The Thermal Degradation of Model Compounds of Amine-Cured Epoxide Resins.   II.   The Thermal Degradation of 1,3-Diphenoxypropan-2-ol and 1,3-Diphenoxypropene

J. C. PATERSON-JONES and V. A. PERCY, *Council for Scientific and Industrial Research, Somerset West, Cape, South Africa,* and R. G. F. GILES and A. M. STEPHEN, *Department of Chemistry, University of Cape Town, Rondebosch, Cape, South Africa*

Synopsis

The thermal degradations in an inert atmosphere, in air, and over alumina of 1,3-diphenoxypropan-2-ol and 1,3-diphenoxypropene were studied with the aim of investigating the thermal stability of the glyceryl portion of bisphenol A-based epoxide resins. Degradation products were characterized.   The thermal stability of the glyceryl group relative to that of the cure linkage in aromatic amine-cured epoxide resins is discussed.

INTRODUCTION

The thermal stability of aromatic amine-cured epoxide resins depends on the stability of the aliphatic portions of the network.[1]   The cure linkage
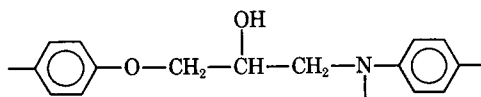
differs from the glyceryl portion of bisphenol A-based epoxide resins
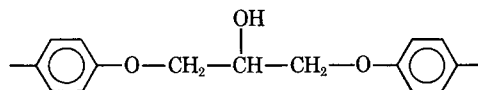
in that the nitrogen function replaces an oxygen atom.   In the present study the thermal stability of a model for the glyceryl group, 1,3-diphenoxypropan-2-ol, is compared with that of the model for the cure linkage, 1-(N-ethylanilino)-3-phenoxypropan-2-ol, discussed previously.[2] Phenolic compounds are major products of the degradation of uncured epoxide resins.[3,4]   Breakdown of the glyceryl group may contribute to the production of phenolic compounds in the degradation of aromatic amine-cured bisphenol A-based resins.

The nature of the products of the degradation of a model for the dehydrated glyceryl group, 1,3-diphenoxypropene, is also investigated with the aim of determining whether 1,3-diphenoxypropan-2-ol undergoes dehydration prior to degradation.

EXPERIMENTAL

Degradation products were identified by the techniques previously outlined.[2] GLC retention times of standard compounds not given previously[2] are listed in Table I.

TABLE I
GLC Retention Times of Standard Compounds

Compound	GLC Retention time,[a] min
Propionaldehyde	1.7
Acrolein	1.9
Phenyl allyl ether	13.3
Phenylacetaldehyde	19.8

[a] Column, 4.57 m $\times$ 0.953 cm diameter glass preparative column packed with 25% polyethylene glycol PEG 20M on 60–72 mesh silanized Celite; operating temperature, 180–181°C; carrier gas (N_2) flow rate, 206.9 ml/min; column pressure, 30–31 psi.

Syntheses

1,3-Diphenoxypropan-2-ol. Epichlorohydrin (39 ml; 0.5 mole) was added dropwise to a stirred solution of phenol (94 g; 1 mole) in 40% aqueous sodium hydroxide (55 ml; 0.55 mole). The mixture was heated under reflux for 2–3 hr. On cooling, a precipitate formed which was filtered, washed, and recrystallized from a mixture of acetone and water; white prisms (98.1 g; 80.4%), mp 81–2°C (lit.[5] mp 81–2°C), were obtained.

ANAL. Calcd for $C_{15}H_{16}O_3$: C, 73.8%; H, 6.6%. Found: C, 73.8%; H, 6.6%.

1,3-Diphenoxypropene. (i) *1,3-Diphenoxyprop-2-yl p-Toluenesulfonate:* 1,3-Diphenoxypropan-2-ol (104 g; 0.43 mole) and p-toluenesulfonyl chloride (134 g; 0,71 mole) were dissolved in pyridine and allowed to stand (17 hr) at room temperature. The mixture was poured into 10% sulfuric acid (1.5 liter), and the precipitate which formed was filtered, washed, dried, and recrystallized from ethanol (800 ml)–acetone (300 ml) (162.7 g; 95.9%), mp 117–8°C.

