

The Thermal Degradation of Model Compounds of Amine-Cured Epoxide Resins. III. The Thermal Degradation of 1-(N-Ethylanilino)-3-phenoxyprop-2-yl Acetate, Trifluoroacetate, and Methyl Ether and O-Deuterated 1-(N-Ethylanilino)-3- phenoxypropan-2-ol

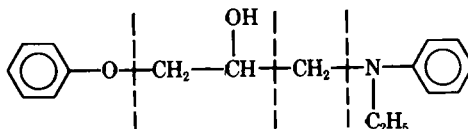
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Synopsis

The thermal degradations of 1-(N-ethylanilino)-3-phenoxyprop-2-yl acetate, trifluoroacetate, and methyl ether were studied. Major products were characterized. 1-(N-Ethylanilino)-3-phenoxypropan-2-ol in which the hydroxyl hydrogen was replaced with deuterium was degraded and the extent of deuteration of the one product, N-ethyl-N-methylaniline, was measured by mass spectrometry. The results were used to investigate the mechanism of the thermal degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol, a model compound for the cure linkage in aromatic amine-cured epoxide resins.

INTRODUCTION

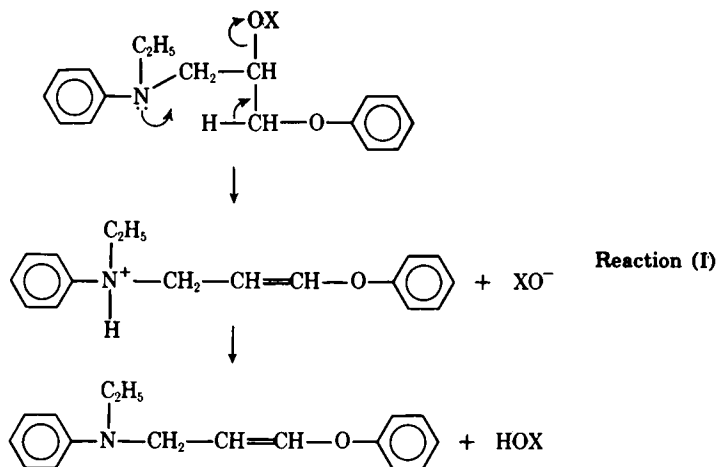
The thermal degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol, a model compound for the cure linkage of aromatic amine-cured epoxide resins, has been discussed in previous papers.^{1,2} The reaction showed several characteristic features: (i) 1-(N-Ethylanilino)-3-phenoxypropan-2-ol is readily degraded, whereas 1,3-diphenoxypropan-2-ol in which the nitrogen function is replaced by oxygen is relatively very stable under the same conditions.² (ii) Dehydration is a major process during degradation. (iii) The major products of the degradation show that bond scission is confined almost exclusively to three out of four possible sites (excluding loss of hydroxyl):



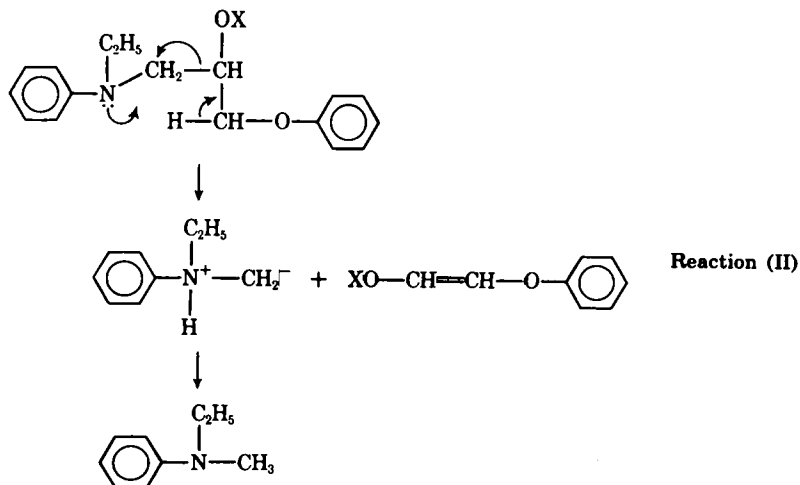
It was suggested, therefore, that the nitrogen atom acted as a nucleophile in two reactions which governed the course of the degradation—an intramolecular β -elimination of water ($\text{X} = \text{H}$) (reaction I):

