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Reaction of Epoxides. V.[1] 1,3-Dipolar Cycloaddition Reaction of Epoxides with Carbon-Nitrogen Double Bond Compounds

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The reaction of epoxides with several conjugated C–N double bond compounds was attempted. Aromatic aldazines were found to undergo criss-cross cycloaddition toward epoxides. On the other hand, aromatic ketazines gave the oxazolidines formed by the cycloaddition of one molecule of epoxides to one of the C–N double bond of the ketazines. Moreover, in the reaction with N,N'-bis-benzylidene-*p*-phenylenediamine and N,N'-*p*-phenylene-bis-methylidenaniline, cycloaddition of two molecules of epoxides to two C–N double bonds of these compounds occurred to give the corresponding *p*-phenylene-bis-oxazolidines.

The 1,3-dipolar cycloaddition reactions of epoxides to C-N double and triple bonds have been widely investigated and it has been well known that epoxides react with Schiff bases,[3] isocyanates,[4] isothiocyanates,[5] carbodiimides[6] and nitriles[7] to give oxazolidines, oxazolidones, oxazolidinethiones, oxazolidinimides and oxazolines. In this study, the reaction of epoxides with aromatic aldazines and ketazines in which adjacent conjugated C-N double bonds are involved in the molecules were attempted.

Reaction with Aromatic Aldazines

Benzaldazine and *p*-tolualdazine were allowed to react with 2,3-epoxypropyl phenyl and *p*-tolyl ether.[8] The reaction was successfully carried out by heating one mole of the azines with six moles of the epoxides in benzene in the presence of stannic chloride catalyst under reflux to give a corresponding product. The yield of the product varied, depending upon the amount of the epoxides and the conditions employed, but in all cases were below 20%. The mass spectrum of the product exhibited the abundant molecular ion peak corresponding to the 1:2 aldazine–epoxide adduct and the elemental analysis was also in agreement with the adduct.

As the structure assignable for the 1:2 aldazine–epoxide adduct, the following three compounds are possible. 1) The adduct (I) by the electrophilic attack of epoxides to the methylidene carbon atom of the C-N double bonds of aromatic aldazines. 2) The normal

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[1] Part IV: M. Furukawa, M. Sugita, Y. Kojima and S. Hayashi, *Chem. Pharm. Bull.* (Tokyo), **21**, 2099 (1973).

[2] Location: *Oe-hon machi, Kumamoto.*

[3] *a*) R. Oda, M. Okano, S. Tokiura and A. Miyano, *Bull. Chem. Soc. Japan*, **35**, 1216 (1962); *b*) S. Hayashi, M. Furukawa, Y. Fujino, H. Okabe and T. Nakao, *Chem. Pharm. Bull.* (Tokyo), **19**, 2404 (1971).

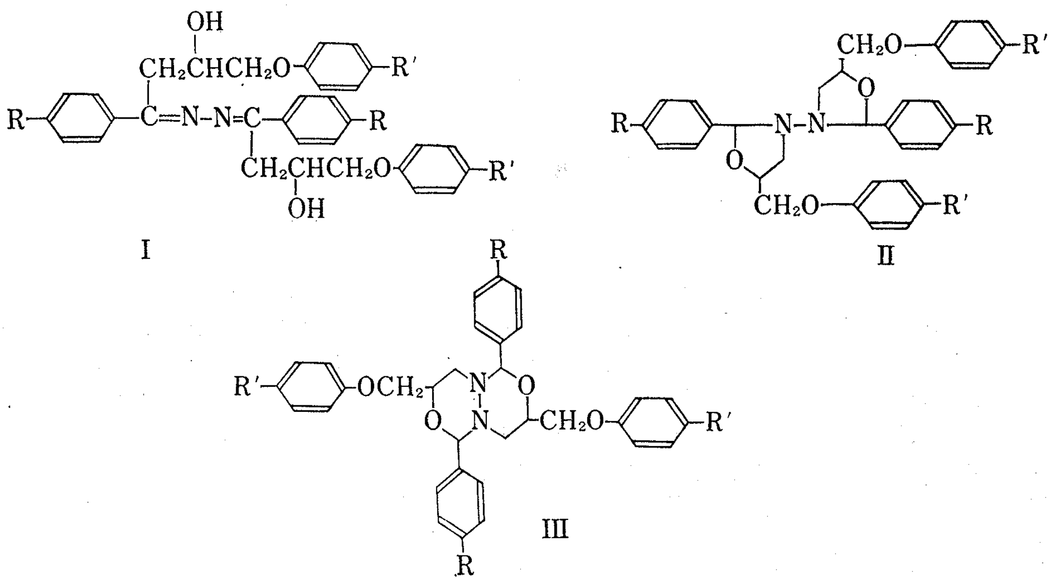
[4] *a*) K. Gulbins and K. Hamann, *Angew. Chem.*, **70**, 705 (1958); *b*) G.P. Speranza and W.J. Peppel, *J. Org. Chem.*, **23**, 1922 (1958).

[5] *a*) G.A. Razuvaev, A.N. Egorochkin, V.S. Etlis and A.P. Sineokov, *Chem. Abstr.*, **59**, 13789*c* (1963); *b*) V.S. Etlis, A.P. Sineokov and G.A. Razuvaev, *ibid.* **61**, 3112*a* (1964).

[6] *a*) K. Gulbins and K. Hamann, *Chem. Ber.*, **94**, 3287 (1961); *b*) K. Gulbins, M. Roth and K. Hamann, *Angew. Chem.*, **73**, 434 (1961).

[7] *a*) R. Oda, M. Okano, S. Tokiura and F. Misumi, *Bull. Chem. Soc. Japan*, **35**, 1219 (1962); *b*) M. Taguchi and K. Nagano, *Chem. Abstr.*, **71**, 124477*w* (1969).

[8] S. Hayashi, M. Furukawa, Y. Fujino, T. Nakao and K. Nagato, *Chem. Pharm. Bull.* (Tokyo), **19**, 1594 (1971).