(ii) *1,3-Diphenoxypropene:* 1,3-Diphenoxyprop-2-yl p-toluenesulfonate (70 g; 0.18 mole) and powdered potassium hydroxide (16.5 g; 0.30 mole) were mixed and dry distilled under vacuum. The distillate (23 g) was collected and dissolved in ether. The ethereal solution was washed successively with 10% aqueous sodium hydroxide and water, dried over anhydrous sodium sulfate, and distilled, bp 66–200°C/approx. 7 mm Hg. An IR spectrum of the distillate showed the presence of hydroxyl-containing compounds, which were removed by column chromatography

(column, 40 × 2.3 cm I.D. silica gel; eluent, chloroform). Distillation of the chromatographed solution yielded 1,3-diphenoxypropene as a pale-yellow liquid (5.96 g; 15%), bp 172–6°C/6.3 mm Hg (approximately 1:1 mixture of cis and trans isomers from PMR spectrum).

ANAL. Calcd for $C_{15}H_{14}O_2$: C, 79.6%; H, 6.2%. Found: C, 79.4%; H, 6.4%.

Degradation Procedure

Degradations were carried out in a conventional glass distillation apparatus. 1,3-Diphenoxypropan-2-ol was degraded under four conditions: (1) catalyzed degradation over aluminum oxide "Camag" M.F.C. Brockmann activity 1 (neutral), 100–240 mesh; (2) catalyzed degradation over aluminum oxide "Camag" M.F.C. Brockmann activity 1 (pH 6), 100–240 mesh; (3) catalyzed degradation over aluminum oxide calcined B.D.H. (pH 9); (4) uncatalyzed degradation (a) under nitrogen and (b) in air.

1,3-Diphenoxypropene was degraded under conditions 2 and 4b.

Degradations over alumina employed 50% w/w of the catalyst which had previously been dried for 2 hr at 150°C under vacuum. Before degradation under nitrogen, the apparatus was purged with nitrogen for 15 min, and a small flow of nitrogen was maintained during the degradation. In general, the starting material was heated at such a rate that the temperature of the distilling products did not exceed 250°C. After a certain period, no further products could be distilled at temperatures below 250°C, and heating was discontinued, leaving a very viscous or solid residue. Degradations 4a and 4b of 1,3-diphenoxypropan-2-ol were exceptions. Because of its high stability under these conditions, 1,3-diphenoxypropan-2-ol was heated under reflux (360°C/760 mm Hg) for 2 hr before distillation which yielded only a small quantity of degradation products, leaving a residue of largely unchanged starting material. As a measure of the relative ease of degradation, the times required for degradation were recorded (Table II).

Certain degradation products were collected by preparative GLC and identified by a comparison of their IR, PMR, and mass spectra with those

TABLE II
Degradation Data

Compound	Degradation procedure	Time of degradation, min	Yield of products, % w/w
1,3-Diphenoxypropan-2-ol	1	20	44
	2	30	40
	3	60	40
	4a	120	5
	4b	120	2.5
1,3-Diphenoxypropene	2	10	10
	4b	20	40

of standard compounds.[6] A comparison of the GLC retention times and mass spectra (where available) with those of standards served as identification of the remaining compounds. In some cases, retention times were compared at three different column temperatures (181°, 109°, and 83°C).

RESULTS

Degradation Products

Degradations 1 and 2 of 1,3-diphenoxypropan-2-ol yielded similar products and occurred more readily than degradation 3, which yielded products of a similar nature and distribution to those of degradations 4a and 4b. 1,3-Diphenoxypropene degraded readily under conditions 2 and 4b. The nature and distribution of the products of these two degradations were identical.

Tables III–VI list degradation products in estimated orders of abundance together with their means of identification. Chromatograms of the total products of the degradations are shown in Figures 1–4.

TABLE III
Products of the Degradation over Neutral and Acidic Alumina
of 1,3-Diphenoxypropan-2-ol

Compound	Relative abundance	Means of identification[a]
Phenol	major	RT,A
Phenoxyacetone	major	RT,IR,MS,PMR,N
1-Phenoxypropan-2-ol	minor	RT,IR,MS,PMR,N
2-Methylbenzofuran ⎱	minor	RT,IR,MS,PMR,N
3-Methylbenzofuran ⎰		RT,IR,MS,PMR,N
2-Methylcoumaran	trace	RT,IR,MS,N
Phenyl allyl ether	trace	RT,IR,MS,N
Chroman	trace	RT,IR,MS,N
2-Chromene	trace	RT,N
3-Chromene	trace	RT,N
Acetone ⎱	trace	3RT,N
Propionaldehyde ⎰		3RT,N
1-Propanol	trace	3RT,N
Acetaldehyde	trace	3RT,N

[a] RT = GLC retention time; A = acidity; MS = mass spectrum; N = neutrality; 3RT = RT measured at three different temperatures.

