702. *The Mechanism of Epoxide Reactions. Part II.*[1] *The Reactions of 1,2-Epoxyethylbenzene, 1,2-Epoxy-3-phenylpropane, and 1,2-Epoxy-3-phenoxypropane with Benzylamine.*

By N. S. ISAACS and R. E. PARKER.

Arrhenius parameters have been determined for the reactions in 99·8% ethanol of 1,2-epoxyethylbenzene, 1,2-epoxy-3-phenylpropane, and 1,2-epoxy-3-phenoxypropane with benzylamine and with the products of the first reactions. Product analyses have been carried out by infrared spectroscopy whence it is inferred that the first reactions of 1,2-epoxy-3-phenylpropane and 1,2-epoxy-3-phenoxypropane give entirely " normal " products. The first reaction of 1,2-epoxyethylbenzene, however, gives both " normal " and " abnormal " products, and rate constants and Arrhenius parameters have been calculated for both these reactions. The mechanism of the reactions is discussed and the effect of substituents is analysed in terms of the Taft linear free-energy relation.

THE reactions of piperidine in 99·8% ethanol with 1,2-epoxyethylbenzene, 1,2-epoxy-3-phenylpropane, and 1,2-epoxy-3-phenoxypropane, reported in Part I,[1] all give entirely or almost entirely " normal " products (*i.e.*, products corresponding to attack of piperidine at the less substituted carbon atom). The only one of these reactions to give a detectable amount of " abnormal " isomer (*i.e.*, the isomer corresponding to attack of piperidine at the more substituted carbon atom) is that between piperidine and 1,2-epoxyethylbenzene, and even this gives only 4% of abnormal isomer at 60°. A consideration of the relative

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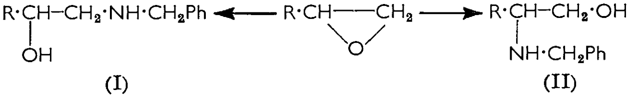
[1] Part I, Chapman, Isaacs, and Parker, *J.*, 1959, 1925.

amounts of normal and abnormal products obtained in the ring-opening reactions of mono-substituted ethylene oxides [2] has led us to the conclusion that one of the main factors determining orientation in these reactions is steric hindrance (primary steric effect)

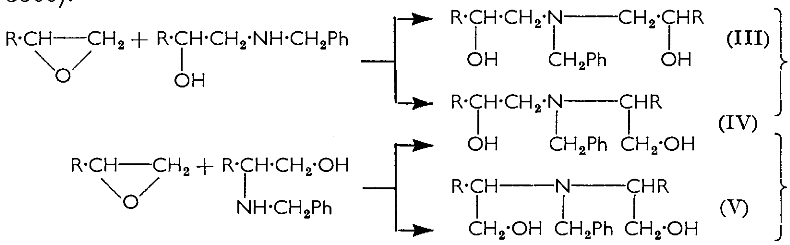


. . . . (i)

between the reagent and the substituent group of the ethylene oxide. This factor inhibits attack at the abnormal (adjacent) position. Since one of the main objects of our work is to study the kinetics of both normal and abnormal ring-opening, it was necessary to find a reaction which gives appreciable amounts of both products. One obvious way to do this was to use a reagent less bulky than piperidine. For this reason we chose the primary amine, benzylamine, and the present paper records a kinetic study of its reactions with the three epoxides mentioned above.

The choice of benzylamine instead of piperidine introduces additional analytical difficulties. In the reactions with piperidine the products are tertiary amines and the reactions were followed by potentiometric titration with perchloric acid in glacial acetic acid, after acetylation of the unchanged piperidine. In the reactions with benzylamine the first products are the secondary amines (I) (normal) and (II) (abnormal). Each of these products can, however, react with further epoxide at either the normal or the abnormal position. Four further reactions are therefore possible, giving rise to three tertiary amines (III—V).

