A STUDY OF THE THERMAL DEGRADATION OF MODEL COMPOUNDS OF AMINE-CURED EPOXIDE RESINS

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MASTER OF SCIENCE

by

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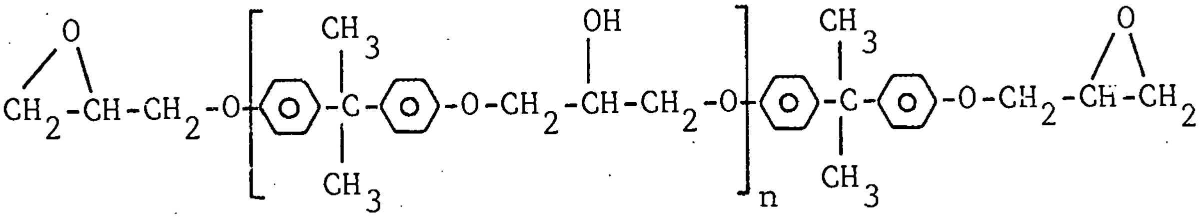
CONTENTS

SUMMARY

The thermal degradation of model compounds of amine-cured epoxide resins has been studied with the aim of investigating the thermal stability of the "cure-linkage". 1,3-Diphenoxypropan-2-ol and 1-(N-ethylanilino)-3-phenoxypropan-2-ol have been synthesised and degraded under various conditions. The results of these degradations are presented and their relevance to the thermal degradation of amine-cured epoxide resins is discussed. The effect of the presence of alumina, which has been used as a filler for epoxide resins, on the thermal stability of the model compounds has been examined. The possibility that the degradation of model compounds may be used as a synthetic route to benzofuran has been investigated.

I. INTRODUCTION

The demand for materials possessing good thermal stability for use in many fields, particularly in aerospace applications, has led to considerable interest in the behaviour of thermosetting resins at high temperatures[1]. Particular attention has been paid to epoxide resins which are noted for their good mechanical, electrical and adhesive properties[1]. The maximum operating temperatures of conventional epoxide resins are in the region of 200 to 260°C but it is considered that they can be modified for use at higher temperatures[2]. A typical and commonly used epoxide resin is based on Bisphenol A and has the following structure[3]:



Where n may vary from 0 to 20.

Epoxide resins may be cured by reaction with a variety of cross-linking agents (hardeners) including aliphatic and aromatic diamines, acid anhydrides and dicarboxylic acids. The thermal stability of the cured resin depends on the particular epoxide/hardener combination. An amine-cured epoxide resin based on Bisphenol A has the following part-structure:

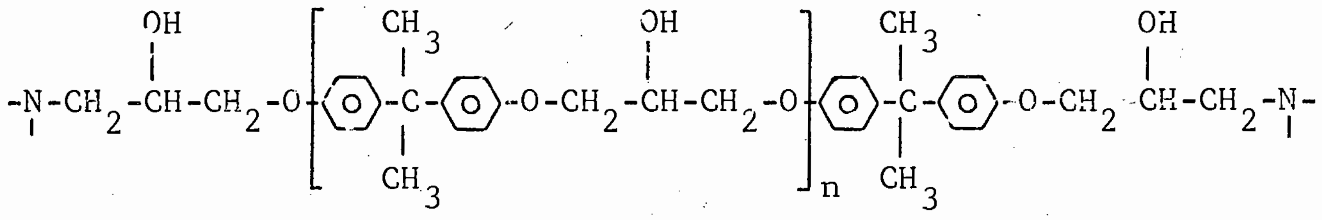
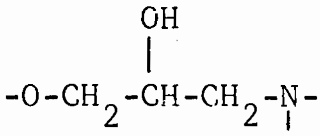


FIGURE 1.



The "cure-linkage" is represented by the $-O-CH_2-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_2-\underset{|}{N}-$ group.

Investigations of the thermal behaviour of cured epoxide resins which attempt to determine the initial point of breakdown of the resin network and the mechanism of degradation may provide a rational basis for improving the thermal properties of these materials. An appreciable amount of work in this direction has been done.

The effect of oxidising conditions on the thermal degradation of epoxide resins was studied[1,4]. Results showed that oxidation of the hydroxyl group to a carbonyl group occurred at relatively low temperatures (150 - 200°C) [5,6]. DANTE and CONLEY[6] suggested that in amine-cured resins oxidation occurred at the nitrogen atoms followed by fission of the network and rearrangement to form keto groups.

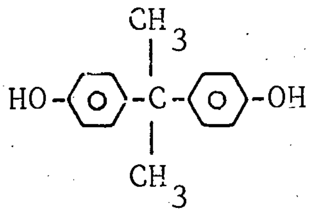
The thermal degradation <u>in vacuo</u> of amine- and anhydride-cured resins provided much useful information on the degradation reactions[1].

Much work carried out on the uncured or incompletely cured epoxide led to the postulation of reaction mechanisms which depended on the presence of free epoxide groups. These mechanisms, postulated by LEE[7,8] and NIEMAN and coworkers[9-11], were used to account for the more volatile degradation products. LEE[7] also postulated a mechanism for the formation of higher boiling degradation products, which were mostly phenols and cresols, from uncured epoxide resins. These mechanisms did not account for the differing stabilities imparted to the network by different hardeners. Furthermore, infra-red studies showed that very few epoxide groups remain in a properly cured resin[12].

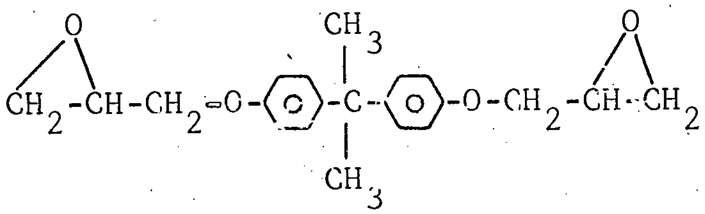
The suggestion that dehydration reactions occur during the degradation of epoxide resins, originally put forward by LEE[7,8], was supported by many workers in this field[13-15]. In fact it was shown that dehydration is an early step in the degradation of amine-cured epoxide resins[1,16]. Water was positively identified as a degradation product and infra-red studies indicated that double bond structures were formed during the early stages of degradation[1,15,16]. LEISEGANG, STEPHEN and PATERSON-JONES[17] suggested that dehydration preceded to a large extent any further degradation of the resin network and that the driving force behind the reaction was the increased stability of the system which resulted from cross-conjugation.

BISHOP and SMITH[18] showed that initial degradation of amine-cured epoxide resins at 400°C led to the formation of hydrogen, methane and water, a process which, they suggested, did not involve breakdown of the network structure. Methane was shown by ^{14}C-labelling to be liberated initially from the isopropylidene group. These workers postulated that hydrogen and water were formed by competing dehydrogenation and dehydration reactions associated with the secondary alcohol groups in the cured resin structures.

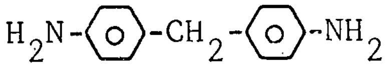
A study[16] of the changes in dielectric properties of an epoxide resin based on the diglycidyl ether of Bisphenol A cross-linked with p,p'-diaminodiphenylmethane (DDM) (fig.2) post-cured at temperatures ranging from 200 to 310°C revealed two dispersion regions : A high temperature/low frequency region associated with the glass transition of the network and a broad low temperature/high frequency region attributed to movement of the hydroxyl dipole of the glyceryl portion of the network. Other workers[19,20] attributed the latter dispersion region to movement of the entire glyceryl portion of the network. In any event absorption would depend on the presence of the hydroxyl group and the extent of this absorption would give an estimate of the hydroxyl concentration in the network.



BISPHENOL A



DIGLYCIDYL ETHER OF BISPHENOL A



p,p'-DIAMINODIPHENYLMETHANE (DDM)

A section of the cured resin may be represented as follows:

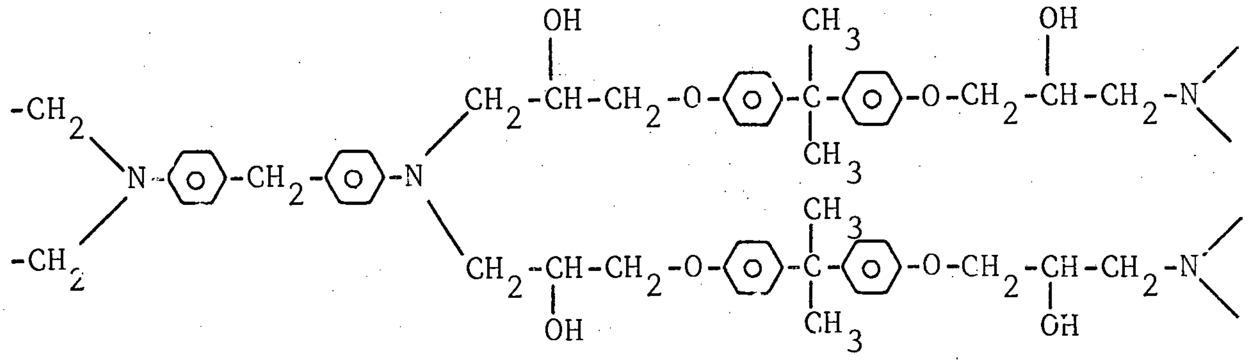


FIGURE 2

The results of PATERSON-JONES[16] et al. indicated that post-cure of the resin at approximately 220°C rather than 200°C increased the cross-linking of the network (reflected by an increase in the hydroxyl concentration) while the glass transition temperature remained approximately constant. Post-cure at approximately 245°C left the concentration of hydroxyl groups unaltered but caused the glass transition temperature to be lowered. This indicated that chain scission reactions were taking place. At a curing temperature of 295°C both the hydroxyl concentration and the glass transition temperature decreased which indicated that both dehydration as well as chain fission reactions had occurred.

Many workers[13,14,16-18] postulated that decomposition of epoxide resins occurred through degradation of the reacted glycidyl group and breakdown of the isopropylidene linkage in the Bisphenol portion of the network. BOWEN[2] investigated the relative thermal stability of these two groups by radiothermal analysis. His results showed that products resulting from the breakdown of the reacted glycidyl group in amine- and anhydride-cured epoxide resins were released at a temperature much lower than that observed for the release of products from the isopropylidene group. This result was confirmed by the work of BISHOP and SMITH[18].

BOWEN's[2] method of studying the liberation of ^{14}C-labelled fragments from the network unfortunately required the scission of two bonds in the network and did not necessarily pinpoint the initial point of breakdown of the resin although his results did suggest that the "cure-linkage" played an important part in the degradation reactions. The production of large quantities of N-substituted anilines in the degradation of the DDM-cured Bisphenol A epoxide resin[16] emphasised the importance of the "cure-linkage" in the degradation process.

A detailed study of the thermal degradation of model compounds of amine-cured epoxide resins was expected to provide further information on the mechanism of the degradation. In the present work model compounds were studied with the aim of investigating the thermal stability of the "cure-linkage". 1,3-Diphenoxypropan-2-ol and 1-(N-ethylanilino)-3-phenoxypropan-2-ol were synthesised and degraded under various conditions.

The degradation of 1,3-diphenoxypropene provided further insight into the mechanism of the degradation of 1,3-diphenoxypropan-2-ol. These results were used to interpret the mechanism involved in the degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol which in turn was related to the degradation of amine-cured epoxide resins.

The study of model compounds has a limitation in that the compounds are degraded in the liquid state and are free to interact with one another. A cured resin, however, exists in the form of a relatively rigid three-dimensional network in which interactions between different portions of the network are less likely[21]. The major products of the degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol were, however, analogous with those found by PATERSON-JONES[22] to result from the degradation of the adduct of the diglycidyl ether of Bisphenol A and p,p'-diaminodiphenylmethane (fig.2), an indication that the mechanism involved in the degradation of the model compound could be related to that of the resin.

A variety of fillers has been used to modify the properties of cured epoxide resins. The thermal stability of a resin may be profoundly modified by the nature of the filler used. The model compounds were degraded over alumina, a material which has been used as a filler, to determine its effect on the degradation reaction.

Products containing the benzofuryl moiety were observed among the major components of the degradation of the DDM-cured diglycidyl ether of Bisphenol A[17]. It was suggested[22] that thermal degradation of model compounds of this resin may provide a synthetic route to benzofuryl compounds. This possibility was investigated.

II. EXPERIMENTAL

II.1. ANALYTICAL TECHNIQUES

II.1.1. Gas Chromatography (GLC)

A Pye series 105 model 15 automatic preparative gas chromatograph was used to isolate and to identify unknown products by a comparison of their retention times with those of standard compounds.

A polar 4,57m x 0,953cm diameter glass preparative column packed with 25% polyethyleneglycol PEG 20M on 60-72 mesh silanised Celite provided a good separation of the products. Permanent gases, aliphatic hydrocarbons and very polar compounds with heavy substituents were, however, not detected and no attempt was made to isolate or to identify these compounds. The operating conditions for each chromatogram were approximately constant:

Operating temperature	180 - 1°C
Carrier gas (N_2) flow rate	206,9 ml/min
Column pressure	30 - 1 p.s.i.

Retention times which were measured from the time of injection of the samples were corrected against the retention times of standard compounds. Corrected retention times were calculated by

$$t_c = t \times t_s/t_{s'}$$

where t_c = corrected retention time

t = measured retention time

t_s = actual retention time of standard

$t_{s'}$ = measured retention time of standard.

II.1.2. Infra-red Spectroscopy

IR spectra were measured on a Perkin-Elmer model 457 grating spectrophotometer scanning from 4000 cm^{-1} to 250 cm^{-1}. The maximum resolution of the spectrophotometer is quoted as 2 cm^{-1} at 3000 cm^{-1} and 1 cm^{-1} at 1000 cm^{-1}.

IR spectra of liquid compounds were determined on liquid films between potassium bromide plates and spectra of solid compounds were measured on potassium bromide discs.

II.1.3. Proton Magnetic Resonance Spectroscopy

PMR spectra were determined on a Varian A-60 Analytical PMR spectrometer. Deuterated chloroform was used as the solvent with tetramethylsilane (TMS) as the internal standard.

II.1.4. Mass Spectroscopy

Mass spectra were used to elucidate chemical structures and also to determine the structures of unknown compounds by a comparison of their mass spectra with those of standard compounds.

In certain cases the products of degradation reactions were separated and collected by preparative GLC and were identified from their mass spectra. In other cases a mass spectrometer coupled to a Perkin-Elmer model 990 gas chromatograph was used to provide the mass spectra of individual compounds which eluted from the chromatograph (this work was performed by Mr. P.R. Boshoff of the Department of Chemistry, University of Stellenbosch). The same chromatograph column was used as in the preparative GLC (section II.1.1.).

II.1.5. Elemental Analyses

Elemental analyses were performed by Dr. K.G. Fuhr of the Department of Chemistry, University of Cape Town and by Dr. F. Pascher, Bonn, Germany. The results are collected in table 1.

II.1.6. Melting Points

All melting points quoted are corrected and were determined on a Kofler hot stage.

II.2. SYNTHETIC METHODS

II.2.1. 1,3-Diphenoxypropan-2-ol

The preparation of 1,3-diphenoxypropan-2-ol was based on the method of KULIEV, ALEKPEROV and AKHMEDOV[23].

Epichlorohydrin (39 ml; 0,5 mole) was added dropwise to a stirred solution of phenol (94g; 1 mole) in a 40% sodium hydroxide solution (55 ml; 0,55 mole). The mixture was heated under reflux on a waterbath for 2 - 3 hr. On cooling the mixture to room temperature a precipitate formed which was filtered, washed and recrystallized from a mixture of acetone and water (white prisms; 98,1g; 80,41%; m.p. 81-2°C; Lit. m.p. 81-2°C[23-26]). The sample's structure was established from IR, PMR and mass spectra. Elemental analyses are given in table 1.

II.2.2. 1-(N-Ethylanilino)-3-phenoxypropan-2-ol

The synthesis of this compound was based on the method suggested by BEASLEY, PETROW and STEPHENSON[25].

Phenyl glycidyl ether (97,3g; 0,649 mole) and N-ethylaniline (78,5g; 0,649 mole) in ethanol (75 ml) were heated under reflux on a waterbath for 4 hr. The solution was distilled under reduced pressure and collected as a pale yellow syrup (138,6g; 78,9%; b.p. 198-200°C/1,1 mm Hg; Lit. b.p. 156°C/

0,1 mm Hg[25]). The structure of the product was confirmed from IR, PMR and mass spectra. Elemental analyses are given in table 1.

II.2.3. Phenyl allyl ether

Phenol (136 g; 1,45 mole) and allyl bromide (132 ml; 1,55 mole) dissolved in dry acetone (800 ml) were heated under reflux for 4,5 hr over anhydrous potassium carbonate (300 g). The mixture was poured into water (1 l) and extracted with ether. The ethereal extract was washed with a 10% sodium hydroxide solution and then with water until neutral, dried over anhydrous sodium sulphate and distilled. Phenyl allyl ether was collected as a colourless liquid (178,5 g; 91,8%; b.p. 83-5°C/10 mm Hg) and characterised from IR, PMR and mass spectra. Elemental analyses are given in table 1.

II.2.4. o-Allylphenol

o-Allylphenol was prepared by the Claisen rearrangement of phenyl allyl ether[27].

Phenyl allyl ether (73 g) was heated under reflux for 5 hr after which time the reflux temperature remained constant (~214°C). The solution was taken up in ether and extracted with a 10% sodium hydroxide solution. The basic solution was acidified and extracted with ether. This ethereal solution was washed, dried over anhydrous sodium sulphate and distilled. o-Allylphenol was collected as a colourless liquid (54,1 g; 74,1%; b.p. 117-9°C/27 mm Hg) and characterised from IR, PMR and mass spectra. Elemental analyses are given in table 1.

II.2.5. 2-Methylcoumaran

2-Methylcoumaran was synthesised by the acid catalysed cyclisation of o-allylphenol[28].

o-Allylphenol (178,5 g; 1,448 mole), glacial acetic acid (750 ml) and hydrobromic acid (400 ml; 48%) were heated under reflux for 30 min, cooled, poured into water (1 l) and extracted with ether. The ethereal solution was washed successively with water, sodium hydroxide (2M) and water, dried over anhydrous sodium sulphate and distilled. The fraction b.p. 94-108°C/14 mm Hg was collected. On redistillation 2-methylcoumaran was collected as a colourless liquid (73,3 g; 41,06%; b.p. 84-5°C/9,5 mm Hg; Lit. b.p. 85-8°C/15 mm Hg[28]) and characterised from IR, PMR and mass spectra. Elemental analyses are given in table 1.

II.2.6. 2-Methylbenzofuran

The dehydrogenation of 2-methylcoumaran to 2-methylbenzofuran using N-bromosuccinimide was based on the method of LOOKER and HOLM[29] for the dehydrogenation of flavones.

2-Methylcoumaran (10g; 0,075 mole) and N-bromosuccinimide (13,5g; 0,075 mole) were heated gently in chloroform (200 ml). The chloroform solution turned orange and violent frothing was controlled by cooling the reaction flask in an icebath. After the reaction had subsided the chloroform solution was colourless and the precipitate was orange. The mixture was heated under reflux until all the N-bromosuccinimide had been converted to the lighter succinimide. A 10% sodium hydroxide solution (100 ml) was added to dissolve the precipitate. The chloroform solution was separated and washed and the chloroform was removed by distillation. Potassium hydroxide (13g) dissolved in ethanol (100 ml) was added to the residue and the solution was heated under reflux for 1 hr. A fraction (5,12g) b.p. 72-102°C/18,5-20 mm Hg was collected and redistilled. A mixture of 2-methylbenzofuran and 2-methylcoumaran (2g; b.p. 194-8°C; Lit. 2-methylbenzofuran b.p. 196-8°C[30]) was collected and separated by preparative gas chromatography (section II.1.1.) to yield 2-methylbenzofuran (∼1 ml) which was characterised from IR, PMR and mass spectra. Elemental analyses are given in table 1.

II.2.7. Phenoxyacetone

Phenoxyacetone was prepared by the method of HURD and PERLETZ[31].

Chloroacetone (24g; 0,26 mole), dry acetone (20 ml) and potassium iodide (0,43g) were allowed to stand overnight. Phenol (14,3g; 0,152 mole), potassium carbonate (5g) and dry acetone (20 ml) were stirred and heated under reflux for 15 min. The chloroacetone mixture was then added slowly. After one quarter of this mixture was added, potassium carbonate (5g) and enough acetone to thin the mixture were added. A second portion of the chloroacetone mixture was added dropwise. This procedure was repeated until 20g of potassium carbonate and all the chloroacetone mixture had been added. The mixture was stirred (15 hr) and filtered. Dry acetone was used to wash the residue. The combined filtrates were distilled and a fraction b.p. 108-134°C/36 mm Hg was collected (17,7g). An IR spectrum showed the presence of hydroxyl groups which suggested the presence of 1-phenoxypropan-2-ol.

The mixture was separated by column chromatography with chloroform as eluent on a 40 x 2,3 cm i.d. silica gel column. Under UV* light two bands could be discerned. The first, a pale green band, was collected and distilled. The fraction b.p. 118-130°C/41 mm Hg (10,4g) was collected and found by IR to have less hydroxyl.

This mixture was rechromatographed. The first band was collected and distilled. The fraction b.p. 134-6°C/30 mm Hg was collected as phenoxyacetone, a colourless liquid which

*UV = ultra-violet

turned black on standing (7,7g; 33,77%). The structure was confirmed from IR, PMR and mass spectra. Elemental analyses are given in table 1.

II.2.8. 3-Methylbenzofuran

The preparation of 3-methylbenzofuran was based on the method of FOSTER and ROBERTSON[32] for the synthesis of benzofuran. Condensation of o-hydroxyacetophenone with ethyl bromoacetate yielded ethyl o-acetylphenoxyacetate. This ester was hydrolysed to o-acetylphenoxyacetic acid which was cyclised to form 3-methylbenzofuran-2-carboxylic acid and 3-methylbenzofuran.

II.2.8.1. o-Hydroxyacetophenone was prepared[33] by the Fries rearrangement of phenyl acetate[34].

II.2.8.2. Ethyl o-acetylphenoxyacetate

o-Hydroxyacetophenone (51g; 0,38 mole), ethyl bromoacetate (66g; 0,38 mole), potassium carbonate (76g) and acetone (300 ml) were heated under reflux (2,5 hr), poured into water (600 ml) and extracted with ether. The ethereal extract was washed with water, dried over anhydrous sodium sulphate and the solvent was removed by distillation. The remaining crude ethyl o-acetylphenoxyacetate weighed 82,68g (98,01%).

II.2.8.3. o-Acetylphenoxyacetic acid

Crude ethyl o-acetylphenoxyacetate (82,68g; 0,37 mole) was dissolved in a 4% sodium hydroxide solution (800 ml). The solution was allowed to stand (24 hr) and hydrochloric acid was added until the solution reached pH2. o-Acetylphenoxyacetic acid (37,14g; 51,74%; m.p. 112-4°C) crystallized from the solution, was filtered, washed and dried.

II.2.8.4. 3-Methylbenzofuran

Crude o-acetylphenoxyacetic acid (37,14g; 0,19 mole) was heated under reflux (2 hr) with acetic anhydride (370 ml) containing anhydrous sodium acetate (111g). The solution was cooled and poured into a water/ice mixture (600g). A cold sodium hydroxide solution was added until the solution reached pH8. The solution was extracted with ether. The ethereal extract was washed with water, dried over anhydrous sodium sulphate and distilled. 3-Methylbenzofuran (9,69g; 38,36%; b.p. 195-8°C/763 mm Hg; Lit. 195-7°C[35]) was collected as a colourless liquid and characterised from IR, PMR and mass spectra. Elemental analyses are given in table 1.

II.2.9. 1-Phenoxypropan-2-ol

The synthesis of 1-phenoxypropan-2-ol was based on the method of McSWEENEY, WIGGINS and WOOD[36].

A mixture of propylene oxide (19g; 0,33 mole) was added to phenol (31g; 0,33 mole) and sodium hydroxide (0,67g; 0,02 mole) in a minimum amount of water and heated under reflux (1 hr). The mixture was taken up in ether. The ethereal extract was washed successively with water, 10% sodium hydroxide and water, dried over anhydrous sodium sulphate and distilled. 1-Phenoxypropan-2-ol (29,74g; 59,8%; b.p. 154-6°C/60 mm Hg; Lit. b.p. 134-6°C/15 mm Hg[36]) was collected as a colourless liquid and characterised from IR, PMR and mass spectra. Elemental analyses are given in table 1.

II.2.10. Chroman

The synthesis of chroman was based on the method of HURD and HOFFMAN[37] in which the acetic ester of _o_-allylphenol was treated with hydrogen bromide in the presence of peroxides.

II.2.10.1. _o_-Allylphenyl acetate

_o_-Allylphenol (75g; 0,56 mole) and acetic anhydride (114g; 1,13 mole) were heated under reflux (3 hr). The mixture was taken up in ether, washed several times with water, dried over anhydrous sodium sulphate and distilled to yield _o_-allylphenyl acetate (85,18g; 86,5%; b.p. 131-2°C/29 mm Hg; Lit. b.p. 110-110,5°C/ 11 mm Hg, 123-4°C/20 mm Hg[37]).

II.2.10.2. Chroman

An excess of hydrogen bromide (prepared by the action of liquid bromine (33 ml) on boiling tetralin (165 ml)) was added slowly (45 min) to o-allylphenyl acetate (85g; 0,49 mole) and benzoyl peroxide (2g) in dry carbon tetrachloride (350 ml).

After addition of the hydrogen bromide the reaction flask was sealed and allowed to stand overnight. The solvent was removed and the reaction mixture was washed with water and a dilute sodium carbonate solution. The water insoluble layer was heated under reflux (5 hr) with potassium hydroxide (60g) dissolved in water (200 ml) and ethanol (350 ml). The mixture was poured into water (600 ml) and extracted with ether. A fraction b.p. 109-12°C/32 mm Hg (44,15g) was collected. This was redistilled to yield chroman (35,3g; 53,76%; b.p. 90-2°C/ 5,6 mm Hg; Lit. b.p. 95-6°C/15 mm Hg[37]) which was characterised from IR, PMR and mass spectra. Elemental analyses are given in table 1.

II.2.11. Benzofuran

Benzofuran was synthesised by the decarboxylation of coumarilic acid. The synthesis of coumarilic acid was based on the method of FUSON, KNEISLEY and KAISER[38].

II.2.11.1. Coumarilic acid

Bromine (66,2g; 0,4 mole) was added dropwise (1 hr) to a stirred solution of coumarin (64,6g; 0,4 mole) in chloroform (150 ml). Excess bromine was removed under vacuum at room temperature. A solution of potassium hydroxide (74,5g; 1,3 mole) in water (350 ml) was added and the mixture was steam-distilled. The remaining solution was cooled, decanted from traces of a heavy brown oil and acidified with dilute hydrochloric acid. The precipitated coumarilic acid was filtered, recrystallized from hot water and dried under vacuum at 65°C (32g; 44,6%; m.p. 190-2°C; Lit. m.p. 190-3°C[38]).

II.2.11.2. Benzofuran

The coumarilic acid (32g) was distilled off soda lime (60g). The distillate was taken up in ether, washed successively with a 10% sodium hydroxide solution and water, dried over anhydrous sodium sulphate and distilled. Benzofuran was collected as a liquid (9g; 39,12%; b.p. 169-73°C; Lit. b.p. 174°C[39]) and characterised from IR, PMR and mass spectra. Elemental analyses are given in table 1.

II.2.12. Phenyl vinyl ether

Phenyl vinyl ether was prepared by the method of WOHL and BERTHOLD[40]. The synthesis of phenyl-β-bromoethyl ether, which was required for this preparation, was based on the method of SCHREIBER[41] for the preparation of p-tolyl-β-bromoethyl ether.

II.2.12.1. Phenyl-β-bromoethyl ether

Sodium (23g; 1 mole) was added slowly to a solution of phenol (94g; 1 mole) in ethanol (250 ml). After complete reaction dibromoethane (300 ml) was added and the solution was allowed to stand (24 hr). A white precipitate (sodium bromide) which formed was removed by filtration and the solution was heated under reflux (1 hr). When further precipitate formed the process of filtration and heating under reflux was repeated until no further precipitation occurred. The ethanol and dibromoethane were removed from the solution by distillation and the diphenoxyethane was removed by steam-distillation. The residue was taken up in ether, washed successively with a 10% sodium hydroxide solution and water, dried over anhydrous sodium sulphate and distilled. Phenyl-β-bromoethyl ether was collected as a colourless liquid which solidified on cooling (62,4g; 31,2%; b.p. 125-6°C/16,5 mm Hg, m.p. 31-3°C; Lit. b.p. 108-10°C/7 mm Hg, m.p. 32-3°C[40]).

II.2.12.2. Phenyl vinyl ether

Phenyl-β-bromoethyl ether (50g; 0,25 mole) was added to copper (2g) and finely powdered anhydrous potassium hydroxide (100g). The mixture was heated gently to ensure that the temperature of the distilling liquid would not rise above 160°C. After 3 hr the mixture was heated strongly and the temperature rose to 220°C. The distillate was taken up in ether, washed with water, dried over anhydrous sodium sulphate and distilled. 8,7g of product (b.p. 120-190°C) was collected and redistilled to give phenyl vinyl ether as a colourless liquid (2,7g; 9%; b.p. 154-7°C; Lit. b.p. 155-6°C[40,42]).

II.2.13. *N*,*N*-Diethylaniline

N,*N*-Diethylaniline was prepared by the *N*-ethylation of *N*-ethylaniline.

A mixture of ethyl iodide (8g; 0,05 mole) and *N*-ethylaniline (6g; 0,05 mole) was allowed to stand (30 min). Ethanol (25 ml) was added and the mixture was heated under reflux (2 hr). A solution of potassium hydroxide (10g) in water (100 ml) was added and the mixture was steam-distilled. The distillate was extracted with chloroform and dried over anhydrous sodium sulphate. The chloroform was removed by distillation from the mixture of *N*-ethylaniline and *N*,*N*-diethylaniline which was separated by column chromatography. A 40 x 2,3 cm i.d. silica gel column was used with chloroform as eluent. The first fraction, which appeared purple under UV light, was collected and distilled. *N*,*N*-Diethylaniline was collected as a pale yellow liquid (2,81g; 38,1%; b.p. 74-6°C/2,9 mm Hg; Lit. b.p. 215,5°C[39]) and characterised from IR, PMR and mass spectra.

II.2.14. N-Ethyl-N-methylaniline

A mixture of N-ethylaniline (5ml; 0,25 mole) and iodomethane (5ml; 0,5 mole) was allowed to stand (19 hr) at room temperature. The iodomethane was removed under vacuum. p-Toluenesulphonyl chloride (3,8g) was added to a solution of the reaction mixture in 10% sodium hydroxide (100 ml). The mixture was shaken (15 min) and extracted with ether. The ethereal solution was washed with water and the ether was removed by distillation. The residue was steam-distilled and the distillate was extracted with ether. The ethereal solution was dried over anhydrous sodium sulphate and distilled. 1,4g of a product (b.p. 199-240°C) was collected as a brown oil. After the oil had cooled a precipitate formed. The solution was filtered and distilled. N-Ethyl-N-methylaniline was collected (0,5g; 1,6%; b.p. 201-3°C; Lit. b.p. 201°C[39]) and characterised from IR, PMR and mass spectra.