DISCUSSION

Degradation Mechanisms

Dehydration to form 1,3-diphenoxypropene does not precede the uncatalyzed degradation of 1,3-diphenoxypropan-2-ol. 1,3-Diphenoxypropene was not observed among the degradation products; and 2-chromene, which is a major product of the degradation of 1,3-diphenoxypropene,

TABLE IV
Products of the Degradation over Basic Alumina of 1,3-Diphenoxypropan-2-ol

Compound	Relative abundance	Means of identification
Phenol	major	RT,MS,A
Benzaldehyde	major	RT,MS,N
Phenylacetaldehyde	minor	RT,MS,N
o-Allylphenol	minor	RT,MS,A
Phenoxyacetone	minor	RT,MS,N
Benzofuran ⎫ Phenyl allyl ether ⎭	minor	RT,MS,N / RT,MS,N
2-Methylbenzofuran ⎫ 3-Methylbenzofuran ⎭	minor	RT,MS,N
2-Methylcoumaran	trace	RT,MS,N
1-Phenoxypropan-2-ol	trace	RT,MS,N
Benzyl alcohol	trace	RT,MS,N
3-Chromene	trace	RT,MS,N
Chroman	trace	RT,MS,N
2-Chromene	trace	RT,MS,N
Anisole	trace	3RT,MS,N
Styrene	trace	RT,MS,N
Toluene	trace	3RT,MS,N
Acetone	trace	3RT,MS,N
Acetaldehyde	trace	3RT,MS,N
Ethylbenzene	trace	RT,MS,N
Benzene	trace	3RT,N
Acrolein	trace	3RT,N

TABLE V
Products of the Uncatalyzed Degradation of 1,3-Diphenoxypropan-2-ol

Compound	Relative abundance	Means of identification
Phenol	major	RT,A
Benzaldehyde	major	RT,N
Phenoxyacetone	minor	RT,N
Phenylacetaldehyde	minor	RT,N
2-Methylbenzofuran ⎫ 3-Methylbenzofuran ⎭	minor	RT,N
o-Allylphenol	trace	RT,A
Benzyl alcohol	trace	RT,N
1-Phenoxypropan-2-ol	trace	RT,N
3-Chromene	trace	RT,N
Benzofuran	trace	RT,MS,N
2-Methylcoumaran	trace	RT,N
Chroman	trace	RT,N
2-Chromene	trace	RT,N
Anisole	trace	RT,N
Styrene	trace	RT,N
Toluene	trace	RT,N
Acetone	trace	RT,N
Acetaldehyde	trace	RT,N
Benzene	trace	RT,N
Ethylbenzene	trace	RT,N
Acrolein	trace	RT,N

