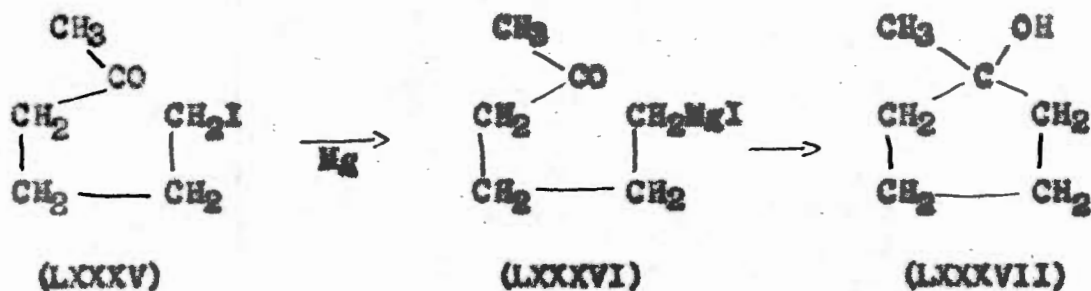
Although the melting points of the 4- and 5- isomers are the same, the new ketone does not exhibit the strong smell of peppermint and bitter almond shown by the 5-isomer.

It is concluded from the investigations outlined, that the products of the reaction of 1,2,3,4-tetrahydro-2-naphthyl-methylamine with nitrous acid are mainly 1,2,3,4-tetrahydro-2-naphthyl-carbinol (LXXX) and 1:2-benz-cyclo-hepten-4-ol (LXXXI) in the ratio of 1/2.8, together with the corresponding olefines.

38/Although...

(B) The Attempted Synthesis of Ring Systems Using an Intramolecular Grignard Reaction.

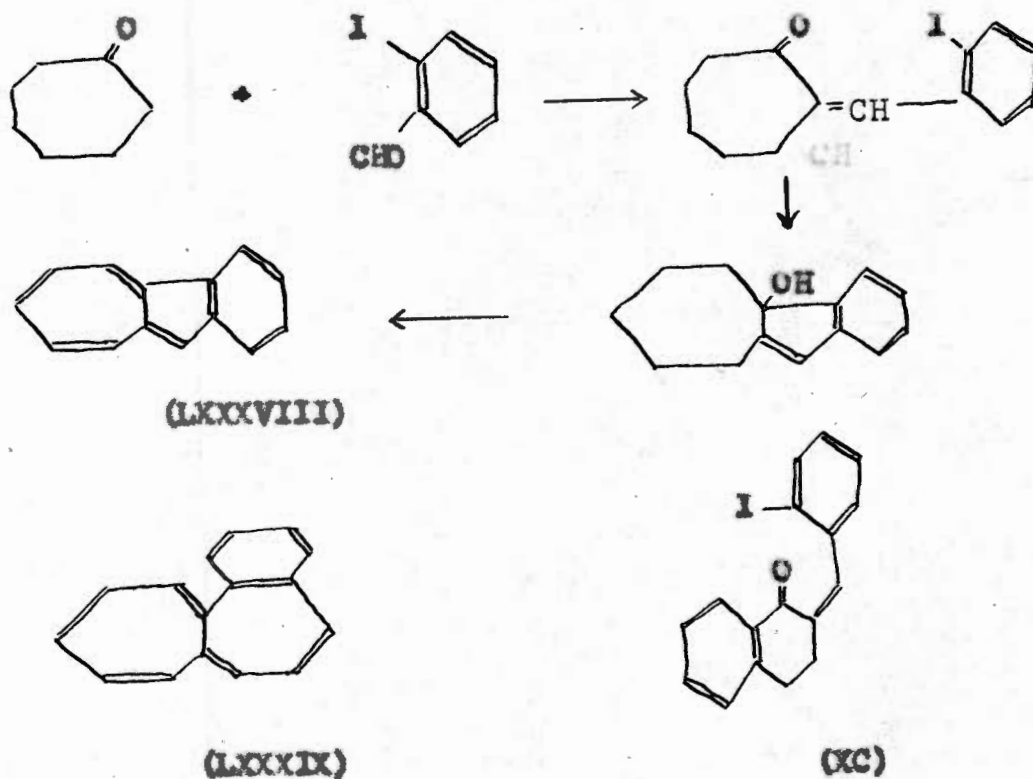
Another reaction which was investigated with a view to the synthesis of azulene and heptalene analogues, was a Grignard ring closure reaction used by Zelinsky and Moser (Ber., 1902, 35, 2684) for the synthesis of 1-methyl cyclo-pentanol (LXXXVII). It depends upon the fact that certain halogen compounds form Grignard reagents which undergo intramolecular condensations to give cyclic structures. Thus 4-iodo-p-butyl methyl ketone (LXXXV) reacts with magnesium to form the Grignard intermediate (LXXXVI) which



undergoes intramolecular condensation to yield 1-methyl cyclo-pentanol (LXXXVII).

Although the yield of cyclic alcohol in this reaction is not very good, it was thought possible to use this ring closure reaction to advantage in the synthesis of fused ring systems such as 1:2-benz-heptalene (LXXXIX).

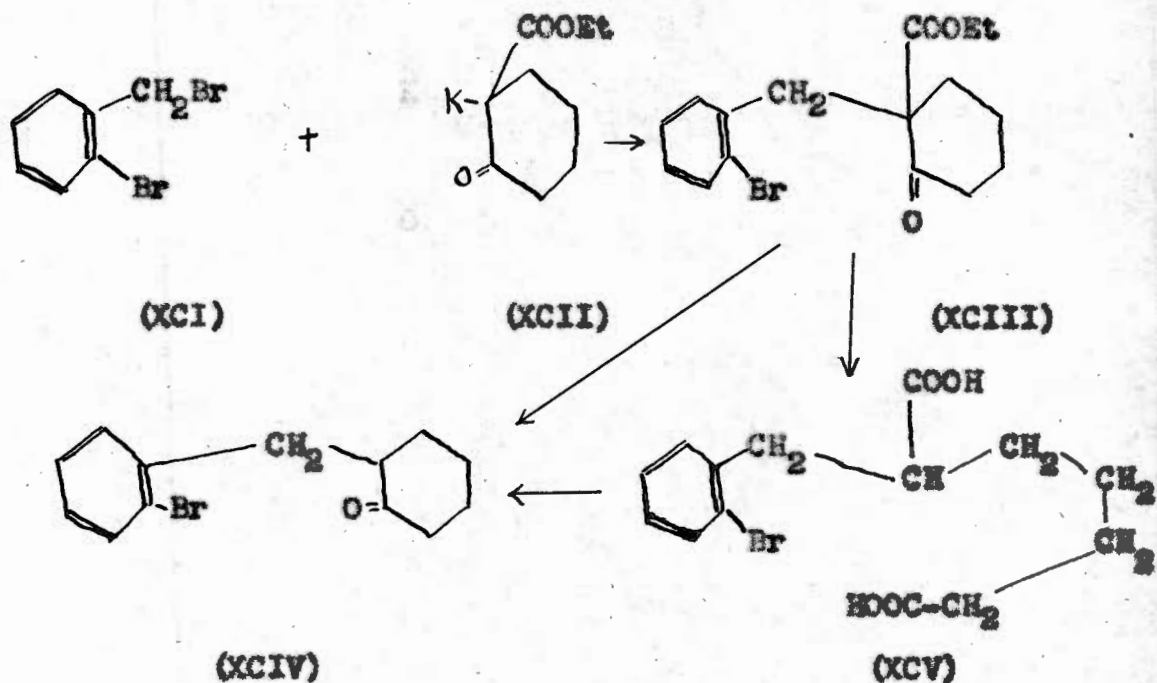
It was planned to do this by the condensation of cyclo-heptanone with the appropriate aryl-halogenated aldehyde to give the required ketalide and then to effect its cyclization with the aid of the Grignard reaction already mentioned, followed by dehydrogenation of the alcohol produced to the required fully conjugated hydrocarbon as shown below:-



In order to gain experience with this method of synthesis 2-(o-iodo-benzylidene)-1-tetralone (XC) was prepared by condensing o-iodobenzaldehyde with 1-tetralone. However all attempts to form a Grignard compound from this

41/keto-halide..

keto-halide failed. As it was considered that this failure to react with magnesium might be due to steric hindrance an attempt was made to hydrogenate catalytically the double bond adjacent to the carbonyl group in (XC). However a resinous high boiling polymer was the only product formed on hydrogenation in the presence of Adam's catalyst. The following route to the benzyl-cyclic ketones was therefore explored.



The potassio-derivative of ethyl-cyclohexanone-2-carboxylate (XCII) was condensed with p-bromo-benzyl bromide (XCI) and the ethyl p-bromo-benzyl-cyclohexanone-2-carboxylate (XCIII) formed, hydrolysed to a mixture of the required p-bromo-benzyl-cyclohexan-2-one (XCIV) and p-bromo-benzyl-2-pimelic acid (XCV). The latter compound was converted to (XCIV) by dry distillation of its thorium salt.

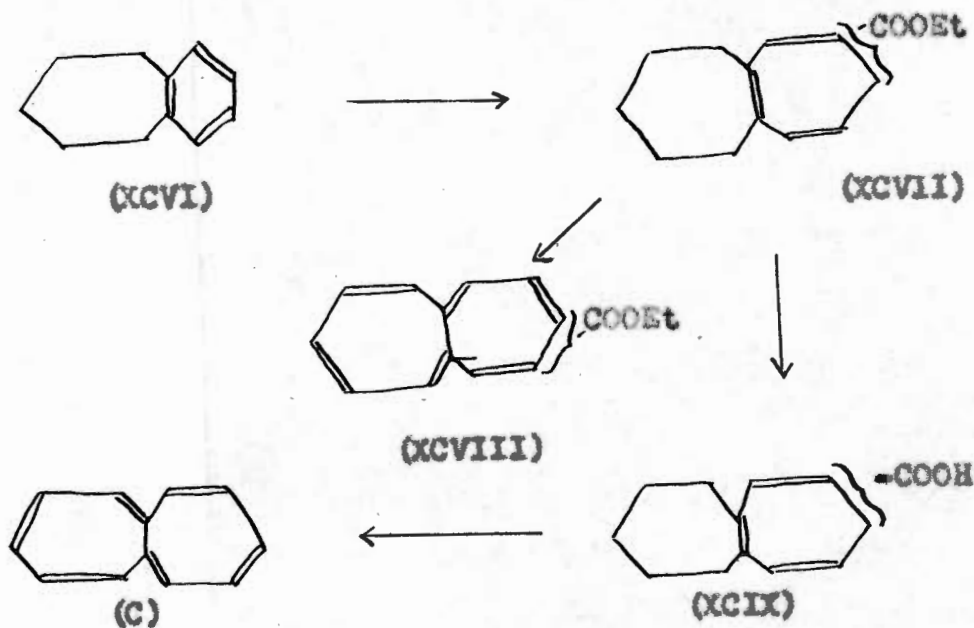
As before, all efforts to prepare the Grignard compound of this aryl halide failed, although the precautions recommended by Gilman (J. Amer. Chem. Soc., 1929, 45, 2412) were rigidly followed. Even when p-bromo-benzyl-cyclo-hexan-2-one (XCIV), (one mole) was mixed with ethyl iodide (0.5 moles) only the iodide reacted with the magnesium, for no bromine was found in the aqueous layer after decomposition of the Grignard complex and the bulk of the ketohalide was recovered unchanged.

The use of lithium in place of magnesium was not explored because of the lack of adequate supplies of this metal.

(C) THE SYNTHESIS AND DEHYDROGENATION OF HEPTATRIENE RING SYSTEMS PREPARED BY RING EXPANSION OF BENZENOID COMPOUNDS WITH ETHYL DIAZOACETATE.

The Buchner rearrangement, as was mentioned in the introductory section, has been applied with considerable success to the synthesis of azulenes, and in this section, various attempts to use this reaction in the synthesis of heptalene derivatives are described.

The first route to be explored, and which closely parallels the synthesis of azulenes from hydrindene (e.g. Plattner and Reniger, Helv. Chim. Acta, 1942, 25, 580) is outlined below:-



It was considered that 1:2-benz-azula-heptene (XCVI) on treatment with diazoacetic ester would undergo ring enlargement in the same manner as hydrindene to yield in this instance ethyl [0.5.5]-bicyclo-dodecatriene carboxylate (XCVII).

which it was planned to convert directly into the heptalene derivative (XCVIII) by dehydrogenation or to heptalene itself (C) by simultaneous decarboxylation and dehydrogenation of the corresponding acid (XCIX).

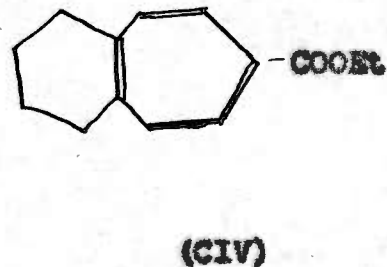
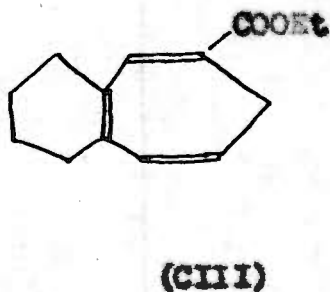
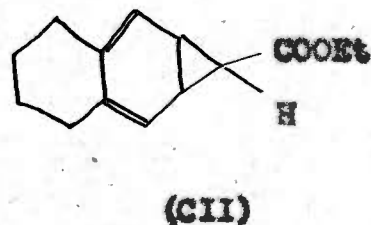
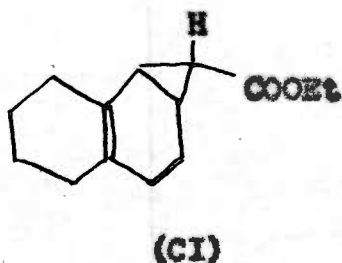
Although the benzenoid ring of hydrindene has been shown to undergo expansion in the normal way, it was not known what effect the fusion of a benzene ring to larger aliphatic rings would have upon the course of the reaction. It had been shown by Buchner (see page 25) that when the benzene ring is fused to another benzene ring as in naphthalene the rearrangement does not take place, ethyl benz-norcaradiene carboxylate (LXX) being the only product of the reaction. It was therefore essential to develop a method of differentiating between the cyclo-heptatriene and norcaradiene ring systems; preferably with small quantities of material, for 1:2-benz-cyclo-heptene is not readily available, being prepared only in rather small yields by long stage syntheses (Borsha and Roth, Exp., 1921, 54, 174).

It was therefore decided to undertake a study of the reaction of diazoacetic ester with tetralin, which is readily available in quantity, before embarking on the synthesis using 1:2-benz-cyclo-heptene.

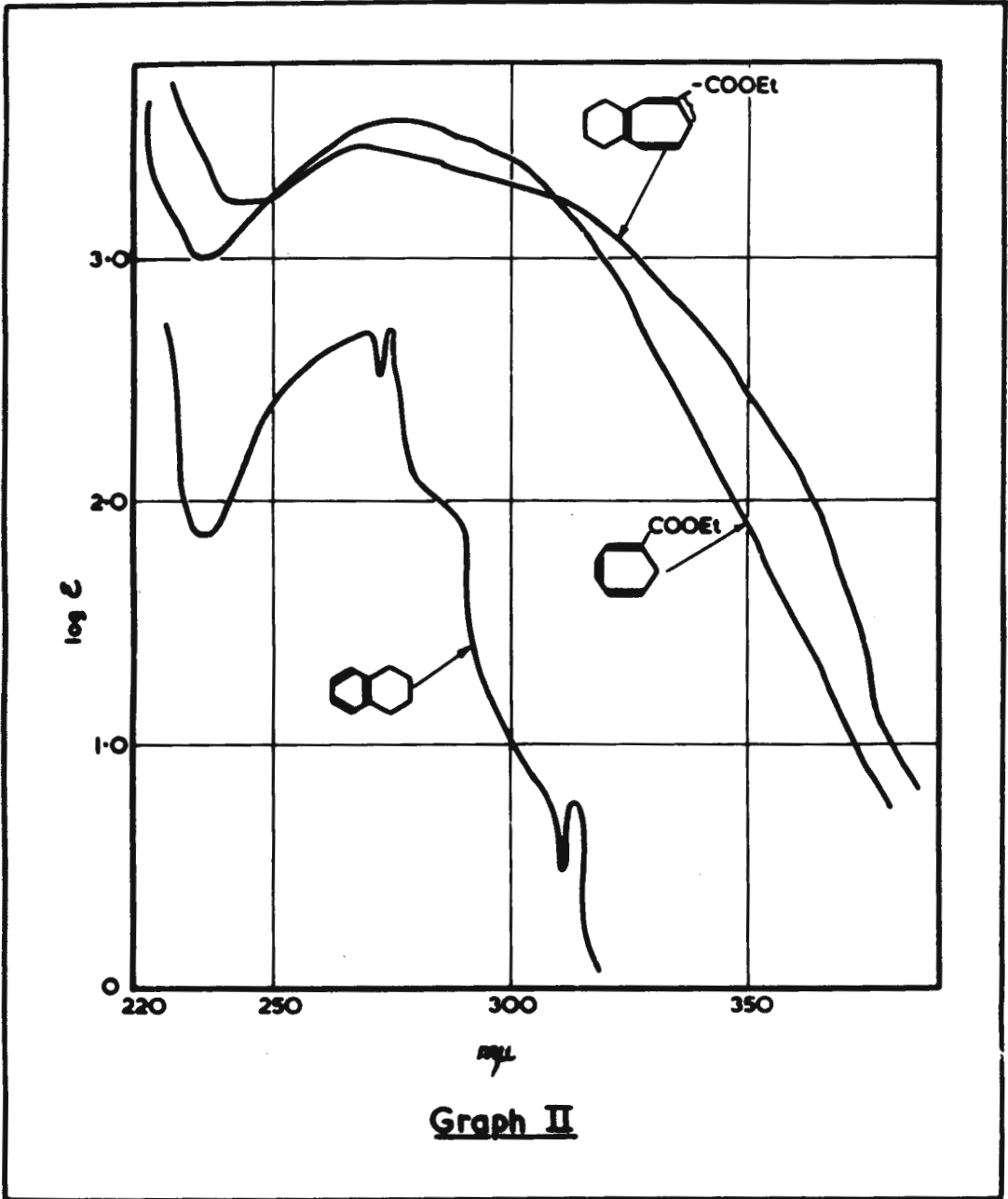
Tetralin was treated with ethyl diazoacetate at 130°C. in the manner used in the azulene syntheses, that is, to favour the formation of the heptatriene product, and

45/yielded....

yielded a high boiling ester, which could not be obtained pure by fractionation, because the nitrogenous impurities formed by the polymerization of some of the diazoacetic ester have a similar boiling range. However it was found possible to obtain a pure product by hydrolysing the ester. In this way most of the impurities were rendered soluble in dilute aqueous acid and the required acid could be extracted out with ether. On distillation the acid came over as a pale yellow resinous substance which could not be crystallized. This is without doubt due to the large number of isomers present. Thus besides the norcaradiene systems (CI) and (CII) and the two heptatriene structures (CIII) and (CIV) a number

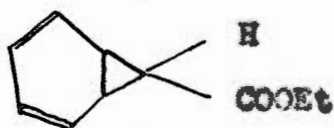


of bond and geometrical isomers are also possible. Thus the substance was not expected to be crystallized readily.

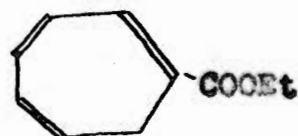


Graph II

As it was expected that the norcaradiene structures (CI) and (CII) might have different ultra violet absorption spectra from the heptatriene ones (CIII) and (CIV), a study of the spectra of ethyl norcaradiene (CV) and ethyl cyclo-heptatriene (CVI) was made for use as standards. The curves of the absorption spectra of these two esters were



(CV)



(CVI)

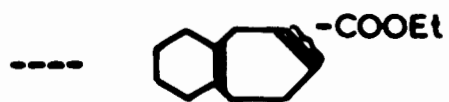
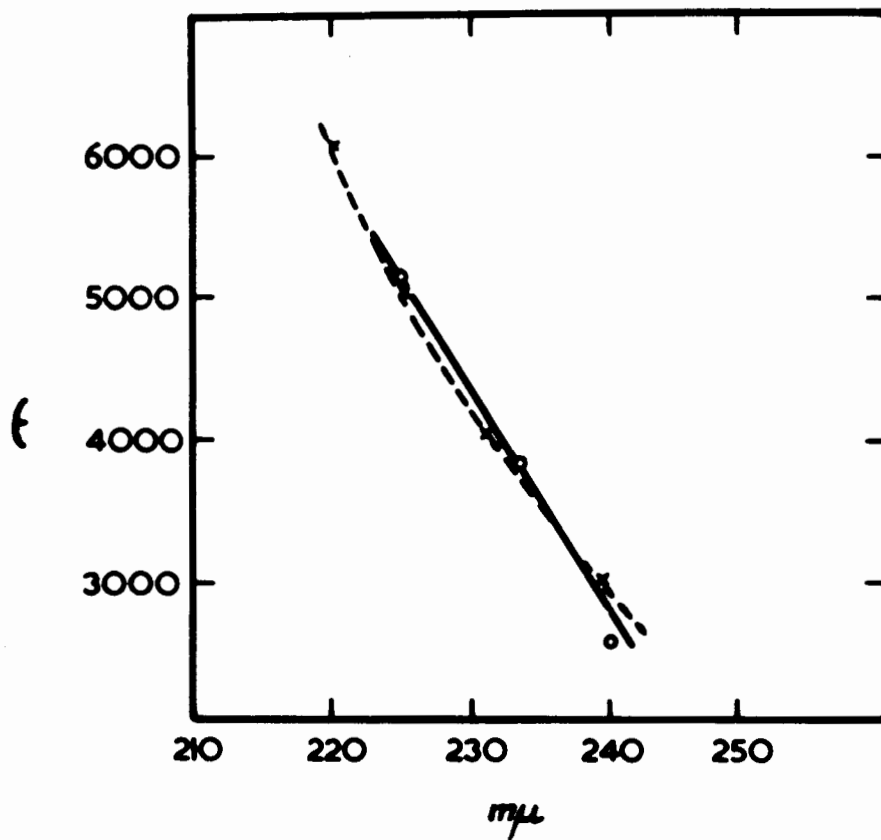
however very similar, doubtless because it is not possible to get the norcaradiene isomer pure, it being always contaminated with ethyl cyclo-heptatriene carboxylate. The latter substance on the other hand is easily obtained pure by warming the mixture to 140°C. Under these conditions all the norcaradiene ester is rearranged to the cyclo-heptatriene form.

Although it was not found possible to develop a clear cut method of differentiating between the two structures using this method, it was found that the absorption spectra of ethyl cyclo-heptatriene carboxylate (CVI), and the product obtained from tetralin (see graph II), were very similar.

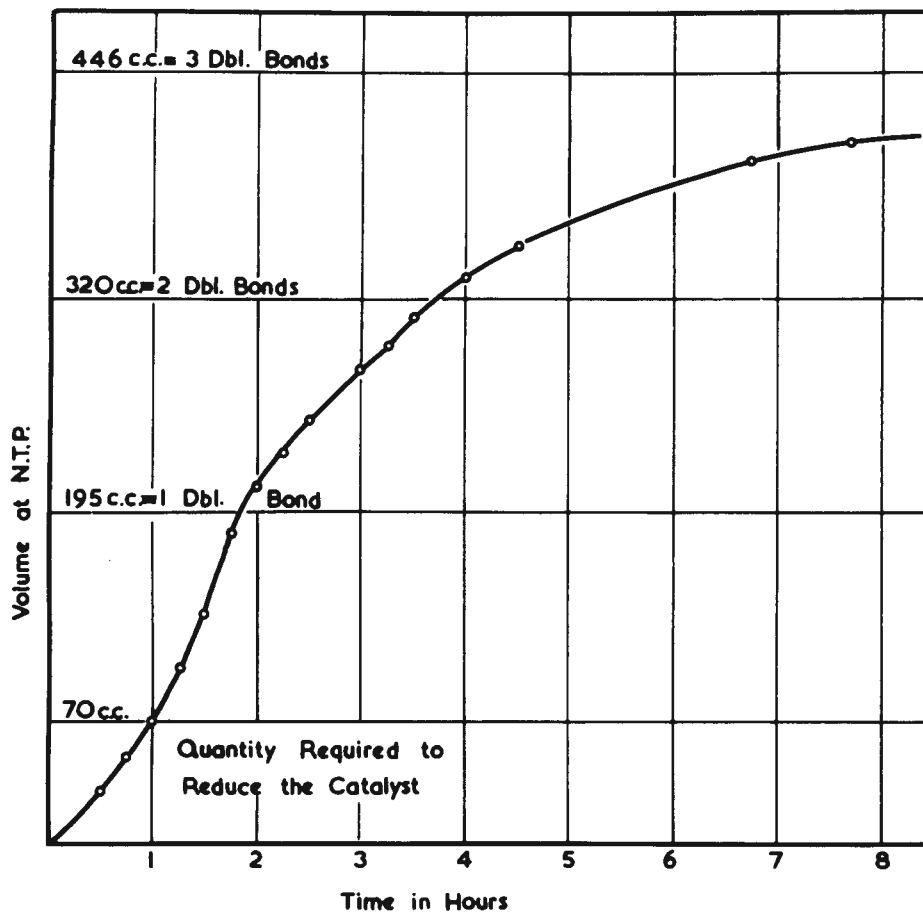
The tetralin condensation product does not give the coloured compounds with concentrated sulphuric acid which are characteristic of most norcaradiene esters. However this

failure to form coloured compounds is not a conclusive proof of the absence of norcaradiene esters because ethyl benz-norcaradiene carboxylate (see page 25) is an exception to this rule and gives no coloured complex with concentrated sulphuric acid.

When the tetralin condensation product was hydrogenated with a palladium calcium carbonate catalyst, hydrogen, equivalent to only one double bond was absorbed. Thus it would appear that if the product has a norcaradiene structure, the hydrogenated material must have one double bond in a strongly protected position. This condition would probably be fulfilled if the material resulting from the hydrogenation has the remaining double bond at the site of fusion of the two six-membered rings, as in (CVII) and (CVIII), the latter isomer being produced by terminal addition of hydrogen to the butadiene system contained in the parent diene (CII). On the other hand if the system has a cycle-heptatriene structure, the two remaining double bonds in the hydrogenated material must exist in protected positions. Here again this would be possible if the hydrogenated compound is an $\alpha\beta$ -unsaturated ester such as (CIX), (CX) or (CXI), with the second double bond situated at the site of fusion of the two rings, for it is known that double bonds adjacent to carboxyl groups are more slowly reduced than isolated double bonds (Farmer and Galley, J. 1933, 687). This is in some measure supported.

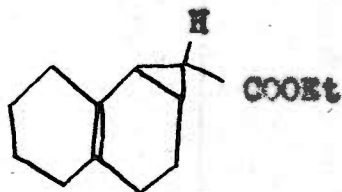


Graph III

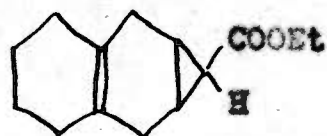


HYDROGENATION OF C1CCC2C(C1)C=CC2C(=O)O IN THE PRESENCE OF
 COLLOIDAL PLATINUM CATALYST

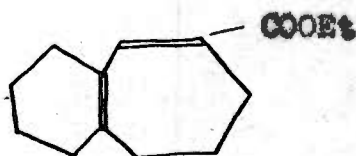
Graph IV



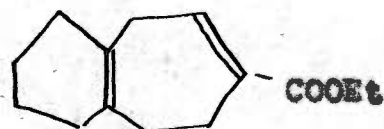
(CVII)



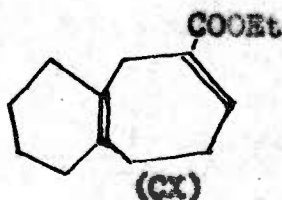
(CVIII)



(CIX)



(CXI)



(CX)

by the fact that the cyclo-heptariene acids isolated by Buchner and Braren, (Ber., 1901, 34, 982.) from the condensation of benzene with ethyl diazoacetate were all β/β -unsaturated acids.

The absorption spectrum of the hydrogenated tetralin condensation product shows a continuous weak absorption, see graph III. The weak absorption of this compound in the near ultra-violet region suggests that the remaining chromophores in the molecule are not conjugated, that is, it is in favour of structures (CVIII), (CX) and (CXI).