II.2.15. N-Allyl-N-ethylaniline

Allyl bromide (7ml; 0,08 mole) was added dropwise to N-ethylaniline (10ml; 0,08 mole). The mixture was heated under reflux on a waterbath (15 min). A 20% potassium hydroxide solution (40ml) was added and the mixture was steam-distilled. The distillate was extracted with chloroform, dried over anhydrous sodium sulphate and filtered. N-Allyl-N-ethylaniline was separated from unreacted N-ethylaniline by column chromatography on a 40 x 2,3 cm i.d. silica gel column with chloroform as eluent. The first band which was yellow was collected and distilled. N-Allyl-N-ethylaniline was collected (7,67g; 60%; b.p. 91-3°C/5 mm Hg) and characterised from IR, PMR and mass spectra.

II.2.16. N-Ethylskatole

N-Ethylskatole was prepared by the N-ethylation of the potassium salt of skatole[43]. Skatole (3,5g; 0,028 mole), ethyl iodide (0,612g; 0,028 mole) and potassium (1,08g; 0,028 mole) were heated under reflux in benzene until all the potassium had reacted. Thin layer chromatography (TLC) showed the presence of unreacted skatole and another product. This product was separated from the skatole by column chromatography (column: 40 x 2,3 cm i.d. silica gel; eluent: chloroform). Repeated passage through the column was required to purify the product. The fractions which TLC showed to contain pure product were combined and distilled. N-Ethylskatole (1,09g; 26%: b.p. 105-6°C/2,9 mm Hg) was collected as a pale yellow liquid. IR, PMR and mass spectra confirmed the expected N-ethylation of the skatole.

II.2.17. N-Ethylindole

The synthesis and isolation of N-ethylindole followed the method used in section II.2.16. for the preparation of N-ethylskatole. N-Ethylindole was obtained in 20% yield as a pale yellow liquid (b.p. 109-12°C/4 mm Hg; Lit. b.p. 252-3°C[44]) and characterised from IR, PMR and mass spectra.

II.2.18. N-Ethyltetrahydroquinoline

Tetrahydroquinoline (5g; 0,038 mole) and ethyl iodide (5,8g; 0,038 mole) were heated under reflux (5 hr). A 25% solution (40ml) of potassium hydroxide was added to the reaction flask and the mixture was steam-distilled. The distillate was extracted with chloroform. The chloroform solution was dried over anhydrous sodium sulphate. The chloroform was removed by distillation and approximately 0,3 ml of product was collected by preparative gas chromatography. N-Ethyltetrahydroquinoline was characterised from IR, PMR and mass spectra. Elemental analyses are given in table 1.

II.2.19. 1,3-Diphenoxypropene

1,3-Diphenoxypropene was prepared by the fusion of the p-toluenesulphonate ester of 1,3-diphenoxypropan-2-ol with powdered potassium hydroxide.

II.2.19.1. 1,3-Diphenoxyprop-2-yl p-toluenesulphonate

1,3-Diphenoxypropan-2-ol (104g; 0,426 mole) and *p*-toluenesulphonyl chloride (134g; 0,705 mole) were dissolved in pyridine (350 ml) and allowed to stand (17 hr) at room temperature. A white solid precipitated from the solution. The entire contents of the flask were poured into 10% sulphuric acid (1,5 l). The precipitate was separated by filtration, washed with water and dried. Recrystallization of the product from a mixture of ethanol (800 ml) and acetone (300 ml) yielded the tosylate (162,7g; 95,9%; m.p. 117-8°C).

II.2.19.2. 1,3-Diphenoxypropene

A mixture of 1,3-diphenoxyprop-2-yl *p*-toluenesulphonate (70g; 0,176 mole) and powdered potassium hydroxide (16,5g; 0,295 mole) was heated under vacuum. Approximately 23g of distillate was collected and taken up in ether. The ethereal solution was washed successively with a 10% sodium hydroxide solution and water, dried over anhydrous sodium sulphate and distilled. An IR spectrum of the distillate (b.p. 66-200°C/ approximately 7 mm Hg) showed the presence of compounds containing hydroxyl groups. These were removed by column chromatography (column: 40 x 2,3 cm i.d. silica gel; eluent: chloroform). The chloroform solution containing the desired product was distilled. 1,3-Diphenoxypropene was obtained as a pale yellow liquid (5,96g; 15%; b.p. 172-6°C/6,3 mm Hg) and characterised from IR and PMR spectra. Elemental analyses are given in table 1.

II.3. DEGRADATION PROCEDURE

1,3-Diphenoxypropan-2-ol was degraded under 4 different conditions:

1 Over aluminium oxide "Camag" M.F.C. Brockmann activity 1 (neutral) 100 - 240 mesh.

2 Over aluminium oxide "Camag" M.F.C. Brockmann activity 1 (pH6) 100 - 240 mesh.

3 Over aluminium oxide calcined B.D.H. (pH9).

4(a) Under nitrogen and (b) in air.

Prior to degradations 1 - 3 the alumina was heated for 2 hr at 150°C under vacuum. The alumina was then mixed with twice its weight of 1,3-diphenoxypropan-2-ol and the reaction mixture heated in an apparatus which allowed the products to be distilled and collected during the degradation. In degradation 4(a) the reaction flask was purged with nitrogen for 15 min prior to degradation and during the degradation. Degradation 4(b) was carried out in air. In each case 1,3-diphenoxypropan-2-ol was heated at such a rate that the distillation temperature remained below 250°C (1,3-diphenoxypropan-2-ol distills at 360°C/760 mm Hg). In most cases degradation was continued until the 1,3-diphenoxypropan-2-ol had decomposed completely.

1,3-Diphenoxypropene and 1-(N-ethylanilino)-3-phenoxypropan-2-ol were degraded under 2 different conditions:

1 Over aluminium oxide "Camag" M.F.C. Brockmann activity 1 (pH6) 100 - 240 mesh.

2(a) Under nitrogen and (b) in air.

The degradation procedures were the same as those used for 1,3-diphenoxypropan-2-ol.

II.3.1. The Degradation of 1,3-Diphenoxypropan-2-ol

II.3.1.1. The degradation of 1,3-diphenoxypropan-2-ol over neutral alumina (pH7)

1,3-Diphenoxypropan-2-ol (20g) was heated over neutral alumina (10g). The temperature of the distilling products rose to a maximum of 210°C. After 20 min the temperature dropped and heating was discontinued. The residue was dark and the distillate which contained some water was reddish-brown. The products (8,8g; 44% w/w) were steam-distilled and the distillate extracted with ether. The ethereal solution was washed successively with a 10% sodium hydroxide solution and water and dried over anhydrous sodium sulphate. A sample was injected into the GLC. A GLC trace of the neutral products is shown in fig.3.

The above procedure was repeated on a larger scale (200g 1,3-diphenoxypropan-2-ol) and the neutral products were separated and collected by preparative GLC (section II.1.1.).

The products and their means of identification are indicated in table 2. The identified compounds were synthesised by alternative routes and their physical characteristics compared with those of the degradation products (table 2).

II.3.1.2. The degradation of 1,3-diphenoxypropan-2-ol over acidic alumina (pH6)

1,3-Diphenoxypropan-2-ol (10g) was heated over acidic alumina (5g) for approximately 30 min when reaction appeared to be complete. The residue was dark and the distillate which contained water was reddish-brown (4g; 40% w/w). The temperature of the distilling products rose to a maximum of 226°C.

A GLC trace of the products is shown in fig.4. The GLC retention times of the products of this degradation were compared with those of standard compounds (table 3) as a means of identification. The relative distribution of products is also indicated in table 3. The more volatile aliphatic compounds were identified by a comparison of their retention times with those of standard compounds at three different temperatures namely 181°C. 108,7°C and 82,5°C (table 4).

The nature and relative abundance of the neutral products of this degradation were identical with those of the degradation over neutral alumina.

II.3.1.3. The degradation of 1,3-diphenoxypropan-2-ol over basic alumina (pH9)

Prior to this degradation the alumina was treated in three different ways;

(1) heated at 75°C under vacuum for 4 hr
(11) heated at 150°C under vacuum for 14 hr
(111) heated at approximately 250°C for 2 hr.

The GLC chromatograms of the products of these degradations were identical (fig.5).

1,3-Diphenoxypropan-2-ol (20g) was heated over basic alumina (10g) for approximately 1 hr after which time degradation appeared complete. The residue was dark and the distillate which contained water was light brown (8,1g; 40% w/w). The distillation temperature rose to a maximum of 200°C. The present degradation did not proceed as readily as the degradations over neutral and acidic alumina. The GLC trace of the degradation products (fig.5) differed from those obtained for the degradations over neutral and acidic alumina (figs. 3 and 4). The GLC retention times of the products of the present degradation were compared with those of standard compounds (table 5) as a means of identification. The relative abundance of the products is also indicated in table 5.

The more volatile products were identified by a comparison of their retention times with those of standard compounds at three different temperatures namely 181°C, 108,7°C and 82,5°C (table 6).

Mass spectra of all the products of the present degradation (except for benzene and acrolein which were present in too small a concentration to analyse) provided identification and further confirmation of the nature of the products of this degradation.

II.3.1.4. The degradation of 1,3-diphenoxypropan-2-ol (1) under nitrogen and (2) in air

On heating 1,3-diphenoxypropan-2-ol under nitrogen and in air the compound distilled largely unreacted at 360°C, but if heated under reflux for approximately 2 hr before distillation a sample of the degradation products could be obtained.

II.3.1.4.1. The degradation under nitrogen of 1,3-diphenoxypropan-2-ol

The reaction flask containing 1,3-diphenoxypropan-2-ol (20g) was purged with nitrogen for 15 min, after which time the compound was heated under reflux for 1,5 hr with a gentle stream of nitrogen passing through the liquid. The degradation products were removed by distillation. The temperature of the distilling products rose to a maximum of 200°C and approximately 1 ml of distillate was collected.

The GLC trace of the products of this degradation (fig.6) was found to correspond with that of the previous degradation over basic alumina (fig.5). The products of the present degradation were identified by a comparison of their GLC retention times with those of standard compounds. The GLC retention times and relative abundance of the products are shown in table 7.

The product represented by the peak at 13,0 min in the gas chromatogram of the products was shown by mass spectroscopy to contain benzofuran only (phenyl allyl ether was not observed).

II.3.1.4.2. The degradation in air of 1,3-diphenoxypropan-2-ol

1,3-Diphenoxypropan-2-ol (5g) was heated under reflux for approximately 2 hr prior to distillation of the products. The distillation temperature did not exceed 200°C and approximately 0,5 ml of distillate was collected. The GLC trace of the products (fig.7) was identical with that of the degradation under nitrogen (fig.6). A comparison of the GLC retention times of the products with those of standard compounds provided identification of the products (table 8).

The nature and relative abundance of the products of this degradation correspond with those of the degradation under nitrogen.

II.3.2. The Degradation of 1-(N-Ethylanilino)-3-phenoxypropan-2-ol

II.3.2.1. The degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol over acidic alumina (pH6)

1-(N-ethylanilino)-3-phenoxypropan-2-ol (40g) was heated over acidic alumina (20g) at such a rate that the temperature of the distilling products did not exceed 242°C. After approximately 37 min reaction appeared complete. The residue had charred and an orange-red distillate (26,13g; 65% w/w) which contained water was collected. The GLC trace of the products is shown in fig.8.

The distillate was taken up in ether (100 ml). The ethereal solution (A) was extracted with a 10% sodium hydroxide solution (3 x 75 ml). The combined aqueous extracts were washed with ether and acidified. The liberated products were taken up in ether. This ethereal solution was washed with water, dried over anhydrous sodium sulphate and stored as the acidic fraction. The ethereal solution (A) was washed successively with a 10% sodium hydroxide solution and water and then extracted with 5% hydrochloric acid (3 x 75 ml). The combined aqueous fractions were washed with ether and basified. The liberated products were taken up in ether. This ethereal solution was washed with water, dried over anhydrous sodium sulphate and stored as the basic fraction. The ethereal solution (A) was further washed with 5% hydrochloric acid and water, dried over anhydrous sodium sulphate and stored as the neutral fraction.

GLC traces of the neutral and basic fractions are shown in figs. 9 and 10 respectively.

A preliminary identification of the degradation products in the neutral and basic fractions was provided by their mass spectra which were determined as they eluted from a gas chromatograph (section II.1.1.). N-Ethylskatole which was not identified from its mass spectrum alone was collected by preparative GLC and identified from its IR and PMR spectra which were identical with those of synthesised N-ethylskatole (section II.2.16.). Mass spectra were not obtained for the compounds 1-phenoxypropan-2-ol, phenol, anisole, phenyl vinyl ether, styrene, ethylbenzene, toluene, acetone and acetaldehyde. These products were identified by their GLC retention times only. GLC retention times were used to confirm the identification of the remainder of the products by a comparison of the retention times of the products with those of standard compounds (table 9). In the case of 3-methyl-N-phenylpyrrole the standard was not a synthesised compound but 3-methyl-N-phenylpyrrole which was separated from the products of the thermal degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol (section II.3.2.2.). The relative abundance of products is indicated in table 9.

II.3.2.2. The thermal degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol

The thermal degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol was carried out under nitrogen and in air. The GLC traces of the products of these two degradations were identical (fig.11).

II.3.2.2.1. The degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol under nitrogen

The reaction flask containing 1-(N-ethylanilino)-3-phenoxypropan-2-ol (20g) was purged with nitrogen (15 min) prior to degradation. Degradation proceeded for approximately 50 min. The temperature of the distilling products rose to a maximum of 212°C and a light brown distillate which contained water was collected (5,5g; 27,5% w/w). The GLC trace of the products (fig.11) did not correspond with that of the degradation over acidic alumina (fig. 8).

The distillate was separated into neutral, basic and acidic fractions by the method outlined in section II.3.2.1. GLC traces of the neutral and basic fractions are shown in figs. 12 and 13 respectively.

Mass spectra were obtained for the products toluene, ethylbenzene, styrene, anisole, phenetole, benzofuran, N,N-dimethylaniline, N-ethyl-N-methylaniline, N-ethylaniline, N-allyl-N-ethylaniline and 3-methyl-N-phenylpyrrole. 3-Methyl-N-phenylpyrrole was collected by preparative GLC and identified from its IR, PMR and mass spectra. The nature of the products of this degradation (excluding 3-methyl-N-phenylpyrrole) was established by a comparison of their GLC retention times with those of standard compounds (table 10). The relative abundance of the products is also indicated in table 10.

II.3.2.2.2. The degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol in air

1-(N-ethylanilino)-3-phenoxypropan-2-ol (20g) was degraded for approximately 45 min after which time reaction appeared complete. The distillation temperature rose to a maximum of 250°C. The residue had charred and a light brown distillate which contained water was collected (7,23g; 36% w/w).

The GLC trace of the products of this degradation compared with that of the degradation under nitrogen (fig.11) and the products were not further investigated.

II.3.3. The Degradation of 1,3-Diphenoxypropene

1,3-Diphenoxypropene was degraded over acidic alumina (pH6) and in air. The nature and distribution of the products of these two degradations were identical.

II.3.3.1. The degradation of 1,3-diphenoxypropene over acidic alumina (pH6)

1,3-Diphenoxypropene (1g) was heated over acidic alumina (0,5g). The compound degraded readily. The temperature of the distilling products rose to a maximum of 206°C. A yellow-brown distillate was collected (0,1g; 10% w/w).

A GLC trace of the products of this degradation is shown in fig.14. The major products phenol, 2-chromene, 3-chromene and 2- and 3-methylbenzofuran were identified from their mass spectra and by a comparison of their GLC retention times with those of standard compounds (table 11).

II.3.3.2. The thermal degradation of 1,3-diphenoxypropene

The thermal degradation of 1,3-diphenoxypropene (1g) occurred readily. The temperature of the distilling products rose to a maximum of 220°C and a pale yellow distillate was collected (0,4g; 40% w/w).

The GLC trace of the products (fig.15) was identical with that of the degradation over acidic alumina (fig.14). The nature of the major products of the present degradation was established by a comparison of their GLC retention times with those of standard compounds (table 12).

III. RESULTS

III.1. ELEMENTAL ANALYSES

TABLE 1

Compound	Calculated %C	Calculated %H	Found %C	Found %H
1,3-diphenoxypropan-2-ol	73,8	6,6	73,8	6,6
1-(N-ethylanilino)-3-phenoxypropan-2-ol	75,3	7,7	75,0	7,7[a]
1,3-diphenoxypropene	79,6	6,2	79,4	6,4
phenyl allyl ether	80,6	7,5	81,2	7,4
2-methylcoumaran	80,6	7,5	80,5	7,7
2-methylbenzofuran	81,8	6,1	82,6	6,6
3-methylbenzofuran	81,8	6,1	81,1	6,6
chroman	80,6	7,5	81,3	7,6
phenoxyacetone	72,0	6,7	71,6	7,0
1-phenoxypropan-2-ol	71,0	8,0	70,5	8,3
o-allylphenol	80,6	7,5	80,4	7,6
benzofuran	81,4	5,1	82,3	5,2
N-ethyltetrahydroquinoline	82,0	9,3	81,6	9,4

[a] N calculated 5,2%; found 5,1%

III.2. DEGRADATION DATA

TABLE 2 : Neutral products of the degradation over neutral alumina of 1,3-diphenoxypropan-2-ol

Compound	GLC Retention Time of standard min	GLC Retention Time of degn.[a] product min	Means of Identification
phenyl allyl ether	13,3	13,2	IR, MS [b,c]
2-methylcoumaran	15,8	15,9	IR, MS [c]
2-methylbenzofuran	17,4	17,7	IR, MS, PMR
3-methylbenzofuran	18,1		
chroman	25,9	25,7	IR, MS [c]
phenoxyacetone	46,1	45,8	IR, MS, PMR
1-phenoxypropan-2-ol	68,1	66,9	IR, MS, PMR

[a] degn. = degradation; [b] MS = mass spectroscopy; [c] insufficient sample was available for PMR to be determined.

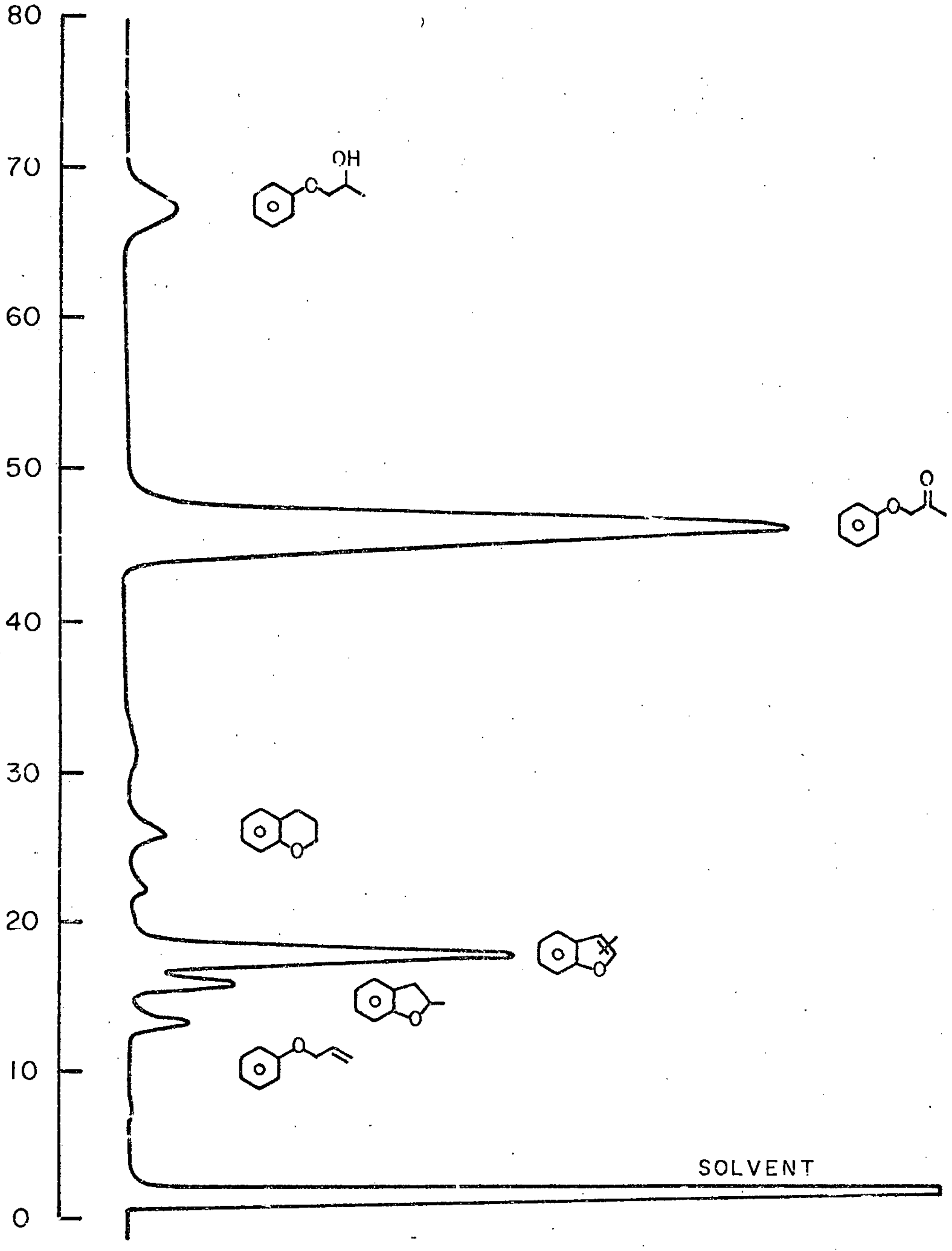


FIGURE 3

GLC trace of the neutral products of the degradation over neutral alumina (pH7) of 1,3-diphenoxypropan-2-ol.

TABLE 3 : Products of the degradation over acidic alumina of 1,3-diphenoxypropan-2-ol

Compound	Relative Abundance	GLC Retention Time	
		of standard min	of degn.product min
Phenol	major	57,2	57,5
phenoxyacetone	"	46,1	46,1
1-phenoxypropan-2-ol	minor	68,1	67,9
2-methylbenzofuran 3-methylbenzofuran	"	17,4 18,1	17,5
2-methylcoumaran	trace	15,8	15,8
phenyl allyl ether	"	13,3	13,1
chroman	"	25,9	25,9
2-chromene	"	22,1	22,4
3-chromene	"	30,7	30,9
acetone propionaldehyde	"	1,8 1,7	1,8
n-propanol	"	2,4	2,4
acetaldehyde	"	1,5	1,5

TABLE 4 : Aliphatic products of the degradation over acidic alumina of 1,3-diphenoxypropan-2-ol

	GLC Retention Time					
	of standard min	of degn. product min	of standard min	of degn. product min	of standard min	of degn. product min
Temperature:	181°C		108,7°C		82,5°C	
Compound						
acetaldehyde	1,5	1,5	1,8	1,9	2,3	-[a]
propionaldehyde	1,7	1,8	2,5	2,5	3,5	3,6
acetone	1,8		2,7	2,8	3,9	4,0
n-propanol	2,4	2,4	6,4	6,5	12,5	12,6

[a] peak too weak to read.

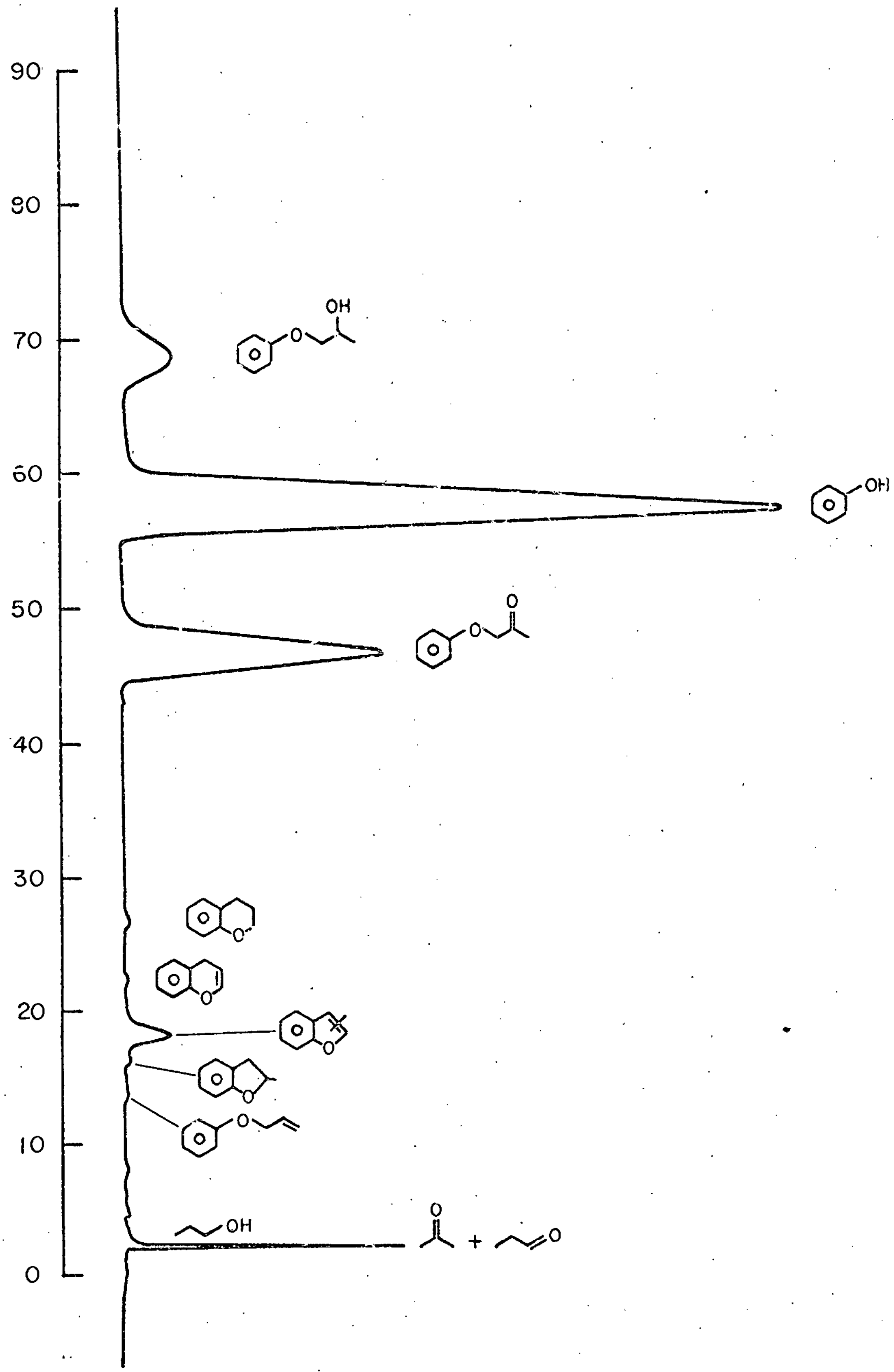


FIGURE 4

GLC trace of the products of the degradation over acidic alumina (pH 6) of 1,3-diphenoxypropan-2-ol.

TABLE 5 : Products of the degradation over basic alumina of 1,3-diphenoxypropan-2-ol

Compound	Relative Abundance	GLC Retention Time	
		of standard min	of degn. product min
Phenol	major	57,2	57,1
benzaldehyde	"	13,8	13,8
phenylacetaldehyde	minor	19,8	19,8
o-allylphenol	"	96,7	96,9
phenoxyacetone	"	46,1	46,3
benzofuran	"	12,9	13,1
phenyl allyl ether		13,3	
2-methylbenzofuran	"	17,4	17,5
3-methylbenzofuran		18,1	
2-methylcoumaran	trace	15,8	15,8
1-phenoxypropan-2-ol	"	68,1	68,5
benzylalcohol	"	38,5	38,6
3-chromene	"	30,7	30,6
chroman	"	25,9	25,9
2-chromene	"	22,1	22,1
anisole	"	7,3	7,3
styrene	"	5,7	5,8
toluene	"	3,1	3,1
acetone	"	1,8	1,8
acetaldehyde	"	1,5	1,5
ethylbenzene	"	3,9	4,0
benzene	"	2,4	2,5
acrolein	"	1,9	1,9

TABLE 6 : Volatile products of the degradation over basic alumina of 1,3-diphenoxypropan-2-ol

	GLC Retention Time					
	of standard min	of degn. product min	of standard min	of degn. product min	of standard min	of degn. product min
Temperature:	181°C		108,7°C		82,5°C	
Compound						
acetaldehyde	1,5	1,5	1,8	1,9	2,3	2,4
acetone	1,8	1,8	2,7	2,8	3,9	4,1
acrolein	1,9	1,9	3,0	3,2	4,6	-[a]
benzene	2,4	2,5	5,1	5,1	8,3	8,3
toluene	3,1	3,1	8,0	8,2	14,6	14,6
anisole	7,3	7,3	35,3	36,4	-	-[a]

[a] peak too weak to read.

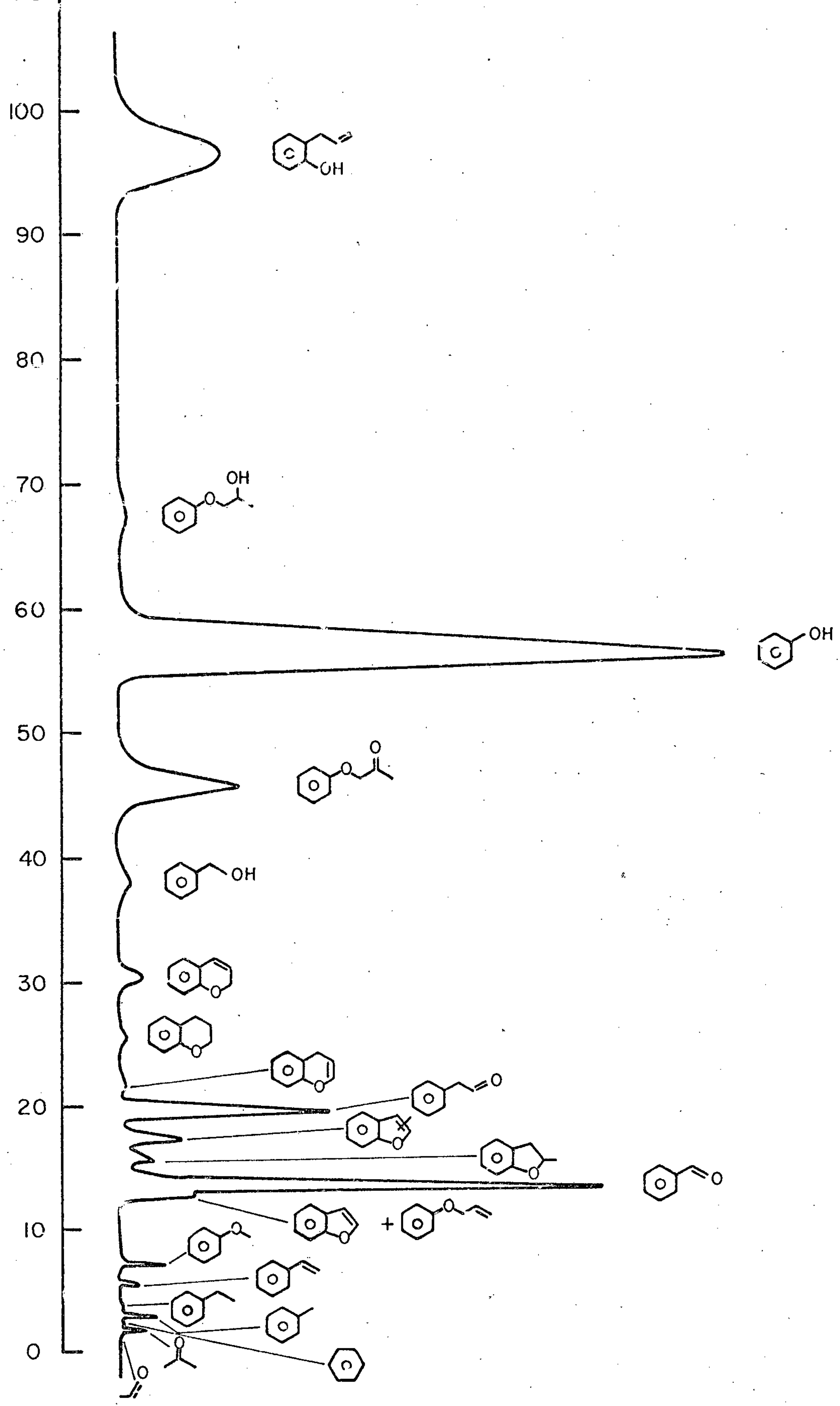


FIGURE 5

GLC trace of the products of the degradation over basic alumina (pH9) of 1,3 - diphenoxypropan-2-ol.