I

II

III

Chart 1

cycloaddition product (II) of two molecules of epoxides to the two C-N double bonds of aromatic aldazines. 3) The criss-cross cycloaddition product (III) of two molecules of epoxides to the conjugated C-N double bonds of aromatic aldazines. R and R′ stand for hydrogen atom and methyl group. In all cases, a position isomer due to the orientation of the cleavage of the epoxide ring is possible.

In the infrared (IR) spectrum of the adduct, no absorption assignable to a hydroxy group was observed. Therefore, the assigned structure I should be apparently denied. The IR and nuclear magnetic resonace (NMR) spectra were consistent with the other assigned structure II and III, though it did not allow an unequivocal choice between II and III. Among these two possible structures, II may be anticipated to show a peak of relatively high intensity at a *m/e* value of one half that of the molecular ion peak in the mass spectrum, because of the

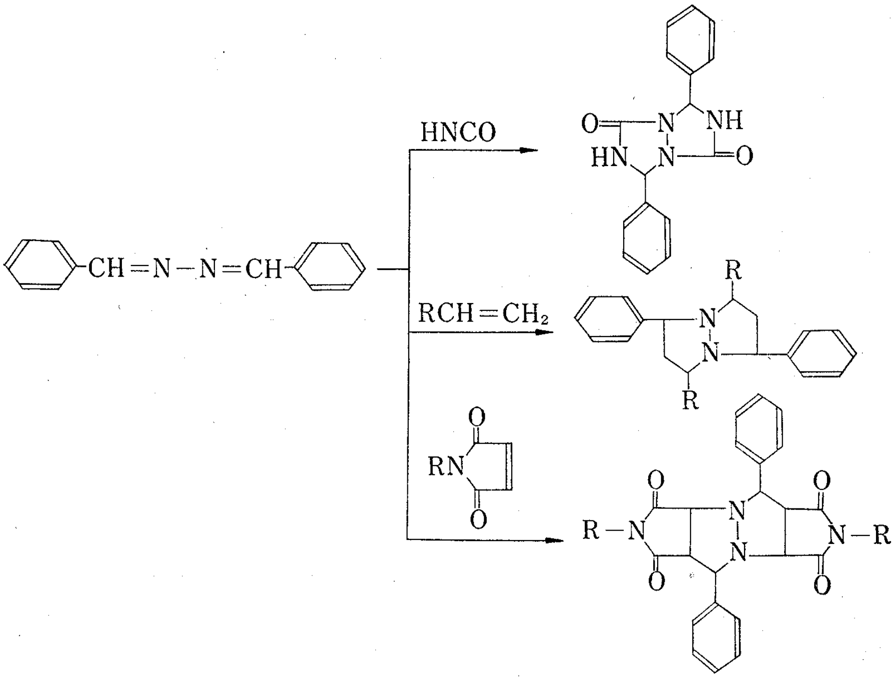


Chart 2

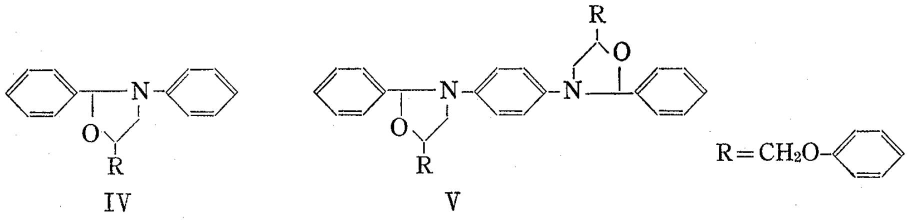


Chart 3

most facile cleavage of the relatively weak N-N bond. However, no such a peak was observed. On the other hand, it has been shown that criss-cross cycloaddition is general for the reaction of aromatic aldazines with certain α,β-unsaturated compounds, such as cyanic acid, thiocyanic acid, isocyanates[9,10] and various electron-deficient olefins[11] in which the double bond is terminal. On considering these facts, the structure III due to the criss-cross cycloaddition would be more likely for the adduct. In order to clarify the distinction between II and III, 2,3-diphenyl-5-phenoxymethyloxazolidine (IV)[3b] and *p*-phenylene-3,3′-bis(2-phenyl-5(or 4)-phenoxymethyloxazolidine) (V), which are quite analogous to II, were synthesized and their spectra were compared with those of the product obtained by the reaction between benzaldazine and 2,3-epoxypropyl phenyl ether. Though the IR and NMR spectra of IV and V exhibited quite analogous pattern, they were different from those of the product. If the product is type II adduct, the formation of 1:1 aldazine–epoxide adduct which is formed by cycloaddition of epoxide with one of C-N double bond of aldazine might be also possible, but in any ratio of the reactants no trace of such a product was observed by pursuance with thin-layer chromatography (TLC). On the basis of these results, it is reasonable to conclude that the structure III is the most likely for the adduct.

Reaction with Aromatic Ketazines

Conjugated ketazines showed behaviors quite different from aldazines toward epodixes. Methylphenylketazine and methyl-*p*-tolylketazine were used as ketazines and allowed to react with 2,3-epoxypropyl phenyl and *p*-tolyl ether. Under the similar reaction conditions, the reaction proceeded with decomposition. Treatment of the ketazines with the epoxides, with a 1:2 molar ratio of the reactants, in benzene in the presence of stannic chloride catalyst at room temperature for 3—4 hours, however, gave successfully a product in a comparatively good yield. The mass spectrum of the product exhibited the molecular ion peak corresponding to 1:1 ketazine–epoxide adduct as the most abundant peak. The elemental analysis agreed with that of such a product.