For the reactions of benzylamine with 1,2-epoxy-3-phenylpropane and with 1,2-epoxy-3-phenoxypropane, the first reaction (i) gives entirely normal product (I) (see below). Since no abnormal isomer (II) is formed, reaction (iii) does not arise. Further, since benzylamine itself gives no abnormal product, it is extremely unlikely that the much bulkier secondary amine (I) will give any abnormal product (IV) in reaction (ii). We therefore assume that, in these cases, the only further reaction is that involving attack at the normal position of the epoxide by the initial product (I), giving the final product (III). This tertiary amine was estimated in the same way as the tertiary amines in Part I.[1] In addition, benzylamine was estimated in a separate aliquot part by converting it into its anil with salicylaldehyde and determining this spectrophotometrically. Thus the amounts of primary and of tertiary amine are known and that of secondary amine is the difference between the sum of these and that of the total initial amine. Under these conditions the rate constants for the first and the second reaction can each be calculated (see p. 3500).



. . . (ii)

. . . (iii)

In the reactions of benzylamine with 1,2-epoxyethylbenzene some abnormal product (II) is formed in the first reaction and the above considerations do not, therefore, apply. However, insofar as the first reaction gives mainly normal product (83% at 20° and 73% at 60°), the above treatment will still be approximately correct and the rate constants have been calculated on this basis. It follows that, while the rate constant calculated for the first reaction of 1,2-epoxyethylbenzene will be correct, the rate constant for the second reaction of this epoxide will be only approximate. To check the accuracy of the latter

[2] Parker and Isaacs, *Chem. Rev.*, 1959, **59**, 737.

it was also determined from the direct reaction of 1,2-epoxyethylbenzene with 2-benzylamino-1-phenylethanol (I; R = Ph). The results obtained were as tabulated.

Second rate constant, benzylamine and 1,2-epoxyethylbenzene, 59·00°	$1·47 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$
Rate constant, 2-benzylamino-1-phenylethanol and 1,2-epoxyethylbenzene, 59·00°	$1·51 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$

Agreement is better than could have been expected and must, to some extent, be fortuitous. Nevertheless, it serves to indicate that there can be no gross error in the calculated values of the second rate constant for the benzylamine reaction.

The product analyses for the first reactions were carried out essentially as in Part I.[1] Reactions, in ethanol, of epoxide with a considerable excess of benzylamine (in order to minimise the second reaction) were allowed to go to completion and the resulting mixtures were distilled in such a way as to give the total secondary amine mixture, free from any other compounds. The infrared spectrum of this mixture was then compared with the spectra of the normal and the abnormal products. The normal products were prepared by reaction of the epoxide with benzylamine and crystallisation of the product to constant melting point. The abnormal products corresponding to 1,2-epoxyethylbenzene and 1,2-epoxy-3-phenylpropane were synthesised unambiguously. The abnormal product corresponding to 1,2-epoxy-3-phenoxypropane was not synthesised, but for this epoxide, as for 1,2-epoxy-3-phenylpropane, the spectrum of the reaction product was identical with that of the normal isomer.

EXPERIMENTAL

Materials.—1,2-Epoxyethylbenzene, 1,2-epoxy-3-phenylpropane, and 1,2-epoxy-3-phenoxypropane were obtained as in Part I.[1]

Benzylamine (from May and Baker, Ltd.) was dried over two portions of sodium hydroxide and then over two portions of sodium. It was fractionated twice through a 40-theoretical-plate column, the middle fraction being collected each time; this had b. p. 185°/768 mm., n_D^{25} 1·5392.

Ethanol was dried and adjusted to 99·80% w/w as in Part I.[1]

Rate Measurements.—The reactions were carried out in the same way as those in Part I,[1] except that rather higher initial concentrations of epoxide and amine were used (0·15M instead of 0·10M). At appropriate intervals pairs of aliquot portions were withdrawn. One portion (5 ml.) of each pair was added to acetic acid and acetic anhydride for determination of tertiary amine as in Part I.[1] The other (1 ml.) was added to 10 ml. of a 1% solution of salicylaldehyde in absolute ethanol; after 30 min. absolute ethanol was added to bring the volume to exactly 100 ml. and the optical density of the solution was measured at 404 mμ, a Unicam S.P. 600 visible spectrophotometer being used. The extinction coefficient of the pure anil from benzylamine and salicylaldehyde was found to be 472 at this wavelength in ethanol and measurement at different concentrations showed that Beer's law is obeyed.