TABLE 7 : Products of the degradation under nitrogen of 1,3-diphenoxypropan-2-ol

Compound	Relative Abundance	GLC Retention Time	
		of standard min	of degn. product min
phenol	major	57,2	57,0
benzaldehyde	"	13,8	13,9
phenoxyacetone	minor	46,1	46,1
phenylacetaldehyde	"	19,8	19,8
2-methylbenzofuran	"	17,4	17,5
3-methylbenzofuran		18,1	
o-allylphenol	trace	96,7	97,3
benzylalcohol	"	38,5	38,5
1-phenoxypropan-2-ol	"	68,1	68,2
3-chromene	"	30,7	30,7
benzofuran	"	12,9	13,0
2-methylcoumaran	"	15,8	15,8
chroman	"	25,9	25,9
2-chromene	"	22,1	22,2
anisole	"	7,3	7,4
styrene	"	5,7	5,8
toluene	"	3,1	3,2
acetone	"	1,8	1,8
acetaldehyde	"	1,5	1,5
benzene	"	2,4	2,5
ethylbenzene	"	3,9	4,0
acrolein	"	1,9	1,9

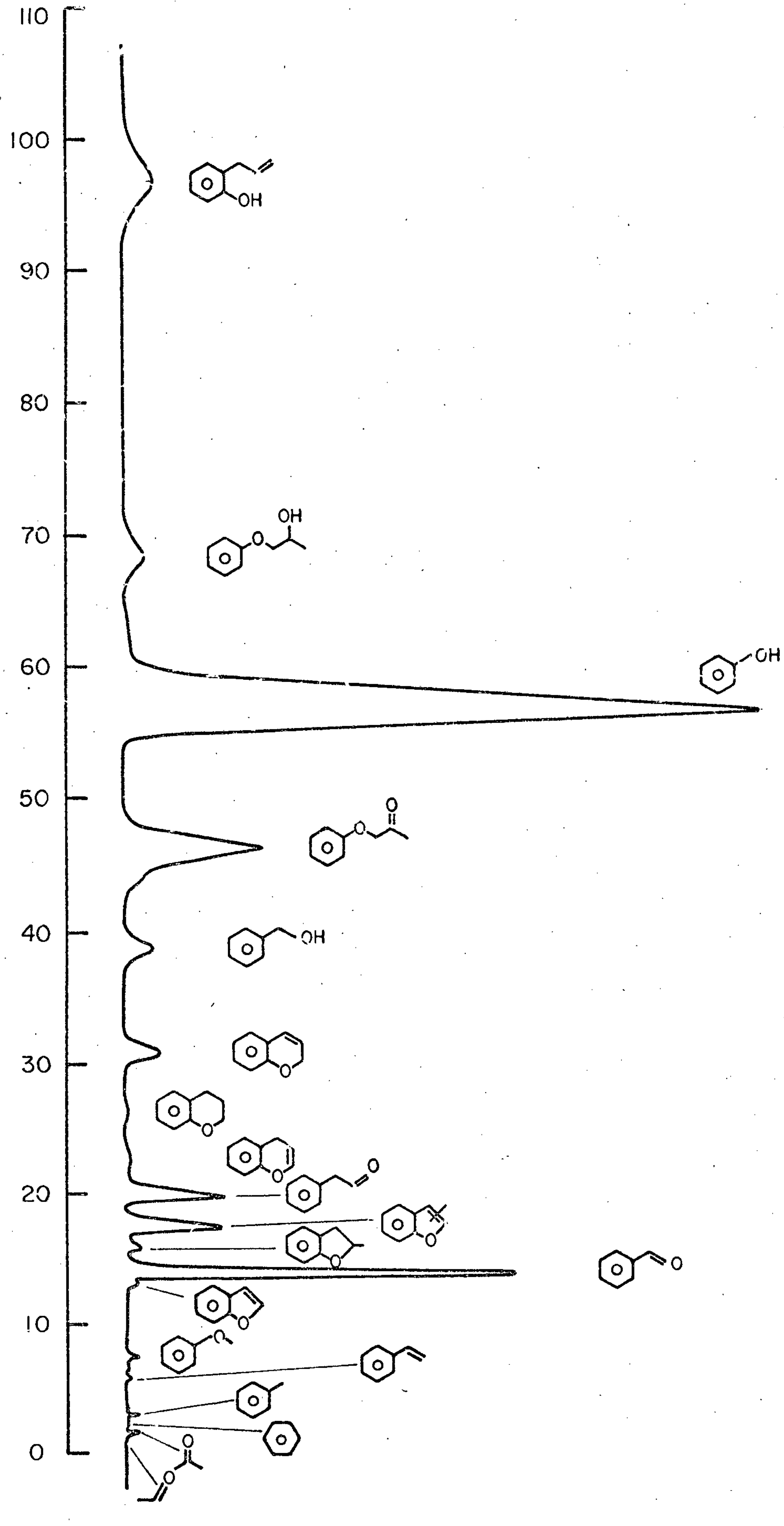


FIGURE 6

GLC trace of the products of the degradation under nitrogen of 1,3- diphenoxypropan-2-ol.

TABLE 8 : Products of the degradation in air of 1,3-diphenoxypropan-2-ol

Compound	Relative Abundance	GLC Retention Time of standard min	GLC Retention Time of degn. product min
phenol	major	57,2	57,1
benzaldehyde	"	13,8	13,8
phenoxyacetone	minor	46,1	46,1
phenylacetaldehyde	"	19,8	19,8
2-methylbenzofuran	"	17,4	17,5
3-methylbenzofuran		18,1	
o-allylphenol	trace	96,7	96,4
benzylalcohol	"	38,5	38,4
1-phenoxypropan-2-ol	"	68,1	68,0
benzofuran	"	12,9	12,9
2-methylcoumaran	"	15,8	15,8
3-chromene	"	30,7	30,7
chroman	"	25,9	25,7
2-chromene	"	22,1	21,6
anisole	"	7,3	7,3
styrene	"	5,7	5,7
toluene	"	3,1	3,1
acetone	"	1,8	1,8
acetaldehyde	"	1,5	1,5
ethylbenzene	"	3,9	3,9
benzene	"	2,4	2,5

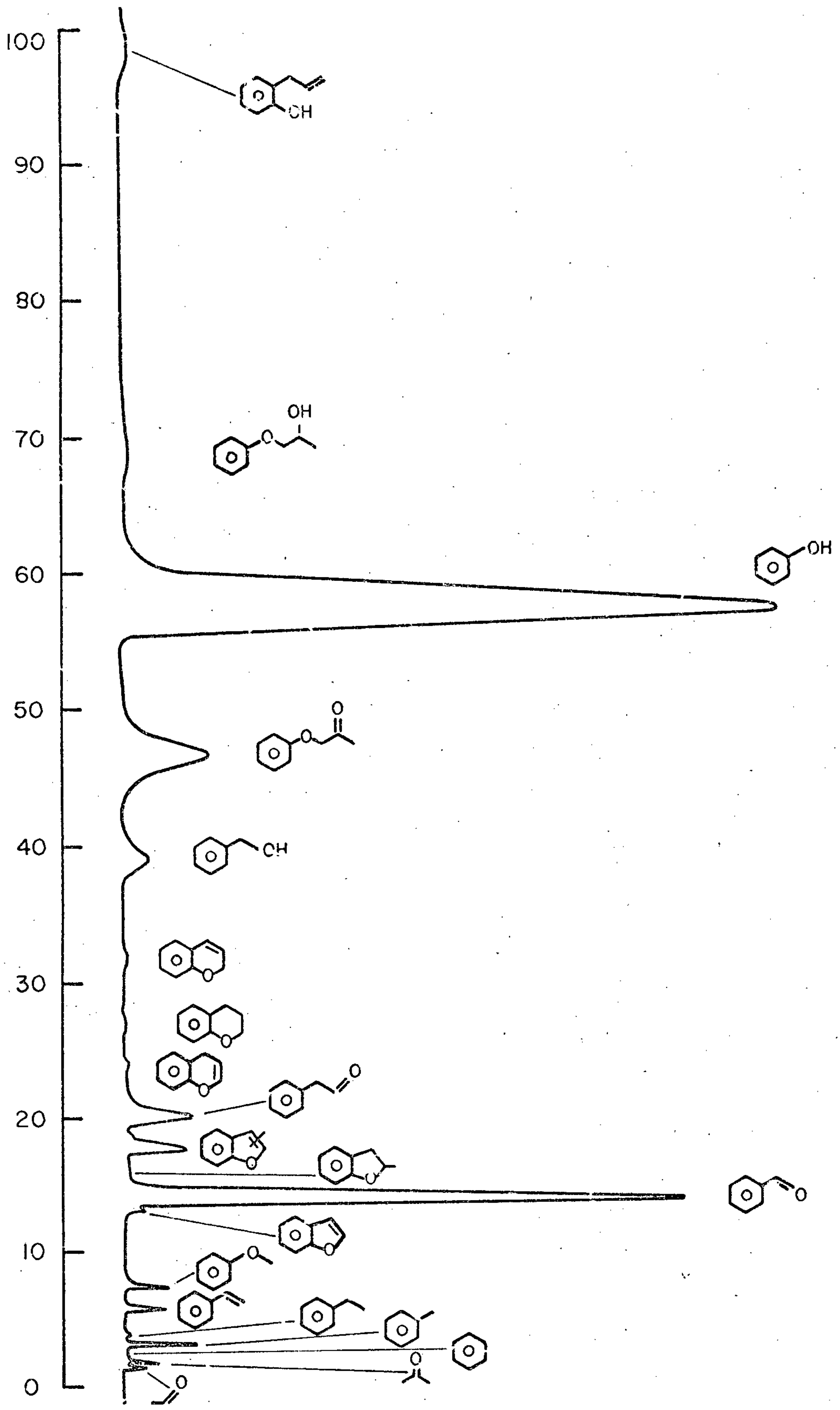


FIGURE 7

GLC trace of the products of the degradation in air of 1,3-diphenoxypropan-2-ol.

TABLE 9 : Products of the degradation over acidic alumina of 1-(N-ethylanilino)-3-phenoxypropan-2-ol

Compound	Relative Abundance	GLC Retention Time of standard min	GLC Retention Time of degn. product min
N-ethylaniline	major	24,6	24,6
phenol	"	57,2	57,4
N-ethylskatole	minor	78,9	79,6
N-ethyl-N-methylaniline	"	17,0	17,0
N,N-diethylaniline	"	18,0	17,9
N-allyl-N-ethylaniline	"	26,6	26,5
N-ethyltetrahydroquinoline	"	54,0	54,0
phenetole	trace	8,1	8,2
phenoxyacetone	"	46,1	46,3
chroman	"	25,9	26,0
2-methylbenzofuran 3-methylbenzofuran	"	17,4 18,1	17,6
2-chromene	"	22,1	22,1
N-ethylindole	"	61,8	62,0
1-phenoxypropan-2-ol	"	68,1	68,0
3-methyl-N-phenylpyrrole	"	66,1	$\sim 66^{a}$
benzofuran	"	12,9	13,0
2-methylcoumaran	"	15,8	15,9
phenyl vinyl ether	"	7,0	7,0
anisole	"	7,3	7,3
3-chromene	"	30,7	30,7
ethanol	"	1,9	1,9
n-propanol	"	2,5	2,4

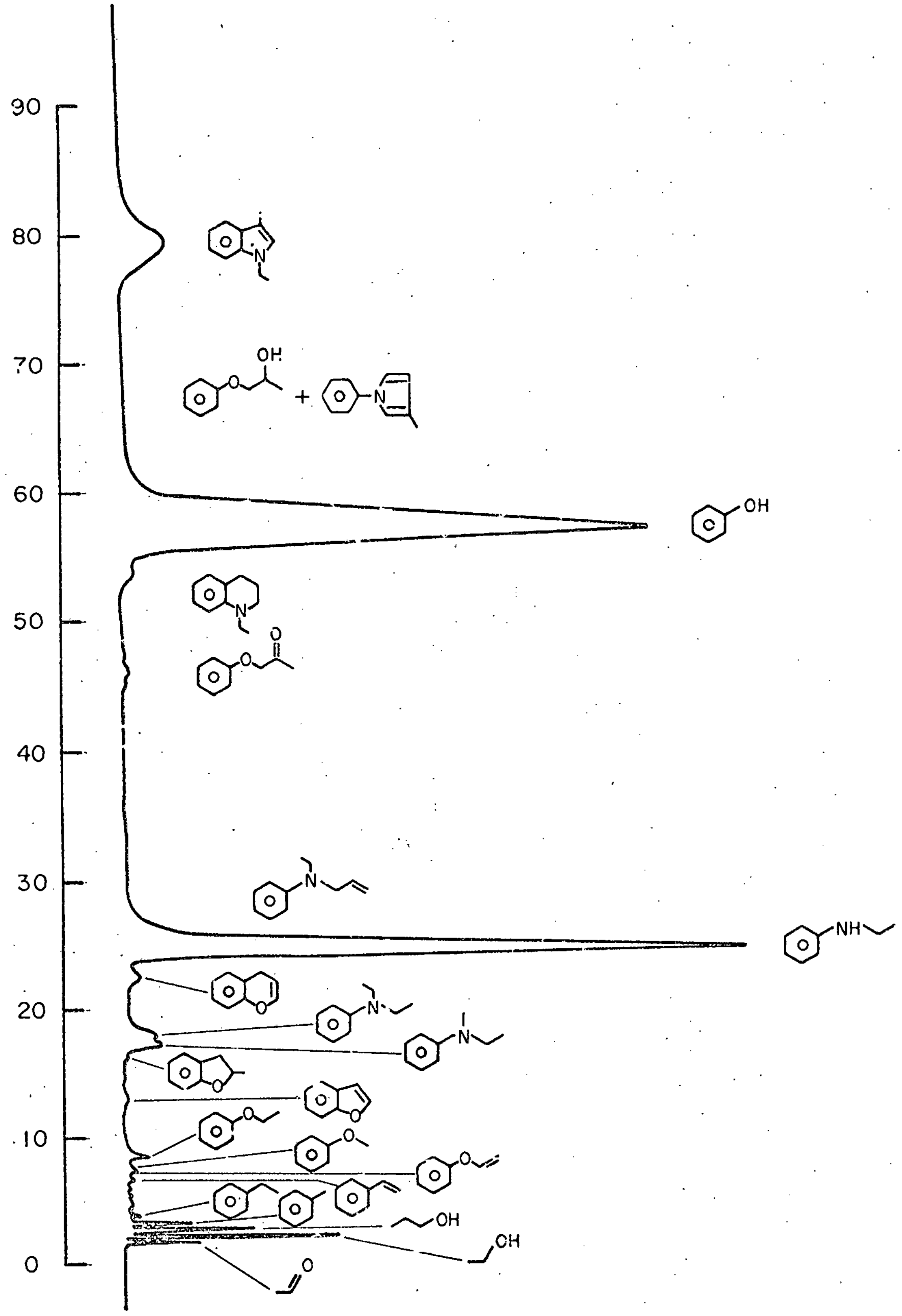


FIGURE 8

GLC trace of the products of the degradation over acidic alumina (pH6) of 1-(N-ethylanilino)-3-phenoxypropan-2-ol.

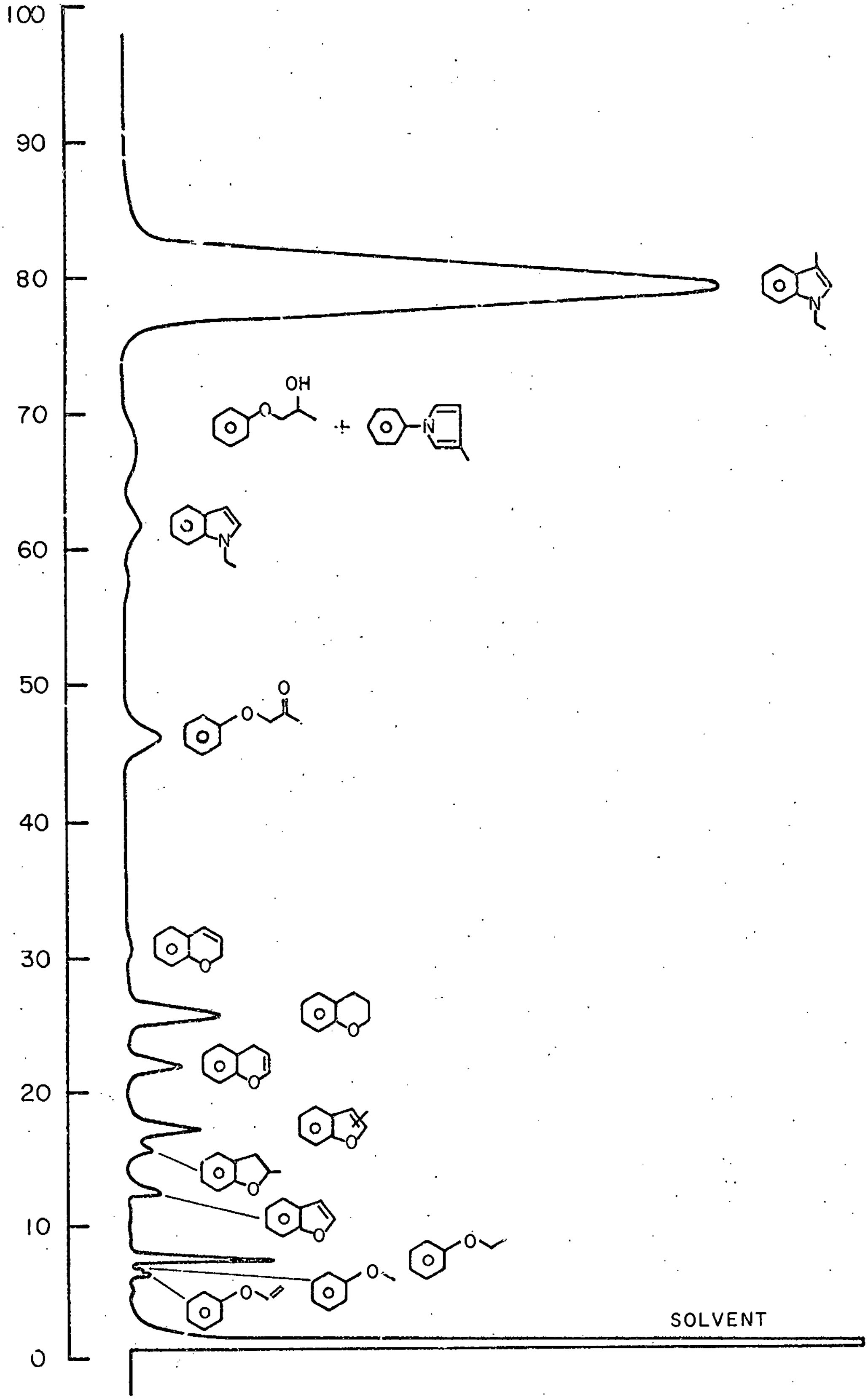


FIGURE 9

GLC trace of the neutral products of the degradation over acidic alumina (pH6) of 1-(N-ethylanilino)-3-phenoxypropan-2-ol.

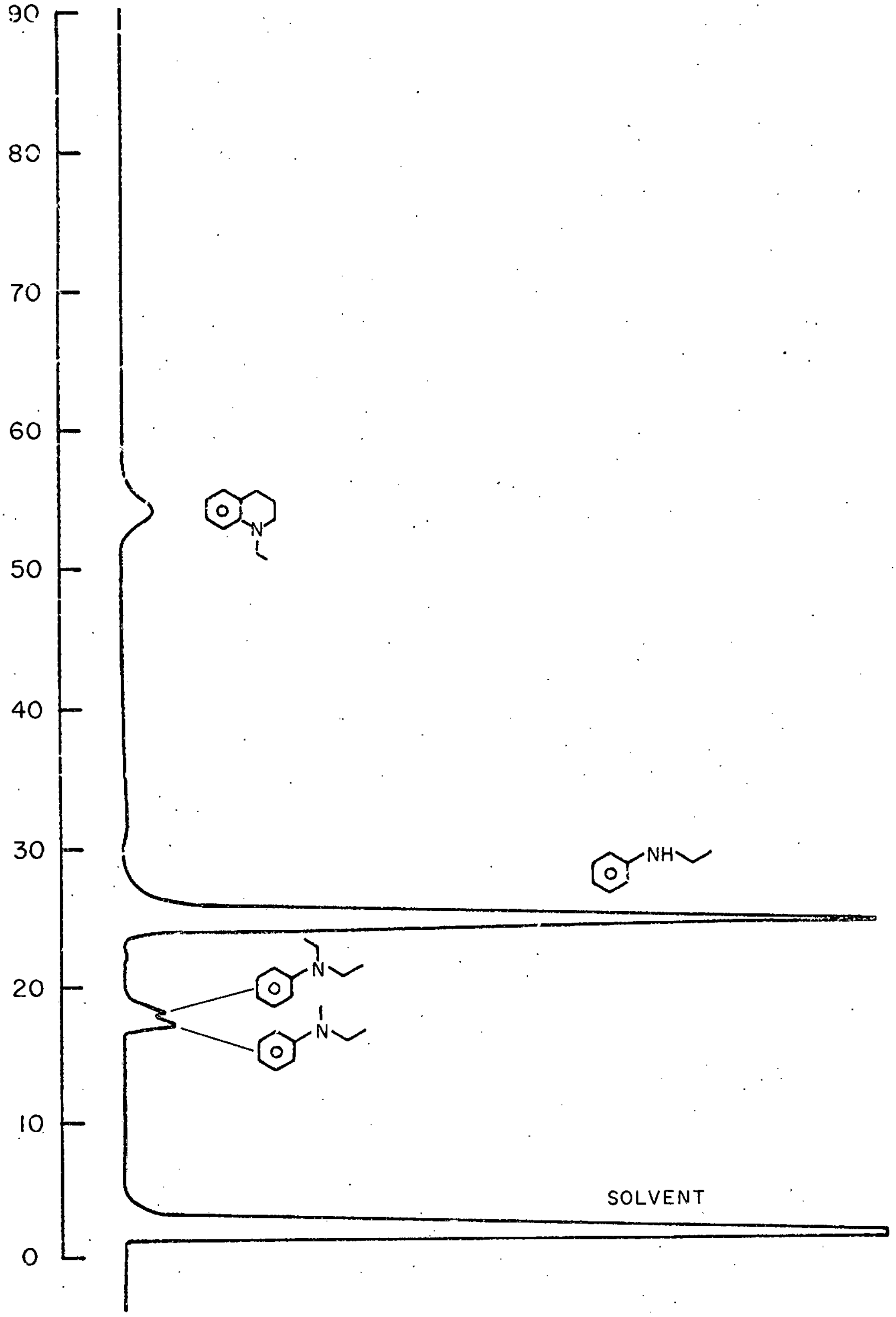


FIGURE 10

GLC trace of the basic products of the degradation over acidic alumina (pH6) of 1-(N-ethylanilino)-3-phenoxypropan-2-ol.

TABLE 10 : Products of the thermal degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol

Compound	Relative Abundance	GLC Retention Time	
		of standard min	of degn. product min.
phenol	major	57,2	57,3
N-ethyl-N-methylaniline	"	17,0	17,0
N-ethylaniline	"	24,6	24,6
3-methyl-N-phenyl-pyrrole	minor	-	66,1
N-allyl-N-ethylaniline	"	26,6	26,5
benzofuran	"	12,9	12,9
benzaldehyde	"	13,8	13,8
2-methylbenzofuran 3-methylbenzofuran	"	17,4 18,1	17,5
o-allylphenol	trace	96,7	95,1
anisole	"	7,3	7,3
N-ethylskatole	"	78,9	78,9
N,N-dimethylaniline	"	14,8	14,9
ethylbenzene	"	3,9	4,0
toluene	"	3,1	3,2
benzene	"	2,4	2,5
styrene	"	5,7	5,7
N-ethyltetra-hydroquinoline	"	54,0	54,2
N-ethylindole	"	61,8	61,8
chroman	"	25,9	25,6
2-chromene	"	22,1	22,5
benzylalcohol	"	38,5	38,6
3-chromene	"	30,7	30,5

TABLE 10 (continued)

Compound	Relative Abundance	GLC Retention Time of standard min	GLC Retention Time of degn. product min
acetone	trace	1,8	1,8
acetaldehyde	"	1,5	1,5
phenetole	"	8,1	8,2

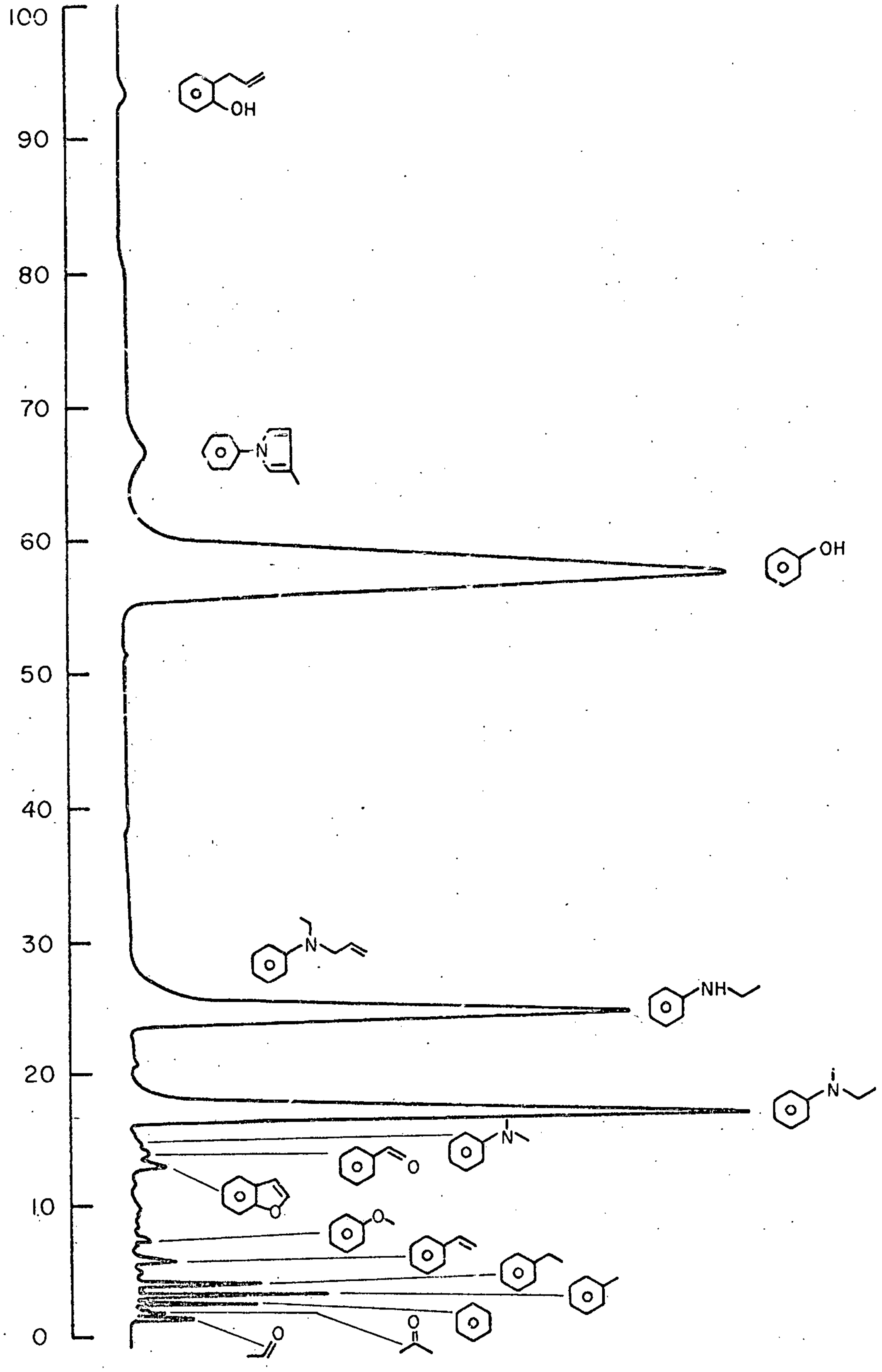


FIGURE 11

GLC trace of the products of the degradation of 1-(N-ethylanilino)-3- phenoxy-propan-2-ol

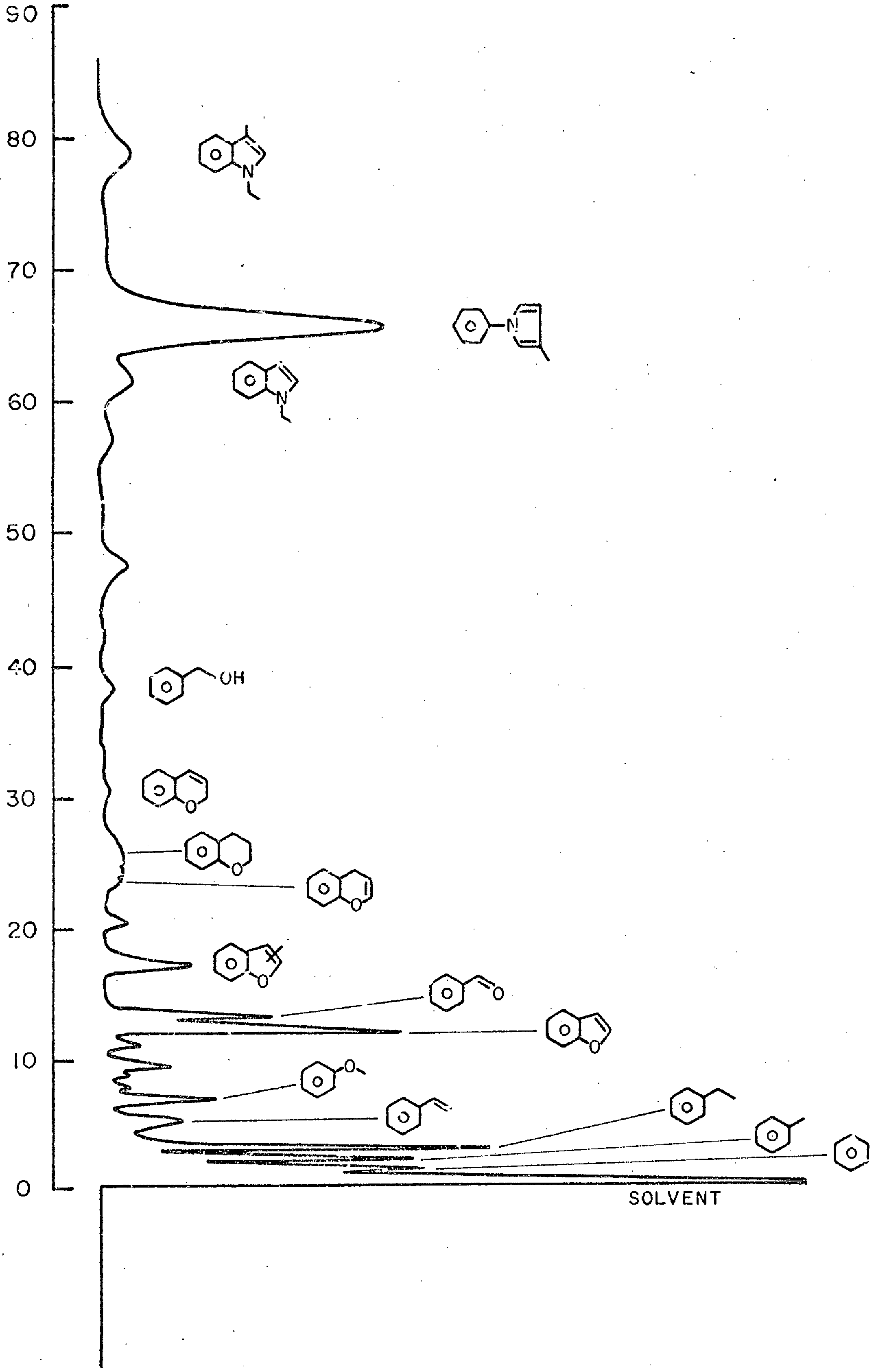


FIGURE 12

GLC trace of the neutral products of the degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol.

