

REACTIONS OF AMINES WITH EPOXIDE GROUP. II.*

KINETICS OF REACTION OF N,N'-DISUBSTITUTED AROMATIC DIAMINES WITH *p*-TOLYL GLYCIDYL ETHER

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N,N'-Dimethyl and N,N'-diethyl derivatives of some aromatic diamines have been synthesized, and the kinetics of their reactions with *p*-tolyl glycidyl ether have been measured. From the rate constants k_1 and k_2 it has been found that the reactivities of the both amino groups with respect to the epoxide group do not differ much from each other, not even in the conjugated diamines.

Kinetics of nucleophilic addition reaction of *ortho*-, *meta*- and *para*-substituted anilines with the epoxide group of 4-tolyl glycidyl ether were studied in our previous paper¹. The rate constant ratio of reactions of the primary and secondary hydrogen atoms of the amino group with epoxide group was found to be within 3.5 and 4.5, no dependence being observed between the ratio k_1/k_2 and the nature of substituent at the aromatic ring.

The aim of this work was to find in what way the completed reaction of the first amino group with epoxide group affected the reactivity of the remaining free amino group in the case of both conjugated and non-conjugated aromatic diamines. N,N'-Dimethyl derivatives of 1,4-diaminobenzene, benzidine, 4,4'-diaminodiphenylmethane and 4,4'-diaminodiphenyl sulphone, and N,N'-diethyl-4,4'-diaminodiphenylmethane were used as model substances in the kinetic measurements. The diamines were chosen to avoid as much as possible the mutual steric interactions of the both reaction centres.

EXPERIMENTAL

Reagents

N,N'-Diethyl-4,4'-diaminodiphenylmethane was prepared by condensation of N-ethylaniline with formaldehyde according to the procedure given for synthesis of 4,4'-diaminodiphenylmethane². The product was purified by two distillations, b.p. 193–195°C/1 Torr; for C₁₇H₂₂N₂ (254.4) calculated: 80.25% C, 8.66% H, 11.01% N; found: 80.10% C, 8.95% H, 11.32% N.

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N,N'-Dimethyl-4,4'-diphenyl sulphone: 5 g 4,4'-dichlorodiphenyl sulphone, 45 ml 20% aqueous methylamine and 0.3 g Cu_2Cl_2 were heated in a sealed ampoule at 220°C 24 h. The product was dissolved in 10% hydrochloric acid, precipitated with 10% sodium hydroxide solution, and crystallized from a mixture ethanol-water 2 : 1. Yield 3 g, m.p. 170–172°C. For $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ (276.4) calculated: 60.82% C, 5.84% H, 10.14% N; found: 61.11% C, 6.12% H, 9.74% N.

N,N'-Dimethyl-4,4'-diaminodiphenylmethane and 1,4-bis-(methylamino)benzene: A solution of 184 g (0.96 mol) *p*-toluenesulphonyl chloride in 250 ml acetone was added to a solution of 0.4 mol of the respective diamine in 400 ml acetone and 100 ml pyridine. The mixture was boiled under reflux condenser 30 minutes and poured onto ice. The precipitate was allowed to crystallize. The product was purified by crystallization (in the second case only boiling) from acetone and gave no colouration with 4-dimethylaminobenzaldehyde (test for primary amines). The *N,N'*-bis(*p*-toluenesulphonyl) derivatives of 1,4-diaminobenzene and 4,4'-diaminodiphenylmethane were dissolved each in 1500 ml mixture acetone-water 2 : 1. After addition of 400 ml 10% sodium hydroxide solution, 150 g (120%) dimethyl sulphate was added with shaking during 2 h. The products were isolated, dried and then heated with 75 ml concentrated sulphuric acid on boiling water bath for 2 hours. The solutions were diluted with 150 ml water each and neutralized with 25% sodium hydroxide solution, and the amines were extracted with diethyl ether. The products were distilled under reduced pressure 1 Torr: 1,4-bis(methylamino)benzene b.p. 100°C, m.p. 51–52°C (53°C ref.³); *N,N'*-dimethyl-4,4'-diaminodiphenylmethane b.p. 200 to 203°C, m.p. 51–53°C; for $\text{C}_{15}\text{H}_{18}\text{N}_2$ (226.3) calculated: 79.62% C, 8.02% H, 12.38% N; found: 79.57% C, 8.02% H, 12.74% N.

N,N'-Dimethylbenzidine: 34 g (0.065 mol) 4,4'-bis(*p*-toluenesulphonylamino)biphenyl was dissolved in 2000 ml acetone whereafter 1000 ml water and 100 ml 10% sodium hydroxide solution were added. During 2 h 35 g dimethyl sulphate was added to the boiling mixture, and boiling was continued for further 2 h. The precipitated product was isolated and recrystallized from dioxane, whereafter it was heated with 5 parts of 25% hydrochloric acid in a sealed ampoule at 160–170°C 6 hours. The amine formed was extracted with diethyl ether, the solvent was evaporated, and the residue was recrystallized from aqueous ethanol. Yield 9 g (65%) of the substance melting at 92–93°C (81–82°C ref.⁴). For $\text{C}_{14}\text{H}_{16}\text{N}_2$ (212.3) calculated: 79.20% C, 7.60% H, 13.19% N; found: 79.23% C, 7.87% H, 13.28% N.

