BRIEF COMMUNICATIONS

# REACTION OF PHENYL GLYCIDYL ETHER WITH N-TRIMETHYLSILYLANILINE AND TRIMETHYLSILOXYBENZENE

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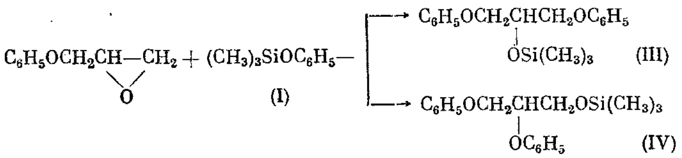
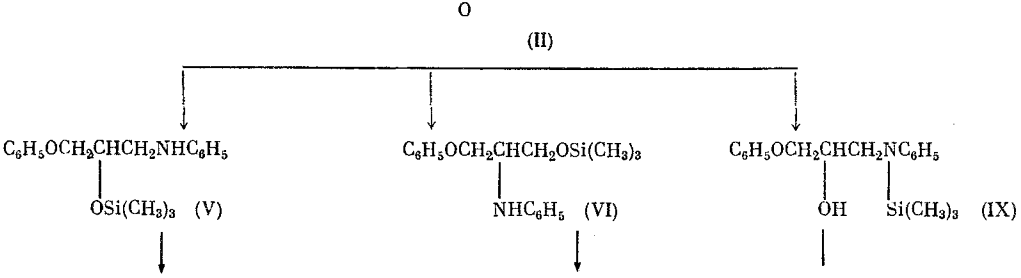
Previously it was shown that silazanes can be used as curing agents for epoxide oligomers (EO) [1, 2]. Taking into account some of the advantages of using silylated compounds as curing agents, we deemed it interesting to make a more detailed study of the model reactions of the α-oxide ring of EO with compounds that contain the $R_3SiO$ and $R_3SiNH$ groups.

The IR spectroscopy method was used to study the reaction of phenyl glycidyl ether (PGE) with trimethylsiloxybenzene (I) and N-trimethylsilylaniline (II). When a mixture of PGE and (I), taken in a 1 : 1 mole ratio, is heated in a stepwise manner from 100 to 250°C the bands in the IR spectrum (Fig. 1), characteristic for the oxirane ring of PGE (3060, 3000, 865 $cm^{-1}$), and the band at 915 $cm^{-1}$, which represents the superimposition of two bands, belonging to the vibrations of the $Ar-O-Si(CH_3)_3$ fragment and the oxirane ring, disappear. Since the bands, caused by the $Si(CH_3)_3$ vibrations (2960, 830 $cm^{-1}$), remain practically unchanged and an increase in the absorption is observed in the region of the stretching vibrations of the ether linkages (1000-1200 $cm^{-1}$), it may be assumed that the reaction goes in the following manner:



A similar picture of the changes in the IR spectrum is observed when a mixture of PGE and (II), taken in a 1 : 1 mole ratio, is heated, and here the bands of the oxirane ring of PGE and the band at 900 $cm^{-1}$, caused by the vibration of the $Ar-\overset{|}{N}-Si(CH_3)_3$ fragment, disappear; the absorption increases in the region of the stretching vibrations of the $C-O$ and $Si-O$ groups (1150-1000 $cm^{-1}$), while the bands of the $Si(CH_3)_3$ group (2960, 830 $cm^{-1}$) remain practically unchanged (Fig. 2).

Beginning with 100°, an increase in the intensity of the band of the stretching vibrations of the OH group is observed during the stepwise heating. This means that the reaction of the oxirane ring at the $N-Si$ bond is accompanied by the usual reaction of opening the oxirane ring of the secondary amino group (with the formation of compounds (VII), (VIII), and (IX)). It may be assumed that (IX) is not formed, since the 900 $cm^{-1}$ band of the $Ar-\overset{|}{N}-Si$ fragment, which contains the $N-Si$ bond, is absent in the spectra of the heated mixture. As a result, the following reaction scheme may be proposed:



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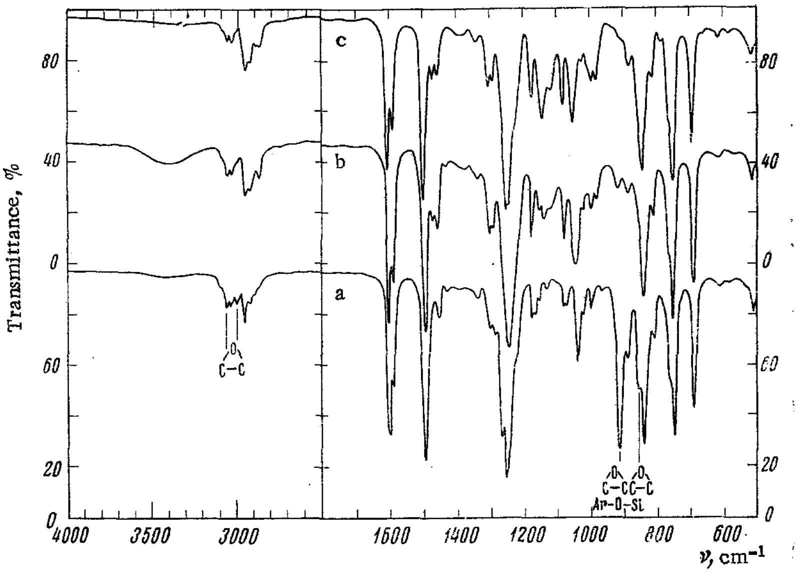
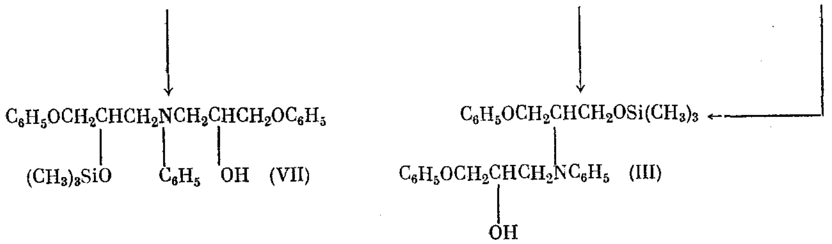


Fig. 1. Infrared spectra: a) of starting mixture of phenyl glycidyl ether (PGE) and trimethylsiloxybenzene (1 : 1 mole ratio); b) of mixture after heating at 175° (10 h); c) of 2-trimethylsiloxy-1,3-diphenoxypropane (III).



$$\mathrm{C_6H_5OCH_2\underset{(CH_3)_3SiO}{CH}CH_2\underset{C_6H_5}{N}CH_2\underset{OH}{CH}CH_2OC_6H_5}$$ (VII)

$$\mathrm{C_6H_5OCH_2CHCH_2OSi(CH_3)_3}$$
$$\mathrm{C_6H_5OCH_2\underset{OH}{CH}CH_2NC_6H_5}$$ (III)

If the mixture of PGE and (II) is not heated in a stepwise manner, but instead directly at 175° for 10 h, then the spectra exhibit a slight increase in the intensity of the absorption band of the stretching vibrations of the OH group and a complete disappearance of the 900 cm$^{-1}$ band (see Fig. 2, $\mathrm{Ar-\overset{|}{N}-Si{<}}$ fragment), with a retention of the intensity of the band at 3370 cm$^{-1}$ of the stretching vibrations of the N — H bond. In the given case, the reaction of the oxirane ring with N-trimethylsilylaniline proceeds at a faster rate at the Si — N bond to give compounds (V) and (VI).

On the basis of the known data regarding the reactions of α-oxides with amines [3], we postulated that the reaction of the oxirane ring of PGE with compounds (I) and (II) should go at the O — Si and N — Si bonds to give compounds (III) and (V), samples of which were specially synthesized. A comparison of the spectral characteristics (position of the bands, halfwidth of the bands, and ratio of intensities) of these compounds and of the heated mixtures of PGE with (I) and (II) disclosed that compounds (III) and (V) make an important contribution in the spectra of the mixtures. Based on an estimate of the optical density of the 830 cm$^{-1}$ band the amount of (III) in the mixture is ~60%.

As a result, it may be concluded that the reactions of trimethylsilyl-substituted derivatives of phenol (I) and aniline (II) with the oxirane ring of PGE proceed at the O — Si and N — Si bonds with the predominant formation of compounds (III) and (V), which, based on the IR spectral data, are stable when heated to 250°. Decomposition at the O — Si bond begins above this temperature with the liberation of hexamethyldisiloxane, the band at 830 cm$^{-1}$ [$\mathrm{(CH_3)_3-Si}$ group] disappears, and the absorption in the region of the stretching vibrations of the OH group increases.