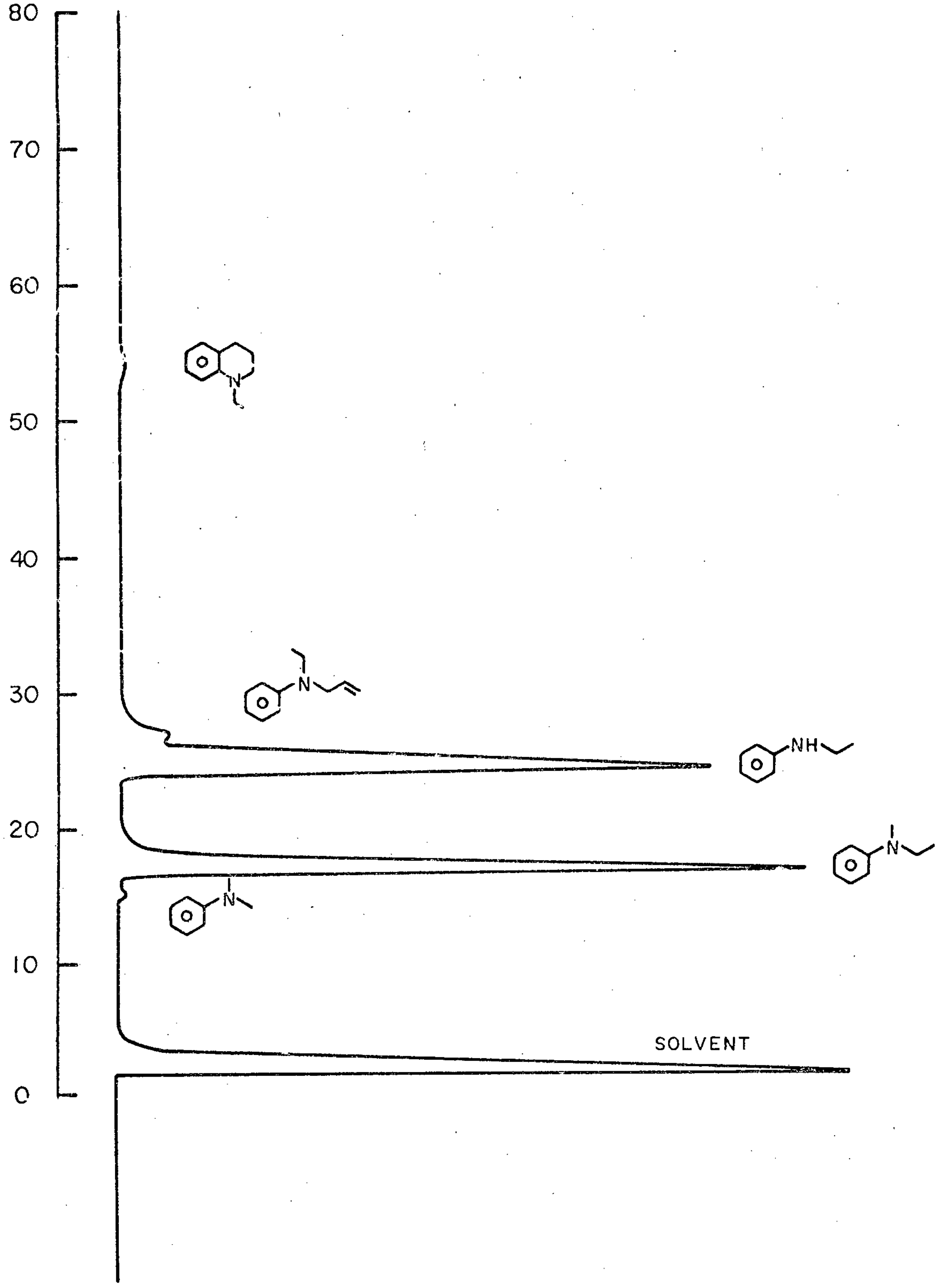


FIGURE 13

GLC trace of the basic products of the degradation of 1-(N-ethylanilino)- 3-phenoxypropan-2-ol.

TABLE 11 : Major products of the degradation over acidic alumina of 1,3-diphenoxypropene

Compound	Relative Abundance	GLC Retention Time	
		of standard min	of degn. product min
phenol	major	57,2	57,2
2-chromene	"	22,1	22,3
3-chromene	minor	30,7	30,9
2-methylbenzofuran	"	17,4	17,7
3-methylbenzofuran		18,1	

TABLE 12 : Major products of the thermal degradation of 1,3-diphenoxypropene

Compound	Relative Abundance	GLC Retention Time	
		of standard min	of degn. product min
phenol	major	57,2	57,2
2-chromene	"	22,1	22,2
3-chromene	minor	30,7	30,8
2-methylbenzofuran	"	17,4	17,6
3-methylbenzofuran		18,1	

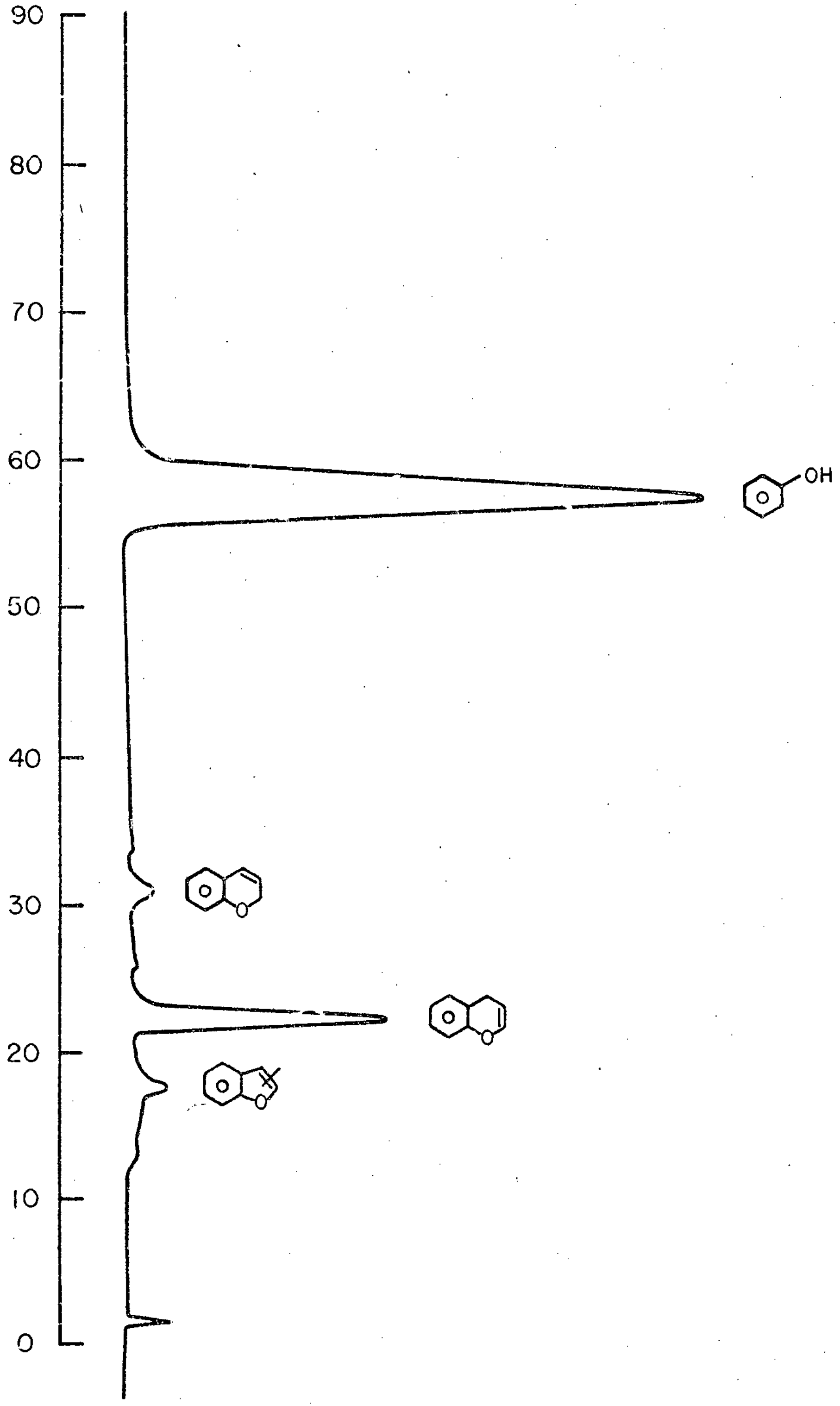


FIGURE 14

GLC trace of the products of the degradation over acidic alumina (pH6) of 1,3-diphenoxypropene.

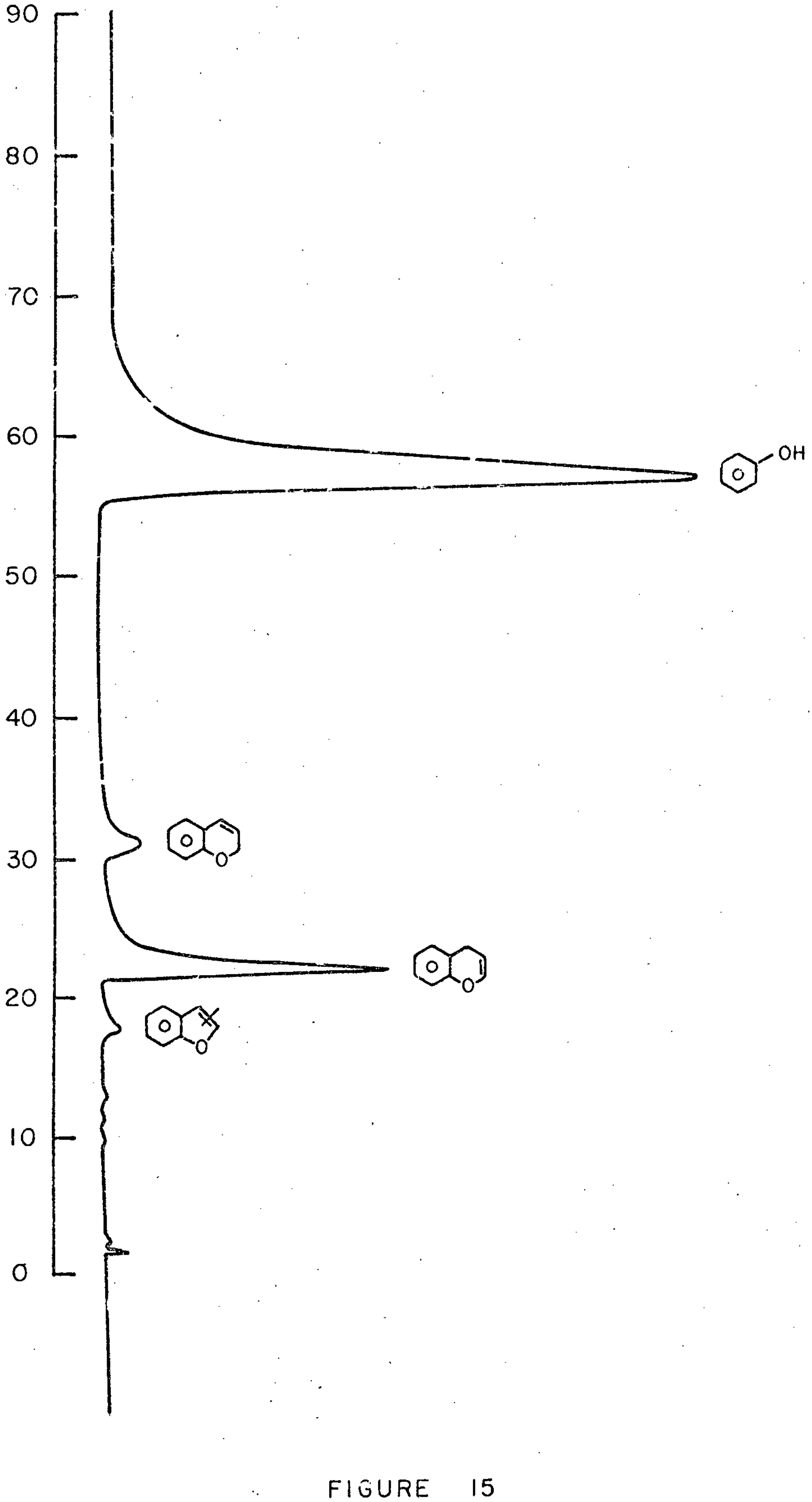


FIGURE 15

GLC trace of the products of the degradation in air of 1,3-diphenoxypropene.

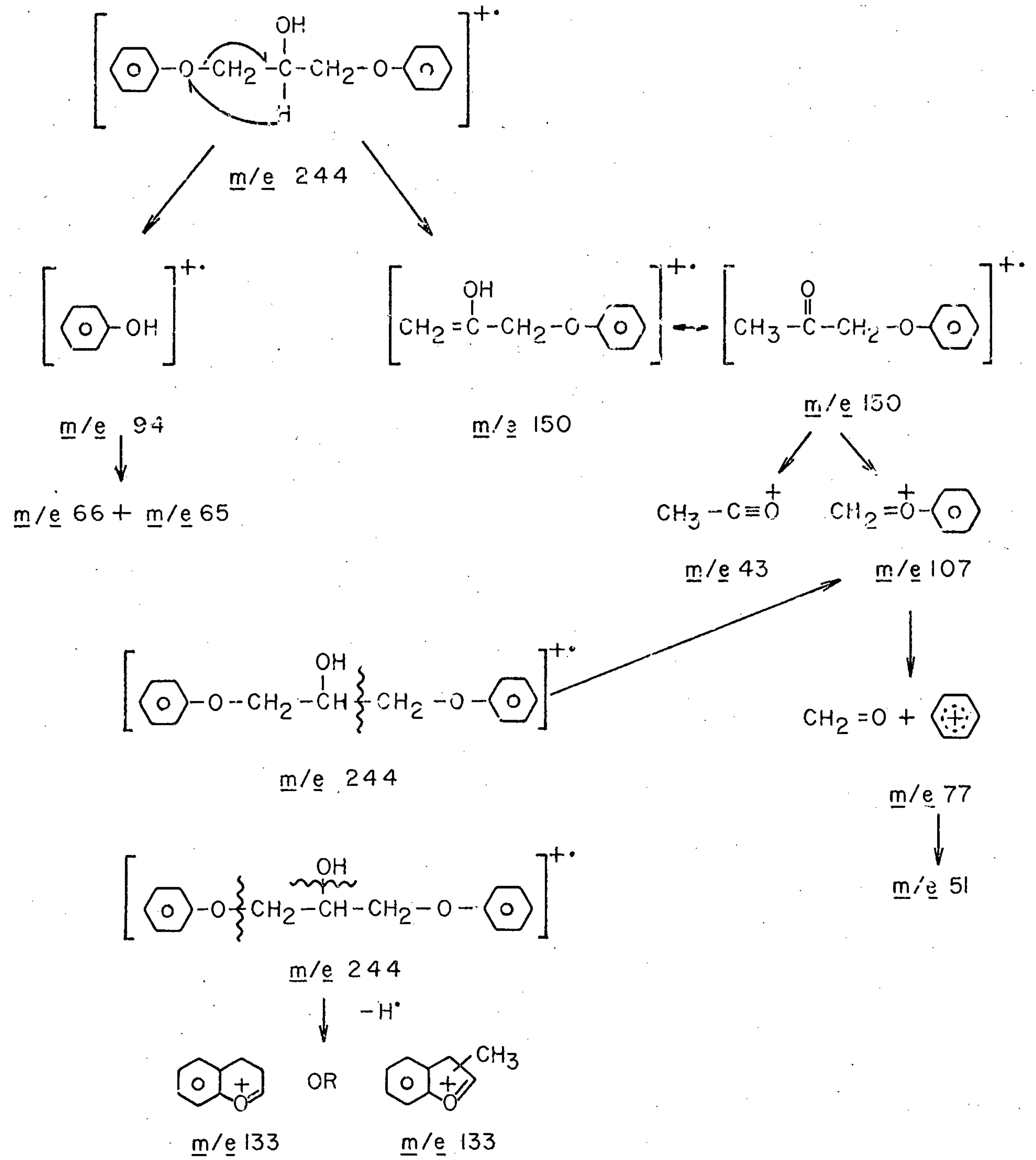
III.3. DISCUSSION OF ANALYTICAL RESULTS

III.3.1. Mass Spectra of the Model Compounds 1,3-Diphenoxypropan-2-ol and 1-(N-Ethylanilino)-3-phenoxypropan-2-ol

III.3.1.1. The mass spectrum of 1,3-diphenoxypropan-2-ol

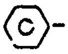
The mass spectrum of 1,3-diphenoxypropan-2-ol contains major peaks at m/e 244, m/e 150, m/e 133, m/e 107, m/e 94 and m/e 77.

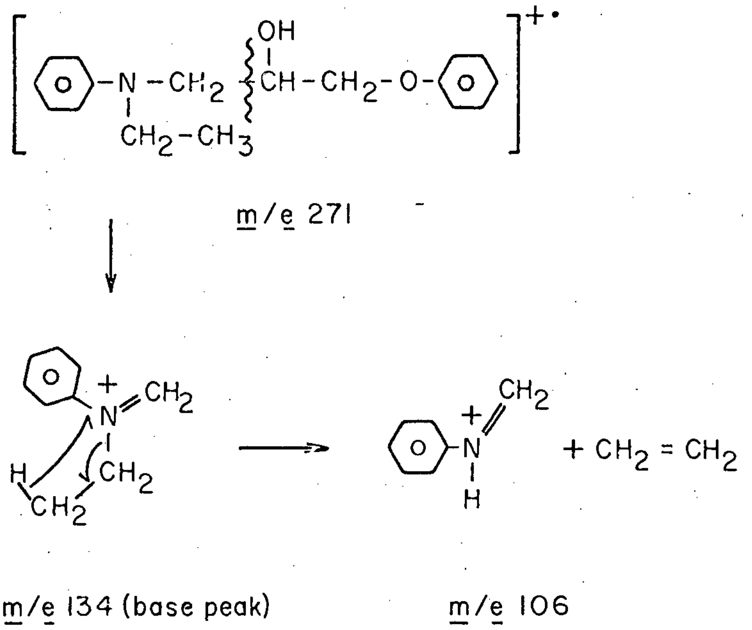
The molecular ion (m/e 244) appears to decompose to the M-94 ion (m/e 150) through the loss of phenol. This process is supported by the appearance of a metastable peak at m/e 92,2 and a strong peak at m/e 94 possibly due to the charged phenol fragment. The m/e 107 fragment which may originate from the molecular ion (supported by a metastable peak at m/e 46,9) or from the M-94 ion (supported by the presence of a metastable peak at m/e 76,4) may decompose to the m/e 77 fragment through the loss of CH_3CO as indicated below. The appearance of a metastable peak at m/e 72,5 indicates that the m/e 133 fragment may originate from the molecular ion. The exact nature of this fragment and the mechanism involved in its formation are not known. A possible fragmentation pattern for the decomposition of 1,3-diphenoxypropan-2-ol may be depicted:



The mass spectrum of phenoxyacetone has major peaks at *m/e* 150, *m/e* 107, *m/e* 77, *m/e* 51 and *m/e* 43 which lend support to the above fragmentation of the *m/e* 150 fragment.

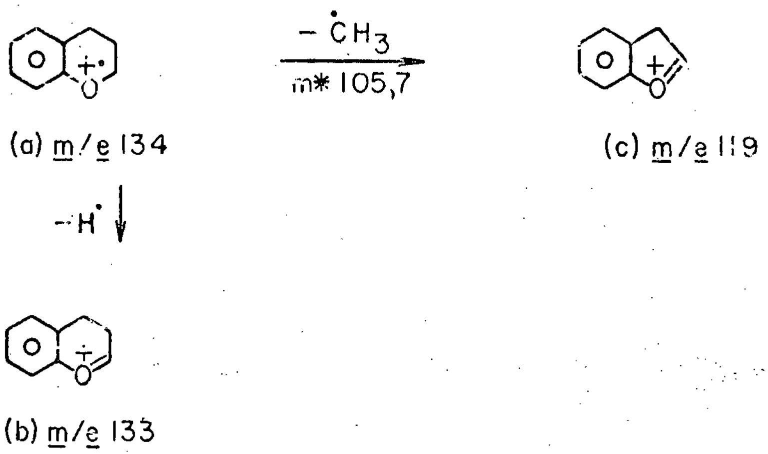
III.3.1.2. The mass spectrum of 1-(*N*-ethylanilino)-3-phenoxypropan-2-ol

The molecular ion (*m/e* 271) of 1-(*N*-ethylanilino)-3-phenoxypropan-2-ol loses -O-CH$_2$-$\dot{C}$HOH to give a strong peak at *m/e* 134 (base peak). This decomposition is supported by the presence of a metastable peak at *m/e* 66,3. The M-137 ion (*m/e* 134) decomposes to the M-165 ion (*m/e* 106) through the loss of ethylene. This process is supported by the presence of a metastable peak at *m/e* 83,9. The decomposition may be represented as follows:



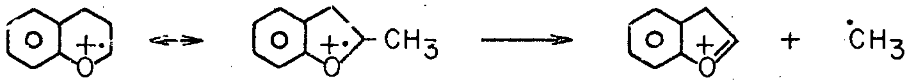
Two other strong peaks in the mass spectrum of 1-(*N*-ethylanilino)-3-phenoxypropan-2-ol occur at *m/e* 86 and *m/e* 84. The fragmentation pattern leading to the formation of these two fragments is not known.

III.3.2. The Mass Spectrum of Chroman

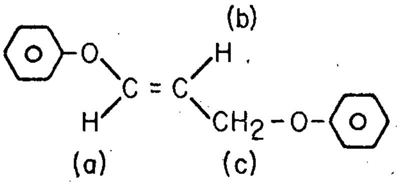


It has been suggested[45] that the M-1 ion (b) derived from chroman decomposes to the M-15 ion (c) through the expulsion of a methylene group. This has been regarded as an unlikely process[45] and it has been suggested[45] that the M-15 peak is due rather to the presence of a contaminating homologue containing one less methyl group.

In the present work a mass spectrum of pure chroman was obtained by determining the mass spectrum on the GLC peak representing chroman as it emerged from a gas chromatograph (section II.1.1.). Contamination of the sample by 2-methylcoumaran (which decomposes to (c) through the loss of $\dot{C}H_3$) is considered unlikely since this compound has a different retention time. The presence of a metastable peak at m/e 105,7 in the mass spectrum of chroman supports the loss of a methyl group from the molecular ion (a) to form the M-15 ion (c). It is possible that chroman rearranges to the 2-methylcoumaran structure prior to loss of $\dot{C}H_3$ to form the M-15 ion (c).

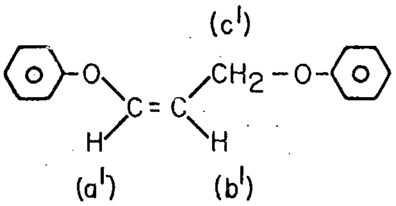


III.3.3. The PMR Spectrum of 1,3-Diphenoxypropene



trans - isomer

a + a' : 3,46 τ (quartet)
b + b' : 4,2 - 5,1 τ (multiplet)
c + c' : 5,4 τ (quartet)

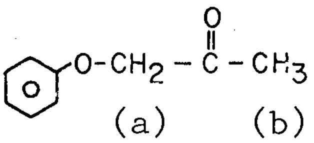


cis - isomer

The PMR spectrum of a mixture of the cis- and trans-isomers of 1,3-diphenoxypropene is complicated by the difference between chemical shifts[46] and coupling constants[47] of corresponding protons in the two isomers. The methine groups a and a' are represented by a pair of doublets around 3,46τ. The methine groups b and b' give rise to a complicated multiplet around 4,65τ. The methylene groups c and c' give rise to a pair of doublets around 5,4τ.

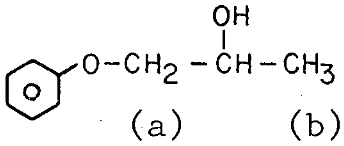
III.3.4. The PMR Spectra of Phenoxyacetone and 1-Phenoxypropan-2-ol

Phenoxyacetone



a : 5,47 τ (singlet)
b : 7,73 τ (singlet)

1-Phenoxypropan-2-ol



a : 6,10 τ (multiplet)
b : 8,75 τ (doublet)

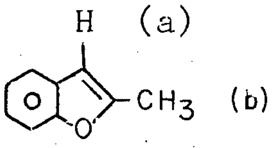
The PMR spectra of phenoxyacetone and 1-phenoxypropan-2-ol which were separated from the products of the degradation over neutral alumina of 1,3-diphenoxypropan-2-ol (section II.3.1.1.) were used to identify these products.

III.3.5. The PMR Spectra of 2- and 3-Methylbenzofuran

2- and 3-Methylbenzofuran were separated from the products of the degradation over neutral alumina of 1,3-diphenoxypropan-2-ol (section II.3.1.1.) as a mixture of the two products.

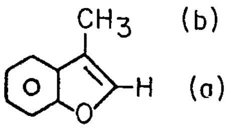
The PMR spectrum of the mixture provided identification of the products. The PMR spectra of the pure synthetic 2- and 3-methylbenzofuran are summarised:

2-methylbenzofuran



a : 3,72 τ
b : 7,62 τ

3-methylbenzofuran



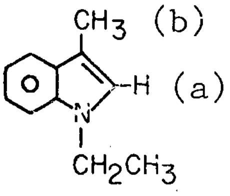
a : ~ 2,63τ
b : 7,79τ

In the spectrum of the mixture two distinct methyl signals are observed at 7,6τ and 7,8τ. The signal at 3,7τ is shown by integration to represent one methine group while 9 aromatic protons including the hydrogen adjacent to oxygen in 3-methylbenzofuran are represented by a multiplet at approximately 2,6τ. IR and mass spectra of the mixture confirmed the presence of both 2- and 3-methylbenzofuran.

III.3.6. The PMR Spectrum of N-Ethylskatole

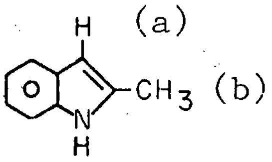
N-Ethylskatole was separated from the products of the degradation over acidic alumina of 1-(N-ethylanilino)-3-phenoxypropan-2-ol (section II.3.2.1.). The GLC retention time, IR and mass spectra indicated that the product was N-ethylskatole. This was confirmed from its PMR spectrum.

N-ethylskatole



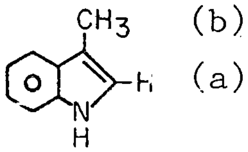
a : 3,16 τ
b : 7,68 τ

2-methylindole



a : 3,79 τ
b : 7,59 τ

skatole



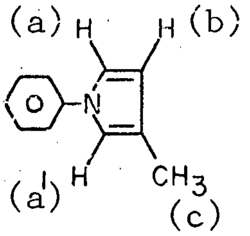
a : 3,14 τ
b : 7,66 τ

The frequencies of the methine and methyl signals of the product N-ethylskatole clearly establish the position of the methyl group on the heterocyclic ring.

III.3.7. The Identification of 3-Methyl-N-phenylpyrrole

3-Methyl-N-phenylpyrrole was separated from the products of the thermal degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol (section II.3.2.2.1.) as a white solid (m.p. 63-4°C, Lit. m.p. 70-1°C[48]).

IR, PMR and mass spectra were used to identify the product. The PMR spectrum clearly indicates the position of the methyl group on the heterocyclic ring.

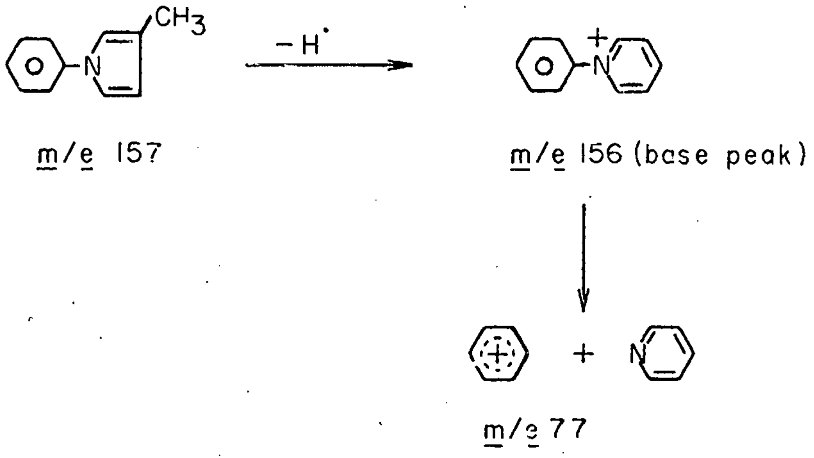


a+a' : 3,0-3,32τ (multiplet)
b : 3,92τ (multiplet)
c : 7,86τ (singlet)

The methine signals at 3,0 - 3,32τ and 3,92τ occur as multiplets because of long-range coupling across the ring[49]. The above assignments are in agreement with the values of the methine groups in the 2 and 3 positions of pyrrole namely 3,40τ and 3,91τ respectively[49]. That the methyl group is in the 3 position on the heterocyclic ring is confirmed by proton integration of the methine signal at the higher frequency (3,92τ).

This result is supported by the fact that whereas the degradation product is a solid, 2-methyl-*N*-phenylpyrrole is a liquid at room temperature[50].