TABLE I
GLC Retention Times of Standard Compounds

Compound	Retention time, min
Acetic acid	6.4
Phenyl acetate	14.2
N-Ethyl-N-methylaniline	14.3
N,N-Diethylaniline	14.5
2-Methylbenzofuran	14.7
N-Ethyltrifluoroacetanilide	17.3
N-Ethylaniline	19.9
N-Allyl-N-ethylaniline	21.9
Phenol	46.0



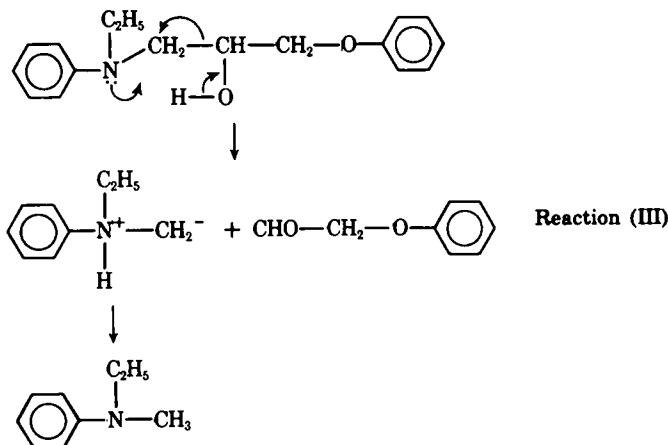
together with an intermolecular dehydration, possibly, and an intramolecular β -elimination of an ylide structure ($X = H$) (reaction II):



These two reactions followed in (I) by allyl-nitrogen bond scission and by isomerization and allyl-oxygen bond scission accounted for the formation of

the major degradation products phenol, N-ethylaniline, and N-ethyl-N-methylaniline.

It has subsequently been suggested³ that an alternative to reaction (II) is the reaction (III); the end result is the same:



The degradations of model compounds in which the hydroxyl hydrogen of 1-(N-ethylanilino)-3-phenoxypropan-2-ol was substituted by acetyl, trifluoroacetyl, methyl, and deuterium were studied in order to provide evidence for, or against, the operation of the above reactions during the model compound's degradation and to distinguish between reactions (II) and (III). If reaction (I) does occur, then varying the ease with which the leaving group can be displaced should have an appreciable effect on the ease of the degradation. In addition, since reaction (I) competes with either or both of reactions (II) and (III), then so should the amount of N-ethyl-N-methylaniline produced relative to N-ethylaniline decrease, the better the leaving group on the central carbon atom. In fact, if N-ethyl-N-methylaniline is formed only by reaction (III), then its production in the degradation of the O-acetyl-, O-trifluoroacetyl-, and O-methyl-substituted compounds should be eliminated entirely. If reaction (III) occurs, then degradation of starting material incorporating a deuterated hydroxyl group will lead to deuterated N-ethyl-N-methylaniline. This hypothesis was tested.

EXPERIMENTAL

In the case of the degradations of 1-(N-ethylanilino)-3-phenoxyprop-2-yl acetate, trifluoroacetate, and methyl ether, only major degradation products were identified except for the product N-ethyl-N-methylaniline which was either present in small quantities or absent. Among the degradation products of O-deuterated 1-(N-ethylanilino)-3-phenoxypropan-2-ol, only N-ethyl-N-methylaniline was investigated. This product was separated from the reaction products by preparative gas chromatography and its percentage deuteration determined by mass spectrometry. As described in a previous paper,¹ permanent gases, low molecular weight hydrocarbons, and high molecular weight or polymeric materials were not investigated.

A Pye Series 105 Model 15 preparative gas-liquid chromatograph (GLC) with a 4.57-m \times 0.953-cm-diameter glass preparative column packed with 25% Carbowax 20M on 60-72 mesh siliconized Diatomite C was used for the separation, identification, and collection of products. The operating conditions were: column temperature, 181°C; carrier gas (N₂) flow rate, 206.9 ml/min; column pressure, 30-31 psi; detector, flame ionization. Retention times were measured against those of standard compounds as described previously.¹ Table I lists standard retention times. Product identification was confirmed by infrared spectra (Perkin-Elmer Model 457), mass spectra, and thin-layer chromatographs.