Purity of the *N,N'*-disubstituted diamines was checked by thin-layer chromatography using the plates Silufol UV₂₅₄ and mixtures benzene-methanol 8 : 2 and benzene-ethyl acetate 8 : 2. The spots were made visible by spraying with acetone solution of *p*-nitrobenzenediazonium tetrafluoroborate. Only traces of impurities were found (probably the respective monomethyl derivatives).

Kinetic Measurements

The kinetic measurements were carried out in 99.9% ethanol at 60°C, the concentrations of amines and *p*-tolyl glycidyl ether being 0.05–0.2 and 0.1–0.4 mol/l, respectively (stoichiometric ratio of amine to epoxide was maintained in each case). The reaction was followed by measuring of the concentration of the epoxide compound. The proper arrangement of the experiments and analytical determination of epoxide groups were described in the previous paper¹. The reaction of 1,4-bis(methylamino)benzene with *p*-tolyl glycidyl ether was carried out under nitrogen gas, because otherwise the reaction mixture turned dark due probably to oxidation of the amine.

The rate constant k_1 and k_2 were calculated by the "times ratio" method devised by Frost and Schwemer^{5,6} and two iteration methods described by Svrbely and Blauer^{7,8} which we used in our previous work, too.¹

TABLE I
Results of Kinetic Measurements

Substance	$cTGE^a$ mol l^{-1}	$k_1 \cdot 10^2$ $\text{l mol}^{-1} \text{min}^{-1}$	$k_2 \cdot 10^2$ $\text{l mol}^{-1} \text{min}^{-1}$	k_1/k_2
N,N'-Diethyl-4,4'-diaminodiphenyl- methane	0.4	2.33	1.79	1.30
	0.2	2.75	1.73	1.59
N,N'-Dimethyl-4,4'-diamino- diphenylmethane	0.4	3.60	2.42	1.49
	0.2	4.33	2.80	1.55
1,4-Bis(methylamino)- benzene	0.1	23.0	14.7	1.57
	0.1	23.5	14.9	1.58
N,N'-Dimethylbenzidine	0.4	2.56	2.03	1.27
	0.2	3.18	2.09	1.52
N,N'-Dimethyl-4,4'-diamino- diphenyl sulphone	0.2	0.0589	0.0449	1.31

^a Concentration of *p*-tolyl glycidyl ether in reaction mixture.

RESULTS AND DISCUSSION

Both amino-hydrogen atoms can react in competitive consecutive reactions of amines with epoxide groups. That is why the aromatic diamines, used in this work for determination of reactivity ratio of the both amino groups, were substituted by a methyl or ethyl group at each amino group. Thus for calculation of the reaction constants k_1 and k_2 we could use the methods the reliability of which was verified in our previous work¹. In the present work, too, a very good agreement has been found between the values of rate constants obtained by individual methods. The values given for k_1 and k_2 in Table I are the arithmetic mean values of those obtained by the individual methods. As it could be expected, the rate constants of the reaction of N,N'-diethyl-4,4'-diaminodiphenylmethane with *p*-tolyl glycidyl ether are lower than those of the corresponding dimethyl derivative, because ethyl group causes a greater steric hindrance at the secondary amino-hydrogen atom. The decrease of the reaction velocity was about 35%. The rate constant ratio k_1/k_2 , however, was not practically influenced by this change. This fact suggests that the ratio of reactivities of the both amino groups of primary diamines is not practically changed by the introduction of N-methyl group. The ratio k_1/k_2 is relatively low and practically the same for all compounds of the series under investigation. A low ratio k_1/k_2 was expected in the case of reactions of N,N'-dimethyl-4,4'-diaminodiphenylmethane and N,N'-dimethyl-4,4'-diaminodiphenyl sulphone with *p*-tolyl glycidyl ether, as the conjugation of the both benzene nuclei was interrupted by the methylene resp. sulphone group, and hence only inductive effects could operate between the both amino groups, which

could be neglected with respect to large distance. On the other hand, a quite different rate constant ratio was expected for the reactions of *p*-tolyl glycidyl ether with *N,N'*-dimethylbenzidine and especially 1,4-bis(methylamino)benzene, their amino groups being conjugated. From the results found it can be concluded that the substitution of one amine-hydrogen of an aromatic diamine by a glycidyl residue does not-substantially affect the reactivity of the remaining free amino group in its reaction with epoxide group, provided that there is no steric hindrance between the first glycidyl residue introduced and the second amino group.

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