The mass spectrum of the degradation product is in agreement with the proposed structure. The molecular ion (*m*/*e* 157) loses a proton to give the very stable M-1 ion (*m*/*e* 156, base peak). Very little further fragmentation occurs but the peak at *m*/*e* 77 may be explained:



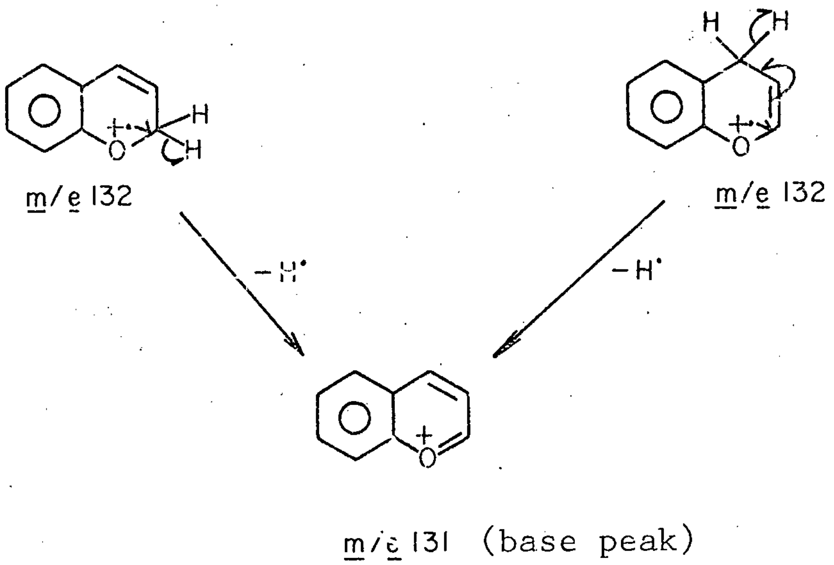
It has been reported[45] that pyrroles containing only C-methyl substituents have their base peaks at M-1 and that other fragmentations are of relatively low abundance (the M-1 ions probably exist as the pyridinium cations[45]).

The IR spectrum of the degradation product is also in agreement with the structure of 3-methyl-N-phenylpyrrole.

III.3.8. The Identification of 2-Chromene

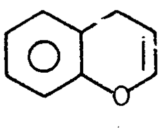
2-Chromene was identified as a degradation product by a comparison of its mass spectrum with that of 3-chromene.

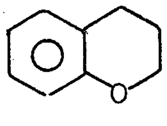
2- and 3-chromene have identical mass spectra. Both molecular ions decompose through the loss of H• to the very stable M-1 ion (m/e 131, base peak). Very little further fragmentation occurs.

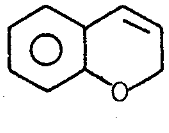


The GLC retention time of 2-chromene (21,1 min) in the degradation over acidic alumina of 1-(N-ethylanilino)-3-phenoxypropan-2-ol (section II.3.2.1.) was used as a standard for comparison with the retention times of 2-chromene in other degradations.

The assignment of the 2-chromene structure to the product eluting at 21,1 min in the gas chromatograms of the degradation products is supported by the retention times of the products 2-chromene, chroman and 3-chromene which elute in the following order:

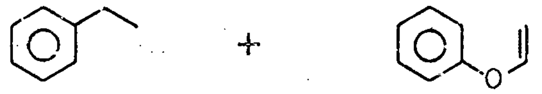

2-chromene
22,1 min


chroman
25,9 min


3-chromene
30,7 min

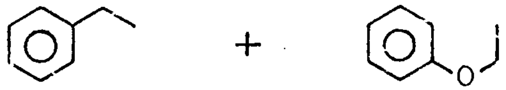
These compounds may be represented by the following part-structures:

2-chromene



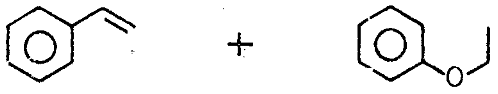
ethylbenzene phenyl vinyl ether

chroman



ethylbenzene phenetole

3-chromene



styrene phenetole

2-chromene and chroman differ in that 2-chromene has the phenyl vinyl ether part-structure whereas chroman has the corresponding phenetole part-structure. That the retention time of chroman is longer than that of 2-chromene is supported by the fact that the retention time of phenetole (8,1 min) is longer than that of phenyl vinyl ether (7,0 min). The difference between chroman and 3-chromene lies in the ethylbenzene part-structure of chroman and the corresponding styrene part-structure of 3-chromene. Their order of elution is supported by the order of elution of ethylbenzene (3,9 min) and styrene (5,7 min).

A similar situation exists in the case of 2-methylbenzofuran which elutes after 2-methylcoumaran. 2-Methylbenzofuran contains overlapping styrene and phenyl vinyl ether part-structures. The effect of the former part-structure appears to predominate because of the longer retention time of 2-methylbenzofuran. In fact the effect of the styrene part-structure appears the stronger since the ratio of the retention times of styrene and ethylbenzene (1,45) is greater than the ratio of the retention times of phenetole and phenyl vinyl ether (1,16).

IV. DISCUSSION

IV.1. THE DEGRADATION OF 1,3-DIPHENOXYPROPAN-2-OL

1,3-Diphenoxypropan-2-ol was degraded under four different conditions;

1 over neutral alumina (pH7)
2 over acidic alumina (pH6)
3 over basic alumina (pH9)
4 under nitrogen and in air.

The products of the first two degradations (tables 2 and 3) were identical and differed from those of the second two degradations (tables 5,7 and 8) which were also identical. The nature of the alumina appeared to modify the degradation reaction.

It has been found[51] that alumina has intrinsic acidity which can undergo profound modifications as a result of the alkali content of the alumina. This varying acidity has been used to explain the disagreement between reports of different investigators not only about the reaction mechanism but also about the nature of the products formed from the same starting materials. Calcined alumina has a pH of 9 and often contains sodium carbonate and bicarbonate[52]. The alkali of alumina may be removed by washing with water or dilute acid giving, on reactivation at 200°C, neutral or acidic alumina[52].

FEACHAM and SWALLOW[53] have shown that a decrease in sodium content enhances the catalytic activity of alumina with respect to the rate of dehydration of ethanol to ethylene. The activity of alumina for dehydration and isomerisation is markedly decreased by adsorbed sodium or potassium ions[54-58] and all of the dehydrating capacity can be removed by impregnation with 0,025-0,3 mmole of sodium ions per gram of alumina[55,59,60].

In the degradation of 1,3-diphenoxypropan-2-ol the effect of this acidity was evident. Interaction with neutral and acidic alumina gave rise to products with three aliphatic carbon atoms which suggested that catalysed carbon-oxygen fission had occurred. Interaction with basic alumina gave rise to the same products as the degradation without alumina in which thermal homolysis might have occurred causing fission of both carbon-oxygen and carbon-carbon bonds. It appeared that the basic alumina had not caused preferential carbon-oxygen fission to any appreciable extent. The degradation over basic alumina, however, proceeded more readily than the degradation without alumina which suggested that basic alumina had in some way accelerated the degradation.

It was found[61,62] that impregnation of alumina with lithium atoms caused an increase in its adsorptive capacity for C_2 to C_4

alcohols. The desorption of ethanol in the form of ethanol and of diethyl ether was intensified and its decomposition to ethylene was inhibited[62]. In a similar manner basic alumina might have restricted the mobility of the 1,3-diphenoxypropan-2-ol molecule, thus facilitating decomposition without necessarily promoting carbon-oxygen fission.

IV.1.1. The Degradation of 1,3-Diphenoxypropan-2-ol over Neutral and Acidic Alumina

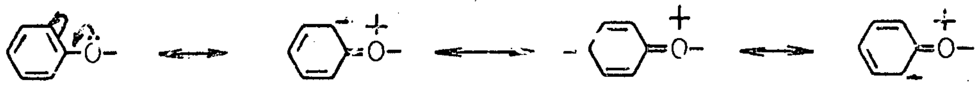
At low temperatures alumina has a strong tendency to be completely hydrated at the surface[51,63]. The temperature of reactivation of the catalyst considerably affects both the nature and relative proportions of the reaction products[63]. Prior heat-treatment of the catalyst above 800°C causes both dehydrogenation and dehydration reactions of alcohols to occur[63]. The formation of trace amounts of butyraldehyde from n-butanol[55], 2-butanone from 2-butanol[56] and acetaldehyde and acetone from ethanol[63-65] has been reported. The formation of carboxylate-like structures by alcohols on the surface of alumina has been reported[66-68] and it has been suggested[68] that dehydrogenation reactions occur via this intermediate.

Reactivation of the alumina at 90°C under vacuum[69] or at 200°C[52] leaves the structure of the surface unchanged[52,63]. In this work, before each degradation, the alumina was heated for at least two hours at 150°C under vacuum to remove adsorbed water without causing a change in the alumina surface which would promote dehydrogenation reactions.

The details of alcohol dehydration reactions on alumina have been summarised by WINFIELD[70], PINES and MANASSEN[54] and more recently by NOTARI[51] and BREMER and coworkers[60]. Most postulates of mechanisms for alcohol dehydration are keyed to the formation of chemisorbed alkoxide species[71-75]. In addition, ethers can be cleaved on alumina to form the same intermediate alkoxide species as the corresponding alcohols[51,62,67,76,77].

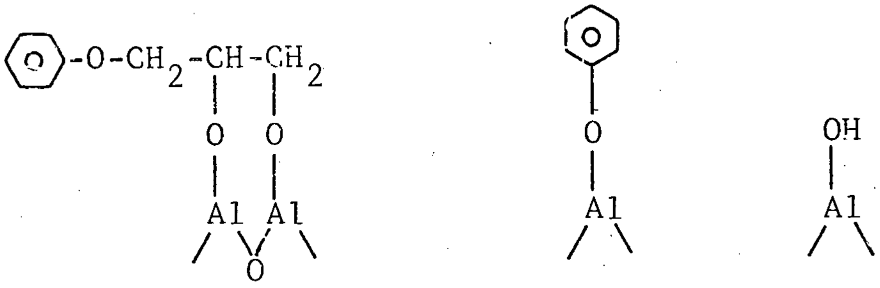
The formation of the surface alkoxide requires the presence of both surface aluminium and oxide ions[51]. The generally accepted model[59,60,66] for the surface of alumina proposed by PERI[78,79] assumes that the surface retains a random configuration of hydroxyl groups after dehydration, which leaves adjoining residual oxide ions and oxide vacancies (exposed aluminium ions). The aluminium ions provide the electric field by which negative oxygen atoms are attracted and chemisorbed and the oxide ions help dissociation of the hydrogen or organic fragment by the formation of OH^- or OR^- groups[51,59,80].

1,3-Diphenoxypropan-2-ol may react with alumina to form alkoxides which result from fission of aliphatic carbon-oxygen bonds. Fission of aromatic carbon-oxygen bonds is not considered likely because of their stability which results from resonance:

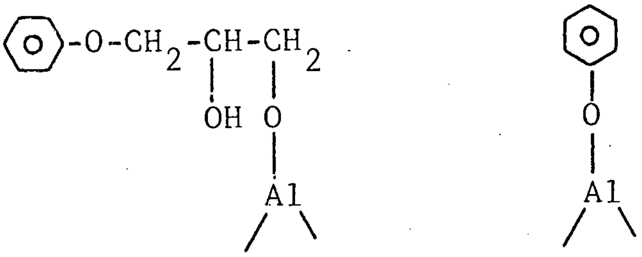


This postulate leads to the following possible intermediates:

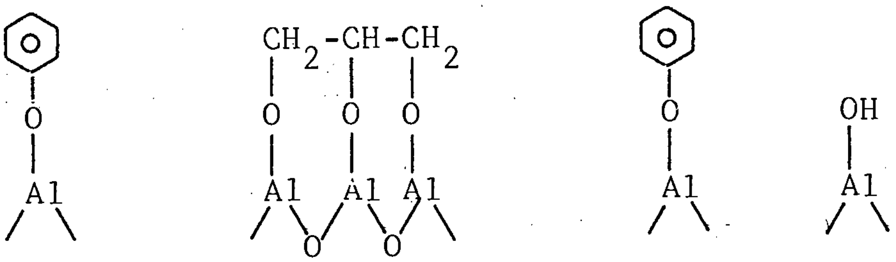
1A



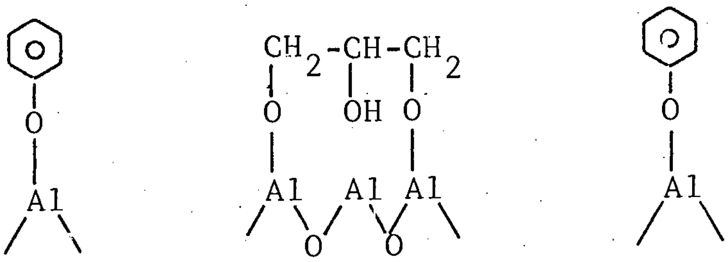
1B



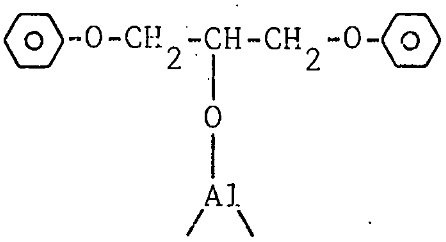
2A



2B



3



The intermediate structures 1A and 2A have two and three oxygen atoms respectively on adjacent carbon atoms bonded to aluminium ions in the alumina. Such a bonding may require a certain amount of distortion of the molecules in order to form these intermediates but this distortion is not considered prohibitive.

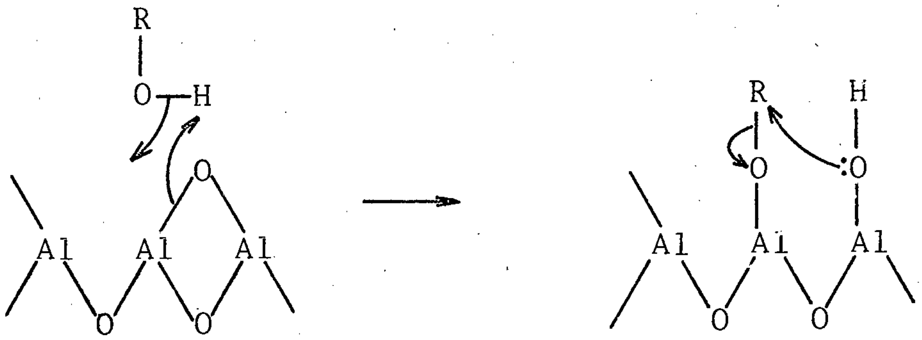
According to PERI[79] an oxide ion on the surface occupies an area of approximately $8\,\text{Å}^2$. The internuclear distance between two oxygen atoms of a molecule occupying adjacent vacancies on the surface would therefore be approximately 2,83Å. If it is assumed that the carbon-carbon and carbon-oxygen bond lengths are the same as those in the free molecule namely 1,54Å and 1,41Å respectively then it can be shown that the required distortion of the carbon-carbon-oxygen bond angle from the normal tetrahedral $109^{\circ}\ 28'$ to approximately 118° is not too severe. The formation of the intermediate 2A with three adjacent carbon atoms having oxygen atoms adsorbed on the surface may require further distortion of the molecule.

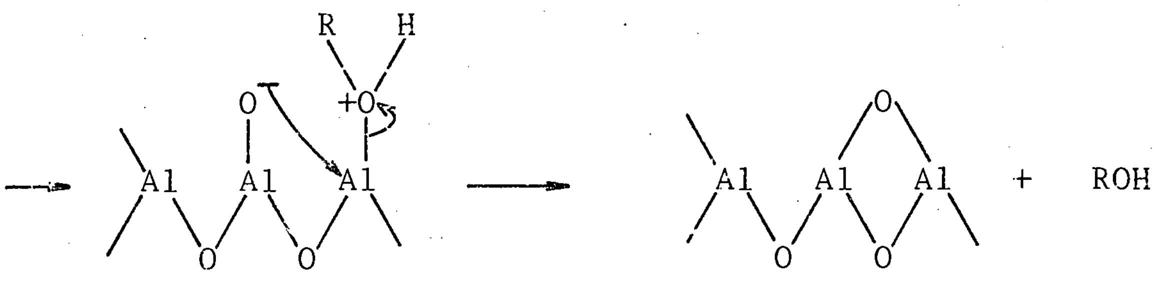
It should be noted, however, that the structure of the alkoxide will be affected by the ionic character of the oxygen to aluminium bond as well as the temperature at which adsorption occurs. The alkoxide chemisorbed surface species of normal alcohols have been reported to exist on the surface between 150°C and 430°C[66,82].

In general, the intermediate structures 1A and 2A suffer a certain degree of distortion but this is not considered sufficient to prevent their formation in view of the relatively small distortions required, the partially ionic bonding and the temperatures involved.

The intermediate alkoxides can undergo reactions which lead to the formation of alcohols, ethers and olefins[51].

The carbon atom attached to oxygen in these intermediate alkoxides is the positive end of a dipole[51] and can therefore be attacked by a nucleophile e.g. OH^- which leads to the generation of a neutral alcohol molecule and leaves an ionic vacancy. This process may be represented as follows[51,59]:





This mechanism has been adopted to explain the possible alcohol desorption reactions in the degradation of 1,3-diphenoxypropan-2-ol over alumina (fig.16.).

A similar mechanism which involves the reaction of two adjacent alkoxide groups can be postulated for ether formation on alumina[51], although many authors[68,71,82-84] claim that ether formation results from the reaction of an alkoxide with a molecularly adsorbed alcohol molecule. HEIBA and LANDIS[76] have, however, shown that aluminium alkoxides decompose to form both ethers and olefins.

1,3-Diphenoxypropan-2-ol was degraded at approximately 360°C with no apparent ether formation. The production of appreciable quantities of any particular ether structure was considered unlikely because of the number of possible alkoxide structures produced on the alumina surface. Furthermore it has been found [56,60,63,67,85] that C_2 to C_8 alcohols do not form ethers above 350°C.

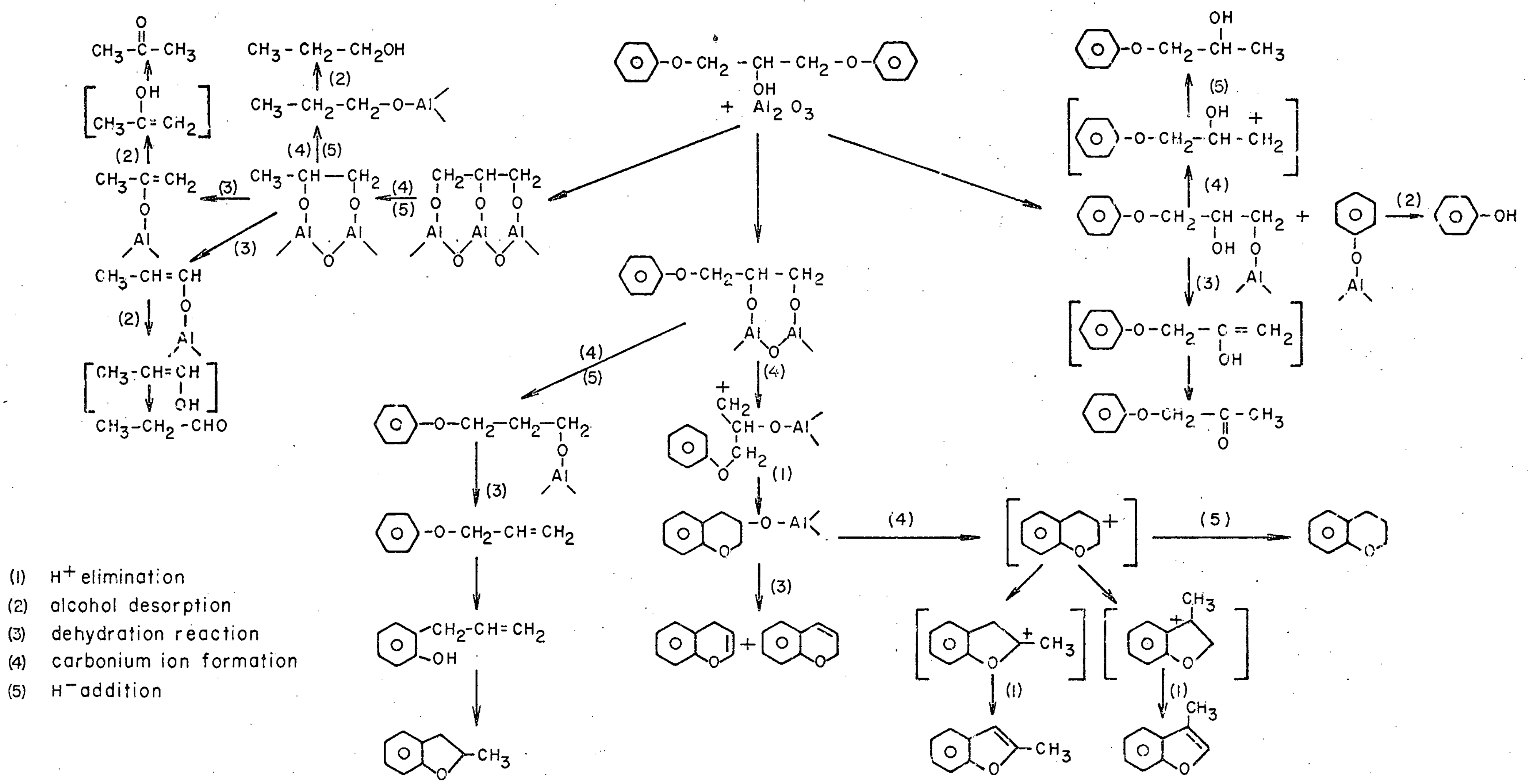


FIGURE 16.

Possible routes to the products of the degradation over alumina of 1,3- diphenoxypropan - 2 - ol.

The dehydration of alcohols over alumina occurs by the concerted or sequential removal of the hydroxyl group of the alcohol by an acidic site of the catalyst and the abstraction of a proton by a base[54,68]. This base may be a basic site on the alumina[51,54,68,86] or another alcohol molecule[87].

Although products of γ-elimination have been reported[86-88] this is not a common mechanism[51]. If the molecule contains β-protons, β-elimination appears to predominate[51,54,68]. It has been suggested that γ-elimination competes with β-elimination only when steric hindrance retards abstraction of the β-hydrogen[87]. Preferential *cis*- or *trans*-elimination of the β-hydrogen has been reported[51,86-88]. In order to explain the *trans*-elimination PINES and MANASSEN[54] have proposed a mechanism similar to solvolytic elimination reactions, for which purpose the concept of alumina acting as a "pseudo-solvent" which surrounds the alcohol molecule has been advanced. The hydroxyl group and the proton are removed from opposite sides of the molecule by the acidic and basic sites of the alumina (fig.17). The reaction takes place within the pores and/or crevices of molecular dimensions of the alumina.

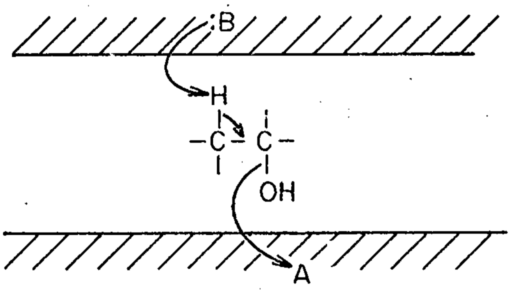


FIGURE 17

Objections to this mechanism are based on the severe steric requirements for accommodation of the alcohol molecules in the cracks and micropores of the alumina[51].

NOTARI[51] has suggested an alternative mechanism of dehydration which explains the formation of either <u>cis</u>- or <u>trans</u>-isomers from alcohols containing two β-hydrogens by invoking a <u>cis</u>-elimination reaction on a single surface of alumina. This mechanism however cannot explain the formation of <u>trans</u>-isomers from alcohols containing only one β-hydrogen. NOTARI's mechanism requires the formation of a cyclic transition state by the alcoholic oxygen atom, the α- and β-carbon atoms, one of the β-hydrogen atoms, one oxide ion of the surface and an aluminium ion in the interior of the solid (fig.18A). In order to form this cyclic transition state a β-hydrogen is directed towards the surface, whether this is the <u>cis</u>- or <u>trans</u>-hydrogen, in an alcohol containing two β-hydrogen atoms, is determined by the steric repulsions between the bulky groups of the molecule and the surface. Steric interaction with the surface may be more important than interaction with the other groups of the molecule; thus, depending on the nature of the alcohol either <u>cis</u>- or <u>trans</u>-isomers may be formed. BREMER and coworkers[60] have postulated the formation of a similar cyclic intermediate (fig.18B) to explain the dehydration mechanism.

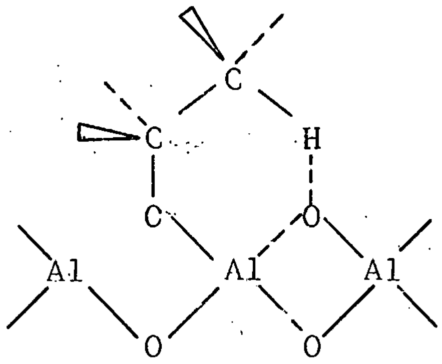


FIGURE 18A

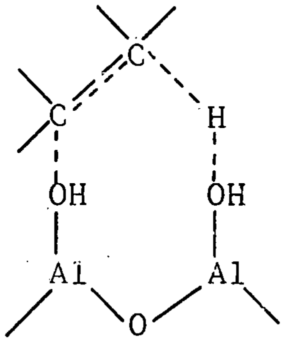


FIGURE 18B

The two intermediate structures are essentially the same; in both cases the adsorbed alcohol forms the same complex with the surface.

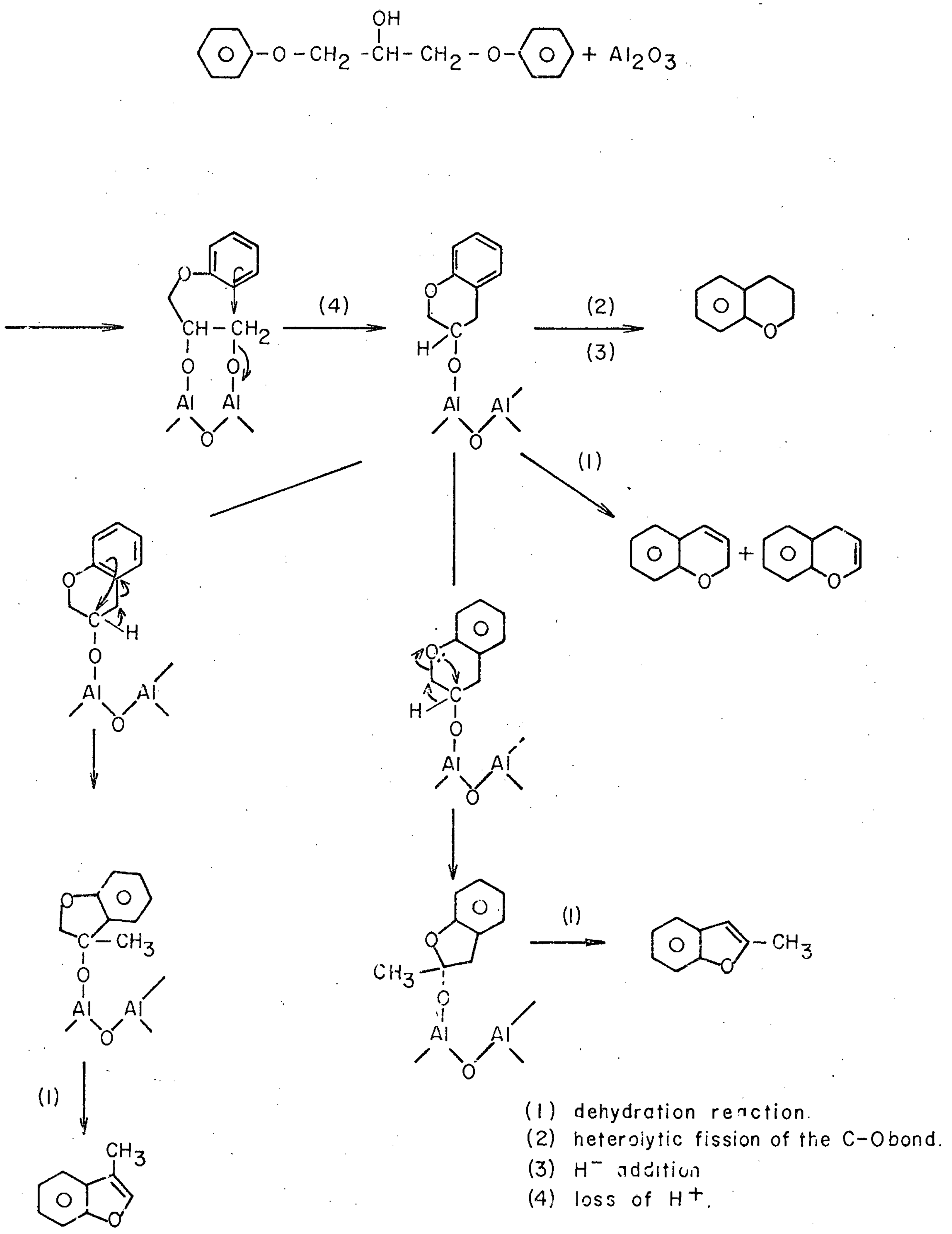
This mechanism which involves the internal degradation of an aluminium alkoxide has been used by many workers to explain olefin formation[67,71,77,89,90].

In the degradation of 1,3-diphenoxypropan-2-ol many products resulting from dehydration reactions were observed. Their formation can be explained by the mechanism proposed by NOTARI[51] i.e. the abstraction of a hydrogen from the aluminium alkoxide by an oxide ion on the surface of alumina (fig.16). Whether this occurs on a single surface of the alumina[51,60] or in a crevice as suggested by PINES and MANASSEN[54] is immaterial since the products involved do not exhibit geometrical isomerism.

In many cases carbonium ion formation has been postulated to explain dehydration reactions which involve skeletal isomerisation or where the preferred cis- or trans-elimination has not occurred[51,54,68,70,91]. The aluminium alkoxide can undergo heterolytic dissociation of the carbon-oxygen bond to form a carbonium ion which can rearrange to a different structure which may be stabilised by the loss of a proton to the surface[51] or by the abstraction of a hydride ion from a neutral molecule. Hydrogenation reactions of alkenes on alumina have been reported[92,93]. The formation of many products in the degradation of 1,3-diphenoxypropan-2-ol over alumina can be explained by postulating carbonium ion formation followed by rearrangement and stabilisation through the loss of a proton to the surface or the abstraction of a hydride from a neighbouring source (fig.16).

An alternative mechanism for the formation of these products which would not liberate free carbonium ions would involve prior rearrangement of the alkoxide group on alumina initiated by the positive character of the carbon adjacent to oxygen in the alkoxide followed by the simultaneous heterolytic fission of the carbon-oxygen bond and stabilisation through either loss of a proton to the surface or hydride abstraction (fig.19).

Possible routes to the products of the degradation over alumina of 1,3-diphenoxypropan-2-ol have been depicted in fig.16.



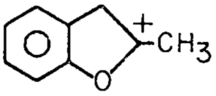
(1) dehydration reaction.
(2) heterolytic fission of the C-O bond.
(3) H^- addition
(4) loss of H^+.

FIGURE 19.

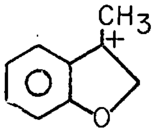
Possible alternative routes to certain products in the degradation over alumina of 1,3-diphenoxypropan-2-ol.