To elucidate the structure of the product, the spectra were compared with those of IV. The IR spectrum of the product formed by the reaction between methylphenylketazine and 2,3-epoxypropyl phenyl ether exhibited a quite similar pattern to that of IV. The mass spectrum of the product also showed a fragmentation pattern analogous to that of IV and abundant peaks corresponding to demethylation and dephenylation from the molecular ion at *m/e* $(M-15)^+$ and $(M-77)^+$, respectively, were observed. Furthermore, the peaks corresponding to acetonitrile and benzonitrile at *m/e* 41 and 103, respectively, were also observed. By these results, it is presumed that the product would be oxazolidine compound formed by the cycloaddition of one molecule of epoxides to one of the C-N double bond of ketazines, though it is impossible to distinguish the possible isomers due to the orientation of the cleavage of the epoxide ring.

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9) *a*) J.R. Bailey and N.H. Moore, *J. Am. Chem. Soc.*, **39**, 279 (1917); *b*) J.R. Bailey and A.T. McPherson, *ibid.*, **39**, 1322 (1917).

10) O. Tsuge, M. Tashiro and S. Kanamasa, The 22nd Annual Meeting of Chemical Society of Japan, 1969.

11) *a*) J. Van Alphen, *Rec. Trav. Chim.*, **61**, 892, 895 (1942); *b*) D.B. Dutt and P.C. Guha, *J. Indian Chem. Soc.*, **27**, 151 (1950); *c*) V. Bruckner, I. Kandel and J. Kovacs, *Acta Chim. Acad. Sci. Hung.*, **1**, 230 (1951); *d*) M. Haring and T. Wagner-Jauregg, *Helv. Chim. Acta*, **40**, 852 (1957).

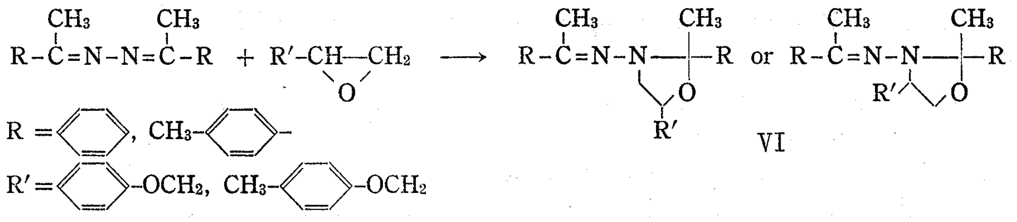


Chart 4

By considering the abundant peaks observed in the mass spectrum, the plausible fragmentation process would be presumed as follows.