Synthesis of Products.—The normal isomers were prepared by reaction of benzylamine with the appropriate oxide in ethanol and crystallisation to constant m. p. In this way were prepared: 2-benzylamino-1-phenylethanol, m. p. 103° (from ethanol) (lit.,[3] 102—103°); 1-*benzylamino*-3-*phenylpropan*-2-*ol*, m. p. 68° (from aqueous ethanol) (Found: C, 79·4; H, 7·9; N, 5·6. $C_{16}H_{19}NO$ requires C, 79·5; H, 7·9; N, 5·8%); and 1-*benzylamino*-3-*phenoxypropan*-2-*ol*, m. p. 74·5° (from ethanol) (Found: C, 74·4; H, 7·5. $C_{16}H_{19}NO_2$ requires C, 74·7; H, 7·4%).

β-*Benzylaminophenethyl alcohol.* Ethyl α-benzylamino-α-phenylacetate was prepared by the action of benzylamine on ethyl α-bromophenylacetate in ether. This ester (23 g., 0·85 mole) was run into a slurry of lithium aluminium hydride (5·0 g., 0·13 mole) in ether (350 ml.) boiling under reflux, and boiled for a further 2 hr. Water was added. After filtration, the ethereal layer was separated and dried (Na_2SO_4), and β-benzylaminophenethyl alcohol obtained upon removal of the ether. Recrystallised from light petroleum, it had m. p. 69° (lit.,[3] 68—69°).

2-*Benzylamino*-3-*phenylpropan*-1-*ol*. α-Bromo-β-phenylpropionic acid[4] (36 g., 0·16 mole) was dissolved in a solution of benzylamine (60 g., 0·56 mole) in water (100 ml.). The mixture

[3] Browne and Lutz, *J. Org. Chem.*, 1952, **17**, 1187.

[4] Fischer, *Ber.*, 1904, **37**, 3062; Fischer and Carl, *Ber.*, 1906, **39**, 3996.

was left for 1 hr., then 2-benzylamino-3-phenylpropionic acid was filtered off as a white powder, m. p. 230—233° [lit.,[5] 225° for the (+)-compound] (22·5 g., 55%), insoluble in all solvents.

This acid (10 g., 0·04 mole) was boiled under reflux with ethanol (>99·9% w/w) (50 ml.), while a stream of hydrogen chloride was passed in. After 3 hr., the ethanol was removed at 100°/15 mm. and the residual ethyl ester, a vitreous solid completely soluble in ethanol (8·5 g., 75%), was dissolved in dry ether and run into a slurry of lithium aluminium hydride (1·0 g., 0·025 mole) in ether (100 ml.). The solution was boiled under reflux for 4 hr. and water (50 ml.) then added. Working up in the usual way gave *2-benzylamino-3-phenylpropan-*1-*ol*, m. p. 67° (from light petroleum) (Found: C, 79·4; H, 7·9; N, 5·6. $C_{16}H_{19}NO$ requires C, 79·5; H, 7·9; N, 5·8%).

Product Analysis.—Infrared analysis. For the reactions of benzylamine with 1,2-epoxyethylbenzene and 1,2-epoxy-3-phenylpropane infrared spectra were determined for (*a*) the actual reaction product (obtained by allowing the reaction in ethanol to go to completion and distilling the product *in vacuo* in such a way as to obtain the total secondary amine fraction free from other compounds), (*b*) the normal product, and (*c*) the abnormal product. For the reaction of benzylamine with 1,2-epoxy-3-phenoxypropane spectra were determined for the actual reaction product and for the normal product. All the measurements were made on chloroform solutions with a Unicam S.P. 100 double-beam, infrared spectrophotometer.