TABLE VI
Major Products of the Degradations of 1,3-Diphenoxypropene

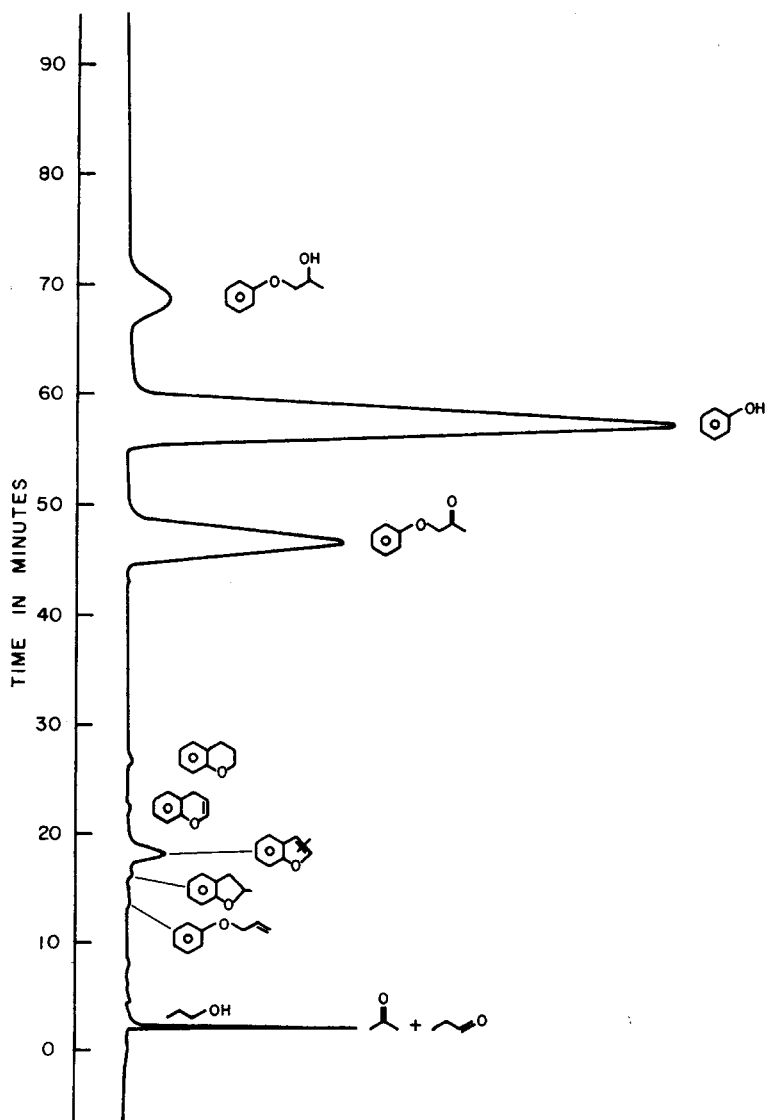| Compound	Relative abundance	Means of identification
Phenol	major	RT,MS
2-Chromene	major	RT,MS
3-Chromene	minor	RT,MS
2-Methylbenzofuran ⎫ 3-Methylbenzofuran ⎭	minor	RT,MS

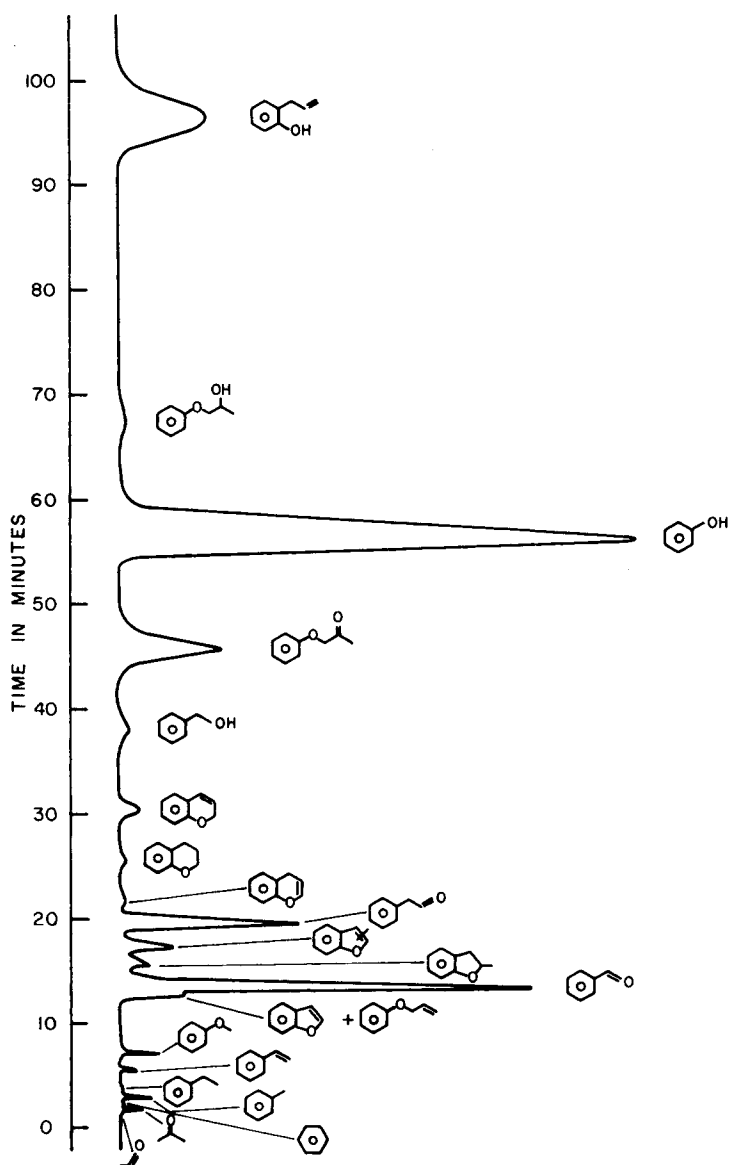Fig. 1. GLC trace of the products of the degradations over neutral and acidic alumina of 1,3-diphenoxypropan-2-ol.