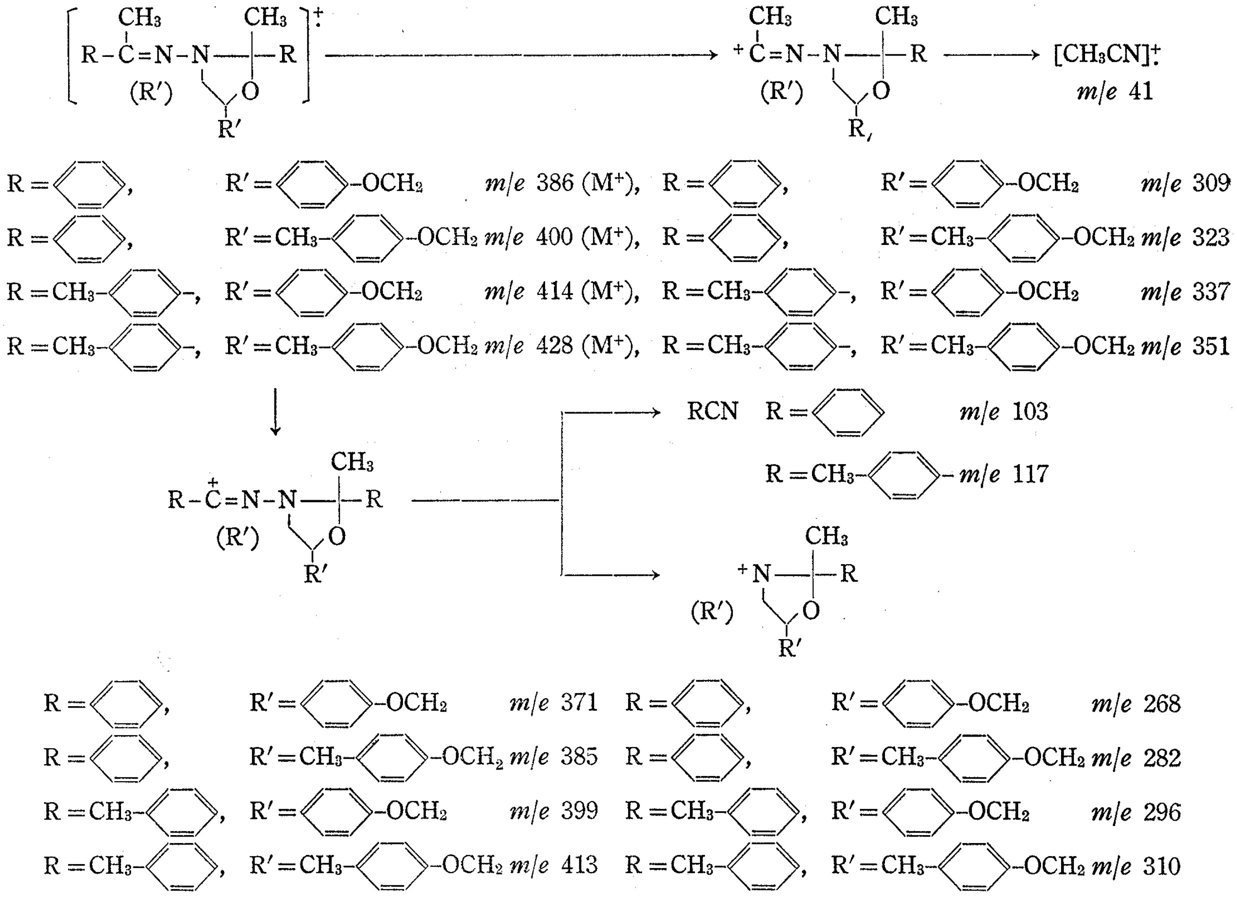


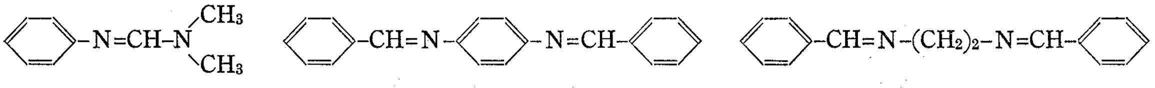
Chart 5

Support for the assigned structure VI was also provided by the NMR spectrum. The material methylphenylketazine exhibited two singlets assignable to the methyl group in extremely close region near τ 7.70 in the NMR spectrum. The two singlets would be probably due to the mixture of the steric isomers, syn and anti forms, of the ketazine. The NMR spectrum of the product analogously showed the characteristic two singlets assignable to the methyl group substituted to the carbon atom of the C-N double bond near τ 7.55 and a singlet due to the methyl group in another ring near τ 8.23.

The same product was also obtained as the only product even in the use of a great excess of epoxides, no trace of any other expected 1: 2 ketazine–epoxide adduct being isolated. Moreover, the product of 1: 1 adduct was allowed to react with epoxides, but no reaction occurred and the materials were recovered unchanged. It would depend upon the decreased nucleophilic property of the adjacent nitrogen atom of C-N double bond due to the oxazolidine ring formed.

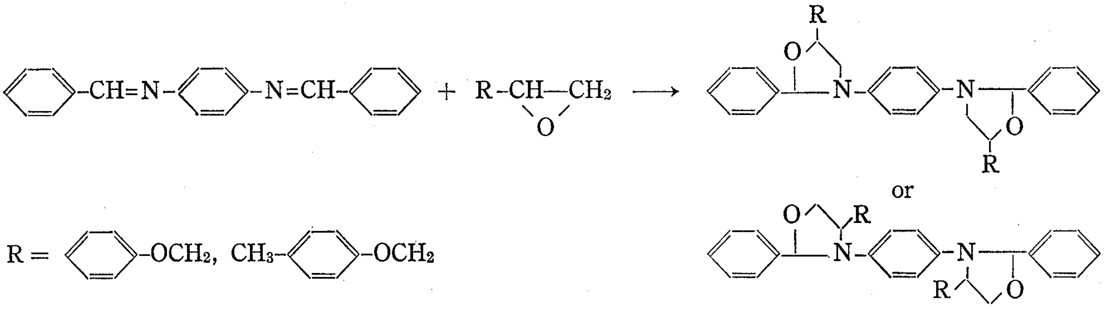
Reaction with N,N′-Bis-benzylidene-*p*-phenylenediamine and N,N′-*p*-Phenylene-bis-methylidenaniline

In the preceding paper,[3b] we reported that benzalaniline of Schiff base reacted with 2,3-epoxypropyl phenyl ether in carbon tetrachloride in the presence of stannic chloride catalyst to give 2,3-diphenyl-5- and 4-phenoxymethyloxazolidine, whose IR and NMR spectra were almost equal. We newly attempted to carry out the reaction between Schiff base of dimethylformaldehyde, N,N-dimethyl-N′-phenylformamidine (VII), and 2,3-epoxypropyl phenyl ether under the similar reaction conditions, but it resulted in failure and the materials were recovered unchanged. We further attempted the reaction of bis-Schiff base in which *p*-phenylene or ethylene group interposed between two C-N double bonds, N,N′-bis-benzylidene-*p*-phenylenediamine (VIII) and N,N′-bis-benzylidenethylenediamine (IX), with 2,3-epoxypropyl phenyl and *p*-tolyl ether. The reaction was successfully carried out with VIII to give a product in a low yield, but not with IX. The product obtained by the reaction with VIII was found to be 1: 2 bis-Schiff base–epoxide adduct by the mass spectrum in which the molecular ion peak was observed as the most abundant peak. The elemental analysis of the product was also in good agreement with such an adduct. The IR and NMR spectra of the product were quite similar to those of IV. Therefore, it is assumed that the product would be N,N′-*p*-phenylene-bis-oxazolidine (V) which was formed by cycloaddition of two molecules of the epoxide to two C-N double bonds, though these spectral data do not allow an equivocal choice between the possible two position isomers due to the orientation of the epoxide ring cleavage. The assigned structure V was supported by NMR spectrum which exhibited a multiplet due to the methylene group at τ 6.80—5.75, a broad multiplet assignable to the methine group between two methylene groups at τ 5.65—5.20 and two singlets assignable to the methine group adjacent to the phenyl group near τ 4.30. The two singlets due to the methine group would be attributed to the mixture of *cis*-trans steric isomers.



VII VIII IX

Chart 6



V

Chart 7

In the mass spectrum of the product, the fragment ion peak corresponding to dephenylation at *m*/*e* $(M-77)^+$ was observed. It was quite similar to the fragmentation of 2,3-diphenyl-4(or 5)-phenoxymethyloxazolidine.

On consideration of these results, it is reasonable to conclude that the structure of the product might be N,N′-*p*-phenylene-bis-4(or 5)-substituted oxazolidine (V).