RESULTS

The first reaction between benzylamine (A) and each epoxide (E) to give secondary amine product (B) may be denoted:

$$\begin{array}{lccccc} & \mathrm{A} & + & \mathrm{E} & \xrightarrow{k_1} & \mathrm{B} \\ t = 0: & a & & e & & 0 \\ t = t: & (a - x) & & (e - x - y) & & (x - y) \end{array} \quad . \; . \; . \; . \; . \; . \; (1)$$

where *a* and *e* are the initial concentrations of amine and epoxide, respectively, *x* is the concentration of B *had no second reaction occurred*, *y* is the concentration of the product (C) of the second reaction, and k_1 is the rate constant for the first reaction. The second reaction, between secondary amine (B) and epoxide (E), is similarly denoted:

$$\begin{array}{lccccc} & \mathrm{B} & + & \mathrm{E} & \xrightarrow{k_2} & \mathrm{C} \\ t = 0: & 0 & & e & & 0 \\ t = t: & (x - y) & & (e - x - y) & & y \end{array} \quad . \; . \; . \; . \; . \; . \; (2)$$

where k_2 is the rate constant for the second reaction. Reactions 1 and 2 give the second-order rate equations 3 and 4, respectively, and these can be re-written in the forms 5 and 6.

$$\mathrm{d}x/\mathrm{d}t = k_1(a - x)(e - x - y) \quad . \; . \; . \; . \; . \; . \; . \; . \; (3)$$

$$\mathrm{d}y/\mathrm{d}t = k_2(x - y)(e - x - y) \quad . \; . \; . \; . \; . \; . \; . \; . \; (4)$$

$$k_1 = \frac{\mathrm{d}x}{\mathrm{d}t} \cdot \frac{1}{(a - x)(e - x - y)} \quad . \; . \; . \; . \; . \; . \; . \; . \; (5)$$

$$k_2 = \frac{\mathrm{d}y}{\mathrm{d}t} \cdot \frac{1}{(x - y)(e - x - y)} \quad . \; . \; . \; . \; . \; . \; . \; . \; (6)$$

Values of d*x*/d*t* were obtained by plotting *x*, the total concentration of secondary and tertiary amine (*i.e.*, total amine minus measured primary amine), against *t* and measuring the slopes of the curve at appropriate values of *t*. Values of d*y*/d*t* were similarly obtained from a plot of *y*, the measured tertiary amine concentration, against *t*.

For the reactions with 1,2-epoxy-3-phenylpropane and 1,2-epoxy-3-phenoxypropane the values of k_1 so obtained can be equated to $k_{1\mathrm{N}}$, the rate constant for attack at the normal position, since the spectra of the products of these reactions were identical with the spectra of the normal isomers. For the reaction with 1,2-epoxyethylbenzene, however, this is no longer true. In this case it was found, from an examination of the spectra of the normal and abnormal isomers and of synthetic mixtures of the two isomers, that the ratio of the peak

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[5] Fischer and Mechel, *Ber.*, 1916, **49**, 1355.

height at 1120 cm.$^{-1}$ to that at 1037 cm.$^{-1}$ varied linearly from 1·32 for pure normal isomer to 0·65 for pure abnormal isomer. It was therefore possible to calculate the fraction of normal isomer (α) and of abnormal isomer (β) in the reaction product at each temperature and to use these values to determine the rate constant for normal attack k_{1N} and the rate constant for abnormal attack k_{1A}, according to equations 7:

$$k_1 = k_{1N} + k_{1A}; \quad \alpha/\beta = k_{1N}/k_{1A} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

The results are summarised in Table 1, and values of k_{1N}, k_{1A}, and k_2, all interpolated to 35°, together with the Arrhenius parameters are collected in Table 2.

TABLE 1. *Isomer proportions and measured rate constants,* 10^4k (l. mole^{-1} sec.$^{-1}$).

	Temp.	α	β	k_{1N}	k_{1A}	k_2
1,2-Epoxyethylbenzene	20·00°	0·83	0·17	0·115	0·024	0·0688
	40·50	0·78	0·22	0·499	0·141	0·366
	59·68	0·73	0·27	1·85	0·68	1·47
1,2-Epoxy-3-phenylpropane ...	20·30	1·00	0·00	0·503	—	0·094
	39·32	1·00	0·00	1·68	—	0·439
	58·92	1·00	0·00	4·66	—	1·80
1,2-Epoxy-3-phenoxypropane ...	20·00	1·00	0·00	1·01	—	0·502
	39·24	1·00	0·00	4·01	—	1·94
	58·80	1·00	0·00	13·8	—	7·25

TABLE 2. *Rate constants interpolated to* 35°, *and Arrhenius parameters.* (k and A in l. mole^{-1} sec.$^{-1}$; E in kcal. mole^{-1}.)