The formation of some products has been depicted for the sake of simplicity as occurring through the reaction of the intermediate alkoxides 1A and 2A where two or three oxygen functions of 1,3-diphenoxypropan-2-ol are simultaneously adsorbed on the alumina surface. In fact these products may be formed by the stepwise addition of the necessary oxygen functions and their subsequent reactions. This would require the liberation of neutral molecules which in turn readsorb onto the surface and undergo further reaction. This is illustrated by the formation of acetone (fig.20).

In fig.16 the loss of a proton from the tertiary carbonium ions

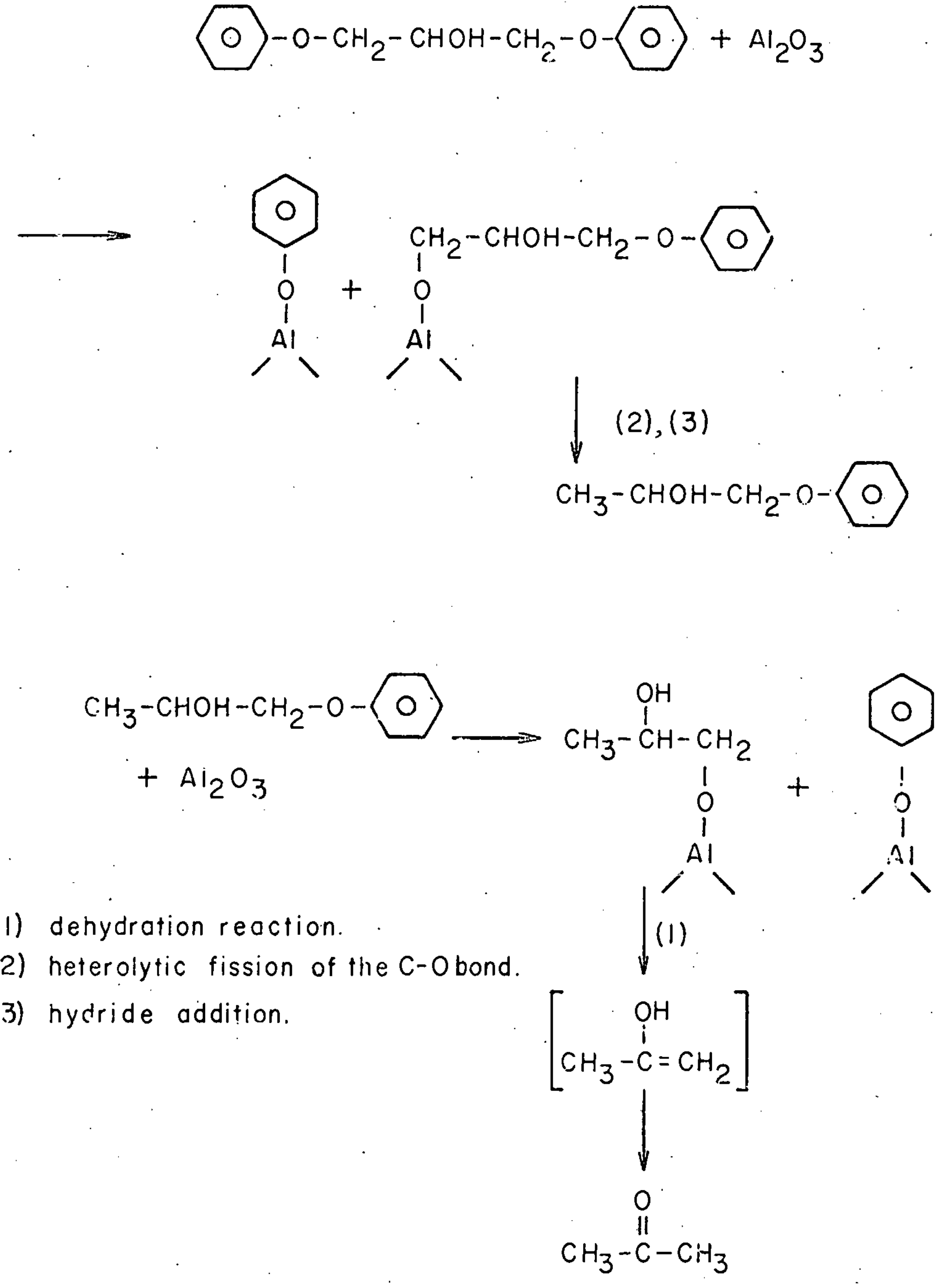


and



to form the aromatic benzofuran structures was considered more likely than the addition of a hydride ion to these ions to form the corresponding coumaran structures. This was supported by the fact that 3-methylcoumaran was not observed amongst the degradation products.

The degradation of 1,3-diphenoxypropan-2-ol over neutral or acidic alumina as depicted in fig.16 explains the formation of the products of this degradation without invoking secondary reactions of the liberated compounds with alumina. In fact it



(1) dehydration reaction.
(2) heterolytic fission of the C-O bond.
(3) hydride addition.

FIGURE 20.

An alternative mechanism leading to the formation of acetone in the degradation over alumina of 1, 3- diphenoxypropan- 2-ol.

is likely that many products once formed may be readsorbed onto the surface of alumina to undergo further reaction and thus provide alternative routes to some of the products of this degradation.

KARAKHANOV and coworkers[94] have found that on heating chroman at 250°C over alumina 2-methylcoumaran is produced. The dehydration of cyclohexanol over alumina gives cyclohexene as the primary product and methylcyclopentenes in a secondary isomerisation reaction[57,72]. 2- and 3-Methylbenzofuran may have been formed by a similar rearrangement of 2- and 3-chromene. Substituted methylbenzofurans have also resulted from photolysis[95,96] and acid treatment of aryloxyacetones[97] and butanones[98]. Phenoxyacetone may be a source of the methylbenzofurans. CORSON and coworkers[99] decomposed 1-phenoxypropan-2-ol over activated alumina at 400°C and obtained a variety of products which were identified as ethylene, propylene, propionaldehyde, acetone, n-propanol, water, phenol, 2-methylcoumaran, 2-methylbenzofuran, phenoxyacetone, o-allylphenol, 1-phenoxypropan-2-ol and high-boiling products.

CORSON et al.[99] found that the decomposition involved mainly the removal of the C_3 side chain and loss of water. A similar result was observed in the present study of the degradation of 1,3-diphenoxypropan-2-ol. They suggested that the precursors of propionaldehyde and acetone might have been enols or propylene oxide which had been reported to rearrange to both propionaldehyde and acetone under similar conditions. In this work the formation of these products has been suggested to have occurred via the enol from (fig.16). CORSON et al. also suggested that dehydration and rearrangement of 1-phenoxypropan-2-ol gave rise to o-allylphenol and 2-methylcoumaran and that dehydrogenation of the latter to 2-methylbenzofuran and oxidation of 1-phenoxypropan-2-ol to phenoxyacetone had occurred. They proposed the scheme for decomposition shown in fig.21.

The products found by CORSON and coworkers[99] correspond with the major products found in the degradation of 1,3-diphenoxypropan-2-ol over neutral and acidic alumina. The discrepancies between the two results may be attributed to the different conditions of the degradations. In the present study the aliphatic hydrocarbons were not investigated and o-allylphenol was not found but was assumed to have been completely converted to 2-methylcoumaran. The absence of phenyl allyl ether in the degradation of 1-phenoxypropan-2-ol might have been due to the operating temperature of 400°C which caused rapid rearrangement to o-allylphenol[27]. Other compounds not found in CORSON's[99] degradation included 3-methylbenzofuran which occurred in a mixture of 2- and 3-methylbenzofuran; and chroman, 2- and 3-chromene and acetaldehyde which occurred in trace amounts in the present degradation.

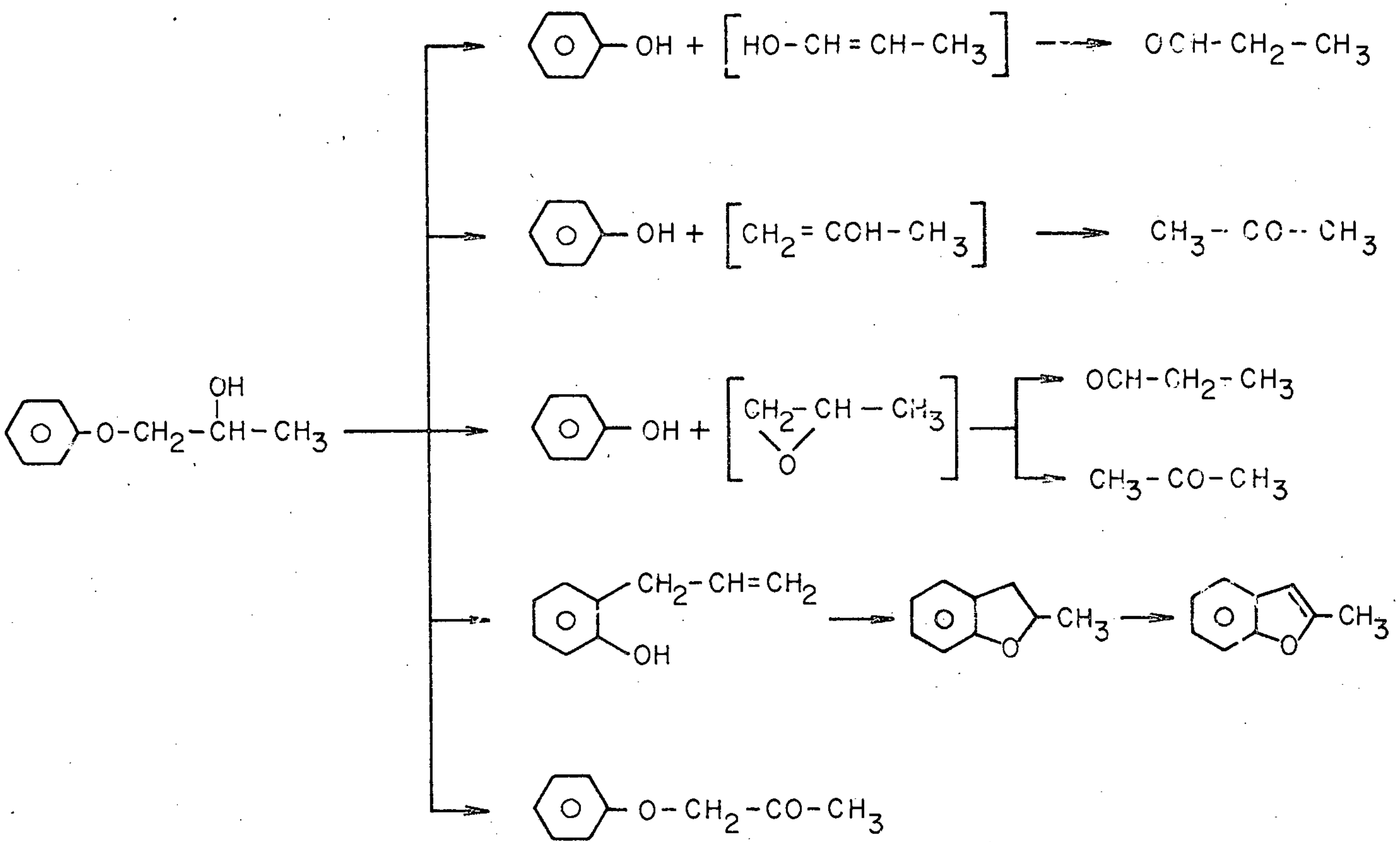


FIGURE 21.

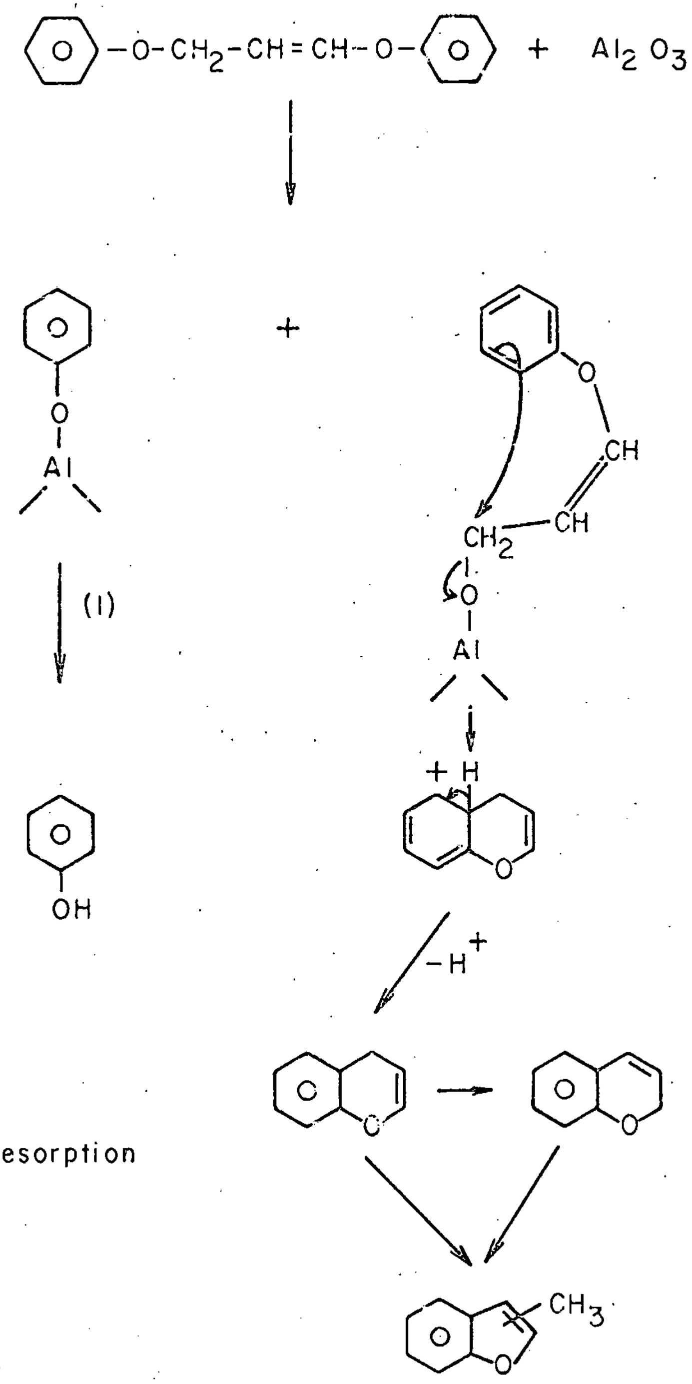
Degradation scheme proposed by CORSON and coworkers [99] for the decomposition over alumina of 1-phenoxypropan-2-ol.

The results of CORSON and coworkers[99] suggest that 1,3-diphenoxypropan-2-ol may be considered to react with alumina to form phenol and 1-phenoxypropan-2-ol. The latter may then react with the surface to form the products obtained in the present degradation.

The possibility that 1,3-diphenoxypropan-2-ol is adsorbed on alumina only at the hydroxyl group to form the intermediate structure 3A was not included in the degradation scheme (fig.16). This intermediate would probably undergo a dehydration reaction to yield 1,3-diphenoxypropene.

IV.1.1.1. The degradation of 1,3-diphenoxypropene over acidic alumina

1,3-Diphenoxypropene was degraded over acidic alumina to yield phenol and 2-chromene as major products. 3-Chromene and 2- and 3-methylbenzofuran were obtained as minor products. Possible routes to these products are indicated in fig.22. The -O-CH= bond in 1,3-diphenoxypropene is stabilised by cross-conjugation and fission may be expected to occur at the $-O-CH_2-$ bond as indicated in fig.22. This will give rise to an intermediate which may cyclise to form 2-chromene. 2-Chromene may isomerise to 3-chromene and further isomerisation of these products may produce the methylbenzofurans. An alternative mechanism for the degradation may involve the Claisen rearrange-



(I) alcohol desorption

FIGURE 22.

Possible routes to the major products of the degradation over alumina of 1, 3-diphenoxypropene.

ment of 1,3-diphenoxypropene and subsequent cyclisation to phenol and 3-chromene which may rearrange under the reaction conditions to form 2-chromene as a major product and the methylbenzofurans as minor products (fig.23).

Since 2-chromene was not produced in any appreciable quantity in the degradation of 1,3-diphenoxypropan-2-ol over neutral or acidic alumina, initial dehydration to 1,3-diphenoxypropene does not appear to have been significant. The conditions of the degradation may, however, have caused almost complete conversion of the chromenes to 2- and 3-methylbenzofuran which occur as minor products in the degradation of 1,3-diphenoxypropan-2-ol. Thus initial dehydration of 1,3-diphenoxypropan-2-ol may occur to a limited extent but fission at the ether linkage is seen to predominate since, after phenol, phenoxyacetone and 1-phenoxypropan-2-ol are the major products.

IV.1.2. The Degradation of 1,3-Diphenoxypropan-2-ol over Basic Alumina, under Nitrogen and in Air.

The nature of the products of the degradations of 1,3-diphenoxypropan-2-ol over basic alumina, under nitrogen and in air indicate that fission of the carbon-carbon bond competes successfully with fission of the carbon-oxygen bond in the molecule. The nature and number of products formed suggest also that homolytic fission of these bonds may have occurred. The

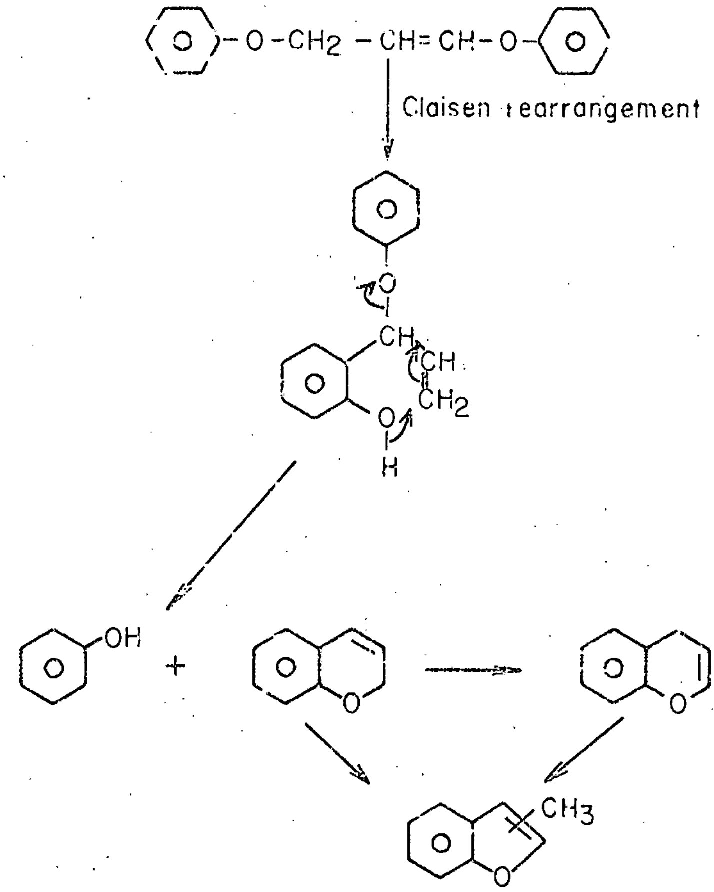
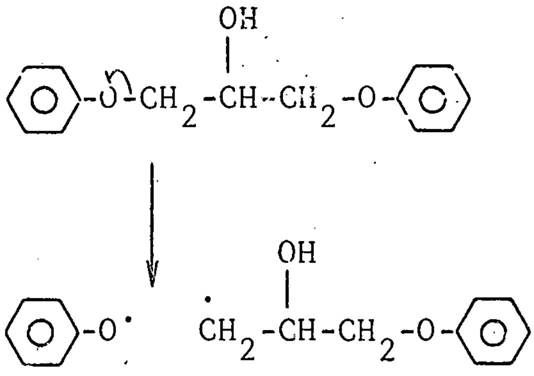
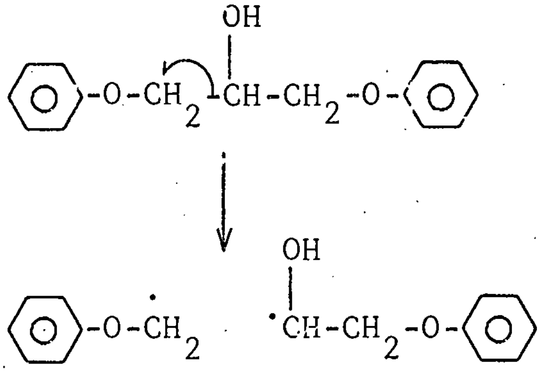


FIGURE 23

An alternative route to the major products of the degradation of 1,3-diphenoxypropene.

formation of all the products found, can be explained by the reaction of the following radical intermediates:





Possible routes to the products of these degradations are given in figs. 24A and 24B.

The mechanisms depicted in figs. 24A and 24B are speculative. Phenyl allyl ether is known to rearrange thermally to o-allylphenol[27,37] which in turn cyclises to form 2-methylcoumaran[37]. Pyrolysis of anisole at 482-700°C has been shown[100] to yield benzene, toluene, benzylalcohol and benzaldehyde. Anisole rearranges to benzylalcohol which decomposes on further heating to benzaldehyde, benzene and toluene[101]. In the degradation schemes the formation of intermediates which have not been identified is postulated but their concentration may have been too low for their

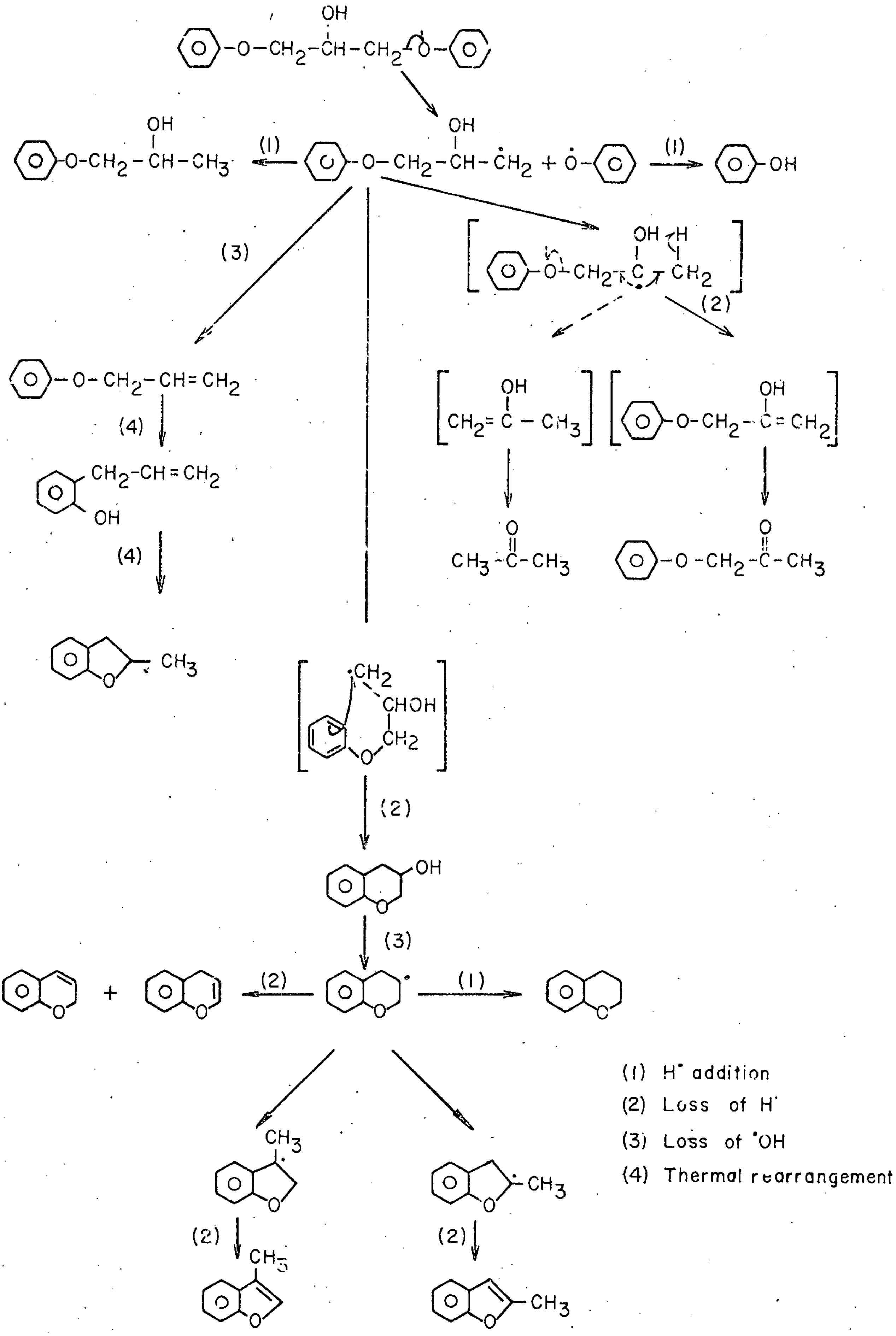


FIGURE 24A.

Possible routes to the products of the thermal degradation of 1,3-diphenoxypropan-2-ol.

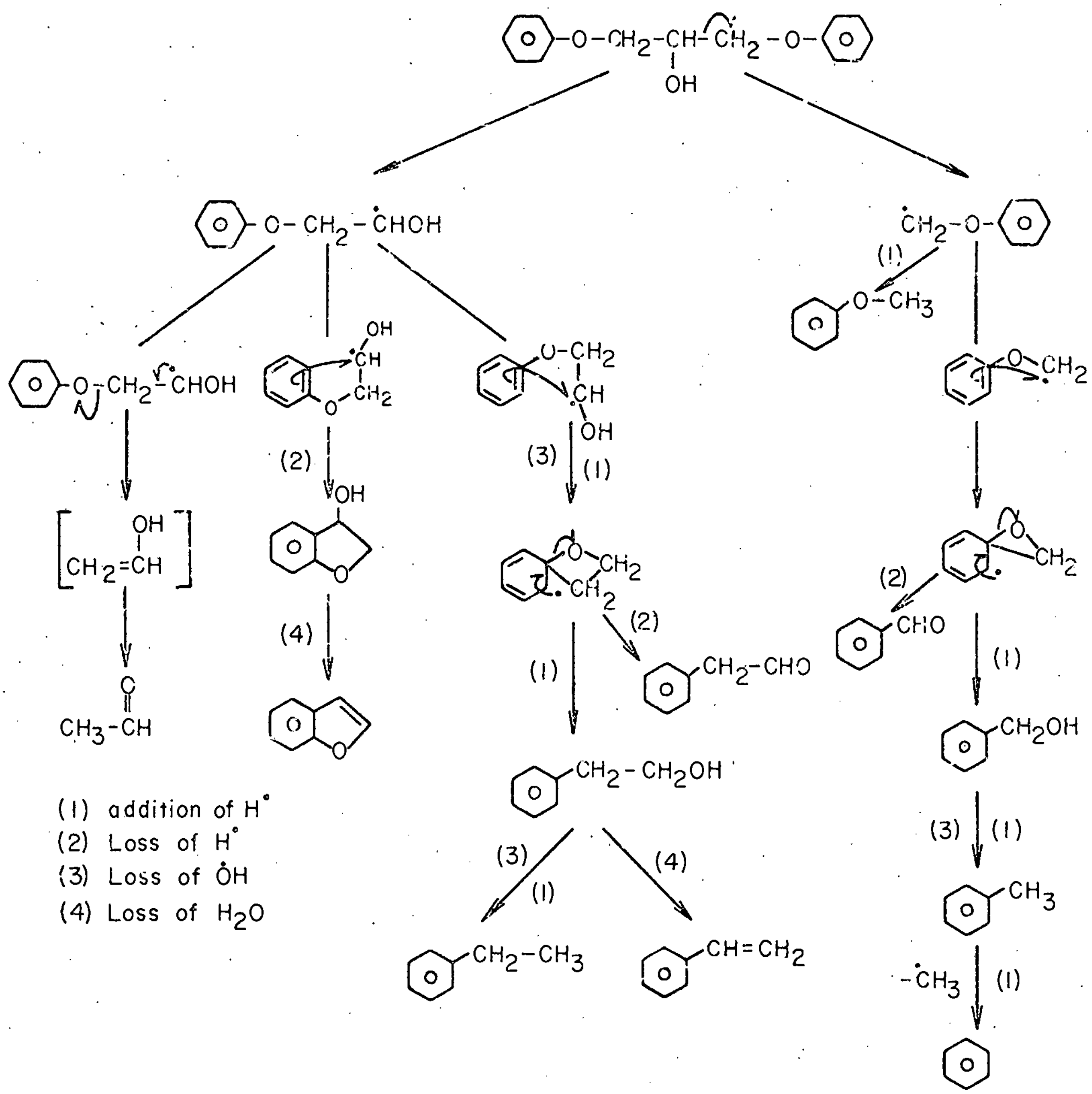
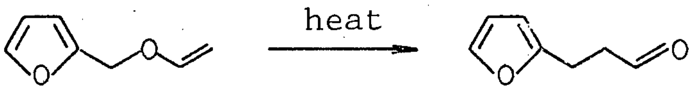


FIGURE 24B.

Possible routes to the products of the thermal degradation of 1,3-diphenoxypropan
-2-ol.

presence to have been detected.

There are many other possible routes to the products of this degradation. Since aryloxyacetones rearrange on photolysis to give 2-methylbenzofurans[95,96] and on acid treatment to give 3-methylbenzofurans[97], it is possible that thermal rearrangement of phenoxyacetone gives rise to one of the methylbenzofurans. Vinyl ethers have been shown to rearrange thermally to form aldehydes[102]. An example is the formation of 3-(fur-2-yl)-propanal (4) from fur-2-ylmethyl vinyl ether (5).

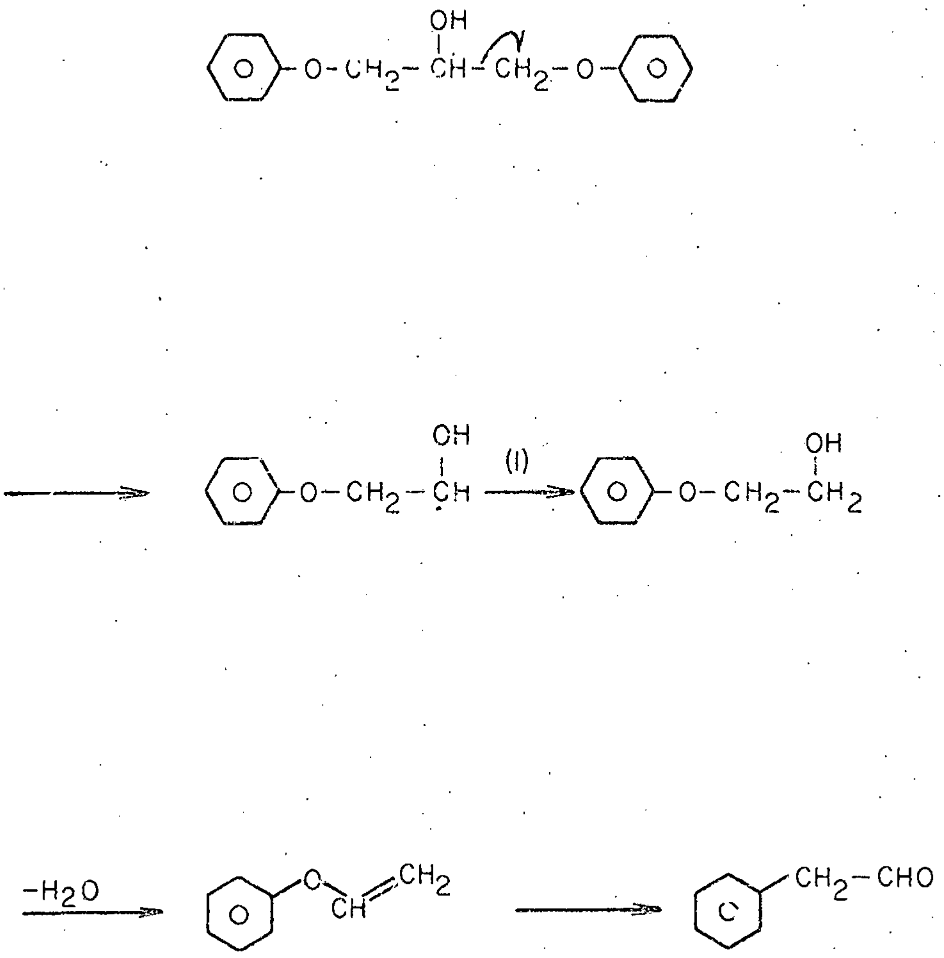


5 4

Phenylacetaldehyde may have resulted from a similar rearrangement of phenyl vinyl ether which could have been formed in the thermal degradation of 1,3-diphenoxypropan-2-ol (fig.25). Products related to phenylacetaldehyde, e.g. styrene and ethylbenzene, possibly resulted from the same reaction.