The reaction of bis-Schiff base in which two C-N double bonds are directly combined at the carbon atoms, benzildianil (X), with 2,3-epoxypropyl phenyl ether was also attempted,

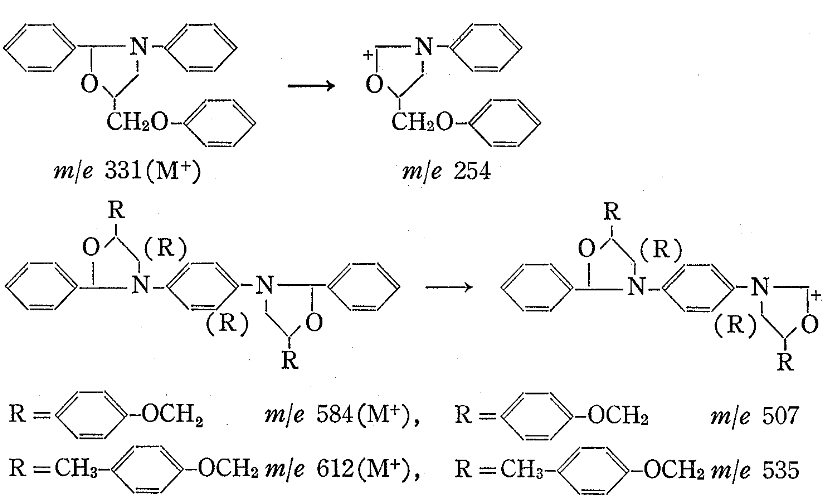
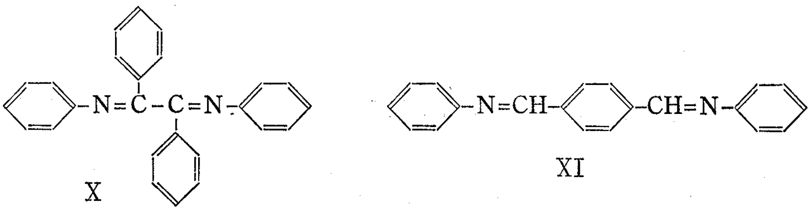


Chart 8

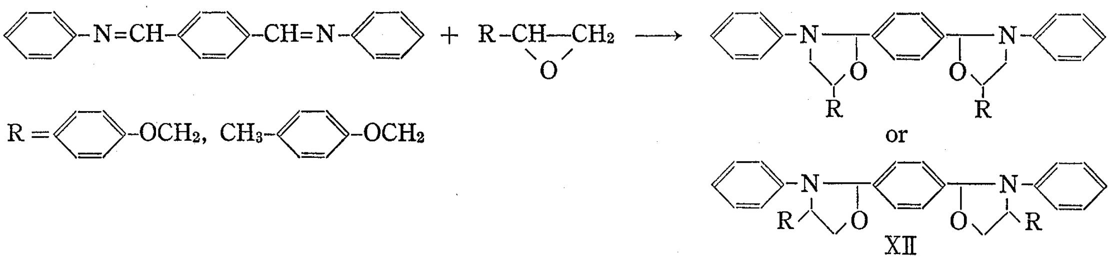
but it resulted in failure, no trace of any product being isolated and the unchanged material being recovered, probably because of the steric hindrance due to the bulkyness of the phenyl group combined to the carbon atom of C-N double bond. However, N,N'-*p*-phenylene-bis-methylidenaniline (XI) in which a *p*-phenylene group was interposed between the carbon atoms of two C-N double bonds successfully reacted with 2,3-epoxypropyl phenyl and *p*-tolyl ether under the similar reaction conditions to give a product in a comparatively good yield.



X XI

Chart 9

By the elemental analysis and the mass spectrum which exhibited the molecular ion peak as the most abundant peak, the product was found to be 1:2 bis-Schiff base–epoxide adduct. The IR and NMR spectra of the product exhibited a quite similar pattern to those of V. Therefore, the product is presumed to be *p*-phenylene-bis-3-phenyl-4(or 5)-substituted oxazolidine (XII) which was formed by cycloaddition of two molecules of the epoxide to the two C-N double bonds. In the NMR spectrum, multiplets assignable to the methylene hydrogens at τ 6.90—5.75, a broad multiplet due to the methine hydrogen between two methylene groups at τ 5.60—5.10 and two singlets attributed to the methine hydrogen adjacent to the *p*-phenylene group near τ 4.00 were observed, providing a support for the assigned structure. The two singlets would be due to the mixture of *cis-trans* steric isomers. In the mass spectrum, the fragment ion peak corresponding to the oxazolidine ring formed by the cleavage between *p*-phenylene group and oxazolidine ring was observed as the most abundant peak. Such a



XII

Chart 10

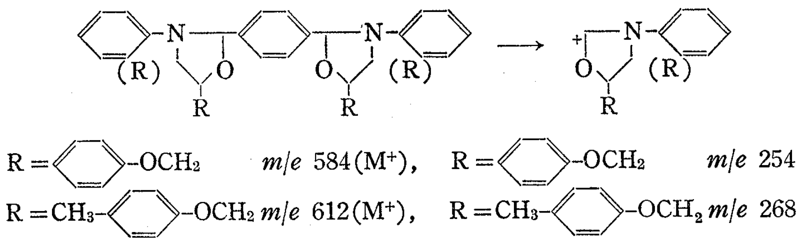
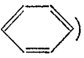
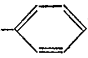
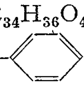
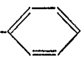


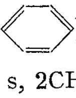
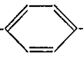
Chart 11

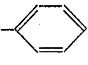
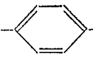
cleavage was quite analogous to that of IV. These results provide a sufficient support for the assigned structure (XII), though it could not distinguish the two possible position isomers.