Fig. 2. GLC trace of the products of the degradation over basic alumina of 1,3-diphen-oxypropan-2-ol.

is found in only trace amounts in the degradation of 1,3-diphenoxypropan-2-ol. The most abundant products other than phenol of the uncatalyzed degradation of 1,3-diphenoxypropan-2-ol retain the oxygen function on the central aliphatic carbon atom. The nature and diversity of the products suggest that degradation of 1,3-diphenoxypropan-2-ol proceeds by homolytic scission of the aliphatic carbon–carbon and carbon–phenoxy bonds. The major scission (which may be induced by the stability of the phenoxy
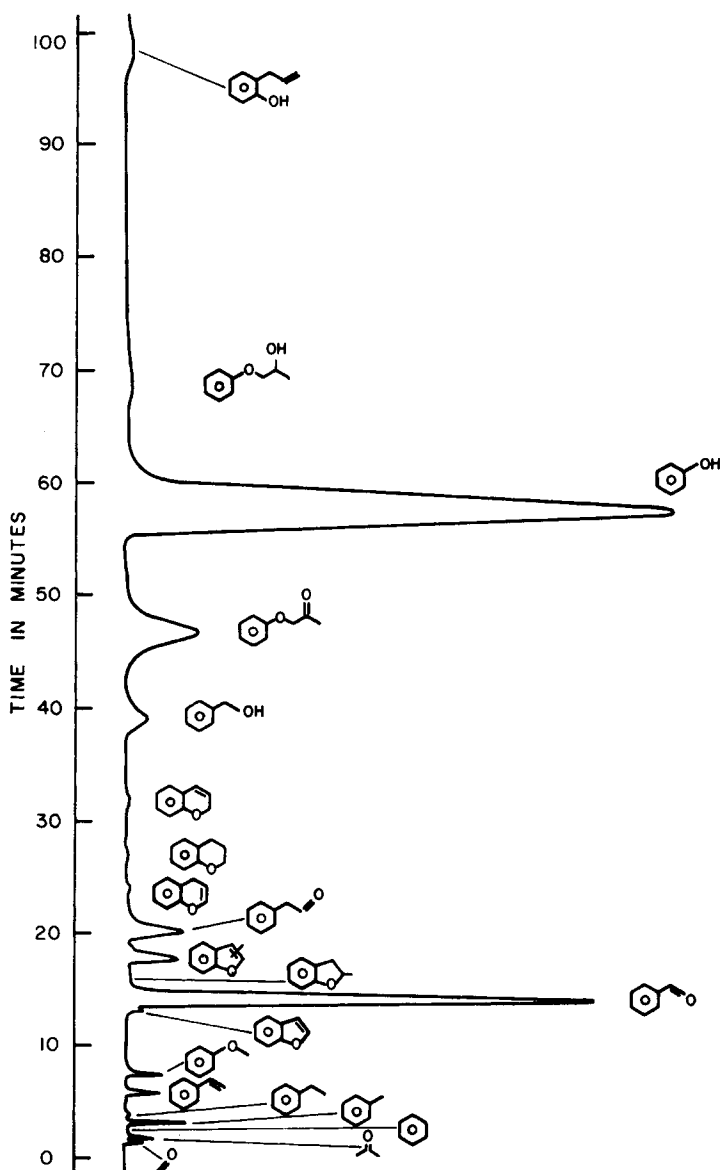
Fig. 3. GLC trace of the products of the uncatalyzed degradations of 1,3-diphenoxy-propan-2-ol.

radical) occurs at the aliphatic carbon–phenoxy bond.   The radicals produced by these reactions are indicated in Figure 5.