IV.1.2.1. The thermal degradation of 1,3-diphenoxypropene

The nature and distribution of the products of the degradations of 1,3-diphenoxypropene in air and over acidic alumina were identical. Phenol and 2-chromene were the major products and smaller amounts of 3-chromene and 2- and 3-methylbenzofuran were



(I) $H^{\bullet}$ addition

FIGURE 25

An alternative mechanism for the formation of phenylacetaldehyde in the thermal degradation of 1,3-diphenoxypropan-2-ol.

also produced (fig.15). Possible routes to the major products of the thermal degradation of 1,3-diphenoxypropene are shown in fig.26. It is possible that Claisen rearrangement and cyclisation of 1,3-diphenoxypropene leads to the formation of phenol and 3-chromene which may isomerise to 2-chromene and the methylbenzofurans (fig.23). This reaction may proceed as indicated since phenol, once produced, may catalyse the cyclisation.

The mechanism of degradation postulated in fig.26 involves homolytic cleavage of the weakest bond in the molecule. The dissociation energy of the $=CH-CH_2-$ bond exceeds that of the $-CH_2-O-$ bond by approximately 19 Kcal/mole (table 13)[103] whereas in the saturated molecule the dissociation energy of the carbon-carbon bond is approximately 7 Kcal/mole less than that of the carbon-oxygen bond. The lower energy required for fission of the carbon-oxygen bond in 1,3-diphenoxypropene (70 Kcal/mole as opposed to 90 Kcal/mole in the saturated compound[103]) provides an explanation for its ready degradation.

Compounds which result from fission of carbon-carbon bonds were not observed in the degradation of 1,3-diphenoxypropene. This indicated that the enhanced thermal stability of the carbon-carbon bond was sufficient to preclude its scission in the degradation. Many products resulting from carbon-carbon fission were observed in the thermal degradation of 1,3-diphenoxypropan-

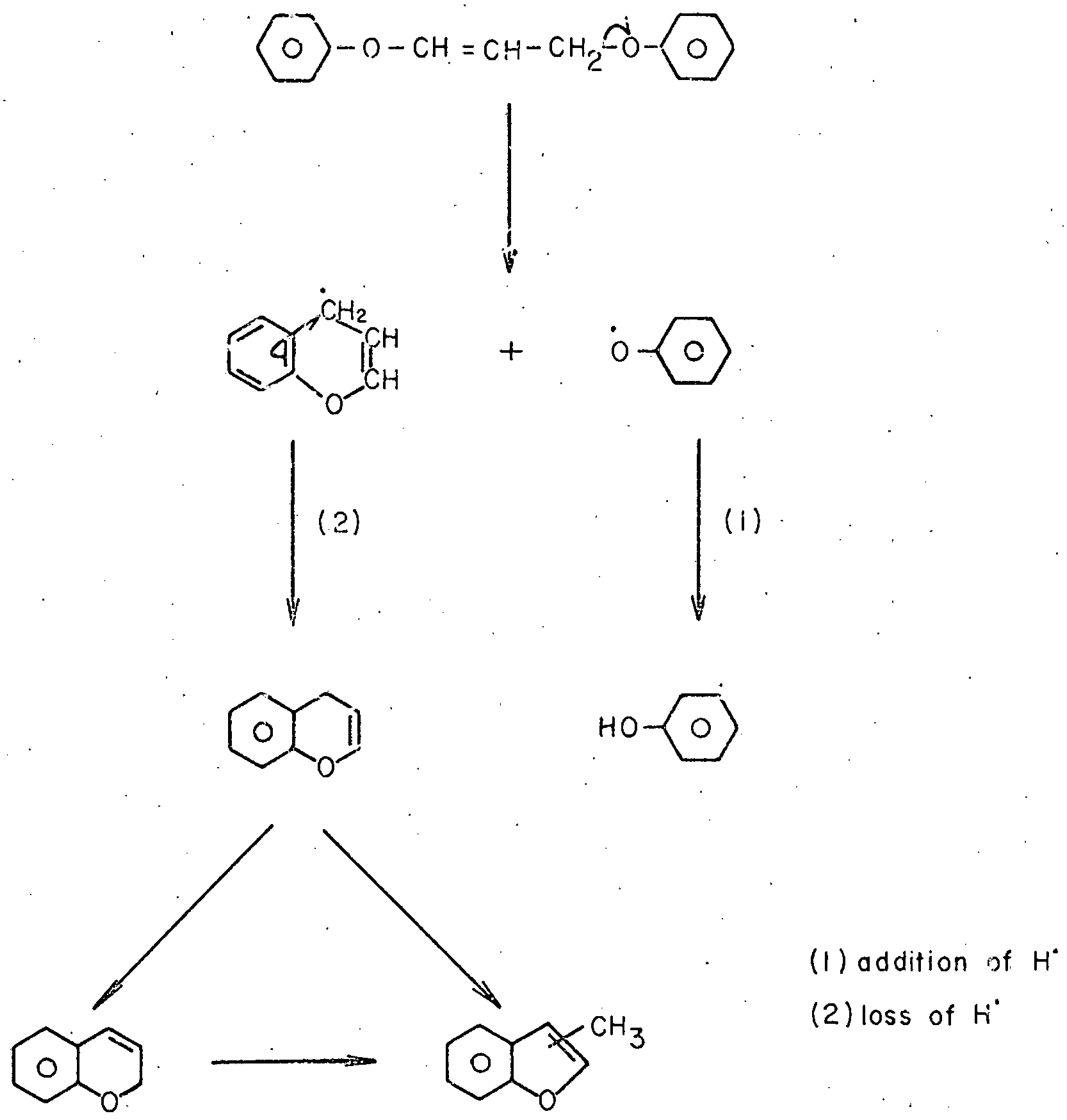
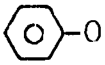
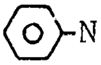


FIGURE 26.

Possible routes to the major products of the thermal degradation of 1,3-diphenoxypropene.

TABLE 13 : Bond dissociation energies[103]

Bond	Approximate bond dissociation energy Kcal/mole
	107
	94
$(CH_2{=}CH)\text{-}O$	>90[17]
$(CH_2{=}CH)\text{-}N$	>90[17]
$(CH_2{=}CH)\text{-}C$	90
C-O	90
C-C	83
C-N	79
$(CH_2{=}CH\text{-}CH_2)\text{-}O$	71
$(CH_2{=}CH\text{-}CH_2)\text{-}N$	64

2-ol. Clearly, reactions leading to their formation occurred prior to the dehydration of 1,3-diphenoxypropan-2-ol to 1,3-diphenoxypropene. In fact the nature of the products of the thermal degradation of 1,3-diphenoxypropan-2-ol (tables 7 and 8) indicate that very little if any dehydration preceded degradation.

IV.2. THE DEGRADATION OF 1-(N-ETHYLANILINO)-3-PHENOXYPROPAN-2-OL

1-(N-Ethylanilino)-3-phenoxypropan-2-ol was degraded under two different conditions;

1 over acidic alumina (pH6)

2 under nitrogen and in air.

The products of these two degradations differed both in nature and in relative abundance. The nature and distributions of the products of these two degradations are indicated by their GLC traces (figs. 8 and 11 respectively) and in tables 9 and 10 respectively.

The degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol occurred more readily than the degradation of 1,3-diphenoxypropan-2-ol. 1,3-Diphenoxypropan-2-ol could be distilled unreacted at 360°C, whereas 1-(N-ethylanilino)-3-phenoxypropan-2-ol showed immediate signs of degradation on the application of strong heat. It appears that the replacement of the oxygen atom in the molecule by a nitrogen atom has caused the thermal stability of the molecule to decrease.

IV.2.1. The Degradation of 1-(N-Ethylanilino)-3-phenoxypropan-2-ol over Acidic Alumina

The nature of the products of this degradation (table 9) indicates that fission has occurred predominantly at the aliphatic carbon-oxygen bond and the aliphatic carbon-nitrogen bond giving rise to phenol and N-ethylaniline as the major products. The fragment remaining after phenol formation appears to have rearranged to form the major neutral product, N-ethylskatole (fig.9). Approximately equal amounts of N-ethyl-N-methylaniline and N,N-diethylaniline were also produced (fig.10). It appears that the alumina has catalysed carbon-oxygen and carbon-nitrogen bond fission but has not precluded carbon-carbon bond fission.

The reactions of nitrogen-containing compounds with alumina are not clearly understood. Infra-red studies have shown that ammonia does not chemisorb on alumina to form NH_4^+ [81,104-6] ions but there is evidence to suggest that ammonia can react with the alumina to form NH_2^- groups[81,105] and possibly NH_3^+ groups[104]. In the former case ammonia dissociates on the surface in a reaction analogous to the adsorption of water[105] (fig.27A). In the latter case a coordinate bond is formed between the nitrogen atom and the aluminium ion by the transfer of an electron from the nitrogen to the aluminium ion which leads to the formation of an NH_3^+ ion[104] (fig.27B).

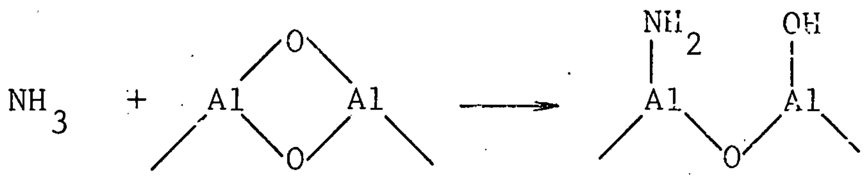


FIGURE 27A

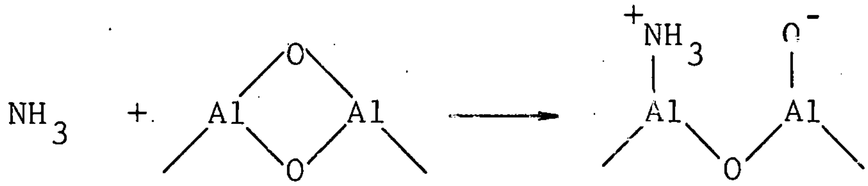
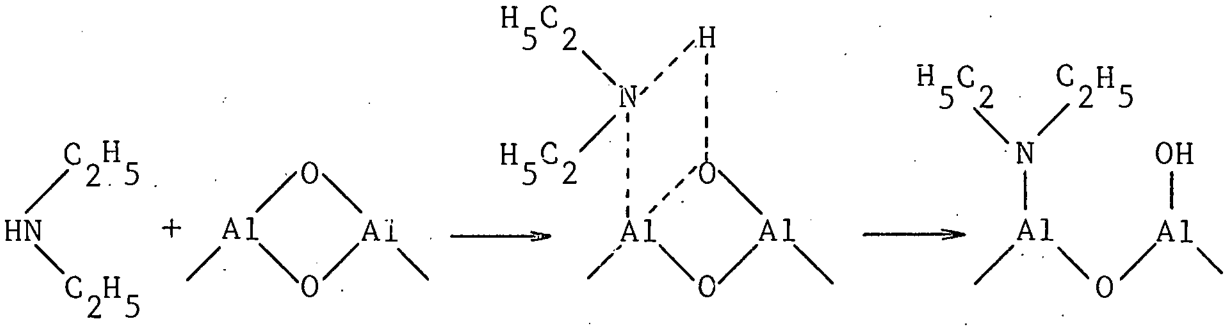


FIGURE 27B

PARERA and FIGOLI[59] suggested that nitrogen bases dissociate on adsorption on alumina. The reaction of diethylamine with alumina is shown below:



The decomposition of nitrogen-containing compounds over alumina gives rise to many complex reactions which include deamination reactions, carbon-carbon bond cleavage and cyclisation reactions[107]. It is difficult to postulate with any certainty a detailed mechanism for the breakdown of 1-(N-ethylanilino)-3-phenoxypropan-2-ol over alumina. A brief outline of the possible decomposition of 1-(N-ethylanilino)-3-phenoxypropan-2-ol in this degradation is given in fig.28.

If it is assumed that the nitrogen function behaves as the oxygen function does on alumina, as suggested by PERI[105] and PARERA and FIGOLI[59], then possible mechanisms can be proposed for the formation of compounds which result from fission of the aliphatic carbon-nitrogen and carbon-oxygen bonds in 1-(N-ethylanilino)-3-phenoxypropan-2-ol (figs. 29 and 30 respectively). It is not known whether carbon-carbon fission in this degradation has occurred heterolytically or homolytically. For this reason a mechanism for the formation of compounds requiring carbon-carbon fission has not been proposed.

IV.2.2. The Thermal Degradation of 1-(N-Ethylanilino)-3-phenoxypropan-2-ol

The nature and distribution of the products of the degradations of 1-(N-ethylanilino)-3-phenoxypropan-2-ol under nitrogen and in air were identical and differed from those of the degradation of this compound over acidic alumina. The catalytic activity of the alumina is, therefore, evident although the precise mechanism of the degradation is not known (section IV.2.1.).

The nature and diversity of the products of the thermal degradation of 1,3-diphenoxypropan-2-ol can be explained by assuming that homolytic scission of aliphatic carbon-oxygen and

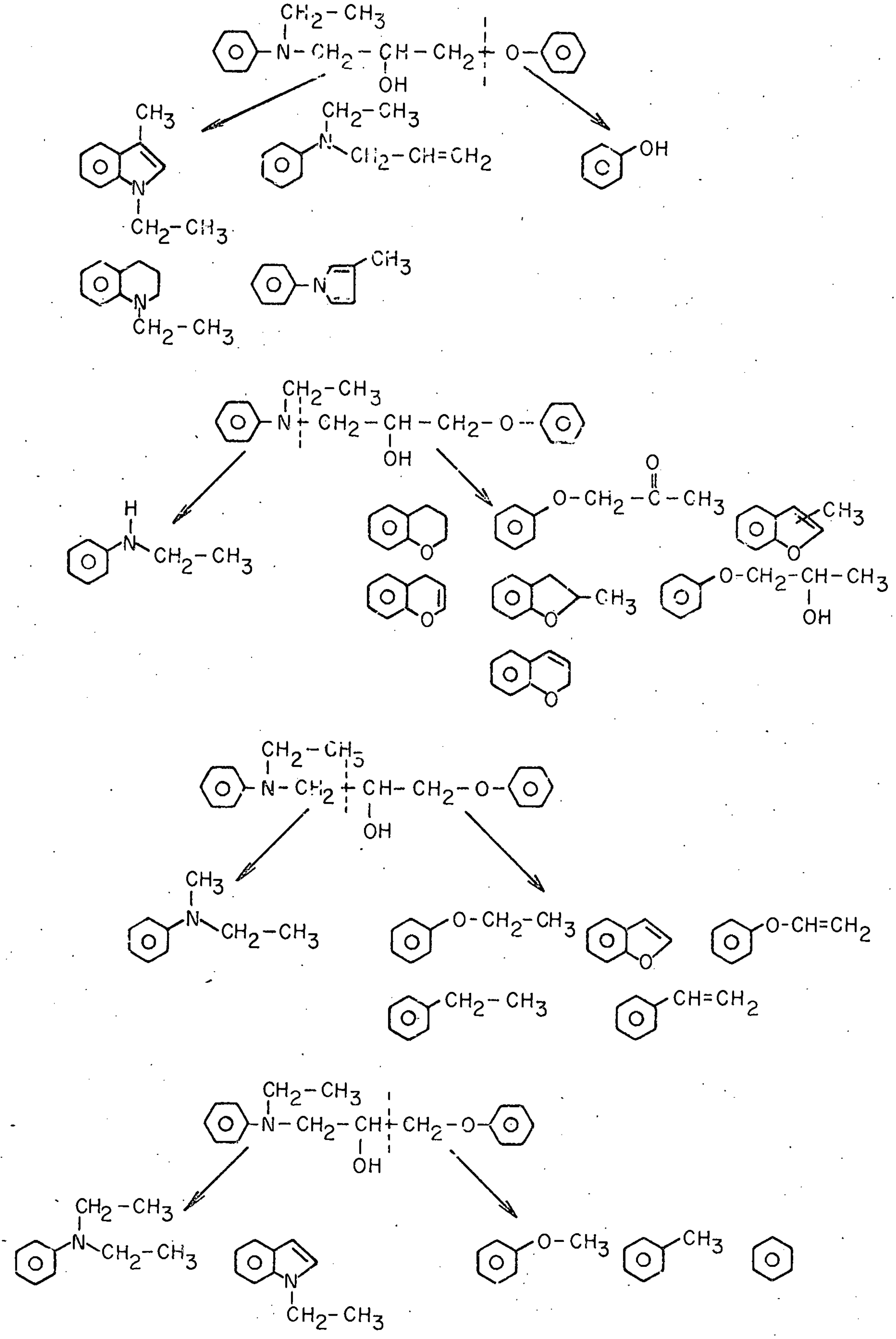
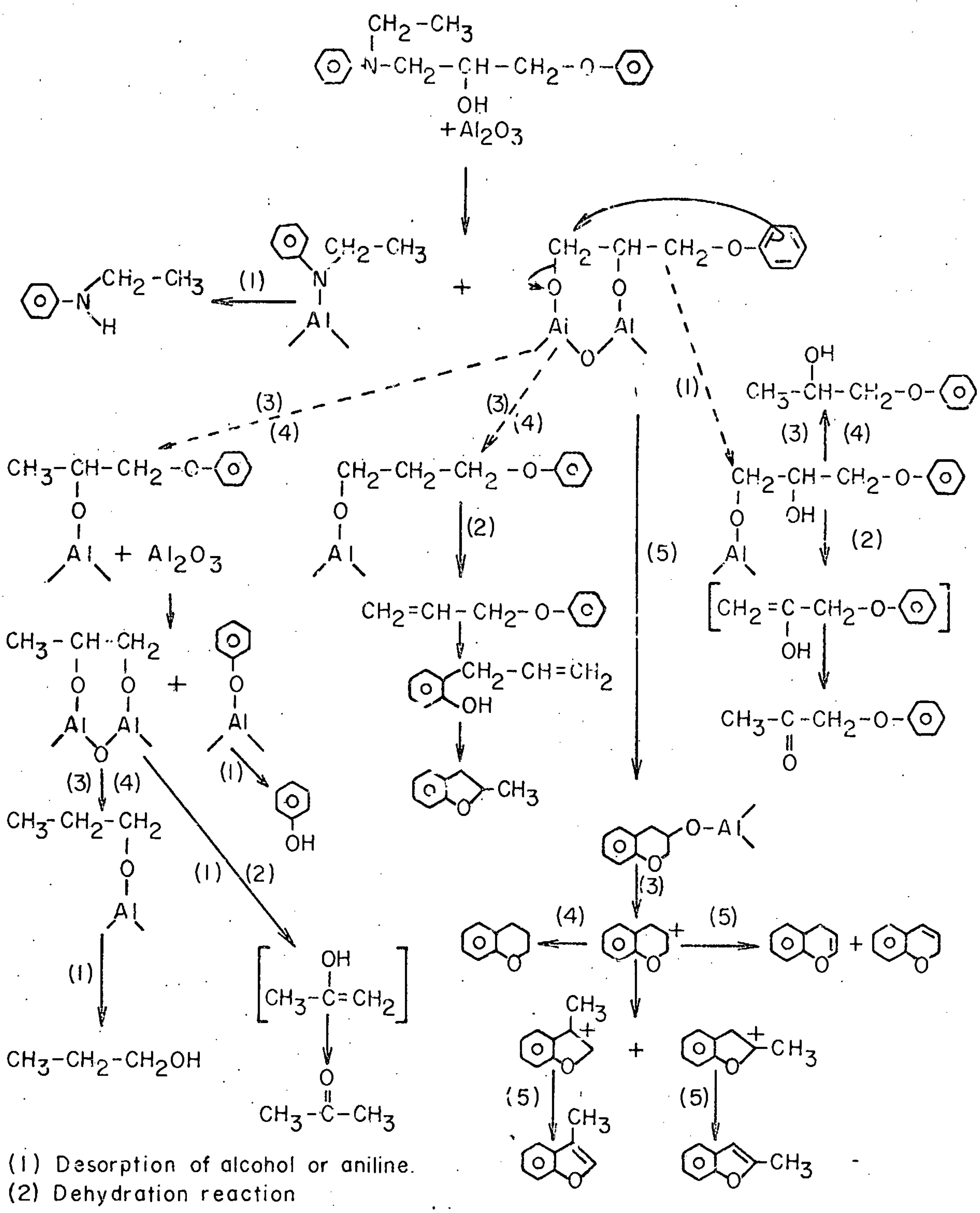


FIGURE 28.

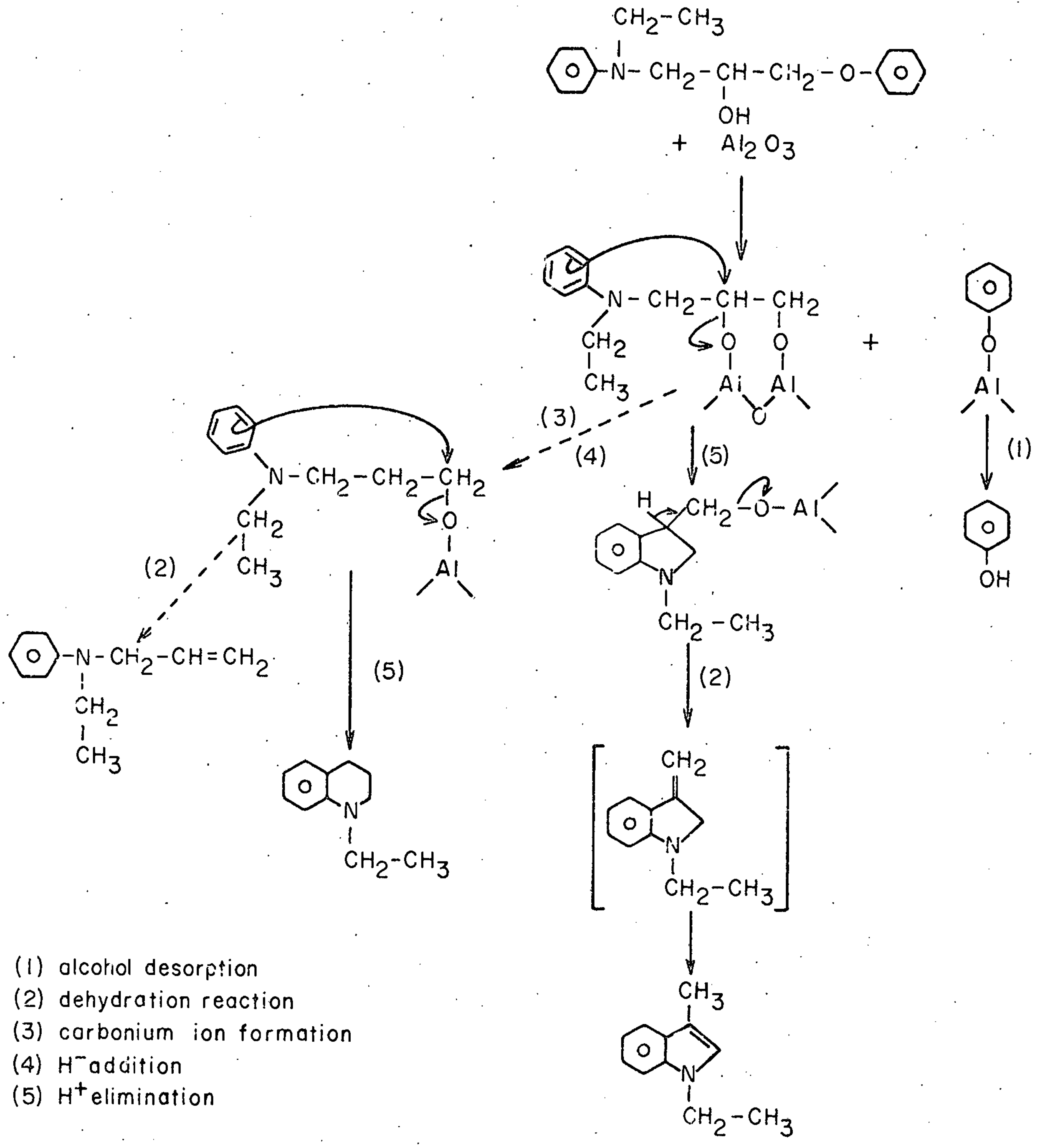
Products of the degradation over alumina of 1-(N-ethylanilino)-3-phenoxypropan-2-ol.



(1) Desorption of alcohol or aniline.
(2) Dehydration reaction
(3) Carbonium ion formation
(4) H^- addition
(5) H^+ elimination

FIGURE 29.

Possible routes to the products of the degradation over alumina of 1-(N-ethylanilino)-3-phenoxypropan-2-ol which result from cleavage of the carbon-nitrogen bond.



(1) alcohol desorption
(2) dehydration reaction
(3) carbonium ion formation
(4) H^- addition
(5) H^+ elimination

FIGURE 30.

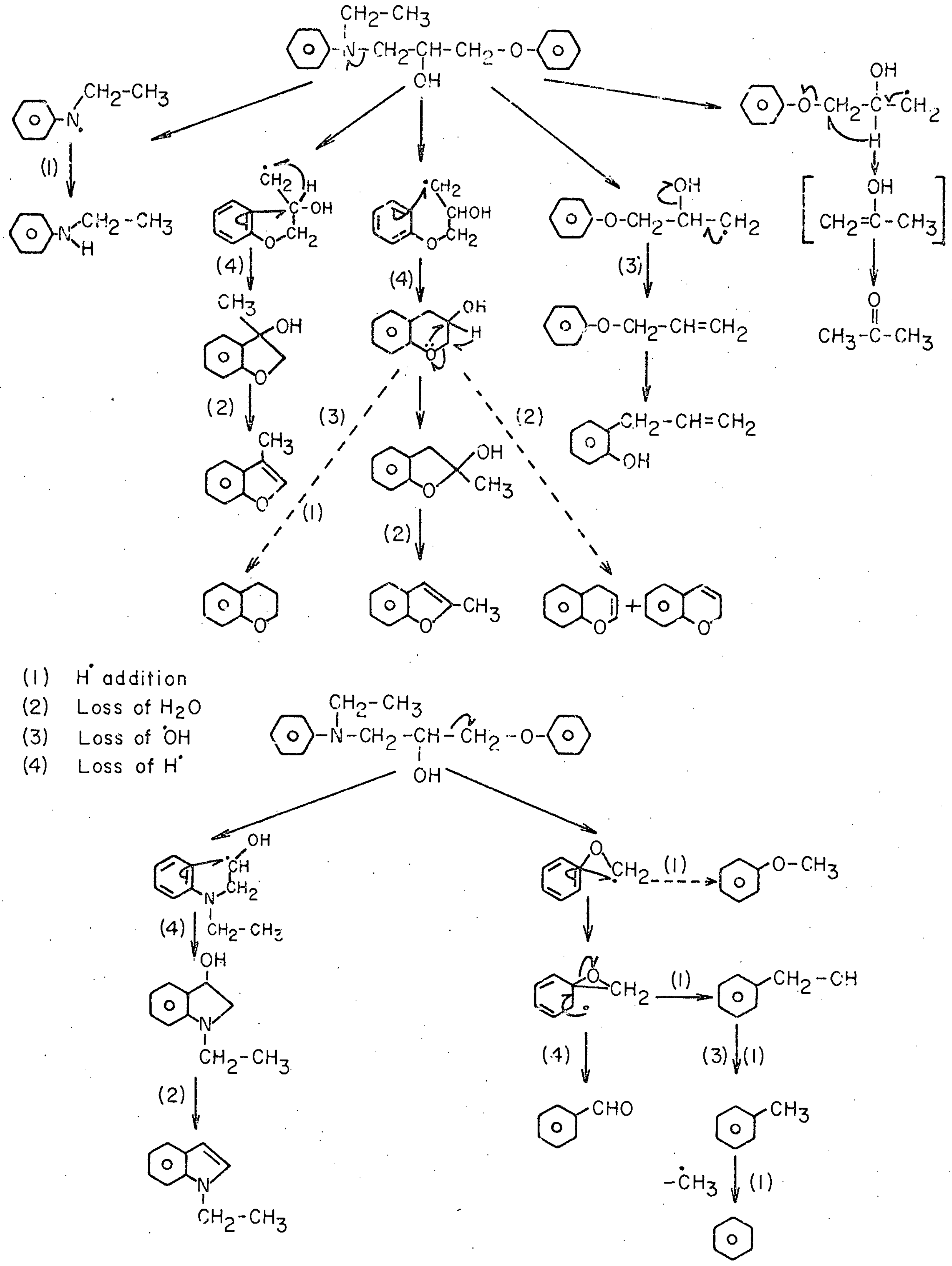
Possible routes to the products of the degradation over alumina of 1-(N-ethylanilino)-3-phenoxypropan-2-ol which result from cleavage of the carbon-oxygen bond.

aliphatic carbon-carbon bonds occurs and is followed by subsequent reactions of the free radicals produced (section IV.1.2.). As may be expected, the products of the thermal degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol are more diverse than those of the thermal degradation of 1,3-diphenoxypropan-2-ol. Their formation can also be explained by postulating scission of aliphatic carbon-oxygen, carbon-nitrogen and carbon-carbon bonds followed by reaction of the radicals produced. Possible routes to the products of this degradation are shown in figs. 31A and 31B. In these schemes which are speculative is postulated the formation of intermediate products which have not in fact been identified. The concentration of intermediates may in any event be too low for their presence to be detected. The schemes are, in addition, not comprehensive. For example N-ethyltetrahydroquinoline may arise from Claisen rearrangement followed by cyclisation of N-allyl-N-ethylaniline.

There are, however, three aspects of this degradation which merit further attention.

(a) Whereas 1,3-diphenoxypropan-2-ol degrades with difficulty at its reflux temperature, the thermal degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol proceeds readily.

(b) None of the products of the degradation of the latter compound appear to have retained the oxygen function of the central aliphatic carbon atom whereas the degradation of 1,3-



(1) $H^{\bullet}$ addition
(2) Loss of H_2O
(3) Loss of $^{\bullet}OH$
(4) Loss of $H^{\bullet}$

FIGURE 31A

Possible routes to the products of the thermal degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol.