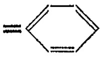
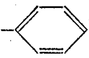
Experimental

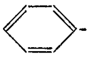
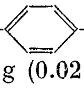
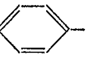
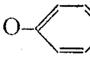
1,5-Diphenyl-3,7-bis-phenoxymethyl-[1,3,4]oxadiazino[4,3-*c*]-[1,3,4]oxadiazine (III, R=R′=H)——To a solution of 2.08 g (0.01 mole) of benzaldazine and 9.0 g (0.06 mole) of 2,3-epoxypropyl phenyl ether in 60 ml of dry benzene was added with stirring a solution of 0.52 g (0.002 mole) of anhyd. stannic chloride in 20 ml of dry benzene below 10° during 20 min and the solution was heated with stirring for 60 hr under reflux. After cooling, the solution was shaken with 50 ml of H_2O and basified with 0.1 N NaOH aqueous solution. The benzene layer was separated, washed with H_2O, dried over Na_2SO_4 and evaporated under reduced pressure. To the residue was added a suitable amount of EtOH and the precipitates deposited on allowing to stand at room temperature were collected by filtration and recrystallized from EtOH to give 0.2 g (3.9%) of needles melting at 140°. *Anal.* Calcd. for $C_{32}H_{32}O_4N_2$: C, 75.57; H, 6.34; N, 5.51. Found: C, 75.45; H, 6.15; N, 5.74. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1250 (C–O–); 1015 (C–O–C). NMR ($CDCl_3$) τ: 6.70—5.35 (10H, m, $2CH_2$–CH–CH_2); 4.43 (2H, s, 2CH–); 3.20—2.35 (20H, m, aromatic hydrogens). Mass Spectrum *m/e*: 508 (M^+).

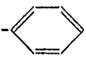
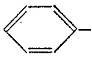
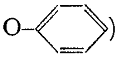
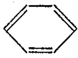
1,5-Diphenyl-3,7-bis-*p*-tolyloxymethyl-[1,3,4]oxadiazino[4,3-*c*]-[1,3,4]oxadiazine (III, R=H, R′=CH_3)——To a solution of 2.08 g (0.01 mole) of benzaldazine and 9.84 g (0.06 mole) of 2,3-epoxypropyl *p*-tolyl ether in 60 ml of dry benzene was added with stirring a solution of 0.52 g (0.002 mole) of anhyd. stannic chloride in 20 ml of dry benzene below 10° during 20 min and the solution was heated with stirring for 38 hr under reflux. The mixture was then treated by the same procedure as described above and the resulting product was recrystallized from benzene–EtOH to give 0.7 g (13%) of prisms melting at 173—173.5°. *Anal.* Calcd. for $C_{34}H_{36}O_4N_2$: C, 76.09; H, 6.76; N, 5.22. Found: C, 76.45; H, 6.43; N, 5.44. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1245 (C–O––CH_3); 1018 (C–O–C). NMR ($CDCl_3$) τ: 7.72 (6H, s, $2CH_3$); 6.75—5.40 (10H, m, $2CH_2$–CH–CH_2); 4.47 (2H, s, 2CH–); 3.25—2.30 (18H, m, aromatic hydrogens). Mass Spectrum *m/e*: 536 $(M)^+$.

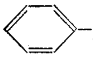
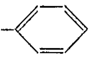
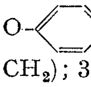
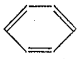
1,5-Bis-*p*-tolyl-3,7-bis-phenoxymethyl-[1,3,4]oxadiazino[4,3-*c*]-[1,3,4]oxadiazine (III, R=CH_3, R′=H)——To a solution of 2.36 g (0.01 mole) of *p*-tolualdazine and 9.0 g (0.06 mole) of 2,3-epoxypropyl phenyl ether in 60 ml of dry benzene was added with stirring a solution of 0.52 g (0.002 mole) of anhyd. stannic chloride in 20 ml of dry benzene below 10° during 20 min and the mixture was heated with stirring for 62 hr under reflux. The mixture was then treated by the same procedure as described above to give 0.6 g (11%) of needles melting at 149°. *Anal.* Calcd. for $C_{34}H_{36}O_4N_2$: C, 76.09; H, 6.76; N, 5.22. Found: C, 76.48; H, 6.65; N, 4.84. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1250 (C–O–); 1033 (C–O–C). NMR ($CDCl_3$) τ: 7.69 (6H, s, $2CH_3$); 6.75—5.40 (10H, m, $2CH_2$–CH–CH_2); 4.47 (2H, s, 2CH––); 3.20—2.45 (18H, m, aromatic hydrogens). Mass Spectrum *m/e*: 535 (M^+).

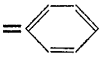
1,5-Bis-*p*-tolyl-3,7-bis-*p*-tolyloxymethyl-[1,3,4]oxadiazino[4,3-*c*]-[1,3,4]oxadiazine (III, R=R′=CH_3)——To a solution of 2.36 g (0.01 mole) of *p*-tolualdazine and 9.84 g (0.06 mole) of 2,3-epoxypropyl *p*-tolyl ether in 60 ml of dry benzene was added with stirring a solution of 0.52 g (0.002 mole) of anhyd. stannic chloride in 20 ml of dry benzene below 10° during 20 min and the mixture was heated with stirring for 30 hr under reflux. The mixture was then treated by the same procedure as described above to give 0.9 g (16%) of needles melting at 151—151.5°. *Anal.* Calcd. for $C_{36}H_{40}O_4N_2$: C, 76.56; H, 7.14; N, 4.96. Found: C, 77.04; H, 7.03; N, 4.86. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1240 (C–O––CH_3); 1030 (C–O–C). NMR ($CDCl_3$) τ: 7.71 (12H, s, $4CH_3$); 6.75—5.45 (10H, m, $2CH_2$–CH–CH_2); 4.50 (2H, s, 2CH––); 3.25—2.45 (16H, m, aromatic hydrogens). Mass Spectrum *m/e*: 564 (M^+).