When the tetralin condensation product was hydrogenated in the presence of colloidal platinum in aqueous acetic acid solution three molecules of hydrogen were absorbed, a fact

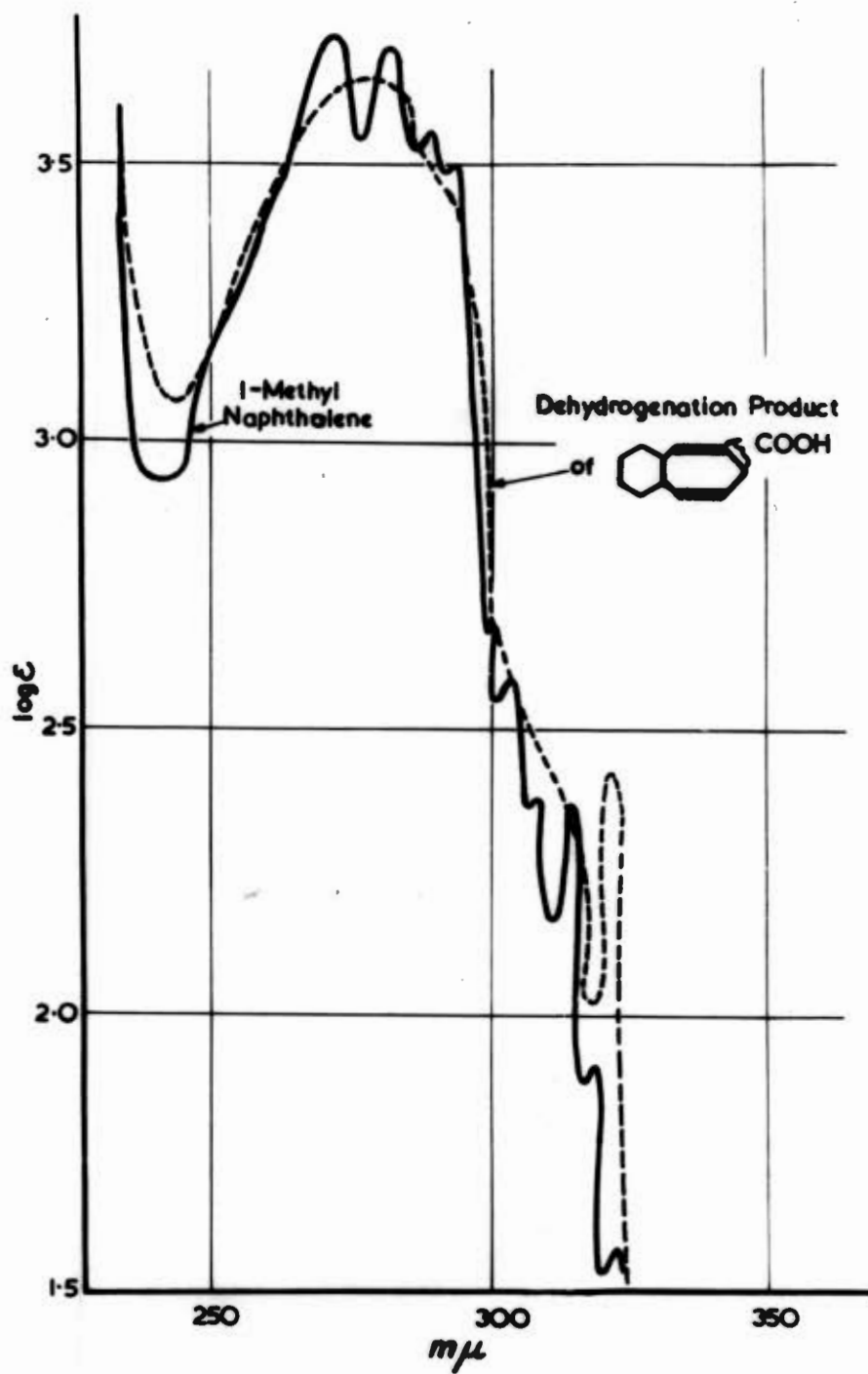
which is more in favour of the cyclo-heptatriene structure. However, the first two molecules of hydrogen were quickly added, see graph IV, but the third much more slowly, and it was thought possible that the slower addition might correspond to the fission of the propene ring in a norcadiene system, with the addition of hydrogen. Thus in another hydrogenation the reaction was stopped when two molecules of hydrogen had been added. The acid produced was found to add bromine readily and decolourise dilute acid potassium permanganate.

A cyclo-propane carboxylic acid ring should be resistant to such reagents (Buchner and Eraren, loc. cit.). It was concluded, from these investigations, that a cyclo-heptatriene structure is more likely than a norcadiene one for the reaction product of tetralin and ethyl diazoacetate.

An attempt was made to separate and characterise the mixture of isomeric acids from the tetralin condensation by fractional crystallization of their amides. It was not found possible to do this by shaking the ester with aqueous ammonia, in the manner described by Buchner, probably because the ester is only sparingly soluble in concentrated aqueous ammonia.

The corresponding acid was therefore converted to the amide by way of the acid chloride in the usual manner, and yielded a semicrystalline mass from which a very small

50/quantity..



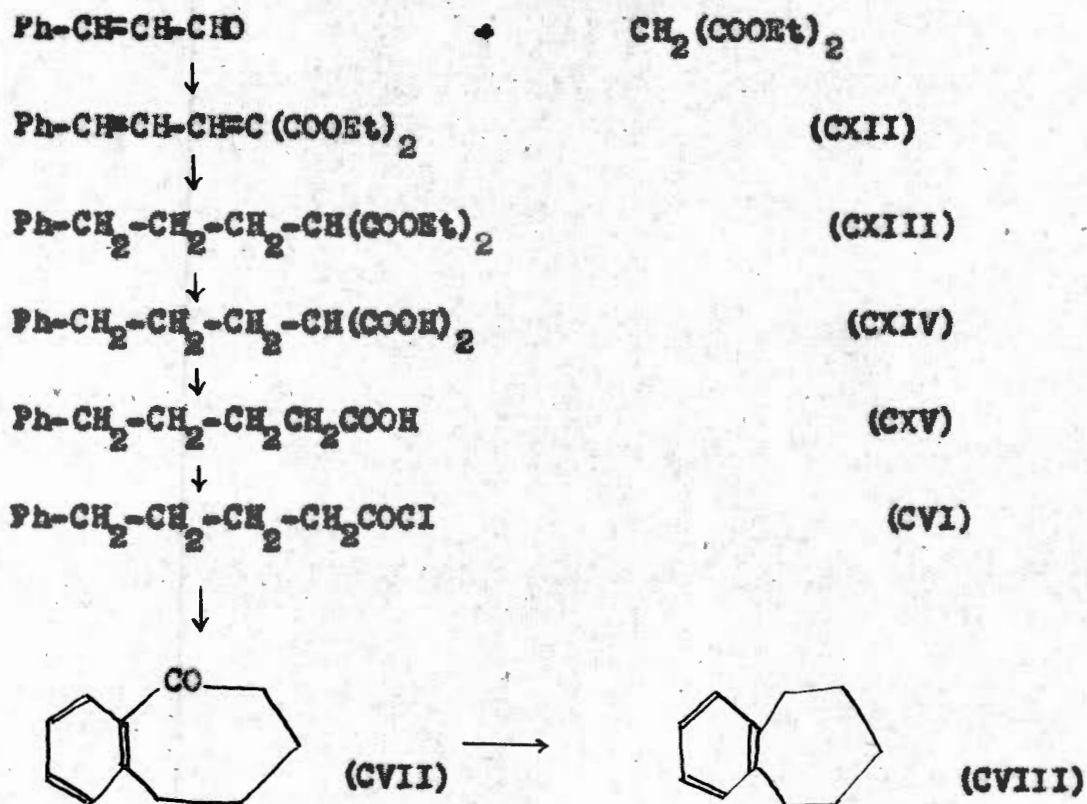
Graph V

quantity of a pure amide (m.p. 119.5-121°C.) was isolated after many recrystallizations; showing that the material is a complex mixture of isomers.

A study of the catalytic dehydrogenation of [0.4.5] bicyclo -undecatriene-carboxylic acid in the liquid phase was made, and revealed a tendency of this system to rearrange to a [0.4.4] -bicyclic structure during the dehydrogenation. Thus the main dehydrogenation product, using a palladium charcoal catalyst (Linstead and Thomas, J., 1940, 1127) in the liquid phase, was a mixture of 1- and 2-methyl naphthalenes in the approximate ratio of 2:1. The constitution was verified by an examination of the ultraviolet spectrum, see graph V. Thus it is seen that the spectrum of the mixture closely resembles that of 1-methyl naphthalene accurately measured by Laszlo (J. prakt. chim., 1926, 117-8, 401). Besides these naphthalenes, hydrogenated naphthalenes, doubtless produced by a process of disproportionation were also detected.

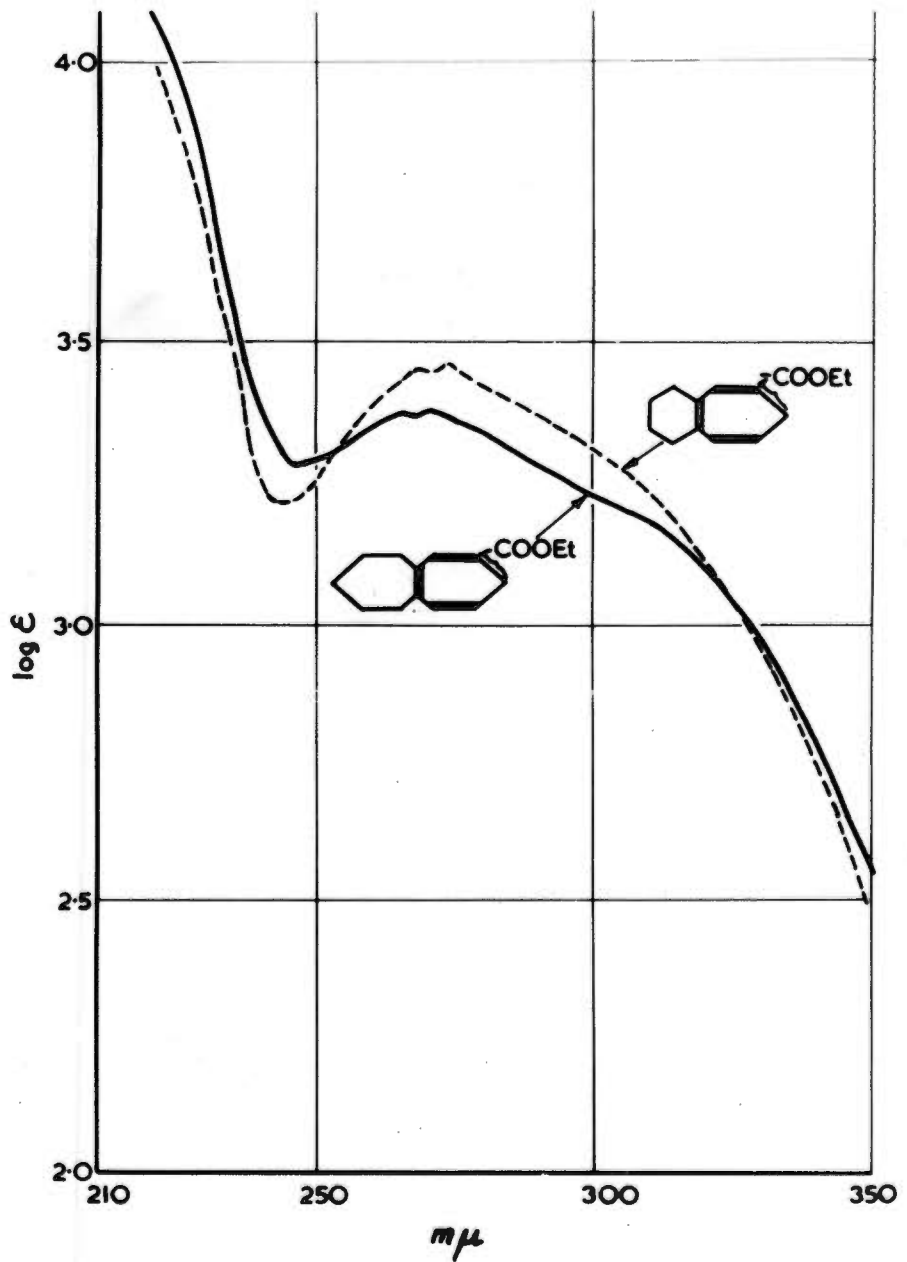
Since the addition compound of ethyl diazoacetate with tetralin was found to undergo the normal rearrangement to a cyclo-heptatriene derivative, it was deemed worthwhile to proceed with the synthesis of heptalenes from 1:2-benz-cyclo-heptene in the manner outlined at the beginning of this section.

The synthesis of 1:2-benz-cyclo-heptene was carried out in good overall yield in seven stages in the following manner:-



Diethyl cinnamylidene malonate (CXII) was prepared in 60% yield by condensing cinnamaldehyde with diethyl malonate in the presence of piperidine. This was hydrogenated in the presence of palladium calcium carbonate catalyst to diethyl 4-phenyl-1:1-butane dicarboxylate (CXIII) in 90% yield. The ester was then hydrolysed and decarboxylated to give 5-phenylvaleric acid (CXV) in the manner recommended by v. Braun and Deutsch (Ber., 1912, 45, 2178) in 73% yield. The acid was converted to the acid chloride (CVI) in 87% yield by treating it in benzene with phosphorus pentachloride. The yield was much lower (viz. 60%) when the method of Kipping and Hunter (J., 1901, 72, 605) was used.

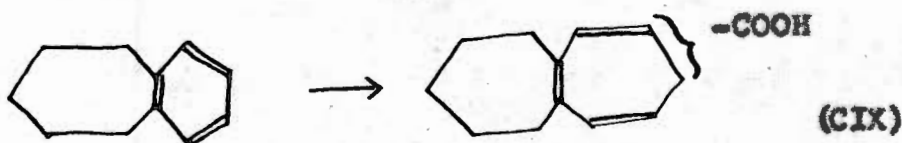
The cyclic ketone 2:3-benz-cyclo-hepten-1-one (CVII)



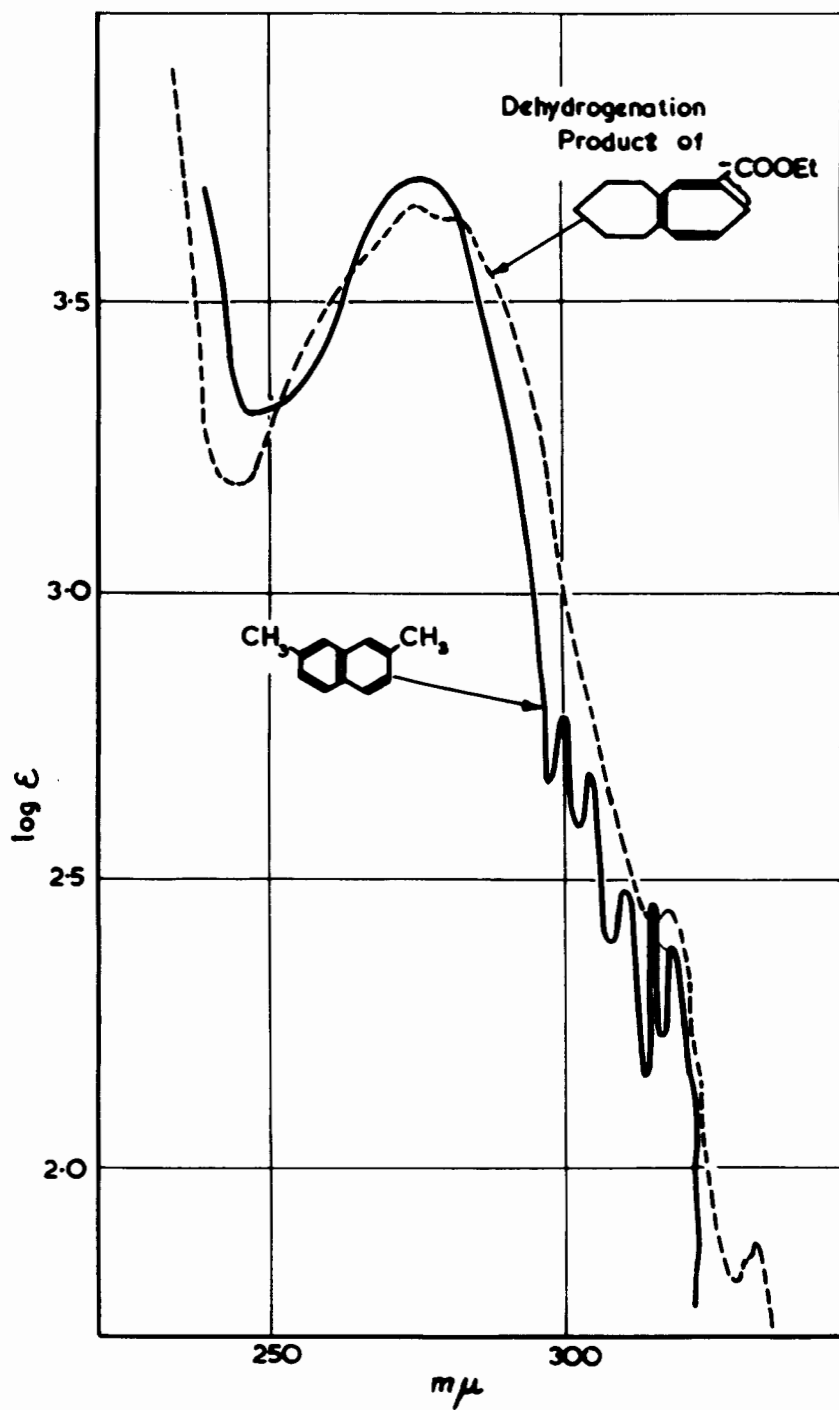
Graph VI

was formed in 82% yield by using an improved Friedel Craft reaction. Finally the 2:3-benz-cyclo-hepten-1-one was reduced by means of Clemmensen's reaction in the manner recommended by Plattner (Helv. Chim. Acta, 1944, 27, 801) to 1:2-benz-cyclo-heptene (CVIII) in 87.5% yield. The overall yield was thus approximately 17-20%.

The 1:2-benz-cyclo-heptene was treated with ethyl diazoacetate in the same way as tetralin and yielded a condensation product which had properties very similar to that of ethyl [0.4.8]-bicyclo-undecatriene carboxylate. The curves of the ultra violet absorption spectra were found to be almost identical, see graph VI. The new acid absorbed hydrogen equivalent to one double bond in the presence of a palladium calcium carbonate catalyst, but absorbed three moles of hydrogen when treated with colloidal platinum catalyst in aqueous acetic acid. It did not give a coloured compound with concentrated sulphuric acid. The acid was therefore concluded to be a [0.5.5]-bicyclo-dodecatriene carboxylic acid such as formulated (CIX).



The study of the dehydrogenation of this acid in the liquid phase using a palladium charcoal catalyst as before, revealed a tendency of this substance to rearrange to a [0.4.4]-bicyclic ring system under these conditions.



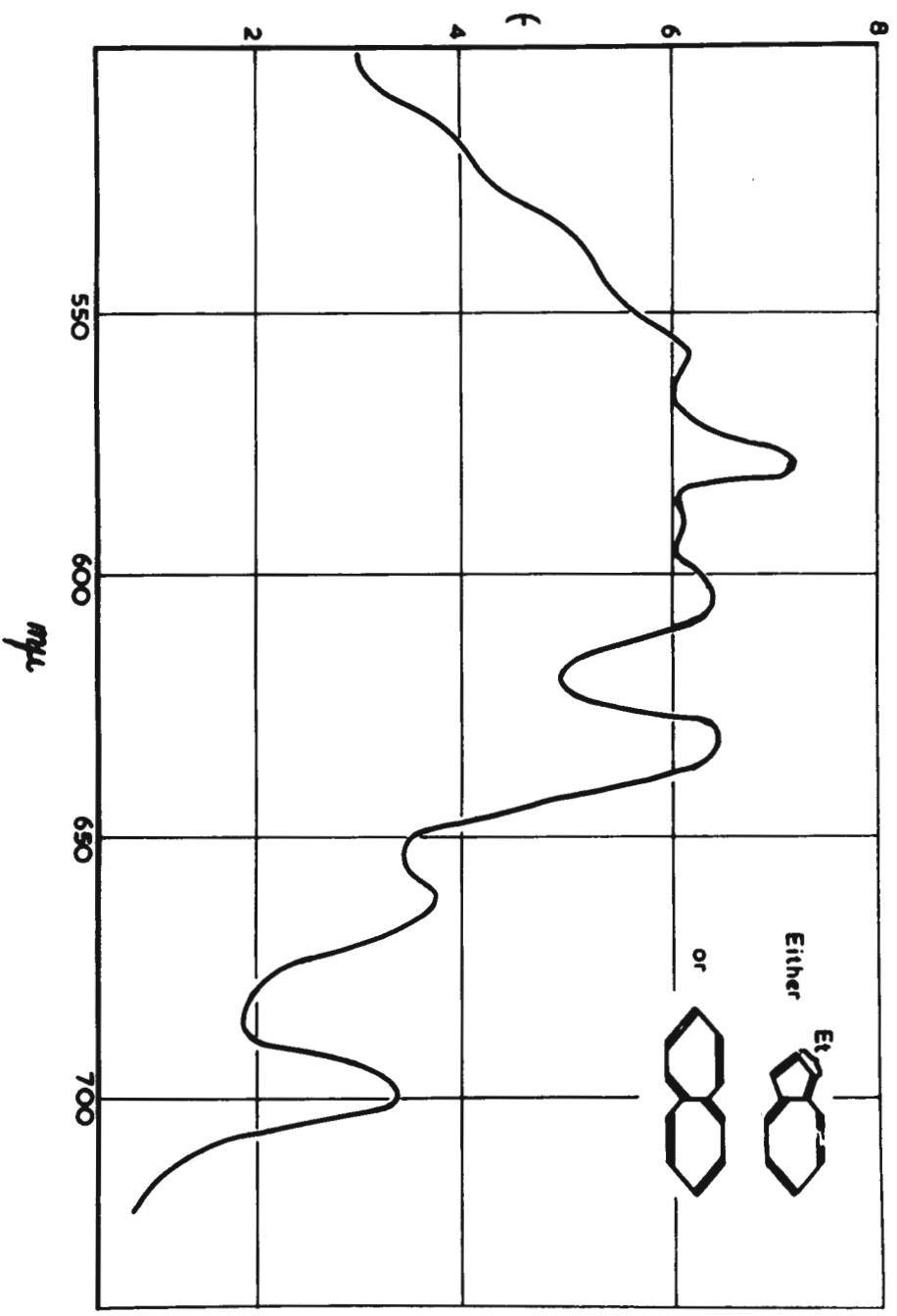
Graph VII

Thus the main product isolated was a colourless hydrocarbon fraction which formed a crystalline picrate m.p. 121-122°C. and which is concluded to be a mixture of dimethyl-naphthalene. The naphthalene structure was definitely confirmed by a comparison of its ultra violet absorption spectrum curve with that of 2,7-dimethyl naphthalene (Leszle, J. prakt. chim., 1925, 117-8, 401), see graph VII.

This rearrangement to a naphthalene structure indicates that the heptalene structure is not a very stable one, and that it cannot be produced by dehydrogenation with the same facility as azulene.

Attempts to produce a heptalene derivative using other standard methods of dehydrogenation were equally unsuccessful. Thus the products from the dehydrogenation with sulphur and with chloranil all showed absorption of ultra violet light less than that of the starting material. Pure heptalene on the other hand would be expected to have a very intense absorption at least equal to that of azulene.

Since it was considered that the long contact of the material with the catalyst in the liquid phase dehydrogenation might be the cause of the rearrangements, attempts were made to dehydrogenate rapidly the material in the vapour phase. An apparatus was therefore constructed to ensure only a brief contact of the vaporised material with the strongly heated catalyst and rapid removal and cooling of the dehydrogenation products in order to avoid rearrangement of the carbon skeleton.

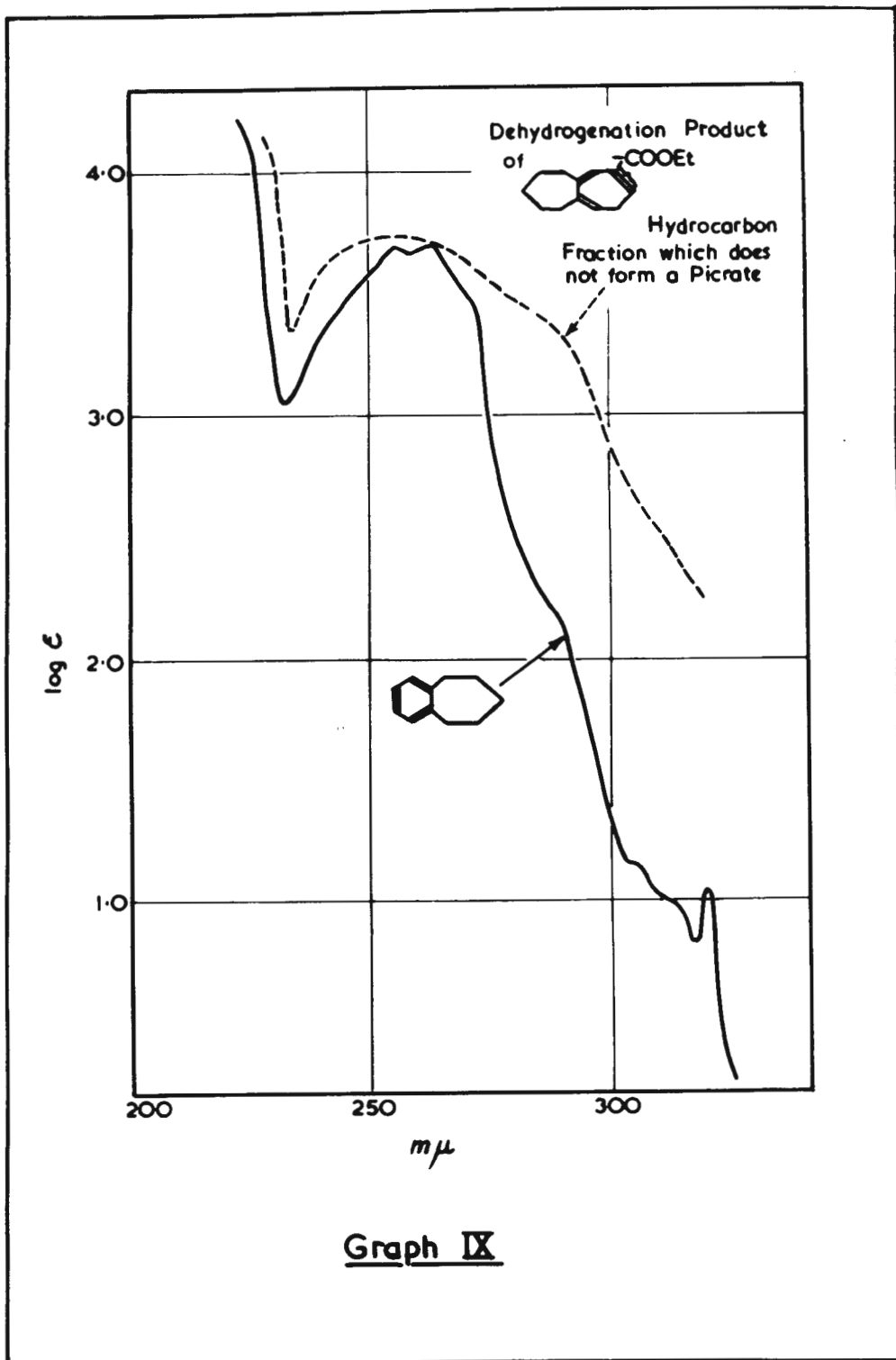


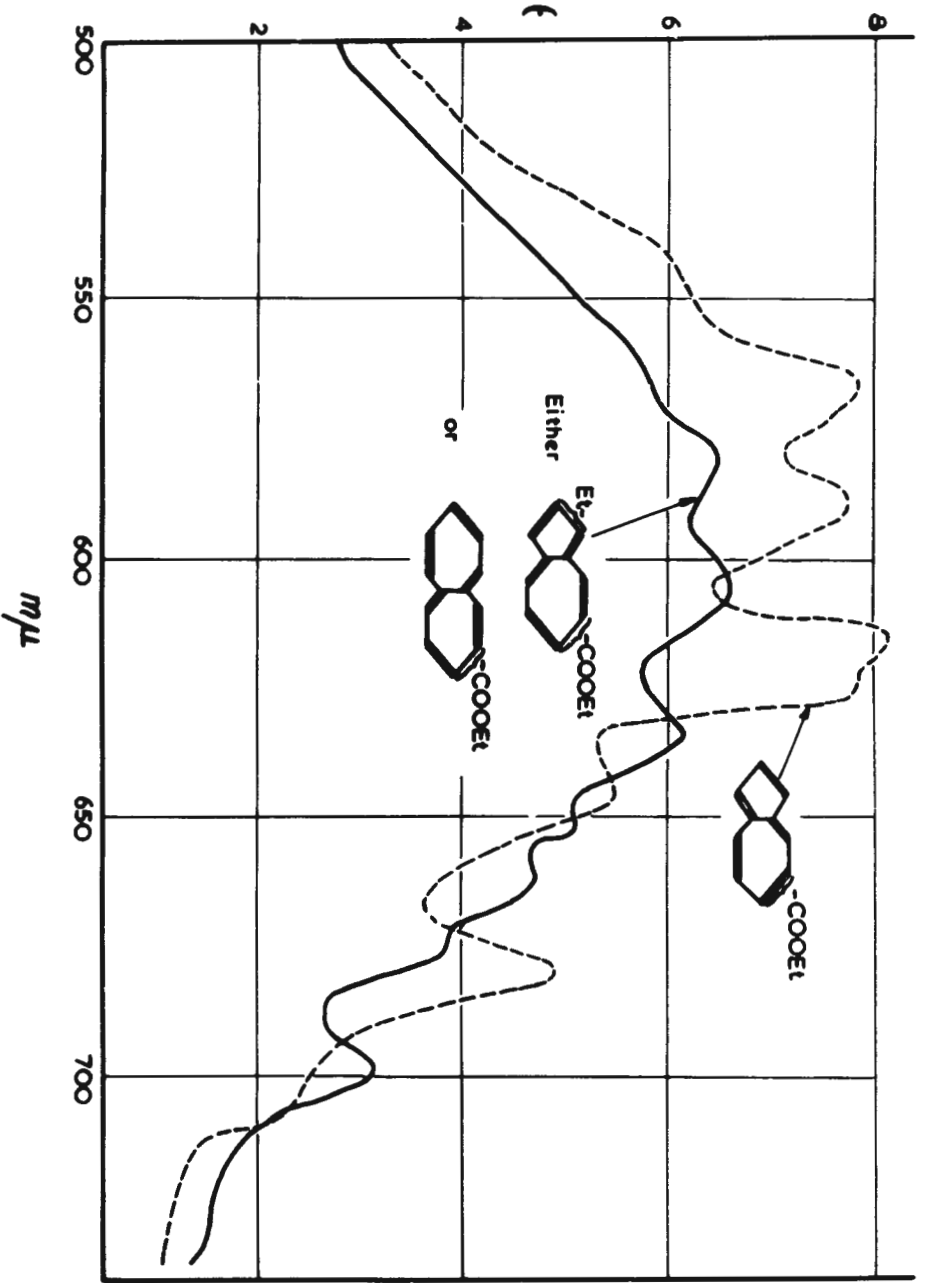
Graph VIII

Under these conditions the product obtained from ethyl [0.5.5]-bicyclo-dodecatriene carboxylate was a deep blue oil, which was divided by distillation at 15 m.m. pressure into two main fractions. The first was a deep blue hydrocarbon fraction b.p. 110-120°C. and the second a deep blue-violet ester fraction b.p. 140-170°C.