The structures of 1-(N-ethylanilino)-3-phenoxyprop-2-yl acetate, trifluoroacetate, and methyl ether were confirmed by proton magnetic resonance spectra.

Syntheses

1-(N-Ethylanilino)-3-phenoxypropan-2-ol. The preparation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol has been reported.¹

ANAL. Calcd for C₁₇H₂₁O₂N: C, 75.3%; H, 7.8%; N, 5.2%. Found: C, 75.3%; H, 7.9%; N, 5.2%.

PMR Spectrum (in Deuteriochloroform). T 8.88 (3H, triplet, J, 7 c/s; —N—CH₂—CH₃), T 7.33 (1H, broad singlet removed by D₂O exchange; —OH), T 6.55 (doublet, J, 6 c/s; —CH—CH₂—N—Ar) superimposed on T 6.58 (multiplet; —N—CH₂—CH₂—),
 (combined resonances totalling 4H), T 6.02 (2H, doublet, J, 4 c/s; Ar—O—CH₂—CH—),
 T 5.82 (1H, poorly resolved multiplet, resolved by D₂O exchange; —CH—OH), T 2.68-3.40 (10H, multiplets; —Ar—H).

1-(N-Ethylanilino)-3-phenoxyprop-2-yl Trifluoroacetate. Trifluoroacetic anhydride (20 ml) was added slowly with mixing under reflux to 1-(N-ethylanilino)-3-phenoxypropan-2-ol (5 g; 0.0185 mole). After the initial rapid reaction, the mixture was heated under reflux for 3 hr and distilled. The fraction, bp 181-184°C/2.6 mm Hg, was collected as a pale-green syrup (5.07 g; 74.9%). The product was stored in a desiccator to prevent hydrolysis.

ANAL. Calcd for C₁₈H₂₀O₃NF₃: C, 62.1%; H, 5.5%; N, 3.8%. Found: C, 62.1%; H, 5.5%; N, 4.0%.

PMR Spectrum (in Deuteriochloroform). T 8.86 (3H, triplet, J, 7 c/s; —N—CH₂—CH₃), T 6.59 (2H, quartet, J, 7 c/s; —N—CH₂—CH₂—), T 6.29 (2H, doublet, J, 6 c/s; —CH—CH₂—N—Ar), T 5.82 (2H, doublet, J, 4 c/s; Ar—O—CH₂—CH—), T 4.46 (1H, 9-plet, J, 4 c/s and 6 c/s; —O—CH₂—CH—CH₂—N—), T 2.58-3.40 (10H, multiplets; —Ar—H).

1-(N-Ethylanilino)-3-phenoxyprop-2-yl Acetate. 1-(N-Ethylanilino)-3-phenoxypropan-2-ol (10.92 g, 0.0403 mole) was heated 4 hr under reflux

with acetic anhydride (30 ml). The reaction mixture was stirred into 200 ml cold water and extracted with 200 ml diethyl ether. The ether extract was washed three times with 100 ml water, dried (Na_2SO_4), and distilled. The fraction boiling at 221–223°C/5.5 mm Hg was collected as a pale straw syrup (10.52 g; 83.4%).

ANAL. Calcd for $\text{C}_{19}\text{H}_{23}\text{O}_3\text{N}$: C, 72.8%; H, 7.4%; N, 4.5%. Found: C, 72.9%; H, 7.5%; N, 4.5%.




PMR Spectrum (in Deuteriochloroform). T 8.88 (3H, triplet, J, 7 c/s; $-\text{N}-\text{CH}_2-$
 CH_3), T 7.99 (3H, singlet; $\text{CH}_3\text{CO}-$), T 6.66 (2H, 8-plet, J, 7 c/s and 11.5 c/s; $-\text{N}-$
 CH_2-CH_3), T 6.39 (2H, doublet, J, 6 c/s; $-\text{CH}-\text{CH}_2-\text{N}-\text{Ar}$), T 5.92 (2H, doublet,
 Et
 J, 4 c/s; $\text{Ar}-\text{O}-\text{CH}_2-\text{CH}-$), T 4.63 (1H, 9-plet, J, 6 c/s and 4 c/s; $-\text{O}-\text{CH}_2-$
 $\text{CH}-\text{CH}_2-\text{N}-$), T 2.66–3.44 (10H, multiplets; $-\text{Ar}-\text{H}$).