	Normal reaction			Abnormal reaction			Second reaction		
	10^4k_{1N}	E	$\log_{10} A$	10^4k_{1A}	E	$\log_{10} A$	10^4k_2	E	$\log_{10} A$
1,2-Epoxyethylbenzene	0·355	13·46	5·09	0·094	14·26	5·09	0·245	15·07	6·09
1,2-Epoxy-3-phenylpropane ...	1·52	11·15	3·97	—	—	—	0·325	14·76	5·96
1,2-Epoxy-3-phenoxypropane	3·09	12·97	5·67	—	—	—	1·57	13·35	5·64

DISCUSSION

Normal Reactions.—The values of k_{1N} at 35° (Table 2) for the reactions of the three epoxides with benzylamine show the same qualitative effect of substituents as in the reactions with secondary amines.[1] Thus, a phenyl substituent (in 1,2-epoxyethylbenzene) gives the lowest rate and a phenoxymethyl substituent (in 1,2-epoxy-3-phenoxypropane) the highest rate. The effects are, however, quantitatively different and an analysis in terms of the modified [1] Taft equation:

$$\log k - \log k_0 = \rho\sigma^* + \rho' E_s$$

gives the values of ρ, ρ' and k_0 shown in Table 3. The Table also contains the corresponding values for the reactions with piperidine, morpholine, and diethanolamine.[1] Although these values are far from certain (because of the small number of epoxides studied and frequent deviations from linear free-energy relations), the reactions with benzylamine are very probably less susceptible to the polar effect of substituent groups (smaller ρ) and more susceptible to the steric effect of substituent groups (larger ρ') than the corresponding reactions with secondary amines. The direction of change is unexpected in both cases.

Benzylamine is intermediate in basic strength between piperidine and morpholine and, as Table 4 shows, it is a weaker nucleophile towards epoxides than either of these secondary amines. It should, therefore, show a greater susceptibility to the polar effect of substituents in its reactions since weaker reagents are generally more selective. Further, a primary amine, with only one bulky group attached to nitrogen, might be expected to be less susceptible to the steric effect of substituents in its reactions than a secondary amine with two bulky groups attached to nitrogen. Even though piperidine and morpholine might be considered special types of secondary amine, with their bulky groups held back by ring-formation, diethanolamine would certainly be expected to be more susceptible to steric effects than benzylamine. In fact, however, the steric reaction constant, ρ', for benzylamine is greater than for diethanolamine.

TABLE 3. *Reactions of epoxides in* 99·8% *ethanol at* 35°. (k_0 is the rate constant for the reaction of the parent 1,2-epoxypropane.)

Reagent	ρ	ρ'	10^4k_0 (l. mole^{-1} sec.$^{-1}$)	Reagent	ρ	ρ'	10^4k_0 (l. mole^{-1} sec.$^{-1}$)
Piperidine	0·8	0·2	3	Diethanolamine	0·9	0·2	0·3
Morpholine	0·9	0·2	1	Benzylamine ...	0·5	0·4	2

TABLE 4. *Rate constants* (k_{1N}) *interpolated to* 35°, *and Arrhenius parameters.* (k_{1N} and A in l. mole^{-1} sec.$^{-1}$; E in kcal. mole^{-1}.)