The hydrocarbon fraction was dissolved in petrol ether and extracted with 85% phosphoric acid. The azulene-like material was regenerated from this extract by addition of cold water as an intense ultramarine coloured oil. The curve of the visible absorption spectrum of this material which was measured with a Beckmann Spectrophotometer is shown in graph VIII and is seen to be very similar to that of 2-ethyl azulene (Wagner-Juregg, *et. al.*, *Ber.* 1941, 74, 1522) which shows strong absorption maxima at 686.5, 623, 579.5 and 570.5 μ ., and weak maxima at 660, 645.5, 634, 601, 589.5 and 586 μ .. The hydrocarbons which were not soluble in 85% phosphoric acid were mixed with picric acid and a very small quantity of a picrate isolated. The absorption spectrum of the regenerated hydrocarbon shows it to be very similar to the dimethyl naphthalene mixture isolated before from another vapour phase dehydrogenation (e.f. graph VII).

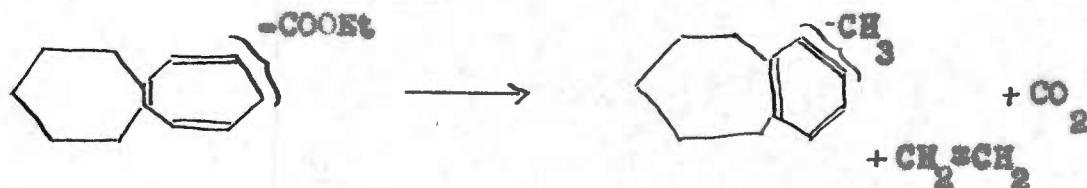
The absorption spectrum of the material which failed to form a picrate has a maximum at 255 μ ., which is at a much lower wavelength than that of the dimethyl naphthalene mixture, which has E_{max} at 280 and is very similar to that of 1:2-benz-cyclo-heptene which has E_{max} at 256 and 263. (see





Graph X

graph IX). It is possible therefore, that it consists mainly of a mixture of methyl 1:2-benz-cyclo-heptenes produced by decarboxylation and rearrangement of the heptatriene ring as shown.



The high boiling ester fraction was extracted with 85% phosphoric acid, as in the case of the lower boiling hydrocarbon fraction, and the azulene-like material regenerated as an intensely blue-violet oil by addition of water. The visible absorption spectrum of this material is shown in graph X. The relatively weak visible absorption of the material compared with that of pure azulenes, indicates that the material contained only a very small quantity of an azulene-like substance. However the yield of even this impure material was very small, and an attempt to obtain the pure substance was not made as it was considered that the impurities would not have any effect upon the position and relative intensities of the absorption bands. The ultra violet absorption spectrum on the other hand would be expected to be considerably affected and cannot be taken to be characteristic of the azulene-like compounds. However the shape of the curve, nevertheless, bears a general resemblance to that of azulene.

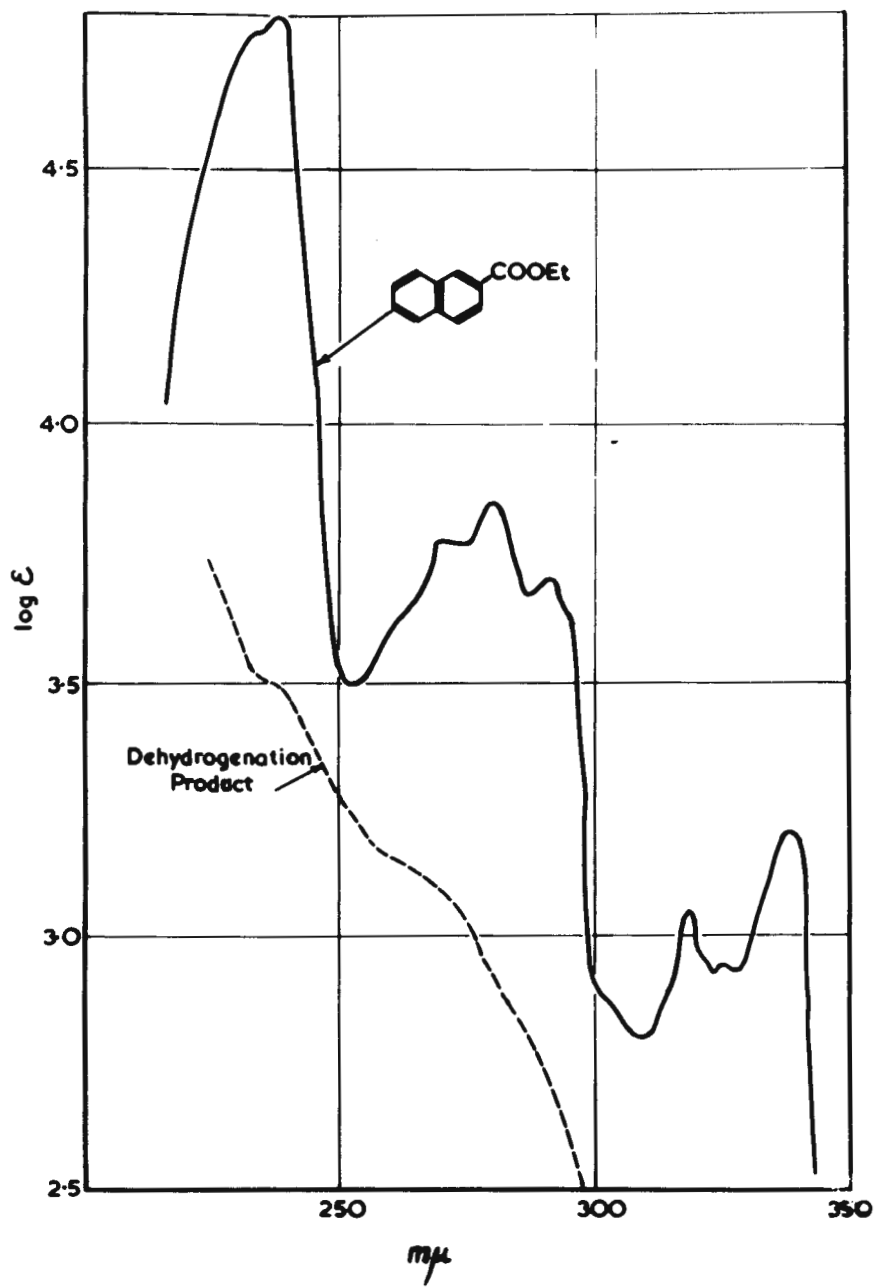
The visible absorption spectrum, though weaker than

that of pure azulenes, is seen to have the same characteristic light absorption of the azulene system, and a comparison of the absorption bands of the blue oil with that of ethyl azulene carboxylate, prepared as a standard for comparison, shows the two substances are very similar, see graph X.

Also the spectral characteristics of 2-ethyl-6-carbethoxy azulene (Wagner-Jauregg *et. al.*, *Ber.*, 1941, 74 1522) which shows strong maxima at 668.5, 608.5, 563 (broad band) and weak maxima at 643, 630.5, 619, 586 and 575.5 μ . are very similar to those of the blue dehydrogenation product.

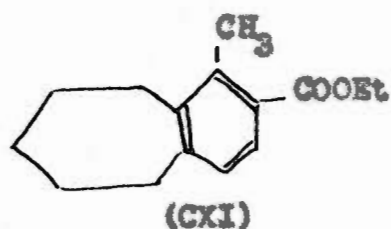
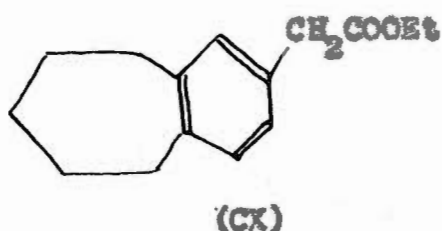
Unfortunately the yield of the blue compounds isolated from the dehydrogenation products of ethyl [0.5.5]-bicyclo-dodecatriene carboxylate was too small to permit a complete study of their structure. However, as these products closely resemble azulene derivatives it seems likely that on catalytic dehydrogenation, the [0.5.5]-bicyclo-dodecatriene carboxylate may have undergone rearrangement to an azulene structure rather than dehydrogenation to a heptalene structure.

The ultra violet absorption spectrum of the ester fraction which did not dissolve in phosphoric acid was found to resemble closely that of ethyl [0.5.5]-bicyclo-dodecatriene carboxylate, and was therefore concluded to be mainly unchanged material. It was not a naphthalene derivative because it rapidly decolourised alkaline potassium permanganate and absorbed much bromine in the cold.



Graph XI

In order to isolate a possible benzenoid rearrangement product from the mixture, the unchanged cyclo-heptatriene acids were removed by oxidation with acetone potassium permanganate and extraction of the acids so formed with weak alkali. The conditions of oxidation were such that all systems containing isolated double bonds would be removed. The product was therefore considered to be either acids having a naphthalene, tetralin or 1:2-benz-cyclo-heptene structure. The study of the absorption spectrum excluded the naphthalene group, because the absorption in the 'near' ultra violet is too weak to be compatible with such a structure (c.f. the absorption spectrum of ethyl 2-naphthoate graph XI). Of the remaining two structures possible, the 1:2-benz-cyclo-heptene rearrangement products such as (CX) and (CXI) are the most probable.



Although these investigations have led to only a partial identification of the dehydrogenation products of ethyl [0.5.5]-bicyclo-dodecatriene carboxylate by a higher speed vapour phase dehydrogenation, they have shown that a high proportion of partially dehydrogenated systems are produced, which are rearrangement products of the [0.5.5]-

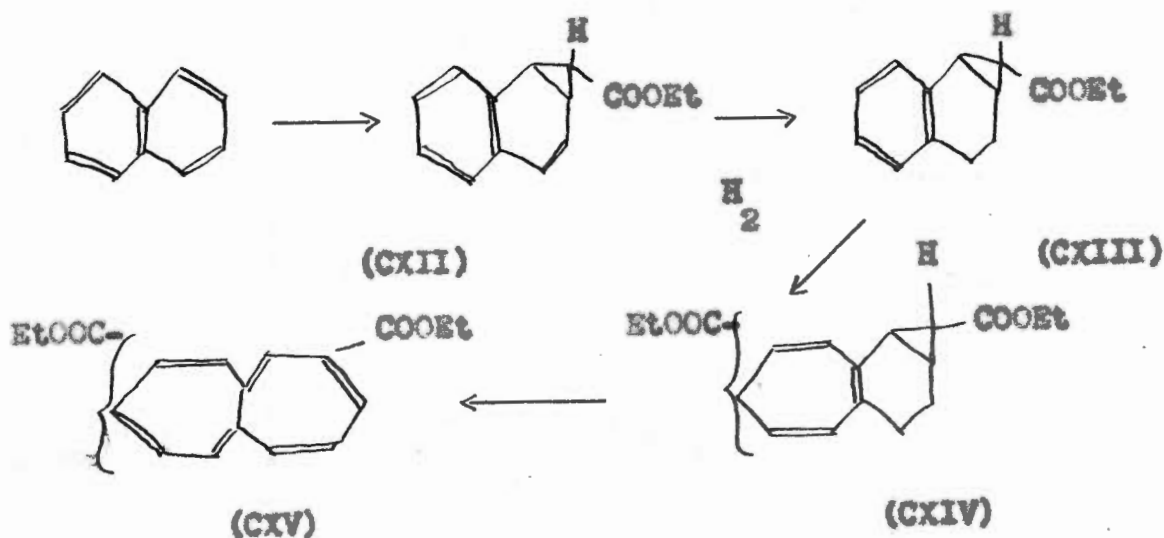
58/bicyclo-...

bicyclo-dodecane ring system. That is, during the reaction, rearrangement of the system precedes its complete dehydrogenation. It is concluded therefore that even if heptalenes derivatives are fairly stable systems, the corresponding partially saturated intermediates containing only three double bonds are not sufficiently stable substances to allow their dehydrogenation to heptalenes by the normal high temperature techniques.

59/Attempted...

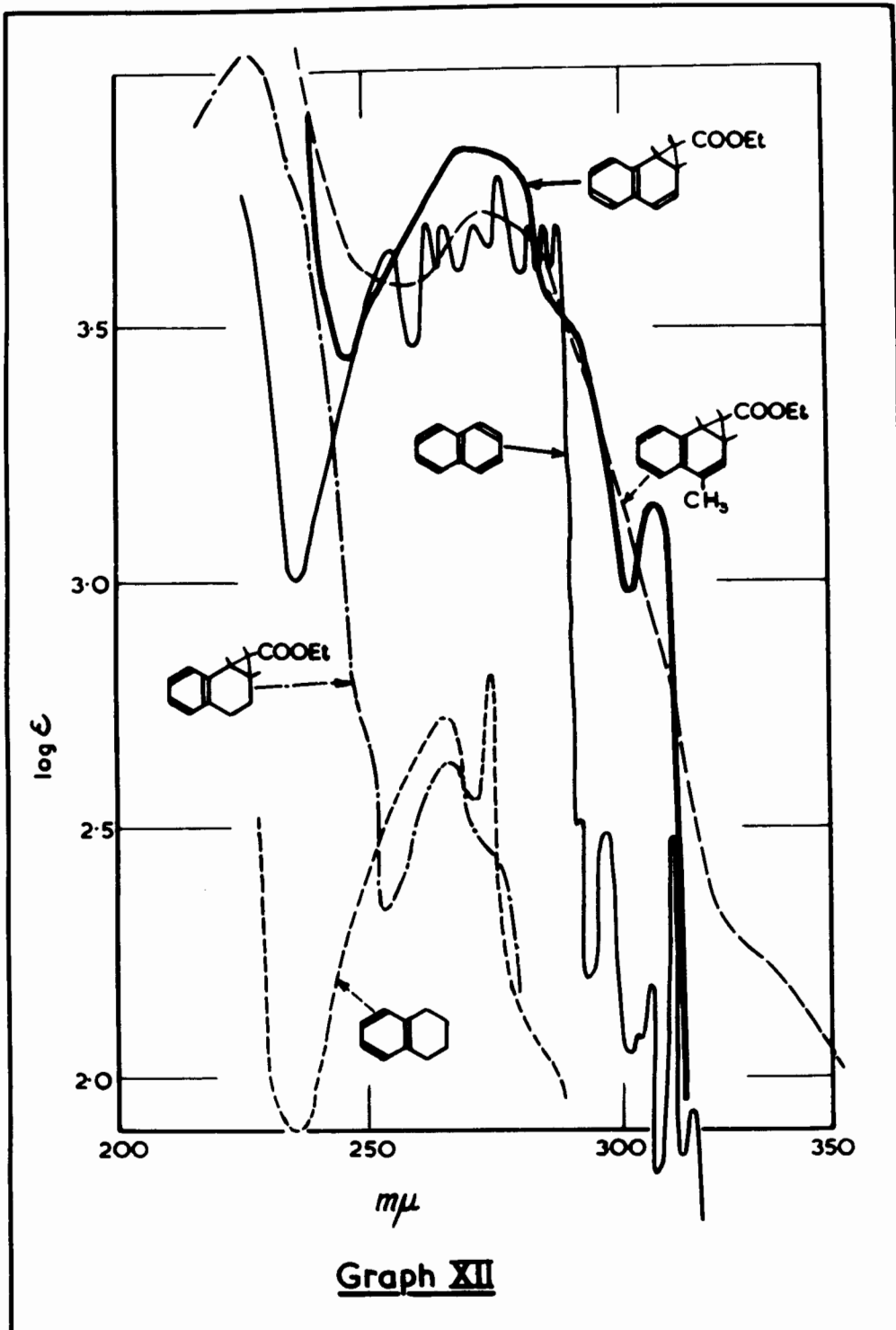
ATTEMPTED SYNTHESIS OF HEPTALENES FROM NAPHTHALENE

Another possible synthesis of heptalene attempted, and which makes use of the Buchner reaction is shown below:-

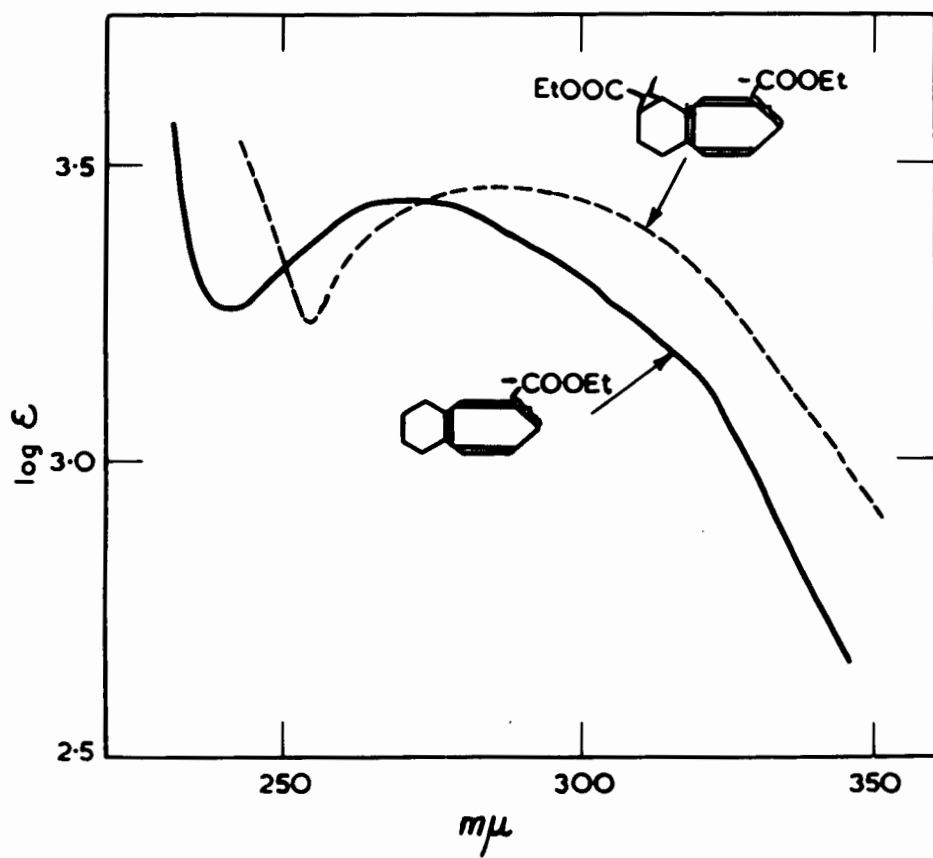


This mode of approach was chosen although the rearrangement in the last stage was open to doubt, because the method has the great advantage of giving compounds which are already highly unsaturated and therefore require but little dehydrogenation to yield the fully unsaturated heptalene derivative (CXV).

The ethyl benz-norcaradiene carboxylate (CXII) was prepared by the method of Buchner and Hadiger (Ber., 1903, 36, 3502) and reduced with hydrogen in the presence of a mild palladium catalyst to ethyl benz-norcaradiene carboxylate (CXIII). Only one molecule of hydrogen was added under these conditions. The hydrogenation of (CXII) to (CXIII) was carried out in order to avoid the possible addition of a second molecule



Graph XII



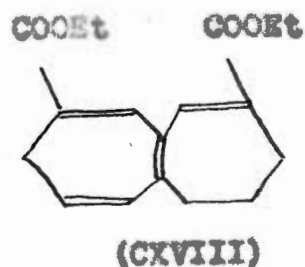
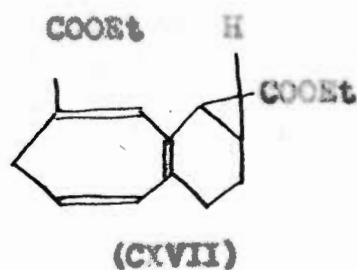
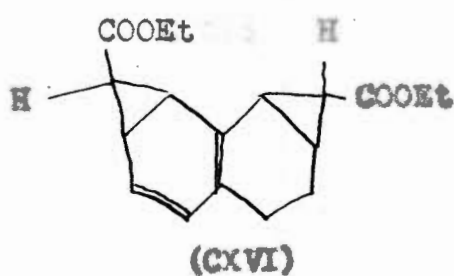
Graph XIII

of ethyl diazoacetate to the naphthalene ring which had already undergone condensation with ethyl diazoacetate. The ethyl benz-norcaradiene carboxylate was then retreated with ethyl diazoacetate under conditions favouring the formation of cyclo-heptatriene derivatives, to yield a complex high boiling product which could not be separated by fractional distillation because the diazoacetate polymerisation products have a similar boiling range. When the mixture was hydrolysed in alcoholic solution, a dark tarry acid mixture was obtained, from which only the acid from (CXIII) could be isolated by crystallization. However, a more tractable mixture was obtained by carrying out the hydrolysis in dilute aqueous alkali. Here again the separation of the mono- and dicarboxy acids could not be achieved by crystallization or chromatography. However it was found possible by esterification and fractional distillation, to get a partial separation of the two esters.

The curve of the absorption spectrum of the new ester is shown in graph XIII. It is quite different from that of the starting material (CXIII) and is very similar to that of cyclo-heptatriene systems.

As in all cases of diazoacetate addition to a benzoid nucleus, two types of condensation product are possible, either the norcaradiene or the cyclo-heptatriene type. Thus in this instance the product could have either of the two types of structure (CXVI) or (CXVII). However if the product

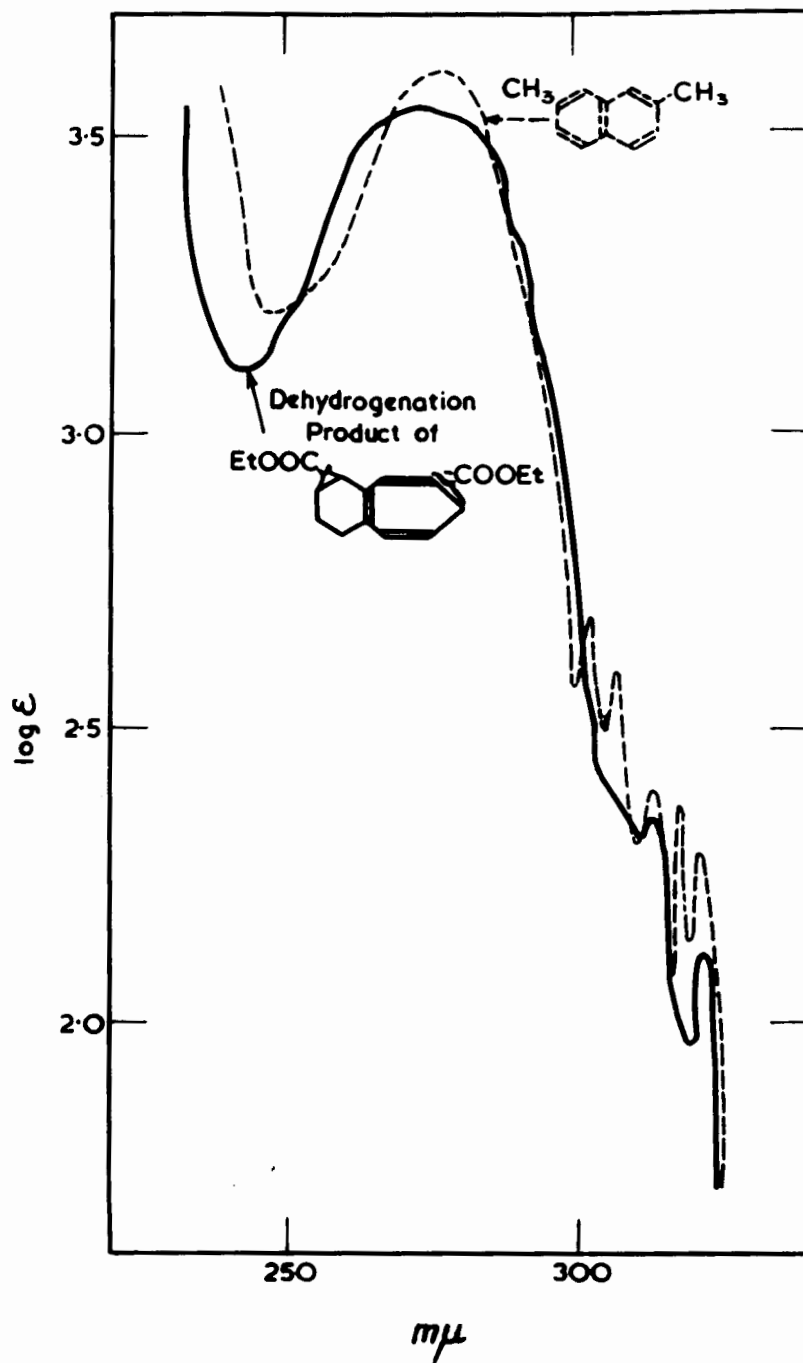
had the structure (CXVI) the ultra violet spectrum would not



be expected to be very different from that of the starting material (CXIII), since by analogy the absorption spectrum of ethyl benz-norcaradiene carboxylate is very similar to that of naphthalene, see graph XII.