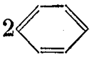
2-Methyl-2-phenyl-3-methylphenylmethylidenimino-4(or 5)-phenoxymethyloxazolidine (VI, R=**-, R′=****-OCH$_2$)**——To a solution of 2.36 g (0.01 mole) of N,N′-bis-methylphenylmethylidenehydrazine and 3.0 g (0.02 mole) of 2,3-epoxypropyl phenyl ether in 60 ml of dry benzene was added with stirring a solution of 0.52 g (0.002 mole) of anhyd. stannic chloride in 20 ml of dry benzene below 10° during 30 min and the mixture was stirred at room temperature for additional 2 hr. The mixture was then shaken with 50 ml of H_2O and neutralized with 0.1 N NaOH aqueous solution. The benzene layer was separated, dried over Na_2SO_4 and evaporated. To the residue was added a suitable amount of EtOH and the precipitates deposited on allowing to stand at room temperature were collected by filtration and recrystallized from EtOH to give 1.3 g (34%) of needles melting at 106.8—107.3°. *Anal.* Calcd. for $C_{25}H_{26}O_2N_2$: C, 77.69; H, 6.78; N, 7.25. Found: C, 78.15; H, 6.79; N, 7.32. IR ν_{max}^{KBr} cm^{-1}: 1240 (C–O–); 1038 (C–O–C). NMR ($CDCl_3$) τ: 8.19 (3H, s, N–C–CH_3); 7.54 and 7.50 (3H, s, CH_3–C=N); 7.30—5.25 (5H, m, CH_2–CH–CH_2); 3.27—2.00 (15H, m, aromatic hydrogens). Mass Spectrum *m/e*: 386 (M^+).

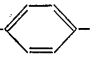
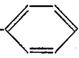
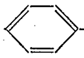
2-Methyl-2-phenyl-3-methylphenylmethylidenimino-4(or 5)-*p*-tolyloxymethyloxazolidine (VI, R=**-, R′=CH$_3$-****-OCH$_2$)**——To a solution of 2.36 g (0.01 mole) of N,N′-bis-methylphenylmethylidenehydrazine and 3.28 g (0.02 mole) of 2,3-epoxypropyl *p*-tolyl ether in 60 ml of dry benzene was added with stirring a solution of 0.52 g (0.002 mole) of anhyd. stannic chloride in 20 ml of dry benzene below 10° during 30 min and the mixture was stirred at room temperature for additional 1.5 hr. The mixture was then treated by the same procedure as described above to give 2.4 g (60%) of needles melting at 109°. *Anal.* Calcd. for $C_{26}H_{28}O_2N_2$: C, 77.97; H, 7.05; N, 7.00. Found: C, 77.66; H, 6.85; N, 6.63. IR ν_{max}^{KBr} cm^{-1}: 1245 (C–O––CH_3); 1037 (C–O–C). NMR ($CDCl_3$) τ: 8.21 (3H, s, N–C–CH_3); 7.76 (3H, s, O––CH_3); 7.55 and 7.52 (3H, s, CH_3–C=N); 7.45—5.15 (5H, m, CH_2–CH–CH_2); 3.45—2.03 (14H, m, aromatic hydrogens). Mass Spectrum *m/e*: 400 (M^+).

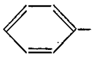
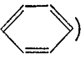
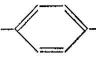
2-Methyl-2-*p*-tolyl-3-methyl-*p*-tolylmethylidenimino-4(or 5)-phenoxymethyloxazolidine(VI,R=CH$_3$-**-, R′=****-OCH$_2$)**——To a solution of 2.64 g (0.01 mole) of N,N′-bis-methyl-*p*-tolylmethylidenehydrazine and 3.0 g (0.02 mole) of 2,3-epoxypropyl phenyl ether in 60 ml of dry benzene was added with stirring a solution of 0.52 g (0.002 mole) of anhyd. stannic chloride in 20 ml of dry benzene below 10° during 30 min and the mixture was stirred at room temperature for additional 3 hr. The mixture was then treated by the same procedure as described above to give 5.7 g (84%) of needles melting at 102—102.5°. *Anal.* Calcd. for $C_{27}H_{30}O_2N_2$: C, 78.23; H, 7.30; N, 6.76. Found: C, 77.94; H, 7.71; N, 6.86. IR ν_{max}^{KBr} cm^{-1}: 1245 (C–O–); 1044 (C–O–C). NMR ($CDCl_3$) τ: 8.25 (3H, s, N–C–CH_3); 7.66 (3H, s, –CH_3); 7.58 and 7.55 (3H, s, CH_3–C=N); 7.50—5.20 (5H, m, CH_2–CH–CH_2); 3.30—2.10 (13H, m, aromatic hydrogens). Mass Spectrum *m/e*: 414 (M^+).

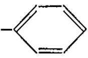
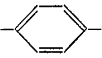
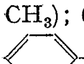
2-Methyl-2-*p*-tolyl-3-methyl-*p*-tolylmethylidenimino-4(or 5)-*p*-tolyloxymethyloxazolidine (VI, R=CH$_3$–**-, R′=CH$_3$-****-OCH$_2$)**——To a solution of 2.64 g (0.01 mole) of N,N′-bis-methyl-*p*-tolylmethylidenehydrazine and 3.28 g (0.02 mole) of 2,3-epoxypropyl *p*-tolyl ether in 60 ml of dry benzene was added with stirring a solution of 0.52 g (0.002 mole) of anhyd. stannic chloride in 20 ml of dry benzene below 10° during 30 min and the mixture was stirred at room temperature for additional 3 hr. The mixture was then treated by the same procedure as described above to give 4.1 g (96%) of needles melting at 114—114.5°. *Anal.* Calcd. for $C_{28}H_{32}O_2N_2$: C, 78.47; H, 7.53; N, 6.54. Found: C, 78.10; H, 7.46; N, 6.79. IR ν_{max}^{KBr} cm^{-1}: 1254 (C–O––CH_3); 1050 (C–O–C). NMR ($CDCl_3$) τ: 8.26 (3H, s, N–C–CH_3); 7.77 (3H, s, O––CH_3); 7.67 (3H, s, –CH_3); 7.60 and 7.57 (3H, s, CH_3–C=N); 7.50—5.25 (5H, m, CH_2–CH–CH_2); 3.40—2.15 (12H, m, aromatic hydrogens). Mass Spectrum *m/e*: 428 (M^+).