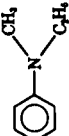



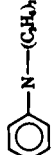
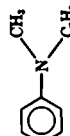
1-(N-Ethylanilino)-2-methoxy-3-phenoxypropane. 1-(N-Ethylanilino)-3-phenoxypropan-2-ol (5 g, 0.0185 mole) was dissolved in 100 ml dry tetrahydrofuran. Potassium (1.2 g, 0.038 mole) was added and the mixture was heated under reflux for 4½ hr and cooled. Pure dry dimethyl sulfate (2 ml, 0.0211 mole) was added and the mixture stirred at ambient temperature for 16 hr. More dimethyl sulfate (0.5 ml, 0.005 mole) was added and the mixture was heated under reflux for 4 hr and cooled. The solidified excess potassium was removed. Sodium hydroxide (1 g, 0.025 mole) in water (20 ml) was added to the reaction mixture which was heated under reflux for 3 hr, cooled, and extracted with diethyl ether (50 ml). The ether extract was washed three times with water (100 ml) and dried (Na_2SO_4). Thin-layer chromatography showed the presence in this solution of the desired product together with some starting material and traces of four other components. The ether solution was applied to ten 20-cm × 20-cm-thick layer chromatography plates (silica gel G, Merck) which were eluted with 1:1 chloroform:benzene. The desired product was located under UV light as a diffuse, dim purple band. The bands were marked and removed from the plates. The combined scrapings were eluted with diethyl ether. This solution was distilled. A fraction boiling 190–191°C/1.6 mm Hg was collected as a pale green syrup (1.91 g; 36.4%) which was shown to be pure by thin-layer chromatography ($R_F = 0.66$; solvent CHCl_3 :benzene 1:1, silica gel G).

ANAL. Calcd for $\text{C}_{18}\text{H}_{23}\text{O}_2\text{N}$: C, 75.9%; H, 8.2%; N, 5.1%. Found: C, 75.8%; H, 8.1%; N, 4.9%.

PMR Spectrum (in Deuteriochloroform). T 8.86 (3H, triplet, J, 7 c/s; $-\text{N}-\text{CH}_2-$
 CH_3), T 6.52 (singlet; $-\text{OCH}_3$), T 6.45 (doublet, J, 6 c/s; $-\text{CH}-\text{CH}_2-\text{N}-\text{Ar}$), T?—T
 Et
 6.8 (obscured by previous two resonances, multiplet; $-\text{N}-\text{CH}_2-\text{CH}_3$), (total for
 previous three resonances 7H), T 6.24 (1H, multiplet; $-\text{O}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{N}-$),
 Et
 T 5.98 (2H, doublet, J, 4 c/s; $\text{Ar}-\text{O}-\text{CH}_2-\text{CH}-$), T 2.64–3.46 (10H, multiplets;
 $\text{Ar}-\text{H}$).

TABLE II
 Products of the Thermal Degradation of 1-(N-Ethylanilino)-3-phenoxyprop-2-yl Acetate, Trifluoroacetate, and Methyl Ether

Compound	Major degradation products	Relative abundances	Means of identification ^b
$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{C}_6\text{H}_5-\text{N}-\text{CH}_2-\text{CH}(\text{OX})-\text{CH}_2-\text{O}-\text{C}_6\text{H}_5 \\ \\ \text{X} \end{array}$			
—CH ₃		major	RT, IR, I
		major	RT, IR, S
		minor	RT, IR, S
		absent	
		major	RT, IR, I
—COCH ₃		major	RT, IR, S
	CH ₃ COOH	major	RT, IR, I

	minor	RT, IR, I
	minor	RT, IR, I
	small traces	RT, TC, S
	major	RT, IR
	major	RT, IR
	minor	RT, IR, MS
	small amount	RT, IR
	small traces	RT

—COCF₃

Note: CF₃COOH not investigated

^a The relative abundance of products was obtained by an estimation of the relative peak areas in the GLC chromatogram. The relative sensitivity of the flame ionization detector to individual compounds was not measured.