The cyclo-heptatriene configuration (CXVII) is more likely to be the structure of the product, for it is not likely that the isolated propane ring system would play much part in the absorption of the molecule in the region measured. This is supported by the observation that the absorption spectrum of ethyl benz-norcaradiene carboxylate is very similar to that of tetralin, see graph XII, the propane ring system having very little effect upon the position or intensity of absorption of the hydroaromatic system. The structure (CXVIII) is definitely excluded, for such a molecule would undoubtedly show much stronger absorption of ultra violet light than that of the product obtained.

Although, as was expected, only one ring had undergone expansion, it seemed possible that catalytic dehydrogenation might bring about a rearrangement, together with removal of hydrogen, to yield the required heptalene system.



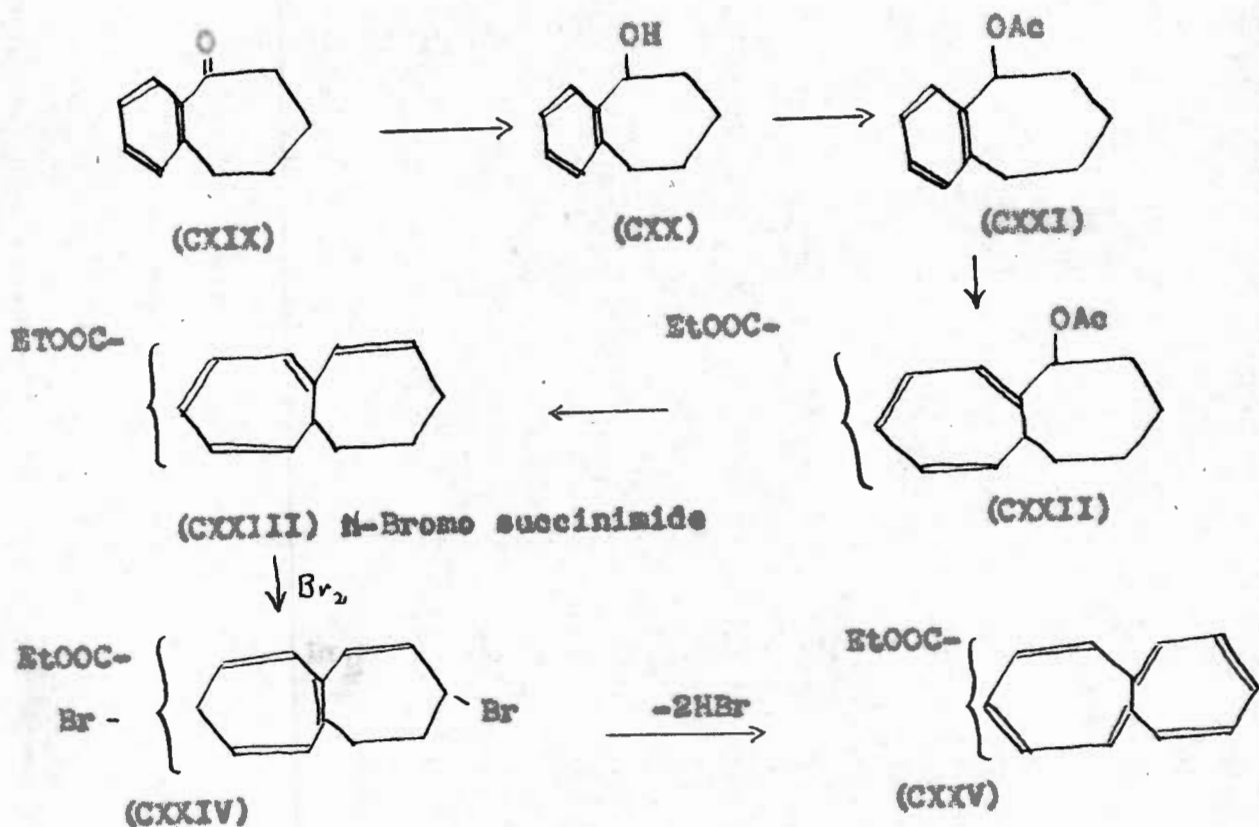
Graph XIV

However, the product of dehydrogenation was a hydrocarbon mixture with a naphthalene structure, as was clearly shown by the curve of the absorption spectrum (see graph (XIV)).

When first distilled the hydrocarbon had a pale blue colour which may have been due to the presence of azulene-like material.

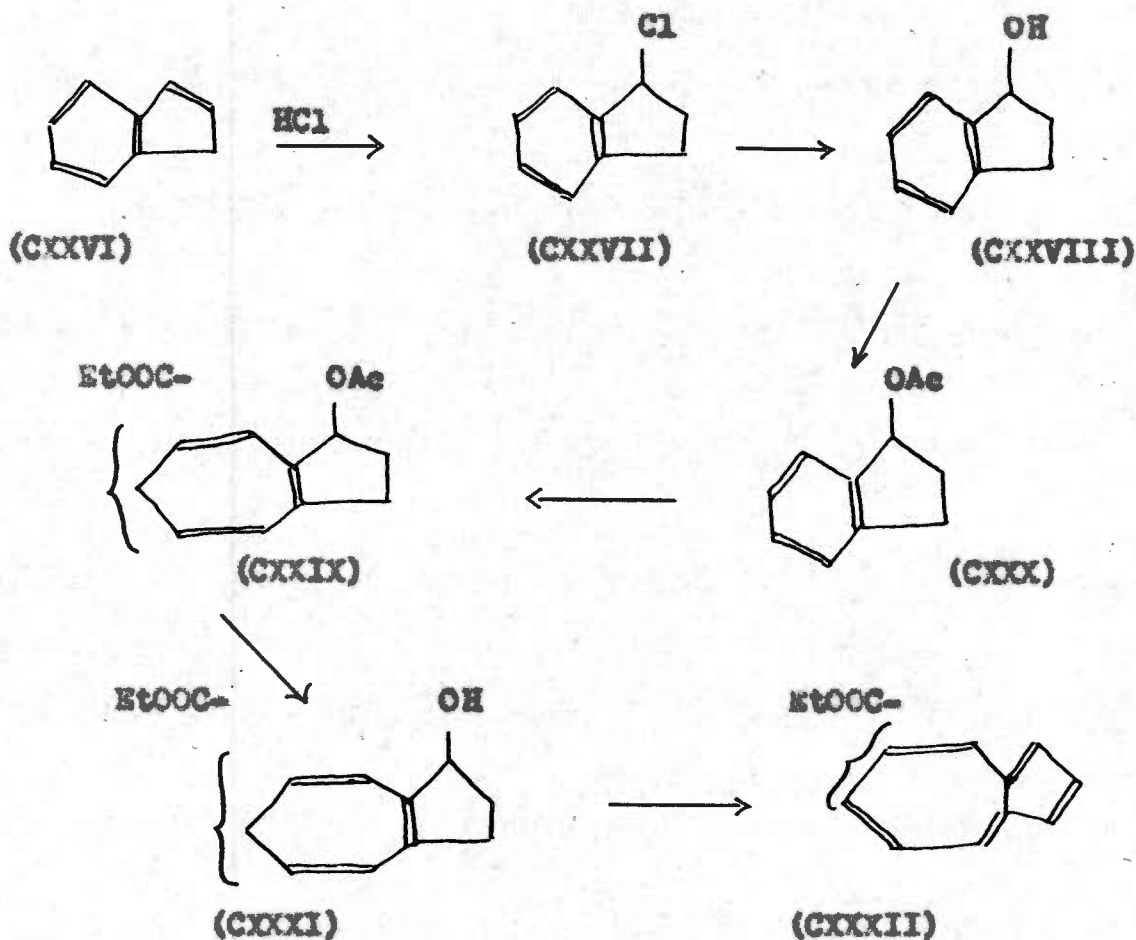
ATTEMPTED SYNTHESIS OF HEPTALENES USING DEHYDROBROMINATION REACTIONS.

Although the repeated failure to prepare heptalene derivatives by dehydrogenation techniques does not prove that this system is not capable of existence it does suggest that the system is not as stable as was expected on theoretical grounds, and that milder reactions than catalytic dehydrogenation must be employed in building up this structure. It was therefore decided to attempt to synthesise heptalenes in the following manner:-



However, as few of these steps have been investigated, a

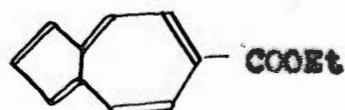
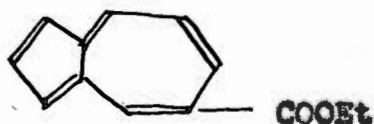
model synthesis of azulene was carried out because of the greater ease of elucidating the structure of the products. It was proposed to carry out the synthesis in the following manner:-



Chlor-hydrindene (CXXVII) was prepared by the method of Haworth (J. 1947, 369) from indene (CXXVI) and converted to hydroxy-hydrindene (CXXVIII), using a method similar to that of Weingerber (Ber., 1911, 44, 1944). The acetoxy-hydrindene (CXXX) was then obtained by acetylation at 100°C. with acetic anhydride.

The condensation of the acetate with ethyl

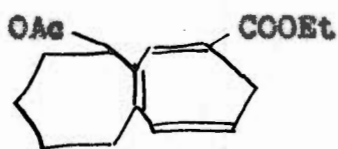
diazosacetate was carried out in the normal manner and yielded a deep blue product which obviously contained some azulene compounds. It was not possible to isolate the cycloheptatriene intermediate (CXXIX) or the corresponding alcohol (CXXXI), because of the ease with which these compounds eliminate hydrogen to yield azulene derivatives. Thus ethyl azulene carboxylate was formed by distillation of the crude acetate (CXXXIX) from sodium carbonate, the product formed being probably a mixture of the 5- and 6-isomers (CXXXIII) and (CXXXIV), respectively.



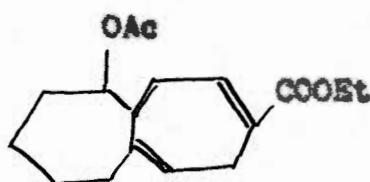
Azulene was produced by distillation of the acid mixture from its copper salt.

Since the course of these reactions clearly indicated that acetates such as (CXXX) undergo the normal Buchner rearrangement reaction 2:3 benz-cyclohepten-1-yl acetate (CXXI) was prepared from 2:3-benz-cyclohepten-1-ol (CXIX) by reducing it to 2:3-benz-cyclohepten-1-ol,^(CXX) in 80% yield with sodium and alcohol. The 2:3-benz-cyclohepten-1-yl acetate (CXXI) was then prepared in 94% yield by heating it with acetic anhydride. This acetate was found to be much more stable than the corresponding hydrindyl acetate, which easily eliminated acetic acid to give indene on heating.

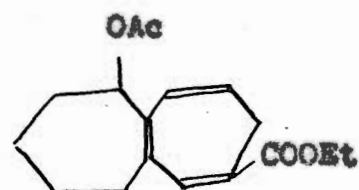
2:3-Benz-cyclo-hepten-1-yl acetate was then treated with ethyl diazoacetate in the usual way, and yielded a high boiling product which could not be obtained pure by fractionation because the nitrogenous impurities have a similar boiling range. The product of the reaction is probably a mixture of the three possible isomers (CXXXV), (CXXXVI) and (CXXXVII), together with bond and stereoisomers.



(CXXXV)



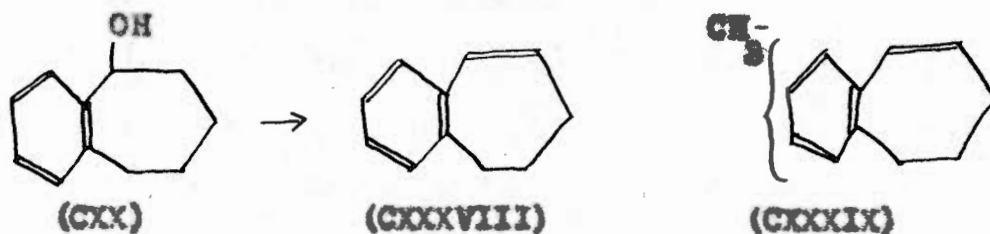
(CXXXVI)



(CXXXVII)

Hydrolysis yielded the corresponding hydroxy acids but satisfactory analytical figures could not be obtained, for the hydroxy acid mixture probably contains a little of the corresponding [0.5.5]-bicyclo-dodecatetraene carboxylic acids such as (CXXIII). The acids were therefore dehydrated with potassium hydrogen sulphate in order to convert them all to the corresponding tetraene acids. The reaction product was then divisible into two fractions, a lower boiling mobile hydrocarbon fraction, and a higher boiling viscous acid fraction.

A comparison of the physical characteristics of this hydrocarbon fraction with that of 1:2-benz-cyclo-hepta-1:3-diene (CXXXVIII) prepared by dehydration of 2:3-benz-cyclo-hepten-1-ol (CXX) reveals a strong similarity.



Besides this both hydrocarbons which have a pleasant petrol-like odour, rapidly decolourise potassium permanganate and absorb bromine in the cold.

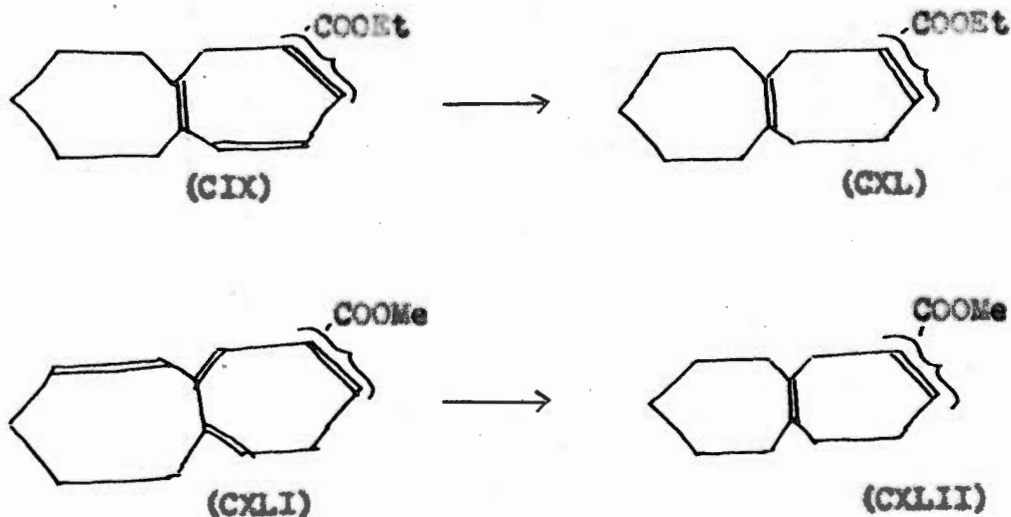
hydrocarbon	b.p.	$n_D^{19.5}$	n_{max}	μ
$C_{12}H_{14}$	air. 100/17 mm	1.5869	13,400	251-7
1:2-Benz- <u>cyclo</u> -heptene	108-110/ 18 m.m	1.5873	15,600	254
$C_{11}H_{12}$				

It was concluded therefore, that under the conditions of dehydration, fission of the carbethoxy group takes place, followed by rearrangement of the heptatriene ring to a benzenoid nucleus, yielding what is probably a mixture of the four possible methyl 1:2-benz-cyclo-hepta-1:3-dienes (CXXXIX).

The higher boiling acid fraction yielded the almost pure [0.5.5]-bicyclo-dodecatetraene carboxylic acid on distillation. The material was not further purified at this 68/stage..

stage because of the difficulty of handling this resinous substance. It was therefore converted to its mobile methyl ester (e.g. CXLI) and purified by fractional distillation.

In order to show that this ester has a [0.5.5]-bicyclo-dodecane structure, and not a rearranged benzenoid one like the low boiling hydrocarbon, the material was hydrogenated in the presence of a mild palladium calcium carbonate catalyst and quickly absorbed hydrogen nearly equivalent to two double bonds; a fact which excludes the presence of a benzenoid nucleus in the molecule. It will be remembered that ethyl [0.5.5]-bicyclo-dodecatriene carboxylate (CIX) (see page 52) under these conditions absorbs hydrogen equivalent to one



double bond, to yield a compound for which the formula (CXL) has been suggested. It follows then if the new acid has the [0.5.5]-bicyclo-dodecatriene structure (CXLI) it would, under the same conditions of hydrogenation, absorb hydrogen equivalent to two double bonds: two double bonds being in

unprotected positions, to yield the same diene ester as ethyl [0.5.5]-bicyclo-dodecatriene carboxylate. In practice the curves of the absorption spectra of (CXL) and (CXLII) were found to be very similar, confirming this hypothesis (see graph III). It was therefore concluded that the new ester is methyl [0.5.5]-bicyclo-dodecatetraene carboxylate.

When this ester was treated with N-bromo-succinimide in the molar ratio of 1:2, bromine equivalent to 1.8 bromine atoms was absorbed. Attempts to purify the bromide for analysis, by distillation, were unsuccessful because the bromide is easily decomposed.

On treatment of the bromide with alcoholic silver nitrate solution, almost all the bromine was removed from the molecule, indicating that the bromine is held as allyl-bromide, not as vinyl-bromide.

The dehydrobromination of this bromide was carried out under varying conditions with different dehydrobrominating agents, but the product always had an absorption of ultra-violet light less than that of the starting material, (CXLI) clearly indicating that rearrangement to weaker absorbing benzenoid structures had taken place.

As the tetraene ester is a very stable compound which may be heated to 250°C. without change, it must be

70/concluded...

concluded that the introduction of two more bonds into the molecule produces some considerable strain which forces it to undergo rearrangement to a more stable structure. Although it has not been found possible to synthesize heptalene derivatives, the work described in this thesis has shown conclusively that heptalenes are not as easily prepared as azulenes, and that the heptalene structure is not likely to be a very stable one.

In considering the stability of the heptalene system it is also significant that material with this structure was not isolated from the products of polymerization of acetylene as were cyclo-octatetraene and azulene, a fact which once again confirms the conclusion that this system does not possess the aromatic stability, predicted for it on theoretical grounds.

EXPERIMENTAL.

The material which did not condense in the distilling flask was collected in a train of wash bottles containing petrol ether (b.p. 80-90°C). When no more nitrile distilled, the petrol solutions were added to the solid nitrile in the distillation flask, the petrol ether evaporated off, and the nitrile distilled at atmospheric pressure as a pale yellow liquid, b.p. 295-310°C. which set to a solid mass on cooling. On redistillation it came over at 304°C. /752 m.m., 40 grams or 17.5% of the theoretical. When the mixture of sulphonate and ferrocyanide was distilled in a glass distilling flask, in 10 gram lots, the yield was much higher, viz 46%. In all, 80 grams of the nitrile was made in two distillations.

2-Aminomethyl-1, 2, 3, 4-tetrahydronaphthalene.

(c.f. Bamberger & Bockmann, Ber., 1887, 20, 1711.)

To 2-naphthonitrile (76.5 g.; 0.5 mol) dissolved in absolute alcohol (800 c.c.) in a round bottom flask (1.5 litre capacity) fitted with a long wide bore copper reflux condenser, was added sodium (80g.) in small pieces. After the first violent reaction, the mixture was heated under reflux until all the sodium was consumed, about two hours. The solution was then added to water (600 c.c.), and acidified with concentrated hydrochloric acid (450 c.c.). The mixture steam distilled free of alcohol and volatile impurities.

The aqueous residue was made alkaline with caustic soda and the liberated amine taken up in ether. The ethereal

solution after drying over calcium chloride, was distilled free of ether and the residue fractionated from sodium at reduced pressure. The fraction boiling at $141^{\circ}\text{C.}/11 \text{ m.m.}$, 38.4 grams or 47% of the theoretical was retained. Bamberger and Bockmann (loc. cit.) report a yield of 54%.

Rearrangement of 2-Aminomethyl-1, 2, 3, 4 -tetrahydronaphthylene

To the freshly distilled amine (38.1 g.), glacial acetic acid (14.2 g.) and water (150 c.c.), contained in a round bottom flask (250 c.c. capacity) was added a solution of sodium nitrite (16.5 g.) dissolved in water (40 c.c.), and the mixture warmed on a water bath for one hour.

The precipitated oil was taken up in ether and after removal of the ether, 16.0 grams of oil remained. The aqueous portion of the reaction mixture was made alkaline and the liberated amine taken up in ether. Removal of the ether left 16.0 grams of recovered amine, which was again treated with nitrous acid to yield a further 10.1 grams of reaction product.

The combined products of the reaction were fractionated at reduced pressure from a claisen flask fitted with a short fractionating column of "Berl saddles". In spite of this it was not found possible to obtain clear-cut fractions (see graph I) and was obviously a mixture of several components. It was however, divided into two main fractions:-

- Fraction (i) b.p. $100-120^{\circ}\text{C.}/13 \text{ m.m.}$ 5.6. grams
- (ii) b.p. $143-153^{\circ}\text{C.}/13 \text{ m.m.}$ 10.0 grams

Fraction (i) contained the isomeric olefins: which reduced potassium permanganate instantaneously in the cold and readily absorbed large quantities of bromine.

Fraction (ii) contained the isomeric alcohols which formed a semicrystalline naphthylurethane, which could not be purified.

Found C, 80.8%; H, 8.7%

C₁₁H₁₄O required C, 81.5% H, 8.6%

Oxidation of Fraction (i)

- c.f. (a) oxidation of 3:4 benz-cyclo-heptadiene
Kipping and Hunter, J.C.S. 1903, 83, 249.
- (b) oxidation of cyclo-heptene
Ruzicka & Brugger, Helv.Chim.Acta. 1926,
9, 399.

The olefin fraction (i) 5.6 g.) was mixed with water (100 c.c.) in a three necked flask equipped with a very rapid stirrer and a dropping funnel. To the vigorously stirred mixture was added potassium permanganate (12.3 g.), dissolved in ice water (500 c.c.), over a period of one hour. When the addition was complete the solution was filtered from the manganese dioxide which was washed with hot water. The combined filtrates were acidified and extracted with a small quantity of ether; ethereal extract I. The aqueous solution was then strongly acidified with concentrated sulphuric acid and then

75/several...

several times extracted with ether, ethereal extract II.

Phthalic Acid

Ethereal extract II on evaporation yielded a crystalline solid which was easily recrystallized from benzene. It was found to melt at about 183°C . with a sublimate of long needles m.p. $128-9^{\circ}\text{C}$. A mixed m.p. with pure phthalic anhydride showed no depression.

The mother liquors from this crystallization were added to the ethereal extract I, which on evaporation yielded an oil (0.8 g.) which could not be crystallized. It was distilled at reduced pressure with some decomposition, and yielded 0.5 grams of a pasty crystalline mass, which was crystallized from benzene.

Homophthalic Acid.

After three crystallizations the melting point was constant m.p. $140-1^{\circ}\text{C}$. (0.0 lg.). Mixed m.p. with phthalic anhydride showed considerable depression. It reduced alkaline potassium permanganate on warming. Davies and Poole, J.C.S., 1928, 1618 give the m.p. of homophthalic anhydride as $141-2^{\circ}\text{C}$. The material was dissolved in a drop of 10% potassium hydroxide and then reprecipitated with dilute sulphuric. The acid was filtered off, dissolved in benzene and allowed to crystallize by evaporation m.p. $178-80^{\circ}\text{C}$. Davies and Poole give the m.p. of homophthalic acid as 181°C . No other acid could be obtained in a pure condition.

Separation of the alcohol fraction (ii)

The alcohol fraction (b.p. 143-153°C./13 m.m. 5.3 g.) was dissolved in benzene (20 c.c.) and refluxed with phthalic anhydride (2.5 g.) for 5 hours. Then a 10% sodium carbonate solution was added until the mixture was faintly alkaline and the insoluble material taken up in ether, ethereal extract III. The aqueous fraction was made strongly alkaline and the mixture placed under reflux for 10 minutes. It was then extracted with ether, ethereal extract IV.

The ethereal extract III after drying over anhydrous sodium sulphate was distilled free of ether. The residual alcohol (3.85 g.) was distilled at reduced pressure. The main fraction boiling 140-148°C./15 m.m. was thought to be benzocyclo-heptenol still contaminated with a little of the isomeric primary alcohol.

The alcohol b.p. 140-8°C./15 m.m. (3.3 g) dissolved in glacial acetic acid (20.0 c.c.) in a three necked flask equipped with a stirrer and a dropping funnel was treated dropwise with a solution of Chromic oxide (2.0 g. i.e. $1\frac{1}{2}$ times the theoretical quantity was added to completely oxidize any of the primary alcohol to the corresponding acid) dissolved in water (20 c.c.) and acetic acid (40 c.c.) at 70°C over a period of one hour. The solution was allowed to stand for a further two hours at 70°C to complete the reaction. The mixture was then poured into an equal volume of water and extracted several times with ether. The combined ethereal

solutions were shaken with an equal volume of 10% caustic soda solution and then washed with water and finally dried over anhydrous sodium sulphate; ethereal extract V. The alkali soluble fraction was acidified and the liberated acid taken up in ether; ethereal extract VI. The solvent was removed under vacuum and left 0.9 grams of oil, which on distillation yielded a crystalline acid (0.6 b.) m.p. 85°C. which could not be purified because of its high solubility in all organic solvents. Mixed m.p. with that obtained from the oxidation of 1,2,3,4-tetrahydro-2-naphthyl carbinol, (described later) viz. impure 1,2,3,4-tetrahydro-2-naphthoic acid, showed some depression.

1,2-Benz-cyclo-hepten-4-one.

The ethereal extract V yielded on removal of the ether 2.1 grams of oil which was dissolved in alcohol (10 c.c.) and heated for 15 minutes under reflux with semicarbazide hydrochloride (2 g.) and Sodium acetate (2.5 g.) in water (10. c.c.). After standing for a week oily crystals separated out and were filtered off at the pump and washed with 50% alcohol (2 c.c.). The semicarbazone was recrystallized from alcohol in large needles m.p. 185-8°C.

	Found	C, 66.1%	H, 6. 7%
$C_{12}H_{15}ON_3$	requires	C, 66.4%	H, 6. 9%

The pure semicarbazone (0.04 g.) was warmed with a few drops of alcohol and diluted hydrochloric acid. The liberated ketone was taken up in ether and after the removal

of the ether under reduced pressure 0.031 grams of oil remained, which quickly set to a mass of colourless, odourless crystals, m.p. 41-2°C.

Phenylhydrazones

The ketone (0.03 g.) was warmed with a solution of phenylhydrazine (0.03g.) in 40% acetic acid (0.4 c.c.). The derivative was filtered off and crystallized as small rhombohedra, m.p. 91-2°C. from dilute acetic acid .

1:2- Benz-cycle-heptenol

The residual alcoholic solution from the preparation of the semicarbazone of 1:2-benz-cycle-hepten-4-one was mixed with an equal volume of water and extracted with ether. The ethereal solution was washed with alkali and dried over sodium sulphate. The ether was removed and the residue (1.9 g.) distilled to yield an alcohol, probably 1:2-benz-cycle-heptenol b.p. 140-1°C /15 m.m. (0.8 b.). The residue was a mixture of high boiling semicarbazones. It was boiled with dilute hydrochloric acid and alcohol and the liberated ketones extracted out with ether. The residue after the removal of the ether was distilled as a colourless, odourless oil b.p. 139-148°C /15 m.m. (0.7 g.). The semicarbazone was then reformed but no new carbonyl compound could be isolated, by fractional crystallization.

1,2,3,4- Tetrahydro-2-naphthyl Carbinol.

The ethereal extract IV (page 76) which contained the primary alcohol (prepared by the hydrolysis of the phthalyl ester) was distilled and boiled at 152-4°C /15 m.m. (1.1g). It is thought to be pure 1,2,3,4-tetrahydro-2-naphthyl carbinol.

Oxidation

The alcohol (0.8 g) was dissolved in acetic acid (5.0 c.c.) and treated dropwise with a solution of chromium oxide (0.33 g.) dissolved in water (5.0 c.c.) and acetic acid (10 c.c.) at a temperature of 70°C over a period of 1½ hours. The mixture was allowed to remain in the bath for another 1½ hours at 70°C. The solution was then mixed with an equal volume of water and extracted with ether. The ethereal solution was extracted with 10% caustic soda solution and finally washed with water and dried over sodium sulphate, ethereal extract VII.