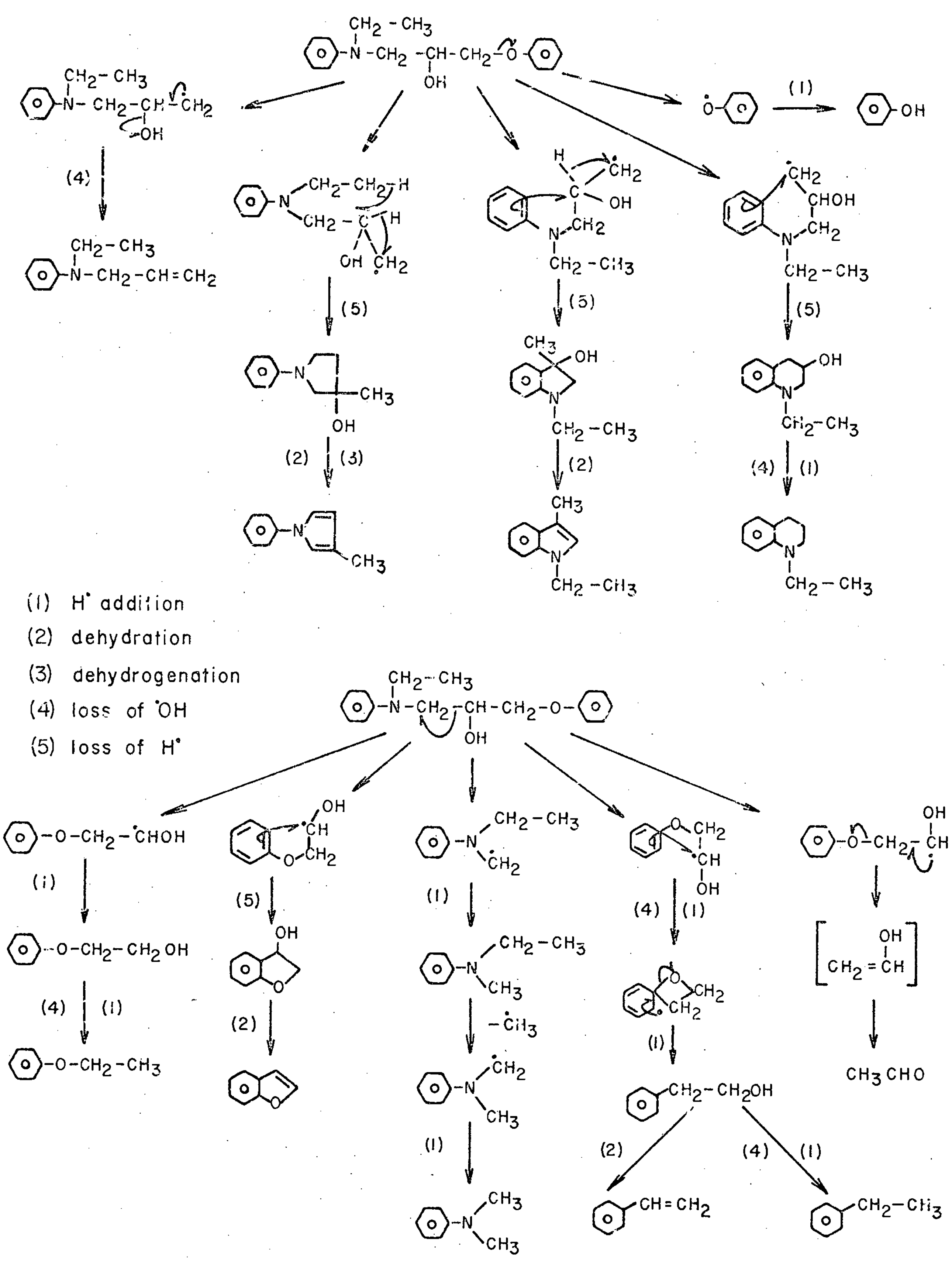


FIGURE 31B

Possible routes to the products of the thermal degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol.

diphenoxypropan-2-ol produces significant quantities of phenoxyacetone and 1-phenoxypropan-2-ol.

(c) The three major products of the present degradation are phenol, N-ethylaniline and N-ethyl-N-methylaniline. If the last product is formed by homolytic scission of the carbon-carbon bond adjacent to nitrogen then this process competes favourably with those giving rise to phenol and N-ethylaniline.

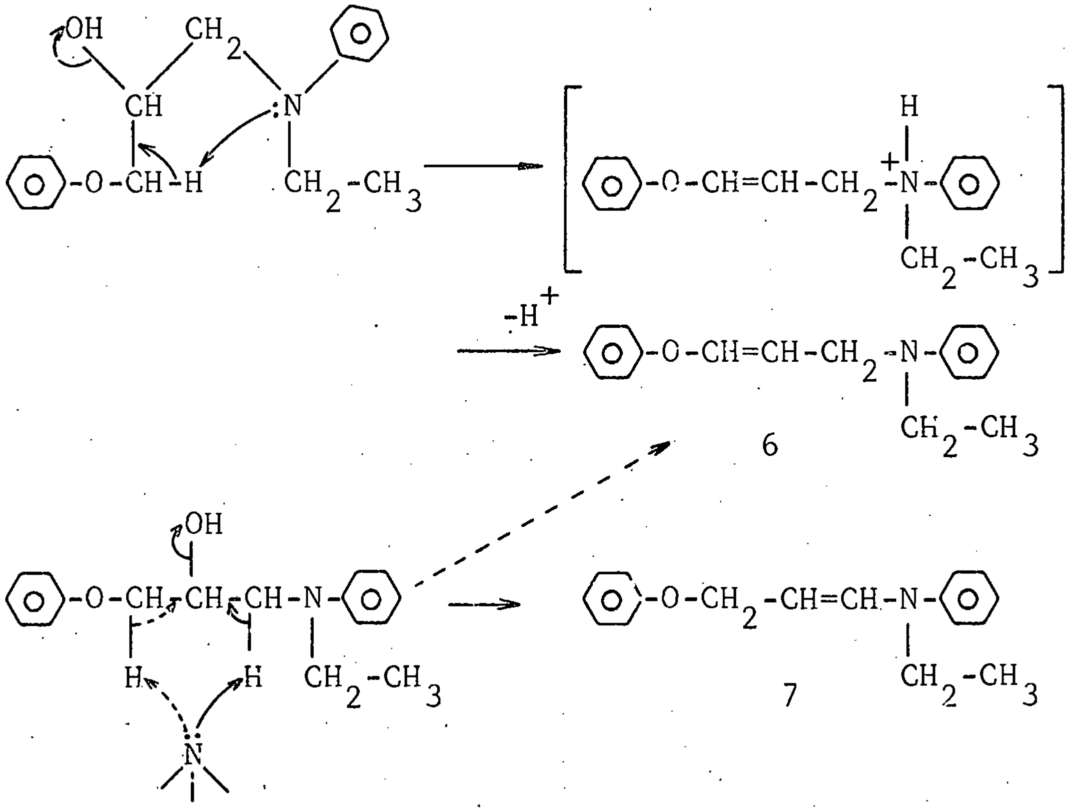
The role that the nitrogen atom plays in the degradation is, therefore, not a trivial one. The effect of the presence of the nitrogen may be twofold.

(a) The presence of the nitrogen may modify the stability of the adjacent aliphatic carbon-carbon bond relative to that of the aliphatic carbon-carbon bond adjacent to oxygen.

(b) The nitrogen may act as a base by virtue of its lone pair of electrons.

Standard bond dissociation energies (table 13) show that whereas aromatic carbon-oxygen and carbon-nitrogen bonds are very stable, aliphatic carbon-nitrogen bonds have approximately the same energy as aliphatic carbon-carbon bonds. On this basis there is, a priori no reason for the ready degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol and, further, no reason for the apparent weakness of the aliphatic carbon-carbon bond adjacent to nitrogen. The values quoted in table 13, however, may be modified by the presence of adjacent groups in the molecule. The quantitative effect of the adjacent oxygen and nitrogen atoms on the bond dissociation energies of the aliphatic carbon-carbon bonds is not known and it is possible that the carbon-carbon bond adjacent to nitrogen in 1-(N-ethylanilino)-3-phenoxypropan-2-ol is the weakest bond in this compound, its scission during degradation giving rise to the large quantity of N-ethyl-N-methylaniline found in the degradation.

Nitrogen may play a catalytic role in the degradation. In particular, by virtue of its lone pair of electrons, the nitrogen may induce, at the temperatures involved, base-catalysed dehydration reactions. Dehydration of the initial compound may lead to the formation of structures 6 and 7.

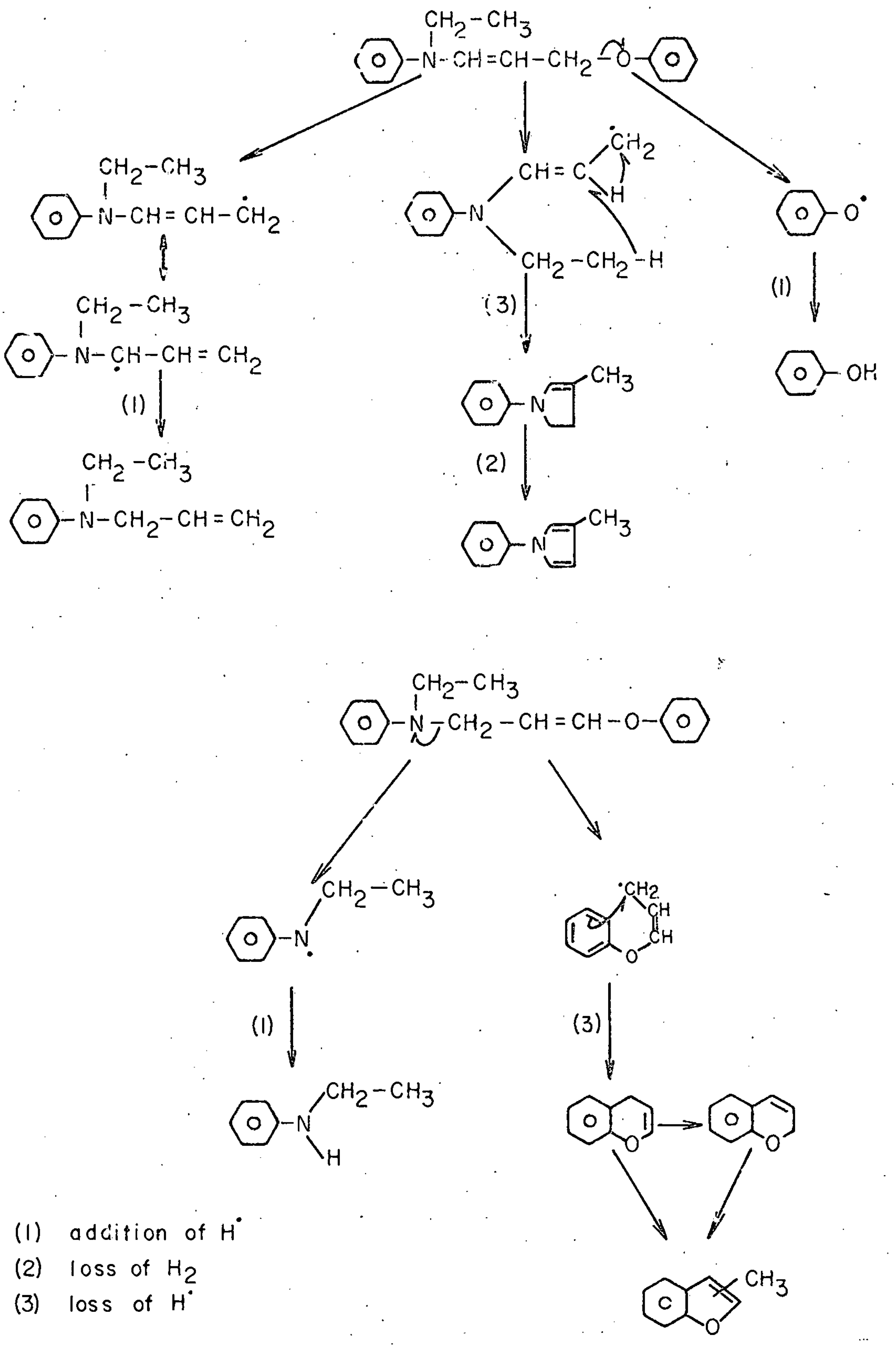


6

7

In structures 6 and 7 the allyl-nitrogen and allyl-oxygen bonds are relatively weak. Homolytic scission of these bonds by analogy with the behaviour of 1,3-diphenoxypropene (section IV.1.2.1.) may occur readily to produce phenol, N-ethylaniline and compounds containing 3 aliphatic carbon atoms as shown in fig.32. The ready degradation of 1-(N-ethylanilino)-3-phenoxy-propan-2-ol may be due, at least in part, to the ease of degradation of structures 6 and 7 which may be formed more easily than 1,3-diphenoxypropene is formed during the degradation of 1,3-diphenoxypropan-2-ol because of the basic nature of the nitrogen present. In addition, dehydration may explain the absence of products containing an oxygen function on the central aliphatic carbon atom.

It is clear from an examination of the products of this degradation (table 10) that dehydration does not precede all further reaction. In particular, the formation of the major product N-ethyl-N-methylaniline and minor products containing one or two aliphatic carbon atoms cannot be rationalised as occurring from structures 6 and 7. The formation of N-ethyl-N-methylaniline as a major product with the probably concurrent formation of benzofuran is a puzzling feature of the degradation. Unless a specific reaction is occurring to form these products by a process other than initial homolysis of the carbon-carbon bond adjacent to nitrogen then the dissociation energy of this



(1) addition of $H^{\cdot}$

(2) loss of H_2

(3) loss of $H^{\cdot}$

FIGURE 32.

Possible routes to the products which may be formed by the thermal degradation of the dehydrated 1-(N-ethylanilino)-3 phenoxypropan - 2-ol structures.

bond must be appreciably lower than those of the other bonds in the molecule and, in fact, must be low enough for its homolysis to compete successfully with fission of the allyl-nitrogen and allyl-oxygen bonds in the dehydrated structures.

In conclusion it is evident that the degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol is an extremely complex reaction which has some features which are not well understood. That dehydration accompanies homolytic fission of bonds appears likely but the nature of the reaction which leads to the formation of benzofuran and N-ethyl-N-methylaniline, two major products, is not clear.

V. CONCLUSION

A comparison of the degradations of 1,3-diphenoxypropan-2-ol and 1-(N-ethylanilino)-3-phenoxypropan-2-ol clearly demonstrates that the presence of the nitrogen atom in the model compound modifies its degradation profoundly. 1-(N-Ethylanilino)-3-phenoxypropan-2-ol degraded more readily than 1,3-diphenoxypropan-2-ol. The degradation of the latter compound apparently proceeded without initial dehydration whereas dehydration of the former compound appeared to accompany its degradation. It has been suggested that dehydration is catalysed by the basic properties of the nitrogen atom and that the ready degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol is due partly to the reduced thermal stability of the dehydrated structure. Furthermore it appears that the aliphatic carbon-carbon bond adjacent to nitrogen in 1-(N-ethylanilino)-3-phenoxypropan-2-ol is particularly unstable and that fission of this bond competes with the degradation of the dehydrated structures.

V.1. AN EXTENSION OF THE RESULTS OF THE PRESENT STUDY TO THE THERMAL DEGRADATION OF AMINE-CURED EPOXIDE RESINS

Conclusions reached about the degradation of the model compounds may be extended to the thermal degradation of amine-cured epoxide resins based on Bisphenol A (fig.2).

The instability of such resins appears to be due to the presence of the nitrogen atom in the "cure-linkage". The section of the resin represented by the 1,3-diphenoxypropan-2-ol model will be more stable than the "cure-linkage" but the presence of the nitrogen atom in the "cure-linkage" may affect the stability of other parts of the network by promoting dehydration reactions. If the 1,3-diphenoxypropan-2-ol part-structure is dehydrated to form a 1,3-diphenoxypropene part-structure, degradation will proceed with ease (1,3-diphenoxypropene degrades more readily than 1,3-diphenoxypropan-2-ol).

The results of the present study suggest that dehydration and fission of the aliphatic carbon-carbon bond adjacent to nitrogen may be competing reactions in the degradation of amine-cured epoxide resins. This is supported by evidence of dehydration reactions[1,13-16,18] and the presence of resonance stabilised free radicals[13,15] in the degraded epoxide resins. Furthermore the degradation[17] at low temperatures (approximately 300°C) of an amine-cured epoxide resin in which the 1,3-diphenoxypropan-2-ol part-structure was absent (n=o in fig.1) produced phenols, _N,N_-dimethylanilines, _N_-methylanilines and benzofuryl structures as major products. This result implies that at low temperatures fission of the aliphatic carbon-carbon bond adjacent to nitrogen competes successfully with dehydration of the resin network. The results of SUGITA[108] indicate that at higher temperatures carbon-

carbon fission adjacent to nitrogen to form N-methyl- and N,N-dimethylanilines and benzofuryl structures is largely overshadowed by dehydration of the resin network to form N-unsubstituted anilines and phenols as major products.

V.2. THE EFFECT OF FILLERS ON THE THERMAL STABILITY OF AMINE-CURED EPOXIDE RESINS

The degradation of the model compounds 1,3-diphenoxypropan-2-ol and 1-(N-ethylanilino)-3-phenoxypropan-2-ol was profoundly affected by the presence of alumina. The alumina appeared not only to promote the degradation of the model compounds but also to modify the degradation mechanisms (sections IV.1. and IV.2.).

The rate and mechanism of decomposition also depended on the nature of the alumina used. Degradation over neutral and acidic alumina proceeded more readily than degradation over basic alumina. The mechanisms involved in these degradations were different (section IV.1.). Neutral and acidic alumina appeared to promote ionic reactions whereas basic alumina allowed thermal homolysis to take place.

It is evident that the presence of fillers, such as alumina and silica flour, which have catalytic properties may alter significantly the thermal stability of amine-cured epoxide resins.

V.3. THE USE OF MODEL COMPOUNDS AS A SYNTHETIC ROUTE TO BENZOFURAN

Benzofuran was not produced in sufficient quantity in the degradations of the model compounds for its isolation to be effected. The largest yield of benzofuran was obtained in the thermal degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol (section IV.2.2.). The nature and distribution of the products of this degradation indicated that many competing reactions were taking place and that the process leading to benzofuran formation was not predominant. Polymerisation of benzofuran may also have reduced its yield.

An appreciable quantity of 2-chromene was produced in the degradation of 1,3-diphenoxypropene but separation of the product from the degradation mixture containing 3-chromene and 2- and 3-methylbenzofuran might prove difficult. Small amounts of 2-chromene may be separated by preparative gas chromatography. The method by which 1,3-diphenoxypropene was synthesised in this work (section II.2.19.) would, however, have to be improved before this technique could be used as an efficient synthetic route to 2-chromene.

VI. REFERENCES

1. D.P. Bishop and D.A. Smith, Ind. Eng. Chem., Int. Edn., 58, 32 (1967).

2. D.O. Bowen, Modern Plastics, p. 127 (1967).

3. R.T. Dowd in F.P. Bruins (Ed.), "Epoxy Resin Technology", Interscience, New York, p. 1 (1968).

4. M.B. Nieman, B.M. Kovarskaya, M. Yazvikova, A. Sidnev and M.S. Akutin, Vysokomol. Soed., 3, 602 (1961).

5. W.R.R. Park and J. Blount, Amer. Chem. Soc., Div. Org. Coatings, Plastics and Printing Inks, 16, 56 (1956).

6. M.F. Dante and R.T. Conley, Amer. Chem. Soc., Div. Org. Coatings and Plastics, Chem. Chicago Meeting, 24, 135 (1964).

7. L.H. Lee, J. Appl. Polymer Sci., 9, 1981 (1965).

8. L.H. Lee, J. Polymer Sci. (A), 3, 859 (1965).

9. M.B. Nieman, B.M. Kovarskaya, L.I. Golubenkova, A.S. Strizhkova, I.I. Levantovskaya and M.S. Akutin, J. Polymer Sci., 56, 383 (1962).

10. V.D. Moiseev, B.M. Kovarskaya, M.B. Nieman, I.E. Zenova and V.V. Guryanova, Soviet Plastics, 6, 12 (1962).

11. M.B. Nieman, L.I. Golubenkova, B.M. Kovarskaya, A.S. Strizhkova, I.I. Levantovskaya, M.S. Akutin and V.D. Moiseev, Vysokomol. Soed., 1, 1531 (1959).

12. H. Dannenburg, J.W. Forbes and A.C. Jones, Anal. Chem., 32, 365 (1960).

13. M.A. Keenan and D.A. Smith, J. Appl. Polymer Sci., 11, 1009 (1967).

14. J.M. Stuart and D.A. Smith, J. Appl. Polymer Sci., 9, 3195 (1965).

15. D.A. Smith, Amer. Chem. Soc., Div. Org. Coatings and Plastics, Chem. Preprints, 27, 321 (1967).

16. J.C. Paterson-Jones and D.A. Smith, J. Appl. Polymer Sci., 12, 1601 (1968).

17. E.C. Leisegang, A.M. Stephen and J.C. Paterson-Jones, J. Appl. Polymer Sci., 14, 1961 (1970).

18. D.P. Bishop and D.A. Smith, J. Appl. Polymer Sci., 14, 205, (1970).

19. N.H. Reinking, A.E. Barnabeo and W.F. Hale, J. Appl. Polymer Sci., 7, 2135, 2145, 2153 (1963).

20. H. van Hoorn, J. Appl. Polymer Sci., 12, 871 (1968).

21. J.C. Paterson-Jones and D.A. Smith, CoA Note Mat. No. 10 (1967), The College of Aeronautics, Cranfield, England.

22. J.C. Paterson-Jones, Ph.D. Thesis, University of Cape Town (1969).

23. A.M. Kuliev, R.K. Alekperov and Sh. T. Akhmedov, Uch. Zap. Azerb. Gos. Univ., Ser. khim. Nauk 1, 31 (1965); Chem. Abs., 67, 32399m (1967).

24. K.A. Andrianov, G.A. Kurakov and C.M. Khananashvili, Zhur. obshchei Khim., 33, 2634 (1963); Chem. Abs., 60, 541c (1964).

25. Y.M. Beasley, V. Petrow and O. Stephenson, J. Pharm. Pharmacol, 10, 47 (1958).

26. J. Munch-Petersen, Acta Chem. Scand., 5, 519 (1951).

27. D.L. Dalrymple, T.L. Kruger and W.N. White in S. Patai (Ed.), "The Chemistry of the Ether Linkage", Interscience, New York, p. 635 (1967).

28. A.O. Fitton and R.K. Smalley, "Practical Heterocyclic Chemistry", Academic Press, New York, p. 16 (1968).

29. J.H. Looker and M.J. Holm, J. Org. Chem., 24, 567 (1959).

30. L. Claisen, Annalen, 418, 69 (1919).

31. C.D. Hurd and P. Perletz, J. Amer. Chem. Soc., 68, 38 (1946).

32. R.T. Foster and A. Robertson, J. Chem. Soc., 921 (1939).

33. A.I. Vogel, "Practical Organic Chemistry", 3rd Edn., Longmans, London, p. 676 (1967).

34. A.I. Vogel, "Practical Organic Chemistry", 3rd Edn., Longmans, London, p. 669 (1967).

35. W.R. Boehme, Org. Synth., 33, 43 (1953).

36. G.P. McSweeney, L.F. Wiggins and D.J.C. Wood, J. Chem. Soc., 37 (1952).

37. C.D. Hurd and W.A. Hoffman, J. Org. Chem., 5, 212 (1940).

38. R.C. Fuson, J.W. Kneisley and E.W. Kaiser, Org. Synth., Coll. Vol. 3, 209 (1955).

39. C.D. Hodgman (Ed.), "Handbook of Chemistry and Physics", 44th Edn., Chemical Rubber Publishing Co., Cleveland (1963).

40. A. Wohl and E. Berthold, Chem. Ber., 3, 2178 (1910).

41. R. Schreiber, Chem. Ber., 24, 189 (1891).

42. S.G. Powell and R. Adams, J. Amer. Chem. Soc., 42, 646 (1920).

43. E.H. Rodd, "Chemistry of Carbon Compounds", Elsevier, Amsterdam, 4A, 81 (1957).

44. A. Michaelis, Chem. Ber., 30, 2809 (1897).

45. H. Budzikiewicz, C. Djerassi and D.H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco (1967).

46. L.M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, London, p. 224 (1969).

47. D.W. Mathieson, "Nuclear Magnetic Resonance for Organic Chemists", Academic Press, London, p. 129 (1967).

48. E.S. Levchenko and Ya. G. Bal'on, Zhur. organ. Khim., 1, 305 (1965).

49. M.H. Palmer, "The Structure and Reactions of Heterocyclic Compounds", Edward Arnold, London (1967).

50. A.P. Terent'ev and M.A. Volodina, Doklady Akad. Nauk S.S.S.R., 88, 845 (1953); Chem. Abs., 48, 3338g (1954).

51. B. Notari, Chimica e Industria, 51, 1200 (1969).

52. E. Lederer and M. Lederer, "Chromatography", Elsevier, Amsterdam, p. 19 (1957).

53. G. Feacham and H.T.S. Swallow, J. Chem. Soc., 267 (1948).

54. H. Pines and J. Manassen, Adv. Catalysis, 16, 49 (1966).

55. R.W. Maatman and L.J. Vande-Griend, J. Catalysis, 20, 238 (1971).

56. B. Blouri, M. Laroche, A. Pazdzerski, A. Ahmadi and P. Rumpf, Bull. Soc. chim. France, 2861 (1967).

57. P. Mauret and E. Bordier, C.R. Acad. Sci. Paris, Ser. C, 266, 1078 (1968).

58. R.M. Lane, B.C. Lane and C.S.G. Phillips, J. Catalysis, 18, 281 (1970).

59. J.M. Parera and N.S. Figoli, J. Catalysis, 14, 303 (1969).

60. H. Bremer, K.H. Steinberg, J. Glietsch, H. Lusky, U. Werner and K.D. Wendlandt, Z. Chem. 10, 161 (1970).

61. A.I. Trokhimets, L.I. Vladyko and S.V. Markevich, Doklady Akad. Nauk Beloruss. S.S.R., 19, 428 (1970); Chem. Abs., 73, 91727p (1970).

62. L.I. Vladyko, A.I. Trokhimets and S. Markevich, Vestnik Akad. Navuk Beloruss. S.S.R., Ser. khim. Navuk, 44 (1970).

63. D.E.R. Bennett and R.A. Ross, J. Chem. Soc. (A), 1524 (1968).

64. K. Hauffe, Adv. Catalysis, 7, 213 (1955).

65. H. Knozinger and R. Kohne, J. Catalysis, 5, 264 (1966).

66. R.O. Kagel, J. Phys. Chem., 71, 844 (1967).

67. Y. Soma, T. Onishi and K. Tamaru, Trans. Faraday Soc., 65, 2215 (1969).

68. H. Knozinger, Angew. Chem., Int. Edn., 7, 791 (1968).

69. R.E. Mardaleishvili and S.N. Khadzhiev, Vestnik Mosk. Univ., Ser. 2, 22, 92 (1967); Chem. Abs. 68, 53634v (1968).

70. M.E. Winfield in P.H. Emmett (Ed.), "Catalysis", Reinhold, New York, 7, 93 (1960).

71. J.E. Dabrowski, J.B. Butt and H. Bliss, J. Catalysis, 18, 297 (1970).

72. H. Pines and W.O. Haag, J. Amer. Chem. Soc., 83, 2847 (1961).

73. O.V. Krylov, Zhur. fiz. Khim., 39, 2656 (1965).

74. J.R. Jain and C.N. Pillai, J. Catalysis, 9, 322 (1967).

75. H. Arai, J.I. Jake, Y. Saito and Y. Yoneda, J. Catalysis, 9, 146 (1967).

76. E. Heiba and P.S. Landis, J. Catalysis, 3, 471 (1964).

77. H. Arai, Y. Saito and Y. Yoneda, J. Catalysis, 10, 128 (1968).

78. J.B. Peri, Actes Congr. Intern. Catalyse, 2^e, Paris, 1, 1333 (1960).

79. J.B. Peri, J. Phys. Chem., 69, 220 (1965).

80. M.W. Tamele, Discuss. Faraday Soc., 8, 270 (1950).

81. J.B. Peri and R.B. Hannan, J. Phys. Chem., 64, 1526 (1960).

82. H. Knozinger and E. Ress, Z. phys. Chem. (Frankfurt), 59, 49 (1968).

83. H. Knozinger, A. Scheglila and A.M. Watson, J. Phys. Chem., 72, 2770 (1968).

84. H. Knozinger, H. Buhl and E. Ress, J. Catalysis, 12, 121 (1969).

85. E. Guerrier, M. Polisset and R. Guihaume, Bull. Soc. chim. France, 2882 (1970).

86. S.M. Brown and H. Pines, J. Org. Chem., 35, 1999 (1970).

87. E.J. Blanc and H. Pines, J. Org. Chem., 33, 2035 (1968).

88. J. Herling and H. Pines, Chem. and Ind., 24, 984 (1963).

89. W.H. Wade, S. Teranishi and J.L. Durham, J. Phys. Chem., 69, 590 (1965).

90. H.J. Solomon, H. Bliss and J.B. Butt, Ind. Eng. Chem., 6, 325 (1967).

91. H. Knozinger and A. Scheglila, J. Catalysis, 17, 252 (1970).

92. N.S. Figoli, S.A. Hillar and J.M. Parera, J. Catalysis, 20, 230 (1971).

93. Y. Amenomiya and R.J. Cvetanovic, J. Catalysis, 18, 329 (1970).

94. E.A. Karakhanov, N.N. Khvorostukhina and E.A. Viktorova, Vestnik Mosk. Univ. Khim., 11, 635 (1970).

95. J. Hill, Chem. Comm., 260 (1966).

96. M.K.M. Dirania and J. Hill, J. Chem. Soc. (C), 1311 (1968).

97. B.D. Cavell and J. MacMillan, J. Chem. Soc. (C), 310 (1967).

98. Y. Kawase, Chem. and Ind., 21, 687 (1970).

99. B.B. Corson, W.J. Heintzelman, H.E. Tiefenthal and J.E. Nickels, J. Org. Chem., 17, 971 (1952).

100. L. Kh. Freidlin, A.A. Balandin and N.M. Nazarova, Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk, 1, 102 (1949); Chem. Abs., 43, 5758i (1949).

101. L. Kh. Freidlin, A.A. Balandin and N.M. Nazarova, Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk, 1, 198 (1949); Chem. Abs., 44, 1441f (1950).

102. A.F. Thomas, Helv. Chim. Acta, 53, 605 (1970).

103. N.N. Semenov, "Some Problems of Chemical Kinetics and Reactivity", translated by J.E.S. Bradley, Pergamon Press, New York, 1, 16 (1958).

104. O.V. Bulgakov, A.V. Uvarov and T.V. Antipina, Zhur. fiz. Khim., 44, 17 (1970); Russ. J. Phys. Chem., 44, 9 (1970).

105. J.B. Peri, J. Phys. Chem., 69, 231 (1965).

106. R.P. Eischens and W.A. Pliskin, Adv. Catalysis, 10, 1 (1958).

107. J.A. Vernon, Diss. Abs., 26, 6383 (1966); Ph.D. Thesis, University of Maryland (1965).

108. T. Sugita, J. Polymer Sci. (C), 23, 765 (1968).