^b RT = GLC retention time; IR = infrared spectrum; TC = thin-layer chromatograph; MS = mass spectrum; I (S) = insoluble (soluble) in 5% hydrochloric acid.

TABLE III
Degradation Data

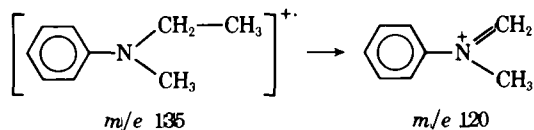
Compound	Yield (w/w), %	Time, min	Peak height ratio	
			N-ethyl-N-methylaniline	N-ethylaniline
$ \begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{N}-\text{CH}_2-\text{CH}(\text{OX})-\text{CH}_2-\text{O}-\text{C}_6\text{H}_5 \\ \text{X} = \end{array} $	36	45	1.24	
-H	20	25	$\ll 0.01$	
-CH ₃	40.5	10	(no trace of N-ethyl-N-methylaniline found)	0.026
-COCH ₃	55	15		0.008
-COCF ₃				

2-Deutoxy-1-(N-ethylanilino)-3-phenoxypropane. 1-(N-Ethylanilino)-3-phenoxypropan-2-ol (2 g; 0.0074 mole) was placed in a glass distillation apparatus connected to a high-vacuum glass line and evacuated. Deuteromethanol (1 ml; 0.0245 mole) was distilled under vacuum from a detachable trap on the vacuum line onto the 1-(N-ethylanilino)-3-phenoxypropan-2-ol. The mixture was warmed to room temperature and allowed to stand for several hours after mixing. The resulting mixture of methanol and deuteromethanol was distilled off under vacuum and a fresh portion of deuteromethanol added. This process was repeated a total of four times. Finally, the 2-deutoxy-1-(N-ethylanilino)-3-phenoxypropane was pumped to remove final traces of deuteromethanol and stored under vacuum to avoid contamination with moisture. The product was calculated to be greater than 99% deuterated.

Degradation

1-(N-Ethylanilino)-3-phenoxyprop-2-yl acetate, trifluoroacetate, and methyl ether were degraded in air in a conventional glass distillation apparatus as described in a previous paper.¹ Table II shows the major products of degradation of these three materials in order of abundance together with the product N-ethyl-N-methylaniline which, although present in only trace quantities or absent, was of special interest. Table III shows the time of degradation and yield of products together with a figure representing the ratio of the peak heights in the chromatogram of the products N-ethyl-N-methylaniline and N-ethylaniline. The corresponding data for 1-(N-ethylanilino)-3-phenoxypropan-2-ol taken from a previous paper¹ is included for comparison.

2-Deutoxy-1-(N-ethylanilino)-3-phenoxypropane was degraded in an atmosphere of pure, dry nitrogen in the distillation apparatus in which it was prepared. The degradation product N-ethyl-N-methylaniline was separated by preparative GLC. The 70-eV mass spectrum of this product was used to estimate its percentage deuteration by comparing peak heights at m/e ratios 119, 120, and 121 and at 134, 135, and 136 with those of pure undeuterated N-ethyl-N-methylaniline whose mass spectrum was run under identical conditions. The product had a percentage deuteration of $39.5 \pm 0.6\%$. Table IV lists normalized peak heights in the mass spectra of the deuterated and pure N-ethyl-N-methylanilines. The peaks at m/e 135 and 120 in the undeuterated sample represent the loss of methyl:



DISCUSSION

Reactions (I) and (II) may be postulated for the degradations of the substituted compounds, 1-(N-ethylanilino)-3-phenoxyprop-2-yl acetate, tri-

TABLE IV
Peak Heights in Mass Spectra of Deuterated and Undeuterated N-Ethyl-N-methylaniline

<i>m/e</i>	Peak height	
	Undeuterated	Deuterated
137	0	9.7
136	7.5	32.6
135	63.0	46.3
134	9.9	8.9
121	14.8	75.5
120	100.0	100.0
119	3.6	16.8
107	2.4	6.1
106	6.2	14.5
105	12.1	14.2
104	12.6	12.5
79	4.6	5.1
78	4.9	6.5
77	25.6	29.2

fluoroacetate, and methyl ether, where X = acetyl, trifluoroacetyl, and methyl, respectively.