1,2,3,4- Tetrahydro-2-naphthoic Acid.

The aqueous layer was strongly acidified with sulphuric acid and extracted with ether. When the ethereal extract was dried over sodium sulphate, the ether removed, 0.16 grams of crystalline acid remained. It was crystallized by evaporation from acetone m.p. 85°C (not sharp). It could

80/ not...

not be further purified because of its high solubility in all organic solvents and because it precipitated as an oil from mixed solvents. However, when mixed with an authentic sample of 1,2,3,4-tetrahydro-2-naphthoic acid m.p. 91°C., the melting point was 89-92°C and it was therefore considered to be mainly 1,2,3,4-tetrahydro-2-naphthoic acid.

1,2,3,4-Tetrahydro-2-naphthaldehyde.

On removal of the ether from the ethereal extract VII, (see above), 0.45 grams of oil remained. It produced a colour with Schiff's reagent, and slowly formed a solid dimedone compound.

Semicarbazone: The remainder of the aldehyde (0.4 g.) was warmed with semicarbazide hydrochloride and sodium acetate in 50% alcohol solution and allowed to stand. After a few days an oily mass of crystals was formed. They were filtered off and washed with 50% alcohol.

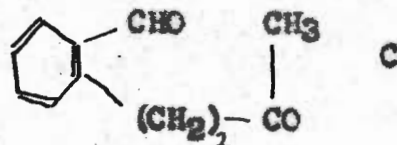
On crystallization of the material from alcohol it was easily separated into a fairly soluble semicarbazone (A) and a rather insoluble semicarbazone (B).

The soluble fraction (A) was recrystallized from alcohol m.p. 188-92°C; less than 0.01 grams. When mixed with the semicarbazone of 1:2-benz-cyclo-hepten-4-one m.p. 185-8°C., a considerable depression was observed. Too little remained for analysis.

The semicarbazone (about 0.005 g) was hydrolysed and the liberated aldehyde treated with a drop of phenyl hydrazine in 50% acetic acid, a crystalline compound was formed but unfortunately there was too little for satisfactory crystallization. The phenyl-hydrazone of 1,2,3,4, - tetrahydro-2-naphthaldehyde has been prepared by Weil and Ostermeier, (Ber., 1921, 51, 3219.) but the semicarbazone is not known.

The rather insoluble semicarbazone

(B) was recrystallized from



alcohol m.p. 218-220°C in very fine crystals. It is thought to be the semicarbazone of a keto-aldehyde such as shown above (C)

Found C, 53.4% ; H, 5.7%

calculated for C₁₃H₁₆O₂N₆ : C, 53.8% ; H, 6.2%

1,2,3,4 - Tetrahydro-2- naphthoic Acid.

(.f. Beeyer. Ann. 1891, 266, 198)

2-Naphthoic acid (1 g.) was dissolved in 30% potassium hydroxide (3 c.c.) and water (10 c.c.) and 4% sodium amalgam (20 g.) added in portions the size of a pea. When the first vigorous reaction had subsided, it was gently heated under reflux. After the solution of the amalgam a fresh portion (20. g) was added and the occasional addition of amalgam continued until a test portion on neutralization was fairly stable to alkaline potassium permanganate, i.e. after the use of about 160 grams of amalgam, over a period of seven hours heating.

After filtration, the acid was precipitated with dilute sulphuric acid and filtered off. It was dissolved in the minimum of sodium carbonate solution, cooled in an ice/salt mixture and concentrated potassium permanganate solution quickly added until the colour remained. The solution was then decolourized with a solution of sodium sulphite and dilute sulphuric acid. The precipitated acid was filtered off, dissolved in methyl alcohol, boiled with animal charcoal and filtered. The material so obtained formed needles m.p. 94.5°C. (Baeyer, loc. cit. records the melting point of the pure acid as 96°C.)

Ortho-iodobenzoylchloride.

Crude ortho-iodobenzoic acid (100 g. ; obtained from anthranilic acid by the Sandmeyer reaction) was refluxed for 1.5 hours with a large excess of thionyl chloride, (4-5 mols). After the removal of the excess thionyl chloride, ortho-iodobenzoyl chloride (97 g. ; 90% of the theoretical) was obtained by distillation, b.p. 162° /25 m.m. m.p. 32°C.

c.f. Cohen and Raper J., 1904, 85, 1272

(Ortho-iodobenzoyl)- aniline.

Ortho-iodobenzoyl chloride (158g.) dissolved in dry benzene (600 c.c.) was cooled in ice and treated slowly with shaking with a solution of aniline (120 g.) in carbon tetrachloride (250 c.c.). The precipitated anilide was filtered off and freed from aniline hydrochloride by thorough washing with dilute hydrochloric acid and water. A further small quantity of anilide was obtained by evaporating the washed and dried benzene/carbon tetrachloride solution. The yield was 185 grams or 97% of the theoretical. It was only slightly soluble in ether, and formed colourless needles, m.p. 142.5° from alcohol.

c.f. Rapson & Shuttleworth J., 1941, 488.

Ortho-iodobenzaldehyde.

The anilide (100 g.) suspended in dry toluene (100 c.c.) was treated with phosphorous penta-chloride (65 g.) and heated

on a water bath until the evolution of hydrochloric acid gas ceased. The residue obtained after the removal of the toluene and phosphorous oxychloride under reduced pressure was dissolved in the minimum of ether, well cooled in a freezing mixture and treated with a solution of anhydrous stannous chloride (120 g.) in dry ethereal hydrochloric acid (200 c.c.). Much heat was produced. After two hours standing and shaking, the clear ether was decanted and the orange yellow crystals added slowly with vigorous stirring to water and ether. (More vigorous conditions caused extensive polymerization).

The mixture was steam-distilled, the aldehyde taken up in ether, washed with sodium carbonate solution and water, and finally dried over anhydrous sodium sulphate. After the removal of the ether the residue was distilled and yielded the pure aldehyde, 55 g. or 77% of the theoretical; b.p. 129°C./15 m.m., m.p. 37°C.

c.f. Stuart J., 1888, 53, 141

Wilgeradt & Rieke, Ber., 1906, 38, 1479.

O-Iodo-2-benzylidene- α -tetralone.

To o-iodo-benzaldehyde (10 g.; 0.072 moles) and α -tetralone (10.5 g.; 0.072 moles) was added potassium hydroxide (2 g.) dissolved in alcohol (7 c.c.). After one hour the precipitated crystals were filtered off and crystallized from alcohol, m.p. 83°C., pale yellow prisms.

Found: C, 56.67% ; H, 3.64%

$C_{17}H_{13}OI$ requires : C, 56.69% ; H, 3.64%

Attempts were made to react this compound with magnesium in the preparation of the Grignard reagent in the normal way but the reaction could not be started with either iodine or ethyl bromide.

In another attempt the magnesium was activated before use by treating it with an ethereal solution of ethyl bromide until a vigorous reaction had set in. The ether was then sucked off, the magnesium quickly covered with dry ether and the aryl halide dissolved in ether added dropwise. The slight reaction still in progress due to the presence of a small quantity of ethyl bromide was immediately stopped and a curdy white precipitate was formed and the reaction could not be started.

Finally when the aryl halide was mixed with ethyl bromide in the molar ratio of 3:1 a sluggish reaction seemed to take place but the bulk of the starting material was recovered from the reaction mixture together with a small quantity of intractable polymer. No iodine was found in the aqueous layer.

Ethyl o-Bromo-benzyl-2-cyclo-hexanone-2-carboxylate.

Potassium (18.5 g.; 0.47 gram atoms, a slight excess), was powdered in boiling toluene (250 c.c.) and ethyl cyclo-hexanone-2-carboxylate (74 g.; 0.44 moles, b.p. 113-6°c./16 m.m.) added a few drops at a time with shaking to prevent the coalescence of the potassium grains, and at such a rate that the mixture was kept in constant ebullition. When the formation of the potassium derivative was complete, the mixture was treated with o-bromo-benzyl-bromide (109.1 g.; 0.44 moles) and heated under

reflux for five hours. The mixture was then washed with water dried and the toluene removed under reduced pressure. The residue was distilled, the fraction b.p. 205-215°C./0.2 m.m. being collected. This slowly set to a pasty mass of crystals (105 g. 60% of the theoretical) from which 72 g. of pure prisms m.p. 56-57°C. were obtained from petrol ether.

Found: C, 56.4%; H, 5.5%

$C_{16}H_{19}O_3Br$ requires: C, 56.7% ; H, 5.6%

The semicarbazone, crystallized from alcohol in small pale yellow rosettes m.p. 186-9°C.

Found; C, 51.6% ; H, 5.7%

$C_{17}H_{22}O_3N_3Br$ requires C, 51.5% ; H, 5.6%

o-Bromo-benzyl-2-cyclohexanone. (prepared by hydrolysis)

Ethyl o-bromo-benzyl-2-cyclo-hexanone-2-carboxylate (58 g. ; 0.17 moles) was refluxed with 5% alcoholic potassium hydroxide (39.5 g. ; 0.71 moles) for three hours. Most of the alcohol was distilled off and the residue distilled free of alcohol with steam. The insoluble material was extracted with ether and the aqueous portion being reserved for the recovery of o-bromo-benzyl-2-pimelic acid. The ethereal extract was dried with calcium chloride, the ether taken off, and the residue distilled at reduced pressure yielded 8 grs. of the required ketone b.p. 113-140°C./0.05 m.m.

The semicarbazone was prepared and crystallized from alcohol in fine rosettes of pale yellow tablets, m.p. 195-6°C. This melting point was not depressed by admixture with the

semicarbazone of the ketone obtained by the dry distillation of the thorium salt of *o*-bromo-benzyl-2-pimelic acid, prepared from the aqueous layer.

Found: C, 52.1% ; H, 6.0%

$C_{14}H_{18}O_3Br$ requires C, 51.9% ; H, 5.6%

o-Bromo-benzyl-2-pimelic Acid.

The aqueous layer from the last reaction was acidified with hydrochloric acid and extracted with ether. The ether removed left 40 grams of very high boiling acid, the fraction b.p. 225-235°C./0.2 m.m., 20.4 g. was collected as a viscous jelly which could not be crystallized.

o-Bromo-benzyl-2-cyclohexanone was prepared from the acid by distillation of the thorium salt, as follows:-

The purified acid (20.4 g.) dissolved in a little alcohol was titrated with caustic soda (48 c.c.; 2.4N) with phenol phthalein as indicator. To this was added a solution of thorium sulphate until no further precipitation took place. The curdy mass was filtered off and dried to constant weight (29.3 g. at 160°C., about eight hours. It was then distilled in small portions from a silica test-tube fitted with an efficient condensing system at reduced pressure. (c.f. Ruzicka et alia, Hely. Chim. Acta., 1926, 9, 249). The bulk of the combined distillates distilled at 115°C./0.02 m.m., yielding 13.5 g. of the crude ketone, (55% of the theory). It was purified via its semicarbazone. The m.p. 195-6°C was not depressed by the semicarbazone of the ketone prepared by

alkaline hydrolysis.

Found: C, 51.5% ; H, 5.6%

$C_{14}H_{18}ON_3Br$ requires C, 51.9% ; H, 5.6%

The ketone was regenerated by refluxing the combined semicarbazones with dilute hydrochloric acid, extracting with ether and distilling in vacuo, b.p. 117-120°C./0.05 m.m. a colourless mobile oil.

Found: C, 58.4% ; H, 5.7%

$C_{13}H_{16}OBr$ requires C, 58.4% ; H, 5.7%

All attempts to prepare the Grignard compound failed although the precautions recommended by Gilman (J. Amer. Chem. Soc., 1923, 45, 2462.) were rigidly followed. When the ketone was mixed with ethyl iodide in the molar ratio of 3:1 roughly 90% of the ketone was recovered unchanged, the remainder being boiling polymer.

Ethyl Aminoacetate Hydrochloride.

Granular aminoacetic acid (500 g.) was mixed with commercial absolute alcohol (1.6 litres) in a three necked flask (3 litre capacity) fitted with a reflux condenser and an inlet (at least 15 m.m. in diameter to avoid blockage) for gaseous hydrogen chloride.

When the mixture, heated on a water bath, was gently refluxing, dry hydrogen chloride was led in at a rapid rate until all the aminoacetic acid was dissolved, about two hours. The mixture was then cooled under the tap with shaking to avoid the formation of hard lumps. The crystalline mass was filtered off at the pump and washed with a little alcohol. By evaporating the mother liquors a further quantity of material was obtained. The crystals were dried for one hour at 100°C. The yield is 90-95% of the theoretical.

c.f. Harries, Ann 1903, 327, 365.

Hantzsch, Ber 1900, 33, 70.

Ethyl Diazoacetate.

The complicated and tedious process recommended by Womack and Nelson, (Org. Syn., 1944, 24, 56) for the preparation of the ethyl diazoacetate was not found to have any advantage over the older method of Silberred, (J. 1902, 81, 600) and the latter method was used with some improvements. However, the method of recovering all the ether from the ethereal extract recommended by Womack and Nelson gives the best yields.

To Ethyl aminooacetate hydrochloride (140 g., 1 mole) and sodium acetate (3 g.) dissolved in water (250 c.c.) in a litre separating funnel, with a very wide bore tap (2 c.m. dia) to facilitate the rapid removal of the contents, was added sodium nitrite (90 g., 1.06 moles) dissolved in water (200 c.c.) and alcohol free ether (150 c.c. prepared by shaking commercial ether with saturated calcium chloride solution). 10% sulphuric acid (about 10 c.c.) was cautiously added; a little at a time until a vigorous reaction had set in. As soon as the reaction slackened the aqueous layer was run quickly into a flask containing ether (about 150 c.c.), the ethereal layer poured into a separating funnel containing 10% sodium carbonate solution (50 c.c.) and quickly shaken with it to prevent the decomposition of the ethyl diazoacetate.

The aqueous layer was returned to the first separating funnel and the process repeated until the ether layer finally became blue-green in colour. The amalgamated ethereal extracts were then dried over calcium chloride, anhydrous sodium sulphate being found to be too feeble a drying agent for this purpose. The use of calcium chloride does not decrease the yield much and the product obtained is free from water and keeps well.

The ethyl diazoacetate was freed from ether by evaporation at reduced pressure in a Claisen distilling flask fitted with a rather wide-bore capillary tube and the bulb immersed in a stream of tap water to maintain a reasonable rate of evaporation.

The deep yellow mobile ester, contrary to the observation of Wormack and Nelson (loc. cit.) was found to keep almost indefinitely in a dark coloured bottle.

The quantity of ethyl diazoacetate in the product was measured by decomposing it with dilute sulphuric acid and measuring the volume of nitrogen evolved. It was found to be 90-95% pure.

10.4.5]-Bicyclo-undecatriene-carboxylic Acid.

The reaction was carried out in a 500 ccs. three necked flask, equipped with a mechanical stirrer, a small dropping funnel and a reflux air condenser. Tetralin (198 g. 1.5 moles) heated to 140-150°C. in an oil bath, was added dropwise, with constant stirring, diazoacetic ester (56.4 g. ; 0.5 moles) over a period of eight hours. The mixture was then heated for one more hour to complete the reaction. The excess tetralin then distilled off under reduced pressure and the fraction boiling 130-200°C./20 m.m. collected. Several attempts were made to purify this material by fractionation in a Claisen flask fitted with a packed fractionating column, but no pure fraction could be isolated, and the pure ester could only be prepared by reesterification of the pure acid, as described later. The purest fraction obtained after several fractionations was analysed.

Found: C, 75.7% ; H, 8.0%

$C_{14}H_{18}O_2$ requires C, 77.1% ; H, 8.2%

It does not give the characteristic colour reaction of norcaradiene esters with concentrated sulphuric acid. To the crude condensation product (86 g. b.p. 130-200°C./20 m.m.) was added aqueous potassium hydroxide (50% ; 80 c.c.s.) and ethyl alcohol (200 c.c.) and placed under reflux for 12 hours. On cooling it was decanted from the crystalline deposit of the potassium salt of maleic acid and steam distilled until free from alcohol. The residue was extracted with ether to remove the unaponified material. The aqueous layer after acidification was extracted with ether, dried over sodium sulphate, the ether taken off and the residue distilled at 2 m.m. pressure.

Fraction (1) -- 168°C. 2.g. semicrystalline

(11) 168-178°C. 40.g. of sticky, light,
yellow oil.

Fraction (11) on redistillation yielded the pure acid b.p. 161-164°C./1.5 m.m., 31.1 g. which could not be crystallized.

Found: C, 77.0% ; H, 8.3% ; neut. equivalent 190.7
 $C_{12}H_{14}O_2$ requires : C, 77.1% ; H, 8.2% ; neut. equivalent 190.8

Ethyl Bicyclo-(0.4.5)-undecatriene Carboxylate.

The pure acid (20 g., b.p. 161-164°C./1.5 m.m.) was dissolved in absolute alcohol (60 c.c.) and conc. sulphuric acid (6 c.c.) added and refluxed for five hours. Most of the alcohol was then distilled off, water was added and the ester taken up in ether, washed with sodium carbonate solution and finally water. The residue, after the removal of the ether was distilled in vacuo the fraction b.p. 175-8°C./m.m., 16 g. being retained.

Found: C, 77.0% ; H, 8.3%

$C_{14}H_{18}O_2$ requires : C, 77.1% ; H, 8.2%

This material was used in the ultraviolet absorption spectrum measurements, graph (11).

Bicyclo- [0.4.5] -undecatriene Amide.

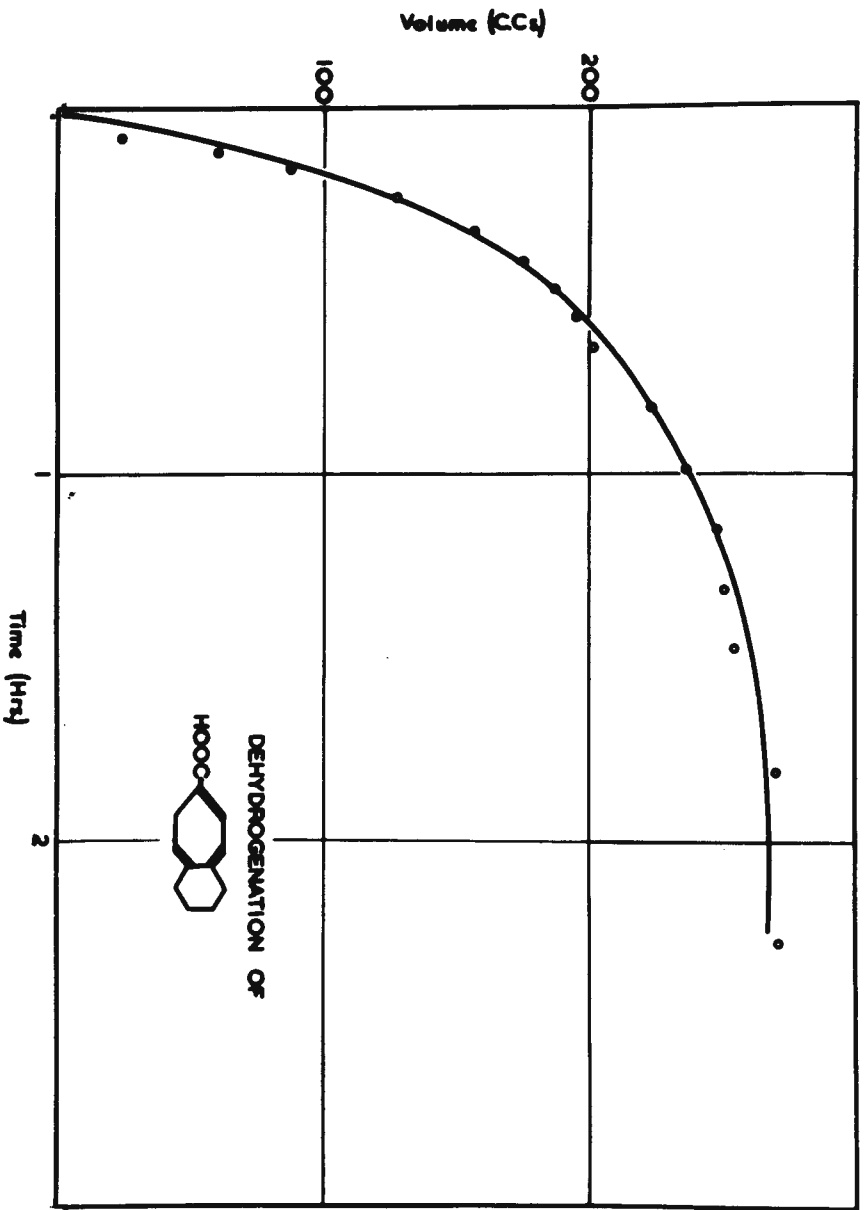
The pure acid (10 g., 0.05 moles) was shaken with phosphorus trichloride (3.6 g. ; 0.026 moles) for one hour and then allowed to stand until the two layers had completely separated. The mixture was then cooled in a freezing mixture and after a short time the acid chloride was easily decanted from the viscous phosphoric acid into a dropping funnel. It was added dropwise to concentrated ammonia solution (50 c.c.) with shaking. A curdy yellow mass, changing to white, was formed. It was taken up in ether and washed with 2% caustic soda solution. On evaporating off the ether a resinous mass remained which was crystallized with difficulty at best from 80% alcohol/water mixture. After five crystallizations a small quantity of the pure amide (0.1 g.) was obtained, m.p. 119.5-121°C

Found: C, 76.2% ; H, 7.9%

$C_{12}H_{15}ON$ requires: C, 75.9% ; H, 7.8%

Bicyclo [0.4.5] -Undecadiene Carboxylic Acid.

The acid was hydrogenated at atmospheric pressure with palladium/calcium carbonate catalyst of Busch and Stöve, (Ber., 1916, 48, 1063); and hydrogen equivalent to 0.9 double bonds was absorbed. The absorption spectrum of the reduced acid is given in graph III. It was an almost colourless, glutinous oil b.p. 155-60°C./1 m.m.



Graph XV

Bicyclo- [0.4.5] -undecane Carboxylic Acid.

Bicyclo- [0.4.5] -undecatriene carboxylic acid (0.647 g.) was dissolved in glacial acetic acid (20 c.c.) and added dropwise with shaking to a mixture of 5% chloroplatinic acid solution (4 c.c.), 2% gum arabic solution (6 c.c.) and glacial acetic acid (5 c.c.) in the hydrogenation flask described by Busch and Stöve (loc. cit.). The material was transferred quantitatively by washing the flasks with a further quantity of glacial acetic acid (N.B. not more than 5 c.c., otherwise there is danger of precipitating the gum arabic.)

The air in the apparatus was replaced with hydrogen and a solution of colloidal platinum, prepared by passing hydrogen for 15 minutes into a mixture of 5% chloroplatinic acid solution (2 c.c.) and 2% gum arabic solution (1 c.c.). The rate of absorption of hydrogen is shown in the graph (IV).

The reaction ceased after hydrogen (326 c.c. at N.T.P., 70 c.c. being subtracted for the reduction of the platinum chloride) equivalent to 2.94 double bonds had been absorbed.

Dehydrogenation Studies

Technique used:-

The material was placed with one tenth of its weight of 20% palladium/charcoal catalyst (Zelinski, Ber., 1925, 58, 1295), in a long necked distilling flask, (25 c.c. capacity) fitted with an inlet tube reaching almost to the bottom of the bulb, which was immersed in a metal bath.

The inlet was connected to a Hein modified Kipp (see "Semimicro Quantitative Organic Analysis-Belcher and Godbert 1945, page 73) for the generation of air-free carbon dioxide, through a purification train consisting of two tubes, the first

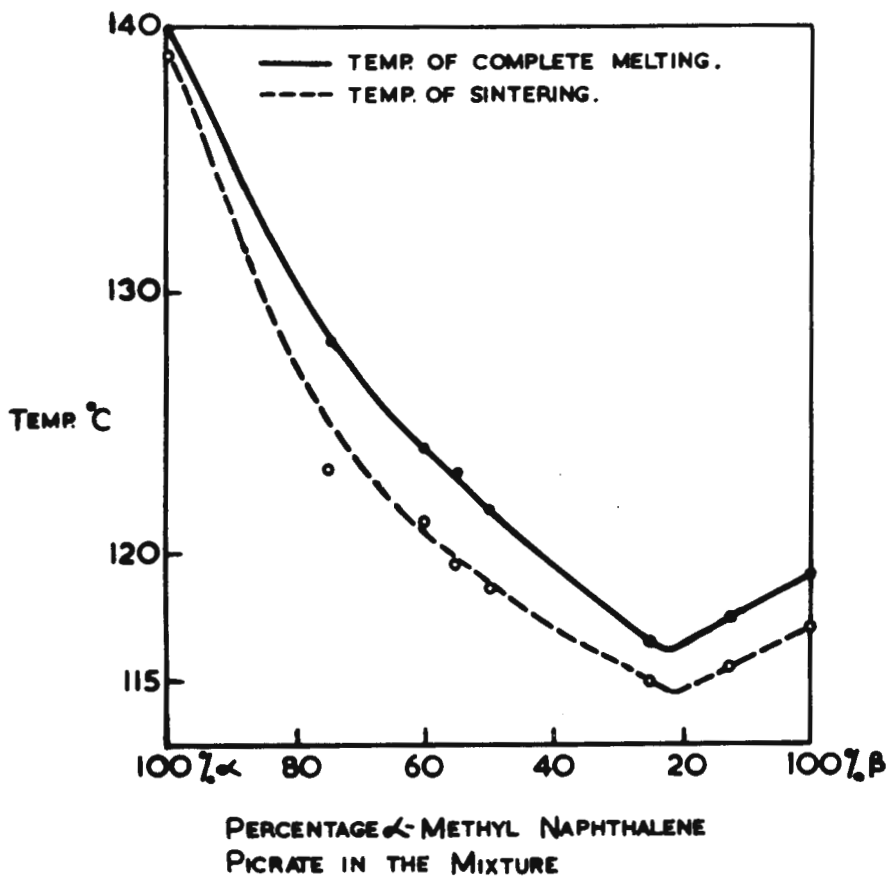
filled with calcium chloride, the second with sodium carbonate monohydrate and finally a sulphuric acid bubbler, i.e. in this order, the calcium chloride tube being nearest to the flask inlet. The flask outlet was connected to a Dumas nitrometer filled with 50% potassium hydroxide and 1% barium hydroxide.

Before heating, the apparatus was swept out with carbon dioxide until free from air, as indicated by the formation of micro-bubbles, as in a nitrogen estimation. The flask was then heated to such a temperature that the liquid was kept boiling. At the same time a slow stream of carbon dioxide was passed through the apparatus. The hydrogen evolved was collected and measured in the nitrometer. It is thought that this apparatus is superior to that used by Linstead et al., (J., 1937, 1146) for dehydrogenation studies as fewer corrections are involved.

Dehydrogenation of Bicyclo-[0.4.5]-undecatriene Carboxylic Acid.

The purified acid (2.14 g., b.p. 161-4°C./15 m.m. was heated with the catalyst (0.21 g.) in the apparatus described. Hydrogen evolution began at 210°C and became vigorous at 270°C. The reaction was complete in two hours. The velocity of dehydrogenation is shown in graph XV. A total of 267 c.c. of hydrogen (at N.T.P.) were evolved, i.e. 53% of the theoretical. The reaction was roughly monomolecular.

For the study of the dehydrogenation products of the acid, a larger quantity (16.5 g.) of material was used. The dehydrogenation was carried out as previously described, except that the hydrogen was not collected. After two hours, when the reaction had ceased, the flask was allowed to cool and the contents extracted with ether. The ethereal solution was washed



MELTING POINTS OF MIXTURES α - & β -METHYL NAPHTHALENE
 PICRATES

with alkali to remove the small quantity of acid present, and dried with calcium chloride. After removal of the ether the following fractions were collected on distillation.

- | | | |
|------|--------------------|--------|
| (I) | 113-133°C./20 m.m. | 7.0 g. |
| (II) | 130-190°C./20 m.m. | 0.3 g. |

Fraction (I) yielded 5.6 g. of colourless mobile oil b.p. 114-122°C./19 m.m. on redistillation. Pure 1-methyl naphthalene distilled from the same flask boiled at 123-4°C under identical conditions.

Picrate.