	1,2-Epoxyethylbenzene			1,2-Epoxy-3-phenylpropane			1,2-Epoxy-3-phenoxypropane		
	10^4k_{1N}	E	log A	10^4k_{1N}	E	log A	10^4k_{1N}	E	log A
Piperidine[1]	3·43	14·42	6·76	4·63	13·81	6·45	14·62	13·87	7·09
Morpholine[1]	1·47	14·40	6·38	1·54	12·97	5·39	5·56	13·30	6·17
Diethanolamine[1] ...	0·271	15·59	6·53	0·436	13·60	5·27	1·70	14·00	6·15
Benzylamine	0·355	13·46	5·09	1·52	11·15	3·97	3·09	12·97	5·67

The clue to these anomalies appears in the values of the Arrhenius parameters in Table 4. The benzylamine reactions have lower energies and entropies of activation than those of the secondary amines. The slowness of the benzylamine reactions is due, in fact, not to a high energy of activation, but to a low entropy of activation; this can be interpreted as indicating more strictly defined transition states. Such strictness could be due either to more closely packed transition states for the benzylamine reactions (more bond-forming and less bond-stretching) or to greater increased solvation in the formation of the benzylamine transition states than in the formation of the secondary amine transition states. While it is true that the transition state from a primary amine (similar to the conjugate acid of a secondary amine) will be more highly solvated than that from a secondary amine (similar to the conjugate acid of a tertiary amine[6]), this effect alone does not seem capable of explaining either the low value of ρ for the benzylamine reactions or the high proportion of abnormal product in the reaction of benzylamine with 1,2-epoxyethylbenzene. We assume, therefore, that the benzylamine transition states are more closely packed (*i.e.*, with both partial bonds shorter) than the secondary amine transition states. Thus the geometry of benzylamine is such that its nitrogen atom, with only one CH_2 group directly attached, can approach quite close to the normal carbon atom of the epoxide, to give a transition state relatively free from steric compression. In each of the secondary amines, on the other hand, the nitrogen atom has two CH_2 groups directly attached to it and is incapable of such a close approach to the epoxide carbon atom (because of steric interaction between the two CH_2 groups and the epoxide substituent group R). The situation is illustrated in Figs. 1 and 2. In the transition states for the benzylamine reactions, depicted in Fig. 1, the steric interaction between the benzyl-CH_2 group and the substituent group R can be eliminated by suitable rotation of the benzylamino-group around the carbon–nitrogen partial bond. Such a condition, however, imposes a restriction on the movement of the benzylamino-group and would lead to a reduced entropy of activation. In the transition states for the piperidine reactions, depicted in Fig. 2, the steric interaction between the two piperidino-CH_2 groups adjacent to the nitrogen atom and the substituent group R is not likely to be significantly affected by rotation of the piperidino-group around the carbon–nitrogen partial bond and in this case, therefore, there will be no restriction on the movement of the piperidino-group and the entropy of activation should be higher than for the benzylamine reactions. The energy of activation should also be higher because of the unavoidable steric interactions. (Although these

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[6] Bell and Trotman-Dickenson, *J.*, 1949, 1288; Trotman-Dickenson, *J.*, 1949, 1293; Bell and Bayles, *J.*, 1952, 1518; Pearson and Williams, *J. Amer. Chem. Soc.*, 1954, **76**, 258.

interactions are reduced by the lengthening of the carbon–nitrogen partial bond, there must be a limit to this lengthening, beyond which there would be a net increase of energy.)

While it seems to us that the above explanation of the lower energies and entropies of activation and of the lower value of ρ for the benzylamine reactions is the most satisfactory one, there will undoubtedly be superimposed on this a differential solvation effect. The NH_2 group of the benzylamine transition states can involve hydrogen bonds to the oxygen atoms of two ethanol molecules, whereas the NH group of the secondary amine transition states can form a hydrogen bond to the oxygen atom of only one ethanol molecule. Since this increased solvation is likely to be considerably more important for the transition states than for the free amine molecules [6] it will also give rise to lower energies and entropies of activation for the benzylamine reactions.