***p*-Phenylene-3,3′-bis(2-phenyl-5(or 4)-phenoxymethyloxazolidine) (V, R=****-OCH$_2$)**——To a mixture of 2.84 g (0.01 mole) of N,N′-bis-benzylidene-*p*-phenylenediamine, 3.0 g (0.02 mole) of 2,3-epoxypropyl phenyl ether and 60 ml of dry CCl_4 was added with stirring a solution of 0.52 g (0.002 mole) of anhyd. stannic chloride in 20 ml of dry CCl_4 below 10° during 40 min and the mixture was stirred at room temperature for additional 18 hr. The mixture was then poured with stirring into 50 ml of H_2O and basified with 0.2 N NaOH aqueous solution. The CCl_4 layer was separated, dried over Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was recrystallized from benzene–EtOH to give 1.1 g (19%) of needles melting at 170°. *Anal.* Calcd. for $C_{38}H_{36}O_4N_2$: C, 78.06; H, 6.21; N, 4.79. Found: C, 77.79; H, 6.04; N, 4.68. IR ν_{max}^{KBr} cm^{-1}:

1245 (C–O–); 1040 (C–O–C). NMR ($CDCl_3$) τ: 6.80—5.75 (8H, m, $2CH_2$–C–CH_2); 5.55—5.20 (2H, broad, m, 2C–CH–C); 4.30 and 4.16 (2H, s, 2–CH–N); 3.65—2.40 (24H, m, aromatic hydrogens). Mass Spectrum *m/e*: 584 (M^+).

***p*-Phenylene-3,3′-bis(2-phenyl-5(or 4)-*p*-tolyloxymethyloxazolidine) (V, R=CH_3––OCH_2)**——To a mixture of 2.84 g (0.01 mole) of N,N′-bis-benzylidene-*p*-phenylenediamine, 3.28 g (0.02 mole) of 2,3-epoxypropyl *p*-tolyl ether and 60 ml of dry CCl_4 was added with stirring a solution of 0.52 g (0.002 mole) of anhyd. stannic chloride in 20 ml of dry CCl_4 below 10° during 40 min and the mixture was stirred at room temperature for additional 20 hr. The mixture was then treated by the same procedure as described above to give 0.9 g (15%) of needles melting at 160—161°. *Anal.* Calcd. for $C_{40}H_{40}O_4N_2$: C, 78.40; H, 6.58; N, 4.57. Found: C, 78.61; H, 6.60; N, 4.19. IR ν_{max}^{KBr} cm^{-1}: 1240 (C–O––CH_3); 1025 (C–O–C). NMR ($CDCl_3$) τ: 7.75 (6H, s, $2CH_3$); 6.80—5.80 (8H, m, $2CH_2$–C–CH_2); 5.65—5.25 (2H, m, 2C–CH–C); 4.38 and 4.25 (2H, s, 2 –CH); 3.70—2.40 (22H, m, aromatic hydrogens). Mass Spectrum *m/e*: 612 (M^+).

***p*-Phenylene-2,2′-bis(3-phenyl-5(or 4)-*p*henoxymethyloxazolidine) (XII, R=–OCH_2)**——To a mixture of 2.84 g (0.01 mole) of N,N′-*p*-phenylene-bis-methylidenaniline, 3.0 g (0.02 mole) of 2,3-epoxypropyl phenyl ether and 60 ml of dry CCl_4 was added with stirring a solution of 0.52 g (0.002 mole) of anhyd. stannic chloride in 20 ml of dry CCl_4 below 10° during 40 min and the mixture was stirred at room temperature for additional 23 hr. The mixture was then poured with stirring into 50 ml of H_2O and basified with 0.2 N NaOH aqueous solution. The CCl_4 layer was separated, dried over Na_2SO_4 and evaporated. The residue was added to a suitable amount of benzene–EtOH and allowed to stand at room temperature overnight. The precipitates deposited were collected by filtration and recrystallized from benzene–EtOH to give needles melting at 178—179°. *Anal.* Calcd. for $C_{38}H_{36}O_4N_2$: C, 78.06; H, 6.21; N, 4.79. Found: C, 78.48; H, 6.15; N, 4.74. IR ν_{max}^{KBr} cm^{-1}: 1253 (C–O–); 1045 (C–O–C). NMR ($CDCl_3$) τ: 6.75—5.75 (8H, m, $2CH_2$–CH–CH_2); 5.57—5.10 (2H, broad m, 2C–CH–C); 4.14 and 3.95 (2H, s, CH––CH); 3.68—2.45 (24H, m, aromatic hydrogens). Mass Spectrum *m/e*: 584 (M^+).

***p*-Phenylene-2,2′-bis(3-phenyl-5(or 4)-*p*-tolyloxymethyloxazolidine) (XII, R=CH_3––OCH_2)**——To a mixture of 2.84 g (0.01 mole) of N,N′-*p*-phenylene-bis-methylidenaniline, 3.28 g (0.02 mole) of 2,3-epoxypropyl *p*-tolyl ether and 60 ml of dry CCl_4 was added with stirring a solution of 0.52 g (0.002 mole) of anhyd. stannic chloride in 20 ml of dry CCl_4 below 10° during 50 min and the mixture was stirred at room temperature for additional 18 hr. The mixture was then treated by the same procedure as described above to give 1.9 g (31%) of needles melting at 173°. *Anal.* Calcd. for $C_{40}H_{40}O_4N_2$: C, 78.40; H, 6.58; N, 4.57. Found: C, 78.70; H, 6.74; N, 4.59. IR ν_{max}^{KBr} tm^{-1}: 1251 (C–O––CH_3); 1050 (C–O–C). NMR ($CDCl_3$) τ: 7.75 (3H, s, CH_3); 6.90—5.75 (8H, m, $2CH_2$–C–CH_2); 5.60—5.15 (2H, broad m, 2C–CH–C); 4.17 and 3.97 (2H, s, CH––CH); 3.70—2.45 (22H, m, aromatic hydrogens). Mass Spectrum *m/e*: 612 (M^+).

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