The hydrocarbon (4.72 g.) was mixed with picric acid (5.7 g., i.e. 75% of the calculated quantity to allow for saturated components formed by disproportionation) dissolved in alcohol (30 c.c.). Pale orange needles (6.02 g., m.p. 120-3°C.) resulted. This was recrystallized from alcohol (40 c.c.) to yield the picrate m.p. 123-4°C. (3.48 g.)

Found: C, 54.7% ; H, 3.4%

$C_{17}H_{13}O_7N_3$ requires: C, 55.0% ; H, 3.5%

This picrate is thought to be a mixture of 1-methyl naphthalene picrate (65%) and 2-methyl naphthalene picrate (35%), see the melting point diagram opposite. When this mixture of 65% was prepared and mixed with the unknown picrate there was no depression of the melting point, although the unknown picrate gave depressions with both 1-, and 2-methyl naphthalene picrates, separately. It was not found possible to separate the two components by recrystallization.

The hydrocarbon was regenerated by shaking the ethereal solution of the picrate (1.6 g.) with 1% caustic soda solution

until colourless. The ether layer was dried over calcium chloride, the ether removed, and the residue distilled at reduced pressure as a colourless mobile oil, b.p. 119-121°C./20 m.m. (Pure methyl naphthalene distilled from the same flask under identical conditions at 120-2°C). It did not reduce aqueous potassium permanganate even on boiling. It was distilled from sodium at atmospheric pressure without change. The absorption spectrum was measured and found to closely resemble that of 1-methyl naphthalene, see graph V.

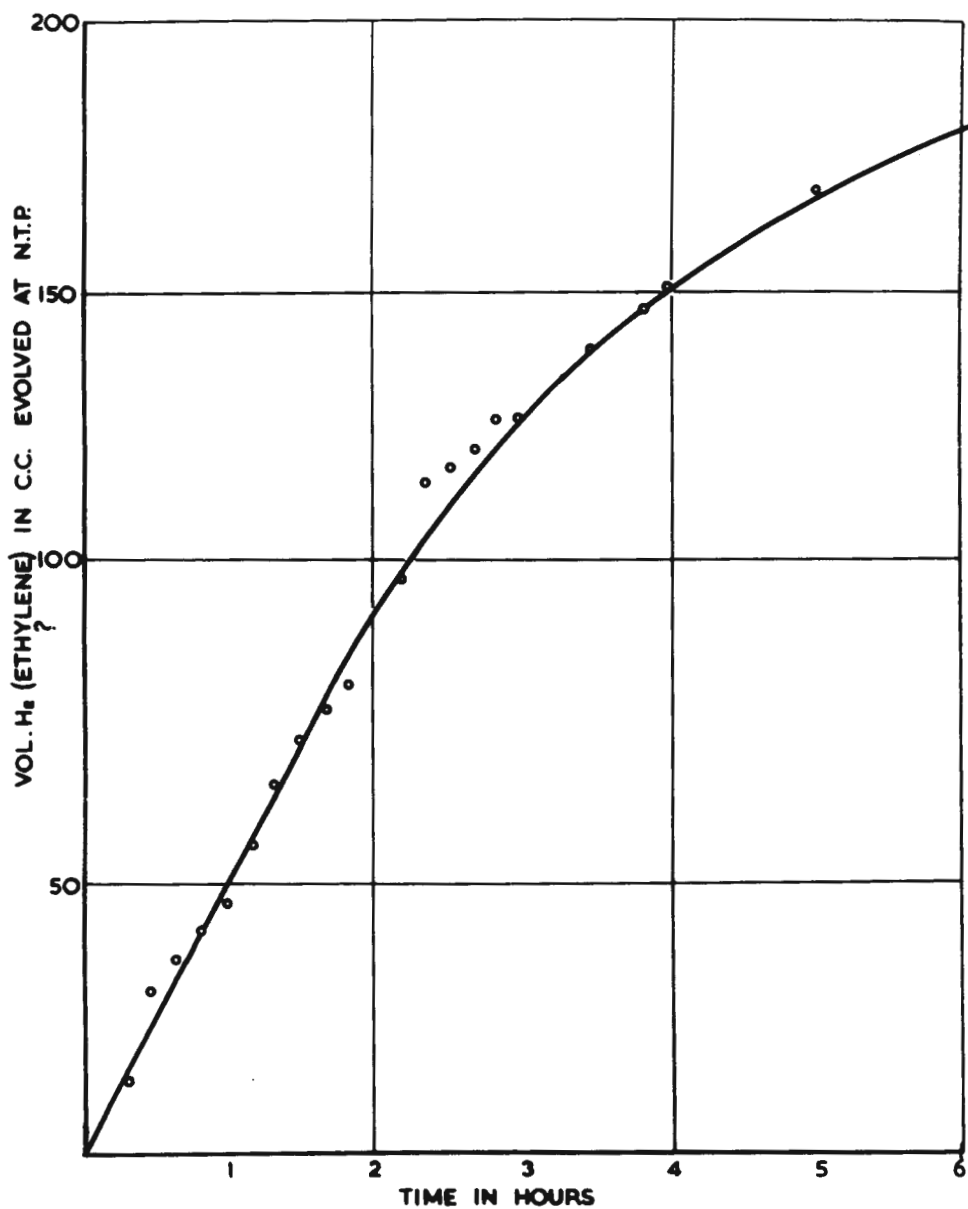
Dehydrogenation of Ethyl-bicyclo-[0.4.5]-undecatriene Carboxylate.

The dehydrogenation of the ester was carried out as before. The ester (2.05 g.) on being heated with the catalyst (0.2 g.) began to effervesce at 310°C. The gas evolution was slower than in the case of the acid and here again less than half the theoretical quantity of hydrogen was evolved, a total of 186 c.c. or 42.5% of the theoretical. The actual quantity of hydrogen produced is probably even less than this, because the gas collected probably contained gaseous hydrocarbons formed by decarboxylation. That fission of the ester grouping had taken place to some extent was confirmed by the isolation of a low boiling hydrocarbon fraction from the dehydrogenation product. The contents of the flask was worked up and distilled under reduced pressure.

Fraction (i) b.p. 120-130 /18 m.m., 0.6 g.

" (ii) b.p. 160-180 /18 m.m., 0.25 g.

The lower fraction resisted hydrolysis and formed a picrate, identical with that derived from the hydrocarbon obtained on dehydrogenation of the acid, already described, m.p. 123-4°C. The higher boiling fraction yielded a small quantity of crystal-
98/line....



DEHYDROGENATION OF



line acid, probably a methyl naphthoic acid. The quantity obtained was too small for satisfactory purification and it was not investigated further.

DIETHYL 4-PHENYL-1:3-BUTADIENE 1:1 DICARBOXYLATE.

(Diethyl cinnamylidene malonate)

Cinnamic aldehyde (132.2 g., 1 mol.) and ethyl malonate (160.2 g.; 1 mol.) were mixed together, piperdine (5 c.c.) added and the mixture allowed to stand for two hours, when a further quantity of piperdine (5 c.c.) was added. After standing overnight, the mixture was taken up in ether and the piperdine washed out with concentrated hydrochloric acid - and then with saturated ammonium sulphate solution. The ethereal solution was dried over sodium sulphate. When the ether had been distilled off, the residue was very slowly distilled in two lots from a Claisen flask (250 c.c. capacity) at high vacuum with the aid of an oil bath. If the oil bath was heated too rapidly, the vacuum could not be maintained, because of a gas evolution, doubtless due to the decomposition of unreacted ethyl malonate.

The first fraction boiling 80-160° /2 m.m. was a mixture of unreacted ethyl malonate and cinnamic aldehyde which was re-treated. The required ester distilled at 170-190° /0.5 m.m. The yield was 170-180 grams, or 60-65% of the theory.

When larger quantities were used, much inferior yields were obtained due to the difficulty of controlling the temperature of the reaction mixture which at best was kept below 30°C.

Diethyl 4-phenyl-1:3-butadiene-1:1-dicarboxylate has also been prepared by Knoevenagel and Henz (Ber., 1904, 37, 4483) but details of the preparation are not given.

Diethyl 4-phenylbutene-1:1-dicarboxylate.

Into a two litre aspirator bottle fitted with an inlet at the bottom and a metal tap at the top, was placed freshly prepared palladium/calcium carbonate hydrogenation catalyst (75 g.) as described by Bush and Stöve (Ber., 1916, 48, 1063) and diethyl 4-phenyl-1:3-butadiene-1:1-dicarboxylate (274 g.; 1 mol.) dissolved in ethyl alcohol (600 c.c.).

The aspirator bottle was then canted at about 45° with the inlet facing upwards, so that with the tap at the top open, it could be flushed out with hydrogen without the gas bubbling through the liquid or coming in contact with the catalyst, which was covered by the alcoholic solution.

When all the air had been replaced with hydrogen, the tap was closed and the bottle was turned on its side and vigorously shaken in a mechanical shaker. Hydrogen was passed in at a pressure of about three atmospheres from a hydrogen cylinder, the pressure being measured by a mercury manometer connected in series with a small bubbler filled with alcohol.

After a few minutes the colour of the catalyst changed from brown to black and a vigorous absorption of hydrogen took place. The reaction was complete after about one hour.

The catalyst was filtered from the alcoholic solution and after distilling off the alcohol the residue was distilled at reduced pressure. The fraction boiling at 141° /0.3 m.m. was collected, about 250 grams or 90% of the theoretical yield. Diethyl 4-phenyl-1:1-dicarboxylate has also been prepared by v.

Braun and Kurber, (Ber., 1912, 45, 384) by treating 3-bromo-1-phenylpropane with the sodio-derivative of ethyl malonate.

4-Phenylbutane-1:1-dicarboxylic Acid.

Diethyl 4-phenylbutane 1:1-dicarboxylate (278 g.; 1 mol.) was mixed with potassium hydroxide (110 g.; 2 moles) dissolved in water (200 c.c., i.e. a 35% solution, D 1.35) and vigorously shaken. After a minute or so, a vigorous reaction set in and the mixture became homogeneous. The solution on cooling was extracted several times with small quantities of ether to remove non saponifiable material. The aqueous layer was acidified with concentrated hydrochloric acid and the liberated acid taken up in a little ether. The ethereal solution was washed with water and dried over sodium sulphate. After removal of the ether, the residue set to a solid crystalline mass which was decarboxylated without further purification.

5-Phenylvaleric Acid.

4-Phenylbutane-1:1-dicarboxylic acid (about 100 g.) was gently heated in a Claisen flask (250 c.c. capacity) under reduced pressure, with a free flame at such a rate that the pressure did not exceed 100 m.m. Under these conditions carbon dioxide was smoothly evolved at about 230°C. and the reaction was complete in about twenty minutes.

When the gas evolution had subsided the phenylvaleric acid was distilled; the fraction boiling 170-200°C./20 m.m. being collected. On cooling, the acid crystallized out in a mush of large plates. These were filtered off at the pump and

washed with small quantities of petrol ether to yield the almost pure 5-phenylvaleric acid. The yield from diethyl 4-phenylbutane-1:1-dicarboxylate (278 g.; 1 mol.) was 128 grams, or 73% of the theory.

The method used in these two stages was essentially that of v. Braun and Deutsch (Ber., 1912, 45, 2178.).

5-Phenyl-valeryl Chloride.

Into a one litre three necked flask fitted with a reflux condenser and a dropping funnel, were placed phosphorus penta-chloride (240 g.; 1.16 mol.) and anhydrous benzene (600 c.c.). The mixture was then heated until solution was complete, and then cooled to room temperature, when a mixture of 5-phenylvaleric acid (174 g.; 1 mol.) dissolved in anhydrous benzene (200 c.c.) was slowly run in with gentle shaking. When the addition was complete the reaction mixture was heated on a water bath until the evolution of hydrochloric acid ceased, about 1 hour.

The benzene and phosphorous oxychloride were then removed by distillation at slightly reduced pressure from a water bath and finally the acid chloride was distilled with the full force of the water pump and came over at 152° /15 m.m. The yield was 170 grams or 87.4% of the theory.

When the preparation was carried out without a solvent the reaction was very vigorous and the yield much lower, about 60% 5-Phenylvaleryl chloride has also been prepared by Kipping and Hunter (J. 1901, 79, 605) but without a solvent. The

boiling point and the yield were not recorded.

1:2-Benz-cyclo-1-hepten-3-one.

(Benz-suberone)

Into a 5 litre round bottom flask fitted with a four necked head to accommodate a reflux condenser, dropping funnel; both protected with calcium chloride tubes, a mercury seal stirrer and an inlet for solid aluminum chloride, was placed powdered aluminium chloride (60 g.) and carbon disulphide (300 c.c.). The flask was heated in a glycerine bath equipped with an immersion heater. Glycerine is preferable to water because the condensation of water vapour on the apparatus is avoided.

The mixture was heated to about 50°C. so that gentle refluxing took place and 6-phenylvaleryl chloride (154.4 g.; 0.8 moles) dissolved in carbon disulphide (3,200 c.c.) was added at the rate of 400 c.c. per hour and at the end of each half hour powdered aluminium chloride (10 g.) was added with vigorous stirring. After eight hours, the stirring was stopped and the mixture was allowed to continue refluxing overnight.

The carbon disulphide was then distilled off and about two kilos of finely crushed ice added. When the reaction was complete the material was extracted with ether. The aqueous portion was filtered, saturated with sodium chloride and twice extracted with ether.

The combined ethereal extracts were shaken with saturated sodium carbonate solution and finally dried over calcium chloride.

A small quantity of acid (about 5 g.) recovered from

the alkali soluble material by acidification and extraction with ether was reworked.

After the removal of the ether, the ketone was distilled the fraction b.p. 148-153° /15 m.m. being collected: 105.3 grams i.e. 82.3% of the theoretical quantity.

In a previous run in which all the aluminium chloride was added at the beginning of the reaction the yield was much lower, 65% of the theoretical quantity.

Benz-suberone has also been prepared by Perkin and Hunter (J. 1901, 72, 605) and Bosche and Reth (Ber. 1921, 54, 174) in much poorer yields, 40% and 50% respectively, and by Plattner (Helv. Chim. Acta. 1944, 27, 801) in 87% yield but with a much more arduous method than the above.

1:2-Benz-cyclo-heptane. (Benz-suberane)

c.f. Method of Plattner, Helv. Chim. Acta. 1944, 27, 174.

Zinc wool (170 g.) was placed in a two litre three necked flask and well shaken with mercuric chloride (12.5 g.) dissolved in water (250 c.c.) and hydrochloric acid (10 c.c.) at 90°C. for two to three minutes and then decanted. The amalgam was shaken with water, 0.1.N hydrochloric acid and finally allowed to stand in cold 1.N hydrochloric acid for half an hour.

The 1.N hydrochloric acid was decanted and water (100 c.c.) and concentrated hydrochloric acid (200 c.c.) were added, and the flask was equipped with a rapid stirrer, a reflux condenser and an inlet for hydrochloric acid gas. The mixture was then brought to boiling with vigorous stirring by means of

an oil bath maintained electrically at 110°C . and 1:2-benz-cyclo-hepten-3-one (20 g.; 0.5 mol.) dissolved in toluene (300 c.c.) gradually added.

After 2, 14, 24, 30 and 36 hours, dry hydrochloric acid gas was passed into the mixture until saturated. Little was necessary towards the end of the reaction. After 48 hours all the zinc was dissolved. The toluene layer separated, washed with alkali and then water. The washings were added to the aqueous layer which was neutralized with caustic soda, so that a slight but permanent precipitate of zinc hydroxide was formed.

These liquids were then several times extracted with ether. The ether was removed and the residual liquid combined with the toluene solution. When the toluene solution had been dried over calcium chloride, the toluene was distilled off through a short fractionating head at atmospheric pressure.

The residue was distilled in vacuo. The main fraction b.p. $96-105^{\circ}$ /15 m.m., 64 grams or 37.5% of the theoretical quantity, was collected.

A portion of this material was twice distilled from sodium and the fraction b.p. 217°C /781 m.m. retained for the absorption spectrum study. See Graph IX.

(0.5.5.)-Bicyclo-dodecatriene Carboxylic Acid.

1:2-Benz-cyclo-heptene (56 g.) was treated dropwise with ethyl diazoacetate (6.0 g. 85% i.e. 0.1 mol.) at $130-5^{\circ}\text{C}$. over a period of two hours. The temperature was then slowly raised to 165°C . during two hours. After cooling to 130°C ., the mixture was retreated with a further quantity of ethyl

105/diazoacetate....

diozoacetate (6.0 g.) and the procedure repeated.

The mixture was then distilled and the following fractions were collected at 15 m.m.

(i) b.p. 100-105°C. 52 grams.

(ii) 120-200°C 9 grams.

The recovered hydrocarbon was retreated as described above. After working the material ten times in this manner, a total of about 25 grams was obtained together with 15 grams of unchanged 1:2-benz-cyclo-heptane.

The combined high boiling fractions were distilled and the portion distilling between 160-190° /13 m.m.; a pale yellow mobile liquid retained (about 16 g.). It did not give the characteristic norceradiene colour reaction with concentrated sulphuric acid.

Since this crude ester could not be obtained pure by fractionation it was saponified with strong alkali to remove nitrogenous material.

To the crude ethyl [0.5.5.]-bicyclo-dodecatriene carboxylate (8.0 g.) was added potassium hydroxide (4 g.) dissolved in water (4 c.c.) and alcohol (20 c.c.) and the mixture placed under reflux for 8 hours. The alcohol was distilled off at reduced pressure, water added, and the solution extracted with ether to remove non-saponified material. The aqueous layer was acidified and the liberated acid taken up in ether. The ethereal extract was washed several times with water to free it from slightly water soluble acids. After drying over sodium

106/sulphate....

sulphate the ether was removed and the acid residue distilled in vacuo. The pure acid distilled as a highly viscous oil, main fraction b.p. 145-155° /0.4 m.m., 3.3 grams or 52% of the theoretical.

Found: C, 76.4% ; H, 7.4%

$C_{13}H_{16}O_2$ requires : C, 76.5% ; H, 7.8%

[0.5.5.]-Bicycle-dodecene Carboxylic Acid.

[0.5.5.]-Bicycle-dodecatriene carboxylic acid (0.593 g.) was dissolved in glacial acetic acid (15 c.c.) and added dropwise to a mixture of 5% palladium chloride solution (4 c.c.) and 2% gum arabic solution (6 c.c.) in the hydrogenation flask (loc.cit.) The air in the flask was replaced with hydrogen and a solution of colloidal palladium, prepared by passing hydrogen into a mixture of 5% palladium chloride solution (2 c.c.) and 2% gum arabic solution (1 c.c.). The mixture was thoroughly shaken and the quantity of hydrogen at atmospheric pressure measured; the reduction was sluggish and stopped after hydrogen (123 c.c. at N.T.P.) had been absorbed (i.e. equivalent to 1.9 double bonds) The mixture was then evaporated to dryness at the water pump. The residue was digested with caustic soda solution and non acid material (less than 0.005 g.) removed by washing with ether. The aqueous layer was then acidified and the liberated acid taken up in ether. On removal of the ether, the acid (0.41 g.) remained behind as a highly viscous, almost colourless oil which slowly reduced acetone permanganate and weakly acid permanganate solutions.

[0.6.5.]-Bicyclo-dodecane Carboxylic Acid.

[0.6.5.]-Bicyclo-dodecatriene carboxylic acid (0.570 g.) was dissolved in glacial acetic acid (10 c.c.) and added dropwise with shaking to a mixture of 5% chloroplatinic acid solution (4 c.c.) and 2% gum arabic solution (5 c.c.) and glacial acetic acid (5 c.c.) in the hydrogenation flask (log. oil.). The flask was washed with a further quantity of glacial acetic acid (5 c.c.) and this also added.

The air in the apparatus was replaced with hydrogen and a solution of colloidal platinum, prepared by passing hydrogen for 15 minutes into a mixture of 5% chloroplatinic acid solution (2 c.c.) and 2% gum arabic solution (1 c.c.) added. The reaction ceased after hydrogen (192 c.c. at N.T.P.), equivalent to 3.07 double bonds had been absorbed.

After the reaction was complete, the mixture was evaporated to dryness at reduced pressure on a water bath. The residue was digested with caustic soda solution and this aqueous solution extracted with ether to remove more acid impurities (less than 0.005 grs.). The aqueous layer was then acidified and the liberated acid taken up in ether and dried over sodium sulphate. On removal of the ether, the acid (0.39 g.), a pale yellow oil remained which did not reduce potassium permanganate solutions.

Ethyl [0.6.5.]-Bicyclo-dodecatriene Carboxylate.

[0.6.5.]-bicyclo-dodecatriene carboxylic acid (b.p. 140-165° /0.4 m.m., 2 g.) was dissolved in absolute alcohol (6 c.c.) and concentrated sulphuric acid (0.6 c.c.) added with

shaking. After refluxing this mixture on a water bath for three hours it was poured into water and the ester taken up in ether. The ethereal extract was washed with 10% sodium carbonate solution and water and finally dried over sodium sulphate. Removal of the ether left the crude ester (2.15 g.) which was distilled, and the fraction b.p. 177-30°C. at 15 m.m. collected as a pale yellow viscous oil, 1.3 grams.

Dehydrogenation Studies. (A) Liquid Phase.

(i) [0.5.5.]-bicyclo-dodecatriene carboxylic acid (1.0 g.) was heated with palladium charcoal catalyst (0.2 g.) in a stream of carbon dioxide at 220°C. for ten minutes. After cooling, the material was extracted out with peroxide free ether. Removal of the ether left a viscous residue which could not be distilled and which was almost completely insoluble in petrol ether.

The petrol solution had a blue-green colour which disappeared when it was shaken with 85% phosphoric acid, but nothing could be regenerated from the solution on adding water.

(ii) [0.5.5.]-bicyclo-dodecatriene carboxylic acid (1.0 g.) was distilled from palladium charcoal catalyst (0.2 g.) in the manner recommended by Plattner and Wyss (Helv., Chim. Acta. 1940, 23, 907), under slight vacuum, but all that was obtained, was a lot of high boiling material and one drop of a mobile pale greenish oil with a smell reminiscent of decalin and which did not readily absorb bromine. It was therefore considered to be possibly a mixture of hydro-naphthalenes.

(iii) Similar trials were carried out with the corresponding ethyl ester of the acid, but with equal failure. Dehydrogenation with sulphur was also unsuccessful.

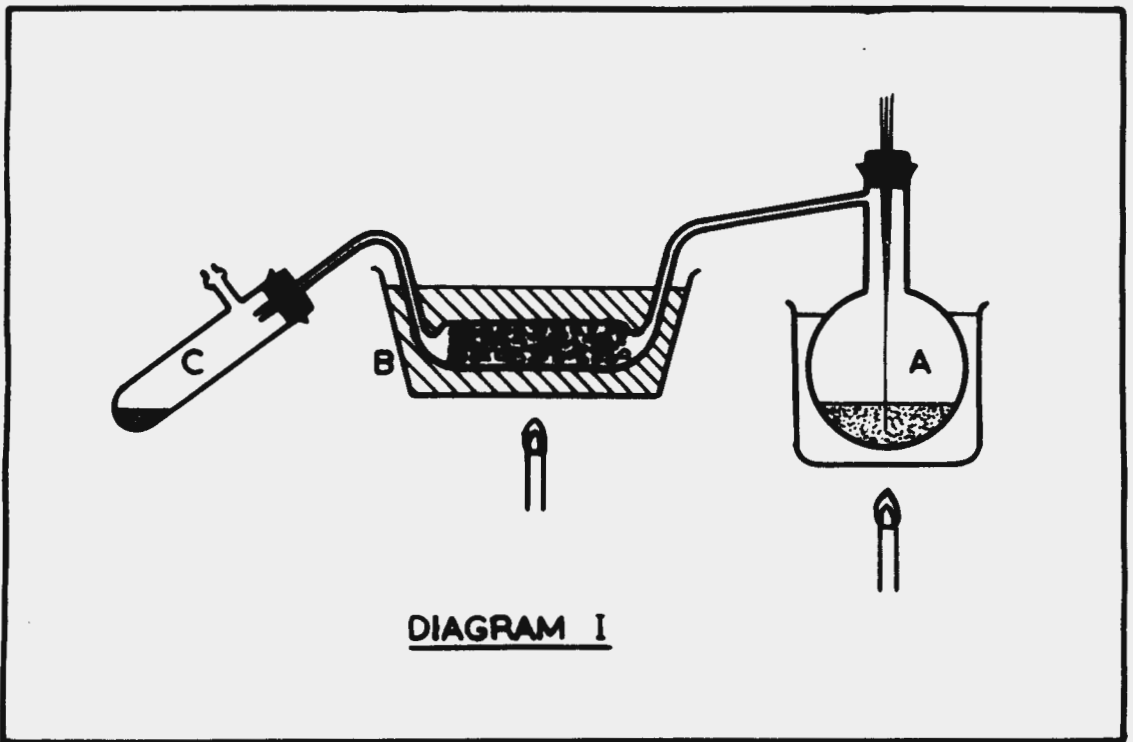
B Vapour Phase.

(1) Ethyl [0.5.5]-bicyclo-dodecatriene carboxylate about (2 g.) was very slowly distilled at 13 m.m. pressure from a small distilling flask (A) immersed in an oil bath, through a catalyst chamber (B) (7.1 c.m. long; 1.5 c.m. in diameter) filled with 30% palladium charcoal catalyst mixed with an equal weight of asbestos, and maintained at a temperature of 325°C. in a metal bath, as shown in the diagram (I).

The first few drops of liquid distilled into the receiver C as a pale blue oil, but as the distillation continued the colour changed to dark green and it was found that the blue coloured material was formed only when the rate of distillation was very slow. However, it was found exceedingly difficult to maintain such a slow rate of distillation with this type of apparatus.

(The apparatus was found to give good yields of ethyl azulene carboxylate by treating ethyl [0.3.5]-bicyclo-decatriene carboxylate in this manner).

When all the ester had been distilled the dehydrogenated material was fractionated at reduced pressure and the first few drops of distillate came over blue in colour, but the bulk of the material distilled at 170-4°C./13 m.m. as a pale green liquid. The ultra violet absorption spectrum of this fraction closely resembled that of the starting material.



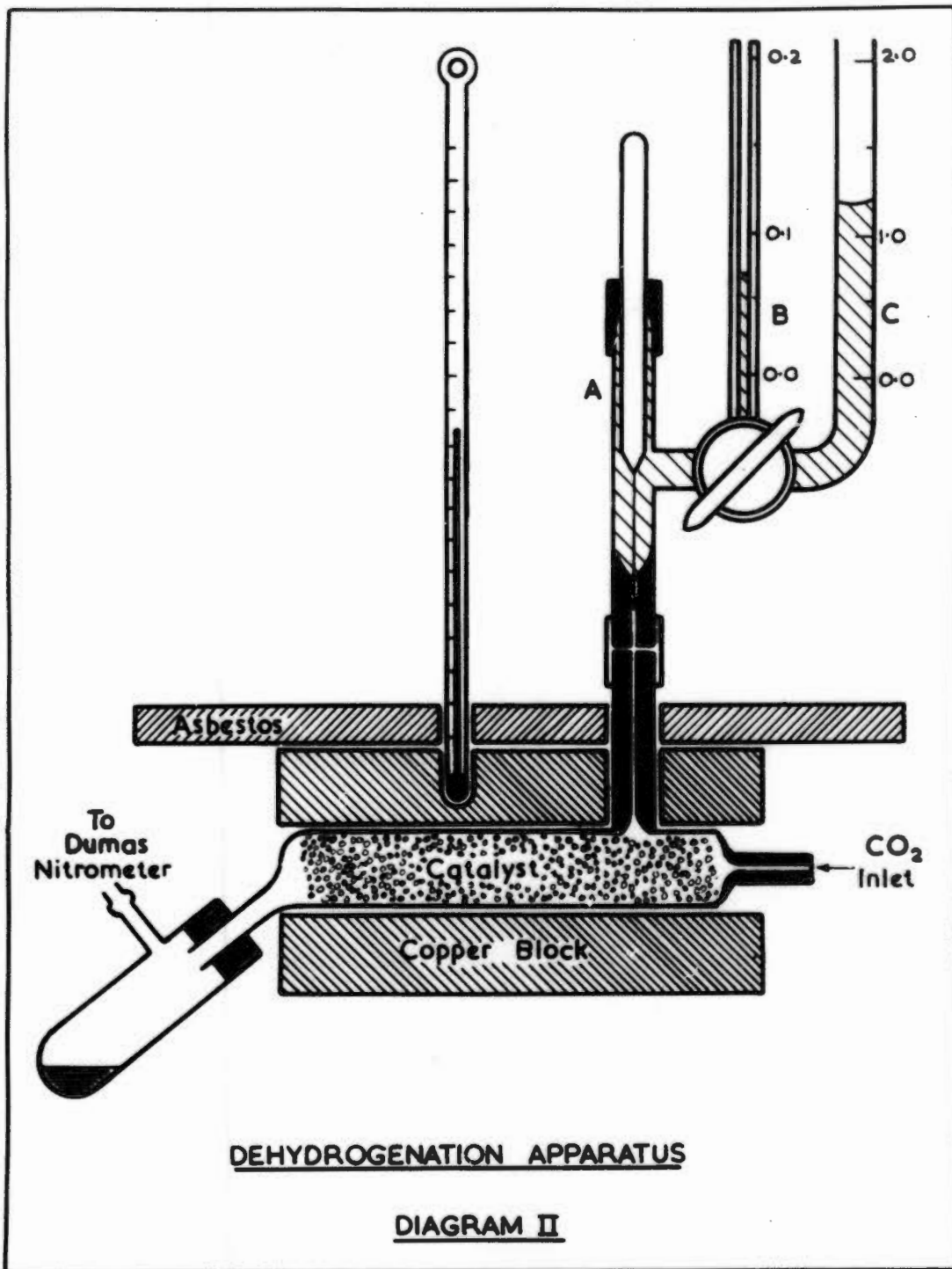
The bluish drops, dissolved in petrol ether, were shaken with 85% phosphoric acid and the complex so formed separated and washed with petrol ether. It was then added with good shaking to a mixture of ether and crushed ice. The blue material regenerated in the ether layer demonstrating the presence of an azulene-like compound. Removal of the ether left an intensely blue oily residue, about 3 mg.