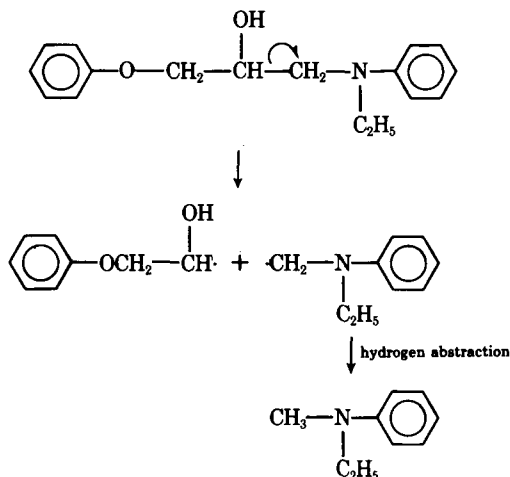
Reaction (III) is clearly not possible for the O-substituted compounds. Reactions (I) and (II) are competing reactions if both occur, the extent to which reaction (I) occurs at the expense of reaction (II) being determined by the effectiveness of the leaving group XO^- since the leaving group in reaction (II) is the same in all cases. The effectiveness of the leaving groups is in the order



On this basis it would be expected that in the degradation of the trifluoroacetyl- and acetyl-substituted compounds, N-ethyl-N-methylaniline production via reaction (II) would be reduced and N-ethylaniline production via reaction (I) increased. Conversely, N-ethyl-N-methylaniline production in the degradation of the methoxy substituted compound would be expected to increase or be the same as in that of 1-(N-ethylanilino)-3-phenoxypropan-2-ol.

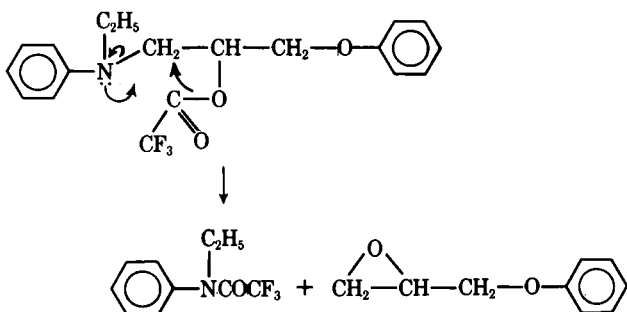
In fact, virtually no N-ethyl-N-methylaniline is produced in the degradation of any of the three O-substituted compounds. Reaction (II), therefore, does not occur to any significant extent. By analogy, reaction (II) plays a negligible role in the degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol.

In fact, it is clear that the production of N-ethyl-N-methylaniline requires the presence of the hydroxyl hydrogen, a feature of reaction (III). It can be argued that N-ethyl-N-methylaniline is formed via simple homolytic scission:



The primary radical formed in this reaction, however, may abstract hydrogen from a very large number of sites in both starting material and products, a process which has very low activation energy.⁴ The extent of deuteration of N-ethyl-N-methylaniline formed by such a process during the degradation of O-deuterated 1-(N-ethylamino)-3-phenoxypropan-2-ol would be small, less than the 39.5% measured, a figure which represents the dilution during degradation of the OD groups on unchanged starting material by exchange with HOD and phenol produced via reaction (I). In addition, N-ethyl-N-methylaniline is formed in only trace amounts or not at all from the O-substituted starting materials. If major quantities of this product are formed via homolytic scission in 1-(N-ethylamino)-3-phenoxypropan-2-ol, there is no reason why similar quantities should not be formed by the same process in the O-substituted compounds. The trace amounts formed by the degradation of acetyl- and trifluoroacetyl-substituted starting materials are probably formed by homolytic scission. The major amounts formed by degradation of 1-(N-ethylamino)-3-phenoxypropan-2-ol are formed by reaction (III).