The presence of neutral or weakly acidic alumina modifies the degradation of 1,3-diphenoxypropan-2-ol.   Degradation proceeds readily, and all the products, with the exception of a trace amount of acetaldehyde, retain the three aliphatic carbon atoms.   Alumina is known[7,8] to promote cleavage
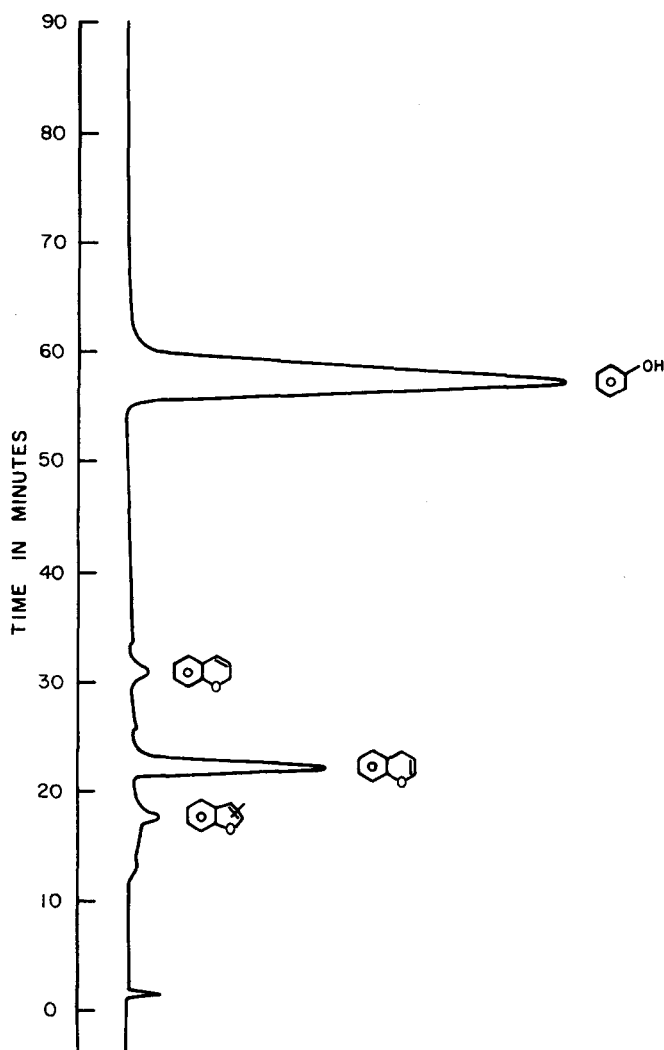
Fig. 4. GLC trace of the products of the degradations of 1,3-diphenoxypropene.

of aliphatic carbon–oxygen bonds in ethers and alcohols. Although degradation proceeds fairly readily over basic alumina, the nature and distribution of the products are similar to those of the products of the uncatalyzed degradation. The failure of the basic alumina to catalyze specifically carbon–oxygen bond fission may be attributed to the poisoning effect[9,10] of its alkali content.[11]