(ii) c.f. Linstead et. al. (J., 1937, 1146).

The apparatus: In this instance the apparatus shown in the diagram (ii) was used. It was designed to operate at a very slow rate of flow as used by Linstead.

The ester was delivered to the catalyst chamber at a rate of 0.005 c.c. per minute, by allowing it to flow through a fine capillary (3 cm. long, and 0.95 m.m. in diameter), the size of the aperture of which, was adjusted by pushing a finely drawn out glass rod with a minimum diameter of 0.80 m.m. and 2 c.m. long into it. The diameter of the glass rod was chosen so that it closely fitted the upper limb (A) to which it was sealed with a piece of rubber tubing lightly smeared with vaseline. The fine capillary burette (B) (0.2 c.c. capacity) was used in the setting of the rate of flow while the larger (C) was used as a reservoir.

The catalyst chamber (dia. 1.5 c.m.; 7.5 c.m. long) was constructed of Duran Jena glass. The inlets were made of fine capillaries to avoid the formation of drops. The tube was packed with a mixture of 30% palladium charcoal (0.78 g.) prepared according to the directions of Linstead (loc.cit.) and 5% palladium asbestos (0.7 g.). The catalyst chamber was
111/heated....



heated in a closely fitting solid copper block made in two halves.

The outlet from the receiver was connected to a Dumas nitrometer, where the volume of gas evolved was collected and measured over 50% potassium hydroxide solution.

The optimum temperature for dehydrogenation was found to be 350-360°C. At 310° the evolution of hydrogen was very slow.

The Dehydrogenation.

Before the reaction was started, the apparatus was swept out with carbon dioxide until micro bubbles were formed in the nitrometer. Ethyl [0.5.5] -bicyclo-dodecatriene carboxylate was then allowed to flow into the catalyst chamber at a rate of 0.005 c.c. per minute. A very slow rate of flow of carbon dioxide was also maintained. A vigorous evolution of gas soon began and after a half hour a drop of colourless oil distilled over.

When the apparatus had reached an equilibrium the volume of gas (320 c.c. at N.T.P.) generated from the ester (0.75 c.c.) was measured. This corresponds to roughly four molecules of hydrogen from every molecule of ester, i.e. one more than was expected due doubtless to the fission of the carbethoxy grouping, and the evolution of gaseous hydrocarbons.

The material obtained from the ester (2.5 g.) was a colourless mobile oil (0.5 c.c.). It was refluxed with potassium hydroxide (0.25 g.) and ethyl alcohol (1 c.c.) for one hour. The alkali solution fractions amounted to less than one drop of dark brown oil. The alkali insoluble hydrocarbon (0.36 g.)

was treated with picric acid (3.7 c.c. of a saturated solution in alcohol, i.e. 0.18 g.)

The picrate separated after warming in orange needles from alcohol m.p. 121-122°C. after two crystallizations. It was much more soluble than picric acid. Mixed melting point with picric about 105°C.

It is considered to be a mixture of isomeric dimethyl naphthalene picrates.

Found: C, 55.8% ; H, 3.9%

$C_{18}H_{16}O_7N_3$ requires: C, 56.1% ; H, 3.9%

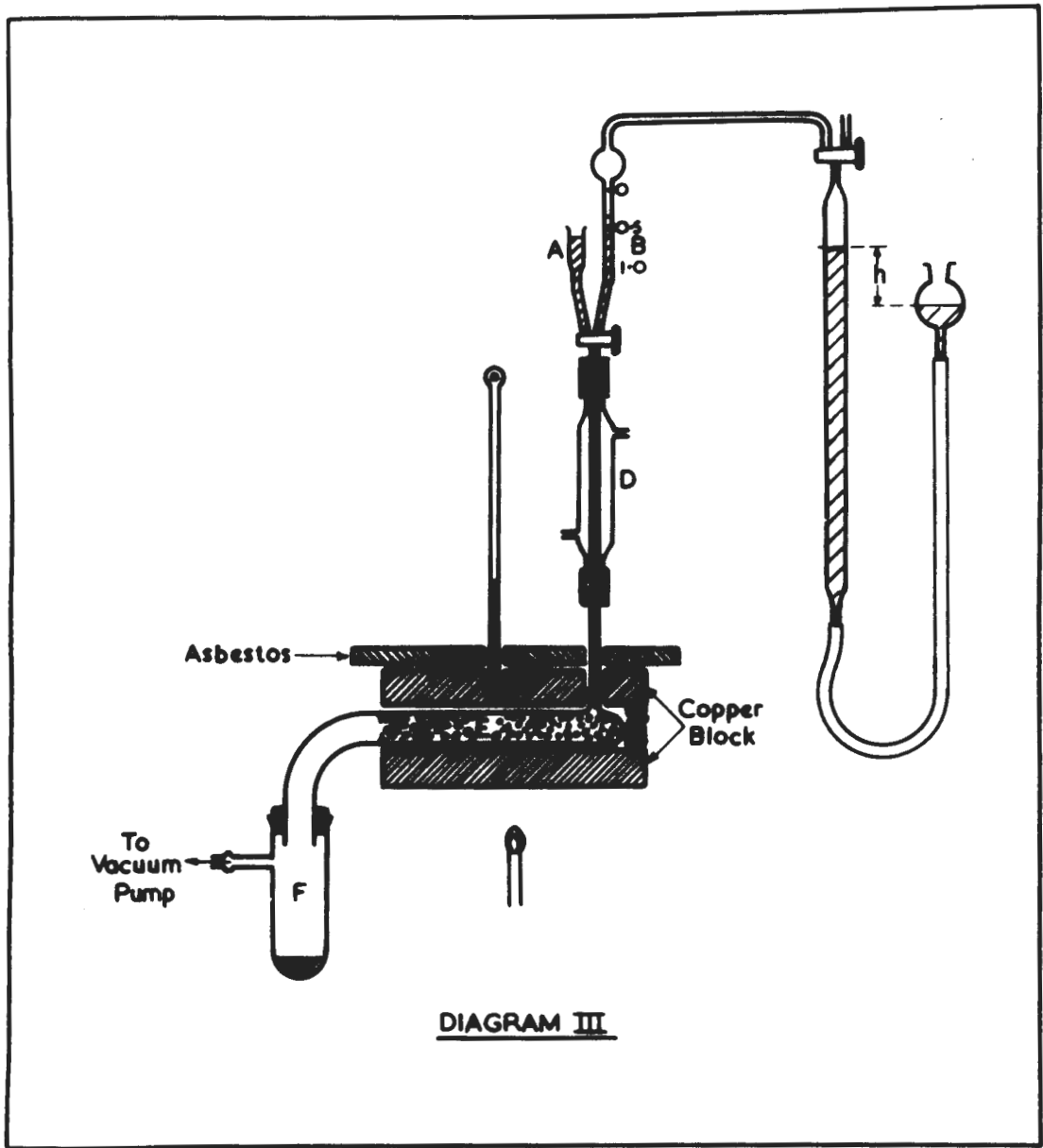
The once crystallized material (m.p. 120-122°C., 0.05 g.) was shaken with dilute caustic soda solution and water until free from picric acid. The ethereal extract was dried over calcium chloride. Removal of the ether left one drop of colourless mobile oil which was used in the ultraviolet absorption spectrum study. The ultra violet absorption spectrum graph (VII) is characteristic of alkylated naphthalenes and this product is thought to be most likely a mixture of dimethyl naphthalenes.

(iii) Higher speed vapour phase dehydrogenation.

The apparatus.

The material for dehydrogenation was supplied as required from the reservoir (A) to the 1 c.c. burette (B), the top of which was connected to a mercury manometer used to adjust the gas pressure in (B), i.e. to control the rate of flow of liquid through the fine capillary, (D) into the catalyst chamber (E). The receiver (F) was connected to a water pump and a pressure of 15 m.m. maintained in the catalyst chamber.

The capillary tube, which was made from a thermometer tube was drawn out so that it delivered the ester at a rate of 0.015-.02 c.c. per minute at a pressure difference of 740 m.m. It was then possible to vary the rate of flow from 0.005-0.02 c.c. per minute by varying "H" from 500-0 m.m.



The capillary which was surrounded by a water condenser to maintain a constant viscosity; was connected to the catalyst chamber below and the burette above with pressure tubing. In order to avoid blockage of the capillary, absolute cleanliness is necessary, and for this reason it is best not to use vaseline in the threeway burette tap. However, to prevent gas leakage it is best smeared with thick grease on the outside. The tap was protected from the heat of the block by several thicknesses of asbestos board. The copper block was maintained throughout at a temperature of 340°C.

The Dehydrogenation.

Ethyl [0.5.5] -bicyclo-duodecatriene carboxylate was allowed to flow into the catalyst chamber at a rate of 0.005 c.c. per minute. The distillate was a colourless oil which was found to be mainly dimethyl naphthalenes. However, when the rate of flow was increased to 0.18 c.c. per minute, the distillate came over deep blue in colour. It was distilled and the following fractions collected at 15 m.m.

Fraction	(i)	b.p. 110-120 deep blue (hydrocarbons)	0.15 g.
	(ii)	120-140 " "	0.03 g.
	(iii)	140-170 intense blue-violet (esters)	0.70 g.
	(iv)	170-175 greenish	0.30 g.

The hydrocarbon fraction b.p. 110-120°C/15 m.m. was dissolved in petrol ether and extracted with ice cold 85% phosphoric acid. The red phosphoric acid extract was washed several times with small portions of petrol ether and the azulene like hydrocarbon regenerated by pouring the mixture into a vigorously

stirred mixture of peroxide free ether, ice and water. The ether layer was then washed with dilute alkali and finally water. This ethereal extract was dried over calcium chloride. Removal of the ether left an intensely ultramarine coloured oil about 5 m.g. The visible absorption spectrum of this material is shown in graph (VIII). It was not found possible to obtain a crystalline derivative.

The ultraviolet absorption spectrum of the deep blue fraction (III) showed that it was mainly unchanged ethyl [0.5.5]-bicyclo-dodecatriene carboxylate. It was dissolved in light petrol ether (25 c.c.) and shaken with small portions of ice-cold 85% phosphoric acid until the petrol ether layer was almost colourless. The dark red phosphoric acid layer was vigorously shaken with six portions of petrol ether (400 c.c. in all). It was then poured with shaking into a mixture of ether (200 c.c.) and crushed ice. The deep blue ethereal solution was washed with sodium carbonate solution, water and finally evaporated to dryness at reduced pressure in an atmosphere of carbon dioxide.

The deep blue oil (0.03 g.) which remained was used in the visible absorption spectrum studies, see graph (x). The study of the visible absorption spectrum and a comparison of it with those described by Plattner and Coworkers indicated that the quantity of azulene like material present did not exceed 5%.

It was not found possible to form a picrate or a troylate, from this material, and all attempts to obtain the pure ester were unsuccessful.

Investigation of the phosphoric acid insoluble fraction.

The combined petrol ether solutions from three dehydrogenation experiments, after the removal of the blue material with 85% phosphoric acid, were evaporated and the residue (about 5 g.), saponified with 10% aqueous potassium hydroxide.

The unsaponified material (0.52 g.) was treated with saturated alcoholic ^{picric} acid solution (5 c.c.; i.e. about 0.26 g. picric acid). It formed a picrate (0.11 g.) m.p. 120-1°C, identical with the isomeric dimethyl naphthalene picrate mixture obtained in a previous dehydrogenation experiment.

The residue which failed to form a picrate was taken up in ether and shaken with 5% aqueous caustic soda until free from picric acid. After removal of the ether, the dark brown oil was distilled from sodium, b.p. about 230°C./750 m.m. The absorption spectrum (c.f. graph vii) was found to be very similar to that of the 2:7-dimethyl naphthalene, and it is concluded that this fraction is mainly a mixture of dimethyl naphthalenes.

The alkali soluble material (2.76 g.) was distilled and yielded a viscous acid b.p. 160-170°C./1.0m.m. pressure. (2.1 g., olive green). It rapidly decolorized potassium permanganate solutions and absorbed much bromine.

Esterification.

The acid mixture (b.p. 160-170°C./1.0 m.m.) was dissolved in absolute alcohol (3 c.c.) and concentrated sulphuric acid (0.3 c.c.) and boiled under reflux for two hours on a water bath. It was then poured into water and extracted with ether. The ethereal solution was washed with sodium carbonate solution and water, and dried over sodium sulphate. Removal of the ether

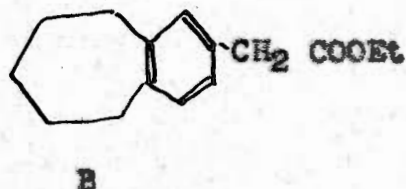
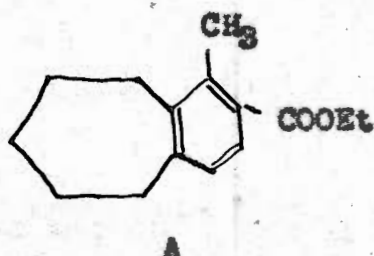
117/yielded....

yielded the crude ester (1.95 g.) which was distilled at 13 m.m. pressure; the following fractions being collected:-

Fraction (i)	b.p. 165-173°C.	0.5 grams.
(ii)	b.p. 173-175°C.	0.8 grams.

The absorption spectra of the two fractions were studied and fraction (i) was without doubt mainly unchanged ethyl dodecatriene carboxylate. Fraction (ii) on the other hand was somewhat different and the presence of aromatic rearrangement products were suspected.

In order to remove all the unchanged ethyl [0.5.5] - bicyclo-dodecatriene carboxylate fraction (ii) (0.5 g.) was refluxed with potassium permanganate (0.2 g.) dissolved in acetone (10 c.c.) and water (10 c.c.) for 15 minutes. A mixture of sodium metabisulphite and 2N sulphuric acid was then added, and the material extracted out with ether. The ethereal solution was washed free of acid oxidation products with 10% sodium carbonate solution, with water and finally dried over sodium sulphate. On removal of the ether, the ester (0.3 g.) remained. It was found ^{to have} too weak an absorption of light to contain much naphthoic ester, (c.f. absorption spectrum of ethyl 2-naphthoate graph xi) and is thought to be either of the type A or B.



Ethyl 2-Naphthoate.

2-Naphthoic acid (Merck) was crystallized from toluene as large flat needles, m.p. 183-4°C. This material (4.5 g.) was dissolved in absolute alcohol (20 c.c.) and concentrated sulphuric acid (1.4 c.c.) added with shaking. After refluxing for three hours the product was poured into 5% sodium carbonate solution and the ester extracted out with ether. The ethereal layer was twice washed with water and dried over sodium sulphate. The ester freed from ether was distilled and the material distilled, b.p. 169° /12 m.m. This material was used for the ultraviolet absorption spectrum study, see graph xi.

c.f. Salkind Bar., 1934, 67, 1033.

3:4-Benz-norcaradiene carboxylic acid.

Naphthalene (1030 g., 8 mol.) was melted into a two and a half litre, three necked flask equipped with an air condenser, a rapid stirrer and a dropping funnel, and maintained at 140-5°C in an oil bath. To the rapidly stirred naphthalene was added ethyl diazoacetate (215 g. 85% i.e. 1.6 mol.) over a period of twelve hours. The mixture was then slowly heated without stirring to 165°C during three hours and finally distilled at reduced pressure. The fraction boiling below 150°C./15 m.m. consisted of unreacted naphthalene, but the fraction coming over from 150-230° /15 m.m. contained the bulk of the crude ethyl benz-norcaradiene carboxylate (154 g.) contaminated with nitrogenous products.

As this ester fraction could not be obtained pure by

fractionation it was directly saponified and the material purified by crystallization of the corresponding acid.

The crude ester (154 g.) was refluxed with potassium hydroxide (70 grs.) dissolved in water (140 c.c.) and ethyl alcohol (500 c.c.). After refluxing for one hour, the mixture was steam distilled free of alcohol and the excess naphthalene removed by extraction with ether. The aqueous layer was then acidified and the liberated acid taken up in ether. After removal of the ether, the crude acid (122 g.) remained. It was purified by crystallization from alcohol and yielded the pure acid (66 grams) m.p. 166-7°C. (Buchner and Hediger loc.cit. 165-6°C.). The melting point is not sharp, probably because it is a mixture of geometric isomers.

The above method is essentially that described by Buchner and Hediger (Ber., 1903, 36, 3502.).

A similar condensation was carried out with 1-methyl naphthalene (114 g.; 0.8 mol.) and the product b.p. 160-250°C./15 m.m. collected (12.0 g.). On hydrolysis 6 grams of a viscous acid was recovered and distilled b.p. 170-80° /2 m.m. as a pale green resinous mass. All attempts to crystallize the material failed and it was not further investigated. The absorption spectrum shows it to be very similar to benz-norcaradiene carboxylate, see graph (xii).

Ethyl Benz-norcaradiene Carboxylate.

The once crystallized benz-norcaradiene carboxylic acid (m.p. 166-7°C., 60 g.) was dissolved in absolute alcohol (210 c.c.

and concentrated sulphuric acid (21 c.c.) added and the mixture placed under reflux for 3 hours. Most of the alcohol was then boiled off, water added and the ester extracted out with ether. The ethereal extract after being washed with 10% sodium sulphate. The ether was removed and the residue distilled at reduced pressure, b.p. 180-3°C./16 m.m. (54 g.)

This material was used for the absorption spectrum study, see graph (XII).

Ethyl benz-norcaradiene Carboxylate.

Ethyl benz-norcaradiene carboxylate (2.609 g.) dissolved in ethyl alcohol was shaken with hydrogen in the presence of a palladium/calcium carbonate catalyst (Busch & Stöve Ber.). A total of 271 c.c. of hydrogen at N.T.P. were absorbed, i.e. equivalent to 0.99 double bonds.

The bulk of the material (50 g.) was then dissolved in alcohol (500 c.c.) and shaken with hydrogen in the presence of the catalyst (10 g.) under a pressure of 3 atmospheres in the manner described on page 10. When the absorption of hydrogen was complete (about 2 hours) the catalyst was filtered off, the alcohol removed and the residue distilled at reduced pressure.

b.p. 179-185°C./16 m.m., 45 grams.

Found: C, 77.6%; H, 7.5%

$C_{14}H_{16}O_2$ requires : C, 77.8%; H, 7.4%

Benz-norcaradiene Carboxylic Acid.

Ethyl benz-norcaradiene carboxylate was hydrolysed with alcoholic potassium hydroxide. The solution after refluxing

121/for....

for half an hour was acidified and the precipitated acid filtered off and recrystallized from alcohol. It does not crystallize well, doubtless due to the increased number of theoretically possible geometrical isomers in the reduced product m.p. 162-4°C.

Found : C, 76.6% ; H, 6.4%

$C_{12}H_{12}O_2$ requires : C, 76.6% ; H, 6.4%

When mixed with benz-norcaradiene carboxylic acid there was a depression of the melting point.

Benz-norcarene carboxylic acid was also prepared by hydrogenation of pure benz-norcaradiene carboxylic acid (2.36 g.) with hydrogen in the presence of palladium/calcium carbonate catalyst. Hydrogen, 275 c.c. at N.T.P. i.e. equivalent to 0.98 double bonds, was absorbed. The material was identical with that already prepared.

Condensation of ethyl benz-norcarene carboxylate with ethyl diazoacetate.

Ethyl benz-norcarene (45 g.) was heated to 145°C., and ethyl diazoacetate (10 g., 0.33 mol.) added dropwise with rapid stirring over a period of five hours. The reaction was completed by slowly heated to 160°C., over a period of three hours. The reaction ^{mixture} was then distilled at reduced pressure, the following fractions being collected:-

Fraction (i) b.p. 130-150°C./1.0 m.m. 38.2 g.

(ii) b.p. 150-200°C./1.0 m.m. 6.0 g.

Fraction (i) which consisted of unchanged ethyl benz-norcarene carboxylate was retreated with ethyl diazoacetic ester as before

and the process repeated several times in order to obtain a substantial yield of condensation product. The high boiling fractions corresponding to fraction (ii), from five such condensations were amalgated (about 18 g.) and redistilled; the fraction boiling 160-190°C./1.0 m.m. (0.7 g.) being collected. As it was not found possible to get a pure product by fractionation, some of the material was hydrolysed as follows:-

The crude ester (3 g.) was mixed with potassium hydroxide (3 g.) dissolved in water (3 c.c.) and alcohol (30 c.c.). This mixture was refluxed for five hours and then extracted with ether to remove unsaponified substances. The aqueous layer was acidified and the liberated acids taken up in ether. The ethereal layer was dried over sodium sulphate. Removal of the ether left a resinous solid which could not be crystallized. On distillation at 0.1 m.m. pressure considerable decomposition took place. The yellow (pale) distillate set to a solid mass of crystals, m.p. 151-2°C. which on recrystallization were identified as benz-norcarene carboxylic acid.

As attempts to separate the two acids chromatographically were equally unsuccessful, an attempt was made to separate them by fractional distillation of their esters. The crude acid mixture (1 g.) was dissolved in absolute alcohol (5 c.c.) and sulphuric acid (0.5 c.c.) added. After refluxing for 5 hours the ester was worked up and distilled at 0.01 pressure.

Fraction (i) b.p. 120-130°C. ; 0.3 g.

Fraction (ii) b.p. 130-150°C. ; 0.5 g.

Although fraction (ii) probably contained a high proportion of

the dicarbethoxy compound the separation was not sufficiently good to obtain satisfactory analytical figures. The absorption of this fraction (see graph XIII) was found to be very different from the starting material and much more like that of an ethyl cyclo-heptatriene carboxylate.

Dehydrogenation.

The crude ester condensation product was distilled from 30% palladium charcoal catalyst at reduced pressure. The material came over pale blue in colour (b.p. 120-140°C./16 m.m.) but was colourless on redistillation. The absorption spectrum of this material was found to closely resemble that of 2:7-dimethyl naphthalene (see graph XIV) and it seems that in this case rearrangement had taken place. A picrate, orange coloured needles m.p. 120-1°C., was prepared but a satisfactory analysis could not be obtained, probably because the dimethyl naphthalenes were contaminated with methyl naphthalenes produced by decarb-ethoxylation and dehydrogenation of the ethyl benz-norbornene carboxylate, known to be present in the crude ester.

1-Chlorohydrindene.

Commercial indene (Eimer and Amend, 90% practical, 450 g.) was shaken with 20% caustic soda, concentrated hydrochloric acid, acid saturated ammonium sulphate in this order and finally dried over calcium chloride. It was then cooled in a freezing mixture to -5° to -10°C. and saturated with dry hydrogen chloride for two hours. After the excess of hydrogen chloride had been removed in a stream of air the residue was distilled at 15 m.m.,

b.p. 105-110°C. A total of 320 grams was obtained together with about 50 c.c. of low boiling material which did not react with hydrogen chloride.

c.f. Haworth J. 1947, 369.

Weingerber Ber. 1911, 44, 1444.

1-Hydroxy-hydrindene.

1-Chloro-hydrindene (305 g. ; 2 mol.), dioxan (300 c.c.) and a solution of potassium bicarbonate (200 g.) dissolved in water (600 c.c.) were separately and concurrently added to water (3000 c.c.) in a five litre flask equipped with a rapid stirrer over a period of four hours. The reaction mixture was then allowed to stand overnight. It was extracted with ether (twice was found sufficient) and the combined extracts after drying over sodium sulphate were distilled free of ether on a water bath at reduced pressure.

The residue was distilled at high vacuum and the following fractions collected at 8-10 m.m. pressure.

(i)	b.p. 70-110°C	70 g.	mainly indene.
(ii)	110-140°C	126 g.	the alcohol.
(iii)	140°	84 g.	the di-indyl-ether.

The yield was thus about 47% of the theoretical quantity.

c.f. Weingerber Ber., 1911, 44, 1444.

1-Acetoxy-hydrindene.

The crude once distilled 1-hydroxy-hydrindene, still containing some indene, fraction (ii), was mixed with acetic anhydride (100 c.c.) and slowly heated to 100° over a period of

five hours. It was then poured into water and sodium carbonate powder added until no more carbon dioxide was evolved. The ester was extracted out with ether and dried over sodium sulphate. After removal of the ether a saponification equivalent showed the presence of 62.5% ester.

The material was distilled and yielded the following fractions at 11 m.m. pressure.

(i) 74-120°C.	40 grams.
(ii) 120-140°C.	70 "
(iii) above 140°C.	20 "

The second fraction was redistilled and the fraction b.p. 125-9° / 11 m.m., 58.2 grams was retained.

The Condensation with Ethyl Diazoacetate.

1-Acetoxy-hydrindene (56 g.) was treated with 90% ethyl diazoacetate (10 c.c.) at 130-5° over a period of five hours with slow stirring. The mixture was then gradually heated to 160° over a period of two hours.

The reaction mixture was then distilled, the following fractions being collected:-

(i) b.p. 83-90° / 0.7 m.m.	51.9 g. recovered ester
(ii) 110-200° / 0.4 m.m.	5.8 g. violet blue.
(iii) high boiling residue	3 g. yellow resin.

Fraction (i) was retreated several times and then the combined condensation products redistilled and the deep blue fraction b.p. 140-160°C./0.5 m.m., 18 g. collected. It was obvious from the blue colour that it already contained azulene compounds.

126/Ethyl.....

Ethyl Azulene Carboxylate.

When this material (5 g.) was heated with sodium carbonate (1.5 g.) in a Claisen flask, immersed in an oil bath at 160-70°C. for half an hour, there was a marked increase in the depth of the colour. The deep violet material produced was fractionated and the main fraction b.p. 160-190°C./12 m.m. collected. Estimation of the quantity of azulene-like material by measuring the light absorption in the visible region showed the presence of not more than 3% of azulene compounds, calculated as ethyl azulene carboxylate.

Distillation of this crude azulene mixture from 30% palladium/charcoal catalyst did not seem to increase the quantity of azulene much. However, much of the impurities were destroyed and the product had a much narrower distillation range 170-180°C./11 m.m. It was estimated to contain 10-12% ethyl azulene carboxylate.

It could not be obtained pure because it was decomposed by 85% phosphoric acid and a crystalline compound with trinitro-toluene could not be formed, owing to the presence of the carbethoxy group. It could not be purified chromatographically. However, as it was considered unlikely that the impurities would effect the visible light absorption much. This material was employed in the spectrographic study.

Azulene.

The crude condensation product b.p. 140-160 /11 m.m. (6 g.) was saponified with potassium hydroxide (6 g.) dissolved in water (120 c.c.) for five hours.