FIG. 1. *Transition states for benzylamine reactions: relatively little freedom of movement of benzylamino-group.*

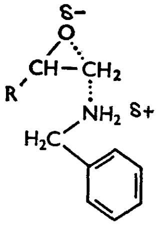


FIG. 2. *Transition states for piperidine reactions: relatively great freedom of movement of piperidino-group.*

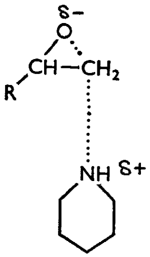
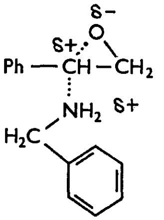


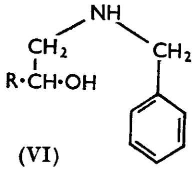
FIG. 3. *Transition state for 1,2-epoxyethylbenzene–benzylamine reaction.*



Abnormal Reaction.—Of the three epoxides studied only 1,2-epoxyethylbenzene gives detectable reaction at the abnormal position. This cannot be ascribed entirely to steric effects, since phenyl has the greatest steric retarding effect of the three substituent groups studied (greatest negative E_s value). Nor can it be due to polar effects, since the value of the polar substituent constant σ^* for phenyl is intermediate between those for benzyl and phenoxymethyl. The only remaining effect of substituent groups on reactivity is the conjugative effect and this is almost certainly responsible for the appearance of abnormal product in the reaction betwen 1,2-epoxyethylbenzene and benzylamine. If we assume that this reaction takes place by a " modified S_N2 mechanism," [2] with a transition state in which both partial bonds are longer than is usual for S_N2 transition states, then it is likely that such a transition state will carry a fractional positive charge on the central carbon atom (Fig. 3). Clearly such a charge would be stabilised by conjugation with the adjacent benzene ring. Such conjugation could not occur with the other two epoxides and these, therefore, undergo no abnormal reaction. That 1,2-epoxyethylbenzene undergoes no abnormal reaction with piperidine, morpholine or diethanolamine [1] must be due to the fact that, with these more bulky amines, the primary steric effect is more important. Thus the conditions necessary for formation of abnormal product in epoxide reactions appear to be that (*a*) the attacking atom of the reagent must be sufficiently unencumbered to keep primary steric effects to a minimum, and (*b*) the " abnormal " carbon atom of the epoxide must be directly attached to a group capable of stabilising a positive charge by conjugative electron-release (or possibly, in some cases, by hyperconjugative or inductive electron-release).

It can be seen in Table 2 that the normal and the abnormal reaction of 1,2-epoxyethylbenzene with benzylamine have the same entropy of activation, but that the abnormal reaction has a higher energy of activation. The lower rate for the abnormal reaction (about 4 times slower at 35°) is, therefore, entirely due to the higher energy of activation (0·8 kcal. mole^{-1} higher). This higher energy of activation is the expected result of attack at a carbon atom adjacent to the bulky phenyl group, rather than at a position one carbon atom further away. The identity of the two entropies of activation is almost certainly fortuitous. The two reactions would not be expected to be isoentropic, and preliminary results for the reactions of nuclear-substituted 1,2-epoxyethylbenzenes with benzylamine show that, in these cases, the normal and the abnormal reaction do not have the same entropy of activation.

Second Reactions.—As already pointed out, the values of the rate constants and Arrhenius parameters for the second reactions (Table 2) are less accurate than for the first reactions. Nevertheless, if it is assumed that the second reactions consist entirely of reaction of the normal product of the first reaction at the normal position of the epoxide, the results are of the expected magnitude. Although the reagents are not the same for the three reactions, they can all be represented by (VI; R = Ph, Ph·CH_2, or Ph·OCH_2), and variations in R will not greatly affect the reactivity of the nitrogen atom. To a first approximation, therefore, the three second reactions may be regarded as the reactions of the three epoxides with a single secondary amine and their rates show the same qualitative sequence as those for the three epoxides with the secondary amines, piperidine, morpholine, and diethanolamine (cf. Table 4). The Arrhenius parameters are also similar to those for the reactions with piperidine, morpholine, and diethanolamine.


(VI)

It is noteworthy that the rate constants for the second reactions are not very much smaller than the total rate constants for the first reactions (2—5 times smaller at 35°). This means that, unless a large excess of benzylamine is used, the second reaction will become significant at quite an early stage in the progress of the first. There is no reason to suppose that the situation will be significantly different for reactions with other primary amines and it follows therefore that, when a primary amine is used to cross-link an epoxide resin,[1] each primary amino-group is likely to combine with two epoxide groups under the conditions normally used.

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