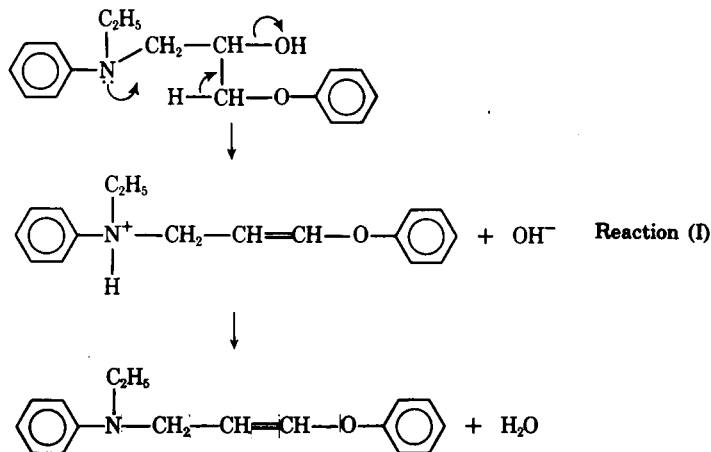
The data presented in Table III shows that there is a correlation between the ease of degradation as measured by time of degradation and yield of products and the effectiveness of the leaving group OX^- as the series $\text{X} = \text{CF}_3\text{CO}-, \text{CH}_3\text{CO}-, \text{H}-, \text{CH}_3-$ is traversed. This is expected if the nitrogen present in the starting material induces the intramolecular β -elimination reaction, reaction (I). Supplementary evidence for the operation of this mechanism is found in the large quantities of acetic acid, both free and in the product phenyl acetate, formed during degradation of 1-(N-ethylamino)-3-phenoxyprop-2-yl acetate (Table II). Trifluoroacetic acid was not investigated as a product of the degradation of 1-(N-ethylamino)-3-phenoxyprop-2-yl trifluoroacetate because of its volatility and the low sensitivity of the GLC detector to it. The product N-ethyltrifluoroacetanilide may be formed by the reaction shown below:



or a similar process. Appreciable quantities of methanol were not found among the degradation products of 1-(N-ethylanilino)-2-methoxy-3-phenoxypropane; in fact, this material was not easily degraded, probably a reflection of the fact that methoxide is not readily displaced in a process such as reaction (I).

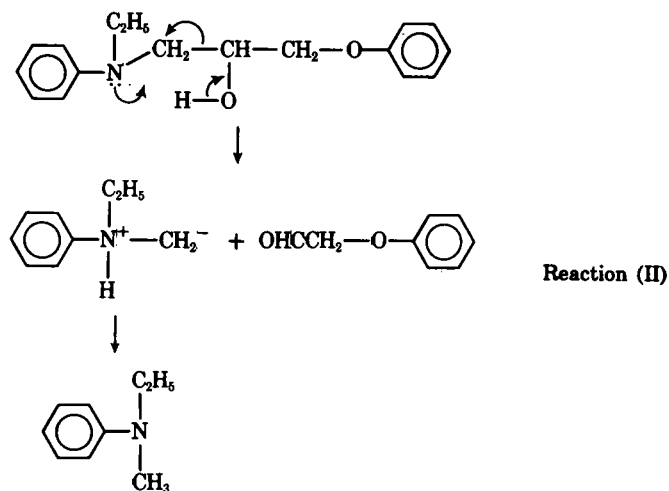
CONCLUSIONS

Two major reactions in which the nitrogen atom acts as nucleophile occur during the thermal degradation of 1-(N-ethylanilino)-3-phenoxypropan-2-ol:



Reaction (I) is written as an intramolecular dehydration. In principle, there is no reason to exclude a β -elimination reaction induced by the nitrogen of another molecule, but steric factors make an intermolecular reaction less likely. A Fisher atomic model of 1-(N-ethylanilino)-3-phenoxypropan-2-ol shows that both the γ -hydrogen involved in reaction (I) and the hydroxyl hydrogen involved in reaction (II) can approach the nitrogen atom very closely without inducing any strain in the molecule.

1-(N-Ethylanilino)-3-phenoxypropan-2-ol is a model compound for the cure linkage in aromatic amine-cured epoxide resins. The significance of



the above reactions in the thermal degradation of these resins will be discussed in a subsequent paper.

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