The unhydrolysed material was removed by ether extraction and the acid recovered by acidification with 5N sulphuric acid. The liberated acid was taken up in ether and the ether layer after several washings with water, was dried over sodium sulphate and evaporated to dryness. The viscous residue (2 g.) was distilled from a 2 c.c. distilling flask containing 30% palladium/mercuric catalyst (0.2 g.). The blue green distillate was redistilled in vacuo. The deep blue oil so obtained (0.3 g.) was mixed with trinitrobenzene (0.15 g.) and ethyl alcohol (1 c.c.) and gently warmed. On cooling a mass of dark brown needles crystallized out, once from alcohol m.p. 160-2°C. (c.f. Plattner. Helv., 1937, 20, 224. m.p. 166.5-167.5°C.).

The azulene was regenerated chromatographically as blue plates with naphthalene-like odour.

2:3-Benz-cyclo-heptanol.

Sodium (30 g.) was added in small pieces over a period of one hour to a boiling solution of 2:3-benz-cyclo-heptenone (benz-suberone, 32 g.) dissolved in absolute alcohol (320 c.c.) When all the sodium was dissolved, the mixture was poured into water and the crystalline alcohol filtered off at the pump. A further quantity of the alcohol was obtained by extracting the filtrate with ether. After drying over sodium sulphate the ether was distilled off.

The combined material was then crystallized from light petrol (b.p. 35-50°C.) and yielded the almost pure alcohol, m.p. 100°C., 23 g. The mother liquors were evaporated to dryness

was treated dropwise with 90% ethyl diazoacetate (12 c.c.) over a period of five hours. The temperature was then slowly raised to 160°C. over a period of three hours. The product was distilled and the low boiling fraction b.p. 105-130°C./1 m.m. which was mainly unchanged acetate, retreated.

The combined high boiling products from four such condensations b.p. 120-170°C./0.4 m.m. (48 c.c.) were redistilled at 0.5 m.m. pressure, the following fractions being collected:-

- (i) 100-145°C. pale yellow mobile oil 5.0 g.
- (ii) 145-185°C. pale orange viscous oil 19.0 g.

As it was not found possible to obtain fraction (ii) pure by fractionation it was directly hydrolysed as follows:-

The ester (3 g.) was refluxed with potassium hydroxide (3 g.) dissolved in water (100 c.c.) until solution was complete, about four hours. The acid was worked up in the usual manner and distilled at 0.2 m.m. pressure, b.p. 150-200°C.

Carbon and hydrogen values suggest that it is a mixture of [0.5.5] -bicyclo-dodecatetraene carboxylic acid and some [0.5.5] -bicyclo-hydroxy-dodecatriene carboxylic acid because it was not found possible to get satisfactory analytical values for any of the fractions taken. Better results could not be obtained with concentrated alcoholic potassium hydroxide for the saponification.

Found : C, 75.3% ; H, 7.2%

The tetraene $C_{13}H_{14}O_2$ requires : C, 77.2% ; H, 6.9%

The alcohol $C_{13}H_{16}O_3$ requires : C, 70.9% ; H, 7.3%

[0.5.5] -Bicyclo-dodecatetraene carboxylic acid.

The mixed acid (b.p. 160-200°C./0.4 m.m., 6.2 g.) obtained by the saponification of the crude ethyl [0.5.5] - bicyclo-acetoxy-dodecaatriene carboxylate was heated to 160°C., in vacuo with finely ground fused potassium hydrogen sulphate (14.0 g.) for half-an-hour. After cooling the material was extracted out with water and ether. The ethereal layer was shaken with 5% caustic soda solution and this aqueous layer twice washed with ether to remove decarboxylated products, ethereal extract A. The aqueous layer after acidification was taken up in ether and the extract B after being washed with water, dried over anhydrous sodium sulphate. The ether from B was removed and the residue (4.06 g.) distilled at 0.4 m.m. pressure b.p. 150-160°C, as a viscous pale yellow oil.

Found : C, 76.7% ; H, 6.7%

$C_{13}H_{14}O_2$ requires : C, 77.2% ; H, 6.9%

Methyl-1:2-benz-cyclo-hepta-1:3-diene.

Ethereal extract A which contained the non-acid material was dried over sodium sulphate and the ether distilled off. A mobile oil with a pleasant petrol-like odour remained. It was distilled and yielded the following fractions at 17 m.m. pressure:-

(i) b.p. 90-100°C. 0.5 g. colourless mobile oil.

(ii) b.p. 200-230°C. 0.2 g. pale yellow viscous oil.

The low boiling fraction was redistilled and the fraction boiling about 100°C. collected; the quantity was too small to get an accurate boiling point.

$n_D^{19.5}$ 1.5869, n_{max} 13,400/251-7 m/u.

Found : C, 80.9% ; H, 9.0%

$C_{12}H_{14}$ requires : C, 81.1% ; H, 8.9%

1:2-Benz-cyclo-hepta-1:3-diene.

Pure 1:2-benz-cyclo-hepten-3-ol (2.21 g.) was mixed with finely ground potassium hydrogen sulphate (4.0 g.) and heated in vacuo at 160°C. for one hour. The hydrocarbon (1.6 g.) was then extracted out with ether and distilled at 10 m.m. pressure.

fraction (i) b.p. 80-85°C. 0.8 g.

(ii) b.p. 140-150°C. 0.6 g.

Fraction (i) was redistilled, the fraction b.p. 108-110°C. at 18 m.m., pressure being collected as a colourless mobile oil with a pleasant petrol-like odour.

$n_D^{19.5}$ 1.5873, n_{max} 15,600/254 m/u.

Found: C, 91.5% ; H, 8.5%

calculated for $C_{11}H_{12}$: C, 91.7% ; H, 8.3%

Methyl [0.5.5] -bicyclo-dodecatetraene Carboxylate.

The pure distilled acid (3.18 g.) was dissolved in absolute methyl alcohol (15 c.c.) and concentrated sulphuric acid (1.5 c.c.). After refluxing the mixture for two hours, it was poured into water and the ester worked up in the usual manner to yield the mobile ester (3.28 g.). This was distilled and the fraction b.p. 95° /0.01 m.m. collected. A pale yellow oil n_D^{18} 1.5682, n_{max} 10, 280/251 m/u E inflex. 1,560/324 m/u.

Found: C, 76.4% ; H, 7.7%

calculated for $C_{14}H_{16}O_2$: C, 76.0% ; H, 7.4%

When hydrogenated in the presence of a palladium calcium carbonate catalyst, hydrogen equivalent 1.8 double bonds was absorbed. The hydrogenated ester was recovered by filtering off the catalyst and distilling off the alcohol. The oily residue was distilled at 0.1 m.m. pressure and the best fraction b.p. $95^{\circ}C$ reserved for the absorption spectrum study. It showed a continuous absorption of light throughout the spectrum without any maxima, see graph (III).

Methyl Dibromo- [0.5.5] -bicyclo-dodecatetraene Carboxylate.

N-Bromo-succinimide (1.67 g., 2 mol.) was added to a solution of pure methyl [0.5.5] -bicyclo-dodecatetraene carboxylate in dry carbon tetrachloride (4 c.c.). Fresh benzoyl peroxide (0.05 g.) was then added and the mixture placed under reflux. No reaction took place in the absence of the catalyst. A reaction quickly set in, as was shown by the tendency of the insoluble material to float on the surface of the carbon tetrachloride. After two hours a test portion of the solid was acidified with dilute acid and a drop of potassium iodide added. Only a pale yellow colour was produced indicating that the reaction was almost complete.

The mixture was then cooled and the succinimide filtered off and dried (0.9 g.). (The theoretical quantity expected 0.93g. The filtered carbon tetrachloride solution was evaporated to dryness and left a dark brown viscous mass. An attempt to obtain

pure material for analysis by distillation proved unsuccessful as the material readily decomposed into a charred mass.

A drop of the material was treated with alcoholic silver nitrate solution and instantaneously yielded a yellow precipitate of silver bromide, clearly demonstrating that the bromine was held in an allylic position in the molecule.

A proportion of the bromo-derivative was heated with the molecular quantity of diethyl aniline for one hour at 100°C. but after working up the product still gave a precipitate with alcoholic silver nitrate, and it was found that the bromide was completely removed only on heating with diethyl aniline for four hours on a steam bath.

The material was then mixed with ether and extracted with dilute acid. The ether layer was washed with water and finally dried over sodium sulphate. Removal of the ether left a viscous oil which was distilled.

Fraction (i) b.p. 100-110°C./0.1 m.m. pale yellow oil 0.1 g.

(ii) b.p. 110-130°C./0.1 m.m. 0.1 g.

The fraction (i) gave a negative test with alcoholic silver nitrate and on analysis it was found to contain only 0.86% bromine, showing that only a negligible quantity of the bromine was held as vinyl bromide.

Absorption study of fraction (i) showed two maxima
E max, 7,560/241 m/μ, E max₂ 7,560/256.

Fraction (ii) E max, 7,000/245 m/μ., E max₂ 7,130/256-μ
m/μ. Thus both fractions had an absorption less than that of methyl [0.5.5] -bicyclo-dodecetetraene carboxylate.

Ethyl Bicyclo- [0.4.5] -Undecatriene Carboxylate.

U.V. Spectrum VIII (see graphs (ii) and (vi).)

<i>mμ</i>	Log E	<i>mμ</i>	Log E	<i>mμ</i>	Log E	<i>mμ</i>	Log E
220	4.340	258	3.37	296	3.33	342	2.70
222	3.95	260	3.38	298	3.32	344	2.63
224	3.90	262	3.40	300	3.31	346	2.59
226	3.84	264	3.42	302	3.29	348	2.53
228	3.78	266	3.44	304	3.28	350	2.46
230	3.69	268	3.45	306	3.27	363	2.164
232	3.58	270	3.44	310	3.23	364	2.061
234	3.51	272	3.44	314	3.19	366	1.997
236	3.42	274	3.46	316	3.17	367	1.923
238	3.33	276	3.45	320	3.11	368	1.832
240	3.25	278	3.43	324	3.05	370	1.797
242	3.22	280	3.42	326	3.02	372	1.672
244	3.21	282	3.41	328	2.99	376	1.164
246	3.22	284	3.40	330	2.96	377	1.134
248	3.23	286	3.39	332	2.92	378	1.097
250	3.26	288	3.38	334	2.87	380	1.041
252	3.28	290	3.37	336	2.83	382	0.948
254	3.30	292	3.35	338	2.79	384	0.832
256	3.33	294	3.34	340	2.75		

Ethyl-cyclo-heptatriene-Carboxylate.

U.V. Spectrum VII (see graph VII).

$m\mu$	Log E	$m\mu$	Log E	$m\mu$	Log E	$m\mu$	Log E
224	3.60	244	3.121	287	3.513	324	2.802
225	3.362	244	3.137	290	3.487	344	2.207
230	3.137	246	3.176	295	3.458	345	2.104
231	3.121	248	3.207	297	3.428	346	2.061
231.2	3.104	251	3.283	300	3.396	347	2.013
231.5	3.083	253	3.324	303	3.362	348	1.964
231.6	3.061	256	3.362	306	3.324	349	1.937
232	3.037	259	3.396	308	3.283	350	1.906
233	3.013	260	3.428	314	3.207	351	1.873
235	2.990	263	3.458	315	3.137	352	1.760
238	3.013	266	3.487	316	3.104	358	1.207
239	3.037	267	3.513	317	3.083	370	1.083
240	3.061	271	3.538	319	3.037	372	1.013
241	3.083	276	3.561	320	3.013	374	0.873
242	3.104	284	3.538	322	2.905	380	0.760

1-, 2- Methyl Naphthalene mixture, by dehydrogenation of ethyl
[0.4.5] -bicyclo-undecatriene carboxylate. (graph V).

μ	Log E	μ	Log E	μ	Log E	μ	Log E
233	3.764	253	3.299	286	3.548	307	2.521
234	3.464	256	3.272	287	3.521	309	2.483
235	3.318	257	3.318	289	3.493	312	2.443
236	3.272	260	3.358	291	3.464	315	2.299
237	3.193	261	3.431	293	3.431	316	2.260
238	3.173	262	3.464	294	3.272	318	1.998
239	3.149	264	3.493	297	3.241	319	2.260
240	3.093	265	3.521	298	3.196	320	2.400
242	3.065	267	3.548	299	3.033	323	2.400
245	3.065	270	3.573	300	2.839	324	1.646
247	3.149	271	3.596	302	2.764	326	1.366
249	3.196	274	3.618	303	2.672	327	1.124
250	3.260	279	3.640	304	2.588	328	0.998
252	3.281	285	3.618	305	2.556		

Ethyl Bicycle [0.5.5]-Dodecatriene Carboxylate

U.V. Spectrum IX (graph VI).

$m\mu$	Log E	$m\mu$	Log E	$m\mu$	Log E	$m\mu$	Log E
218	4.097	246	3.28	278	3.34	310	3.18
220	4.05	248	3.28	280	3.33	312	3.17
222	4.01	250	3.29	282	3.32	314	3.16
224	3.97	252	3.30	284	3.31	316	3.14
226	3.91	254	3.31	286	3.30	318	3.12
228	3.83	256	3.32	288	3.29	320	3.11
230	3.75	258	3.33	290	3.27	322	3.09
232	3.67	260	3.34	292	3.26	324	3.06
234	3.59	262	3.36	294	3.25	326	3.05
235	3.51	264	3.36	296	3.24	328	3.02
236	3.56	266	3.37	298	3.23	330	2.98
237	3.47	268	3.37	300	3.22	332	2.92
238	3.41	270	3.37	302	3.21	336	2.85
240	3.35	272	3.37	304	3.20	340	2.78
242	3.33	274	3.36	306	3.19	344	2.69
244	3.29	276	3.35	308	3.19	350	2.55

Dimethyl Naphthalene Mixture, by dehydrogenation of ethyl
[0.5.5] -bicyclo-dodecatriene carboxylate (graph VII).

$m\mu$	Log E	$m\mu$	Log E	$m\mu$	Log E	$m\mu$	Log E
224	4.009	262	3.516	300	3.093	330	1.826
226	4.068	264	3.544	302	2.982	331	1.792
228	4.111	266	3.574	304	2.863	332	1.790
230	4.127	268	3.594	306	2.778	333	1.826
232	4.065	270	3.620	308	2.724	334	1.839
234	3.821	272	3.644	310	2.608	335	1.865
236	3.535	274	3.650	312	2.556	336	1.834
238	3.324	276	3.660	314	2.513	337	1.766
240	3.230	278	3.654	315	2.477	338	1.716
242	3.196	280	3.647	316	2.446	340	1.644
244	3.176	282	3.647	317	2.430	342	1.583
246	3.182	284	3.625	318	2.446	344	1.519
248	3.248	286	3.591	319	2.461	346	1.400
250	3.272	288	3.559	320	2.461	348	1.384
252	3.324	290	3.505	321	2.447	350	1.335
254	3.366	292	3.462	322	2.413	355	1.248
256	3.405	294	3.407	324	2.238	360	1.204
258	3.444	296	3.314	326	2.029	365	1.124
260	3.471	298	3.186	328	1.899	370	1.107

Alkyl Azulenes or Heptalene, graph VIII.

<i>mu</i>	E	<i>mu</i>	E	<i>mu</i>	E	<i>mu</i>	E
450	1.83	520	4.03	595	6.00	665	3.58
455	1.77	525	4.25	600	6.33	670	3.06
460	1.83	530	4.67	605	6.42	675	2.28
465	1.87	535	5.09	610	6.00	680	1.98
470	1.97	540	5.35	615	5.17	685	1.86
475	2.10	550	5.70	620	4.92	690	2.16
480	2.26	555	6.12	625	5.35	695	3.20
485	2.38	557	6.17	630	6.43	700	3.33
490	2.55	560	6.12	635	6.30	705	2.22
495	2.75	565	6.00	640	5.48	710	1.42
500	3.01	570	6.10	645	4.35	715	1.03
505	3.21	575	6.82	650	3.44	720	0.083
510	3.47	580	7.10	655	3.40	750	0.062
515	3.98	590	6.10	660	3.74		

141/1:2-Benz....

1:2-Benz-cyclo-heptene, graph IX.

<i>mu</i>	Log E	<i>mu</i>	Log E	<i>mu</i>	Log E	<i>mu</i>	Log E
224	4.167	250	3.587	278	2.625	308	1.026
226	4.009	252	3.618	280	2.487	310	0.986
227	3.818	254	3.645	282	2.398	312	0.980
228	3.623	256	3.676	284	2.318	314	0.899
229	3.447	258	3.673	286	2.262	316	0.791
230	3.301	260	3.669	288	2.215	318	0.943
232	3.178	262	3.669	290	2.094	319	1.026
234	3.175	263	3.676	292	1.965	320	0.987
236	3.220	264	3.668	294	1.819	322	0.644
238	3.284	266	3.589	296	1.630	324	0.359
240	3.344	268	3.542	298	1.446	326	0.198
242	3.393	270	3.483	300	1.280	330	T.92
244	3.450	272	3.447	302	1.164	340	T.526
246	3.500	274	3.104	304	1.159		
248	3.543	276	2.815	306	1.136		

Hydrocarbon after removal of Dimethyl Naphthalene (graph IX).

μ	Log E	μ	Log E	μ	Log E	μ	Log E
220	4.41	260	3.725	300	2.816	340	1.838
230	4.188	270	3.616	310	2.575	350	0.959
240	3.613	280	3.452	320	2.225		
250	3.710	290	3.255	330	1.578		

Recovered Ethyl Bicyclo-[0.5.5]-Dodecatriene Carboxylate

224	3.797	266	3.408	300	3.057	334	2.345
230	3.618	268	3.407	304	2.992	336	2.281
235	3.524	270	3.401	306	2.959	338	2.220
240	3.456	272	3.399	308	2.924	340	2.164
245	3.423	274	3.383	310	2.892	342	2.094
250	3.396	276	3.363	312	2.856	344	2.025
252	3.357	278	3.346	316	2.775	348	1.904
254	3.382	280	3.333	320	2.686	350	1.857
256	3.382	282	3.316	324	2.590	355	1.728
258	3.387	286	3.212	326	2.551	360	1.562
260	3.360	290	3.218	328	2.480	370	1.223
262	3.404	292	3.188	330	2.442	380	0.892
264	3.410	296	3.125	332	2.393		

Blue Ester Purified by phosphoric acid treatment, Graph X.

$m\mu$	Log E	$m\mu$	Log E	$m\mu$	Log E	$m\mu$	Log E
230	3.83	320	2.56	355	2.16	400	1.54
240	3.67	330	2.46	360	2.06	410	1.40
250	3.54	340	2.41	365	1.96	420	1.23
260	3.43	350	2.29	370	1.85	430	1.10
270	3.51	342	2.44	375	1.81	440	0.964
280	3.51	344	2.40	380	1.77	450	0.876
290	3.31	346	2.35	385	1.74	460	0.845
300	3.98	348	2.29	390	1.66	470	0.808
310	2.71	350	2.23	395	1.60	480	0.808

Visible Spectrum.

$m\mu$	E	$m\mu$	E	$m\mu$	E	$m\mu$	E
500	5.30	565	10.7	630	11.57	695	5.64
505	5.53	570	11.0	635	11.50	700	5.86
510	5.64	575	11.8	640	10.60	705	4.58
515	6.43	580	12.2	645	9.55	710	3.86
520	6.80	585	12.0	650	8.90	715	3.32
525	7.23	590	11.7	655	8.70	720	3.16
530	7.86	595	11.65	660	8.88	725	3.10
535	8.42	600	12.18	665	8.67	730	2.99
540	8.90	605	12.35	670	7.45	735	2.58
545	9.04	610	12.02	675	7.27		
550	9.62	615	11.30	680	5.67		
555	10.3	620	10.77	685	5.36		
560	10.6	625	10.85	690	5.02		

Ethyl 2- Naphthoate.

Graph XI.

μ	Log E	μ	Log E	μ	Log E	μ	Log E
216	4.062	254	3.509	289	3.692	326	2.945
218	4.285	256	3.544	290	3.699	328	2.926
220	4.382	258	3.578	292	3.679	329	2.964
222	4.464	260	3.603	294	3.502	330	3.025
224	4.532	262	3.626	296	3.225	331	3.100
226	4.600	264	3.655	298	3.004	332	3.180
228	4.677	266	3.708	300	2.875	334	3.205
230	4.742	268	3.777	302	2.870	335	2.966
232	4.765	270	3.774	304	2.846	336	2.768
234	4.767	272	3.774	306	2.808	338	2.301
236	4.787	274	3.774	308	2.802	340	1.700
238	4.817	276	3.804	310	2.835	342	1.470
240	4.690	278	3.842	312	2.850	344	1.157
242	4.446	280	3.854	314	2.882	346	0.888
244	4.191	282	3.816	316	2.985	348	0.706
246	3.750	284	3.735	318	3.053	350	0.569
248	3.590	286	3.676	320	2.975	352	0.138
250	3.517	287	3.676	322	2.932	354	0.016
252	3.495	288	3.684	324	2.946		

Ester obtained by dehydrogenation of Ethyl Bicyclo- [0.5.5] -
Dodecatriene carboxylate- before treatment with potassium
permanganate. Graph XI.

μ	Log E	μ	Log E	μ	Log E	μ	Log E
225	3.758	266	3.263	298	2.836	330	2.312
230	3.638	268	3.249	300	2.790	332	2.284
235	3.553	270	3.232	302	2.747	334	2.248
240	3.484	272	3.216	304	2.710	336	2.202
242	3.458	274	3.187	306	2.677	338	2.155
244	3.418	276	3.161	308	2.646	340	2.103
246	3.395	278	3.139	310	2.618	342	2.050
248	3.366	280	3.124	312	2.590	344	1.998
250	3.353	282	3.101	314	2.560	346	1.948
252	3.333	284	3.076	316	2.532	348	1.895
254	3.313	286	3.055	318	2.506	350	1.842
256	3.302	288	3.030	320	2.473	355	1.701
258	3.293	290	2.997	322	2.450	360	1.553
260	3.286	292	2.965	324	2.418	365	1.406
262	3.285	294	2.927	326	2.381	370	1.232
264	3.276	296	2.882	328	2.346		

Esters obtained by treatment of the Dehydrogenation product
of Ethyl Bicyclo- [0.5.5] -Dodecatriene Carboxylate with
potassium permanganate. Graph XI.

$\mu\mu$	Log E	$\mu\mu$	Log E	$\mu\mu$	Log E	$\mu\mu$	Log E
228	3.651	260	3.171	292	2.681	324	1.732
230	3.586	262	3.155	294	2.618	326	1.688
232	3.549	264	3.145	296	2.537	328	1.640
234	3.518	266	3.128	298	2.435	329	1.632
236	3.508	268	3.104	300	2.342	330	1.623
238	3.498	270	3.082	302	2.250	331	1.641
240	3.472	272	3.066	304	2.161	332	1.655
242	3.435	274	3.018	306	2.082	333	1.654
244	3.393	276	2.982	308	2.022	334	1.625
246	3.348	278	2.952	310	1.971	336	1.591
248	3.308	280	2.925	312	1.921	338	1.461
250	3.288	282	2.898	314	1.884	340	1.366
252	3.262	284	2.860	316	1.854	345	1.117
254	3.229	286	2.827	318	1.828	350	0.898
256	3.208	288	2.790	320	1.791	360	0.629
258	3.190	290	2.738	322	1.760	370	0.560

The crude Ester fraction obtained by Dehydrogenation of
Ethyl Bicyclo- [0.5.5] -Dodecatriene Carboxylate.

$m\mu$	Log E	$m\mu$	Log E	$m\mu$	Log E	$m\mu$	Log E
214	4.199	246	3.521	282	3.305	318	2.403
216	4.170	248	3.509	284	3.283	320	2.350
218	4.193	250	3.505	286	3.246	322	2.318
220	4.193	252	3.502	288	3.223	324	2.270
222	4.201	254	3.490	290	3.176	326	2.218
224	4.166	256	3.483	292	3.130	328	2.164
226	4.164	258	3.474	294	3.053	330	2.130
227	4.114	260	3.464	296	3.072	332	2.104
228	4.053	262	3.459	298	2.927	334	2.072
229	3.982	264	3.452	300	2.845	336	2.033
230	3.911	266	3.446	302	2.799	338	1.992
232	3.769	268	3.430	304	3.722	340	1.943
234	3.662	270	3.408	306	2.669	342	1.907
236	3.613	272	3.395	308	2.628	344	1.860
238	3.581	274	3.373	310	2.572	346	1.821
240	3.562	276	3.354	312	2.537	348	1.771
242	3.547	278	3.335	314	2.498	350	1.735
244	3.534	280	3.318	316	2.441	360	1.568

Ethyl 3:4 - Benz-nor-caradiene Carboxylate.

Graph XII.

$m\mu$	Log E	$m\mu$	Log E	$m\mu$	Log E	$m\mu$	Log E
240	3.751	263	3.751	286	3.625	304	3.041
243	3.516	264	3.785	287	3.574	305	3.087
248	3.450	266	3.817	290	3.516	308	3.149
249	3.516	272	3.848	296	3.369	310	3.087
253	3.574	279	3.817	298	3.256	310	2.892
256	3.625	282	3.785	299	3.183	311	2.751
258	3.670	283	3.751	301	3.041	312	2.369
260	3.713	285	3.713	302	2.972	314	2.0

Ethyl 3:4-Benz-norcarene Carboxylate.

217	3.899	238	3.722	252	2.627	266	2.627
222	3.966	239	3.600	253	2.564	270	2.564
226	4.025	245	3.104	254	2.342	275	2.467
231	3.966	246	2.927	258	2.408	278	2.408
233	3.899	247	2.803	259	2.467	279	2.342
235	3.820	250	2.724	262	2.564	281	2.167

Ethyl Methyl - benz-norcaradiene Carboxylate

Graph XII.

$m\mu$	$\text{Log}_{10} E$	$m\mu$	$\text{Log}_{10} E$
230	4.292	305	3.045
235	4.124	310	2.813
240	3.903	315	2.619
245	3.489	320	2.328
250	3.412	325	2.328
255	3.490	330	2.253
260	3.580	335	2.185
265	3.652	340	2.107
270	3.708	345	2.017
275	3.722	350	1.929
280	3.702	355	1.836
285	3.637	360	1.730
290	3.512	365	1.621
295	3.386	370	1.519
300	3.180	375	1.420

Ethyl Carboethoxy-3:4-cyclo-heptatrienyl-norcarene Carboxylate.

U.V. Spectrum V (graph XIII).

<i>mμ</i>	Log E	<i>mμ</i>	Log E	<i>mμ</i>	Log E	<i>mμ</i>	Log E
233	3.937	245	3.470	259	3.31	305	3.41
235	3.878	246	3.44	262	3.34	310	3.38
237	3.843	248	3.380	266	3.38	314	3.34
239	3.732	249	3.34	269	3.41	323	3.31
240	3.636	251	3.31	276	3.44	326	3.27
241	3.600	252	3.27	280	3.47	328	3.23
242	3.556	254	3.23	290	3.47	332	3.18
243	3.459	257	3.27	297	3.44	340	3.01

Hydrocarbon obtained by dehydrogenation of Ethyl Carboethoxy -
3:4 - cyclo-heptatrienyl norcarene Carboxylate. Graph XIII.

<i>m_u</i>	Log E	<i>m_u</i>	Log E	<i>m_u</i>	Log E	<i>m_u</i>	Log E
234	3.542	258	3.339	281	3.292	315	2.161
235	3.265	259	3.362	293	3.176	316	2.080
236	3.210	260	3.410	296	3.061	317	2.029
237	3.176	262	3.441	297	2.964	319	1.962
238	3.140	263	3.477	299	2.763	320	1.997
243	3.104	266	3.508	300	2.775	322	2.086
248	3.140	273	3.542	301	2.617	323	2.086
249	3.176	282	3.508	302	2.537	324	1.997
253	3.210	285	3.477	303	2.474	325	1.962
255	3.238	288	3.441	306	2.401		
256	3.292	289	3.339	308	2.362		
257	3.316	290	3.316	314	2.265		

ACKNOWLEDGEMENTS.

I wish to put on record my sincere thanks to Dr. W. S. Rapson for his constant help and advice. I am also indebted to Professor W. Pugh for the generous laboratory facilities placed at my disposal and to Dr. M. Lanchen and Dr. F. G. Hellman for their assistance during the latter part of the work.