The Thermal Degradation of Amine-Cured Bisphenol A-Based Epoxide Resins

A comparison of the degradation of the model compounds 1-(N-ethylanilino)-3-phenoxypropan-2-ol, discussed in a previous paper,[2] and 1,3-
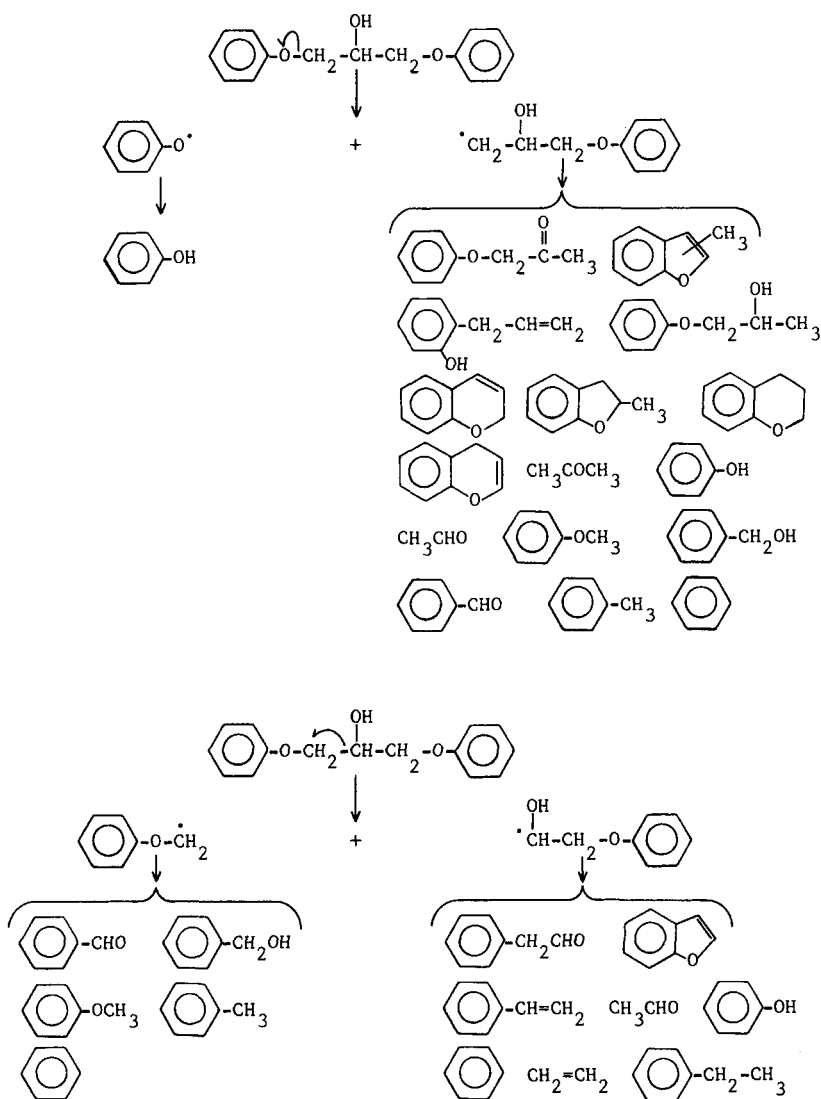
Fig. 5. Products of the degradation of 1,3-diphenoxypropan-2-ol.

diphenoxypropan-2-ol reveals that the presence of the nitrogen atom in the former compound greatly affects its degradation mechanism. 1-(N-Ethylanilino)-3-phenoxypropan-2-ol degrades readily with concurrent dehydration, whereas 1,3-diphenoxypropan-2-ol is relatively stable and dehydration reactions are minor processes in its degradation. Preferential scission of the aliphatic carbon–carbon bond adjacent to nitrogen occurs in the degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol.[2] It is significant that in the mass spectrum of 1-(N-ethylanilino)-3-phenoxypropan-2-ol the base peak (m/e 134) represents the fragment $C_6H_5N^+(C_2H_5)CH_2$,

in which the nitrogen atom has retained the adjacent methylene group, whereas in the mass spectrum of 1,3-diphenoxypropan-2-ol, the peaks representing the $C_6H_5O^+CH_2$ ion (m/e 107) and the charged phenol fragment (m/e 94) are of equal height and together with the m/e 77 peak represent the most abundant ions.

The present results indicate that in aromatic amine-cured bisphenol A-based epoxide resins the cure linkage is less stable than the glyceryl portion of the network. The presence of the nitrogen atom in the cure linkage may, however, modify the stability of adjacent glyceryl groups if the nitrogen atom catalyzes their dehydration to form 1,3-diphenoxypropene part structures which degrade readily.

References

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

2. J. C. Paterson-Jones, V. A. Percy, R. G. F. Giles, and A. M. Stephen, *J. Appl. Polym. Sci.*, **17**, 1869 (1973).

3. L. H. Lee, *J. Appl. Polym. Sci.*, **9**, 1981 (1965).

4. L. H. Lee, *J. Polym. Sci. A*, **3**, 859 (1965).

5. A. M. Kuliev, R. K. Alekperov, and Sh. T. Akhmedov, *Uch. Zap. Azerb. Gos. Univ., Ser. Khim. Nauk*, **1**, 31 (1965); *C.A.*, **67**, 32399m (1967).

6. V. A. Percy, M.Sc. Thesis, University of Cape Town, South Africa, December 1971.

7. B. Notari, *Chim. Ind.*, **51**, 1200 (1969).

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

9. B. Blouri, M. Laroche, A. Pazdzerski, A. Ahmadi, and P. Rumpf, *Bull. Soc. Chim. France*, **8**, 2861 (1967).

10. R. W. Maatman and L. J. Vande-Griend, *J. Catal.*, **20**, 238 (1971).

11. E. Lederer and M. Lederer, *Chromatography*, Elsevier, Amsterdam, 1957, p. 19.