## EXPERIMENTAL

The reaction of phenyl glycidyl ether with trimethylsiloxybenzene and N-trimethylsilylaniline was run in ampuls, sealed under argon, that were heated in a stepwise manner from 25 to 250°C, with holding at 25°C

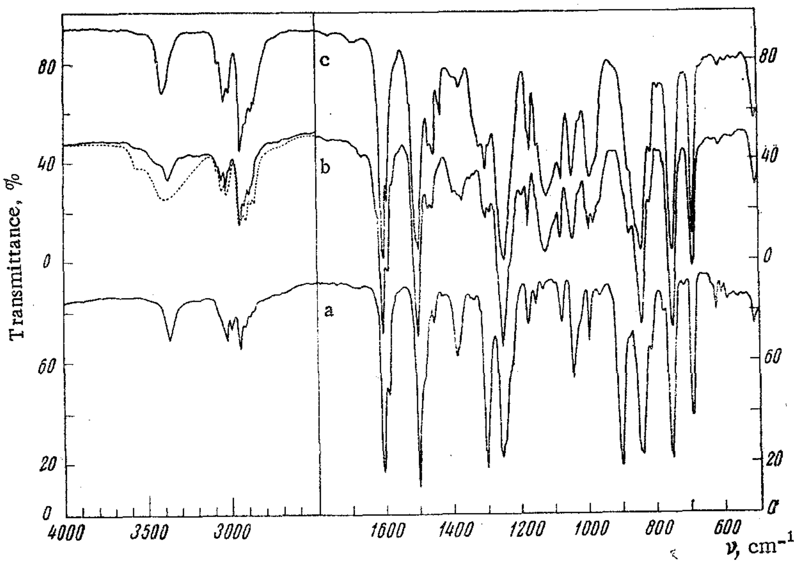


Fig. 2. Infrared spectra: a) of starting mixture of PGE and N-trimethylsilylaniline (1 : 1 mole ratio); b) of mixture after heating at 175° for 10 h (solid line) and after stepwise heating from 25 to 175° (dotted line); c) of 1-phenoxy-2-trimethylsiloxy-3-anilinopropane (V).

intervals for 10 h each. The IR spectra of the samples were taken on a Perkin – Elmer-457 spectrometer (between NaCl plates).

Trimethylsiloxybenzene (I). A mixture of 40.1 g (0.0426 mole) of phenol and 121 ml (0.639 mole) of N-trimethylsilyldiethylamine was stirred at 120-125° in an argon stream. The diethylamine was distilled off during the silylation, and the cessation of its liberation after 5-6 h of condensation testified to completion of reaction. The excess N-trimethylsilyldiethylamine was distilled off at atmospheric pressure, and the residue was vacuum-distilled to give 58.7 g (88%) of (I), bp 80-82° (26 mm); $n_D^{20}$ 1.4782 [4].

N-Trimethylsilylaniline (II). Synthesized in a similar manner from 78.4 ml (0.858 mole) of aniline and 326 ml (1.715 mole) of N-trimethylsilyldiethylamine to give 96.6 g (68%) of (II), bp 88-92° (10-12 mm); $n_D^{20}$ 1.5833 [5].

2-Trimethylsiloxy-1,3-diphenoxypropane (III). Synthesized in a similar manner from 1.5 g (0.006 mole) of 2-hydroxy-1,3-diphenoxypropane and 2.34 ml (0.012 mole) of N-trimethylsilyldiethylamine to give 1.2 g (62%) of (III), bp 144-146° (3 mm); $n_D^{20}$ 1.5257. Found: C 68.30; H 7.75; Si 8.77%. $C_{18}H_{24}SiO_3$. Calculated: C 68.32; H 7.64; Si 8.77%.

1-Phenoxy-2-trimethylsiloxy-3-anilinopropane (V). Synthesized in a similar manner from 16.7 g (0.069 mole) of 1-phenoxy-2-hydroxy-3-anilinopropane and 13.7 ml (0.072 mole) of N-trimethylsilyldiethylamine to give 16.0 g (75%) of (V), bp 214° (8 mm); $n_D^{20}$ 1.5466. Found: C 68.52; H 7.75; Si 8.34%. $C_{18}H_{25}NSiO_2$. Calculated: C 68.53; H 7.99; Si 8.90%.

## CONCLUSIONS

It was shown by the IR spectroscopy method that the reaction of phenyl glycidyl ether with trimethylsiloxybenzene and N-trimethylsilylaniline proceeds via insertion of the opened epoxide ring between the Si – O and Si – N atoms.

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# BISAMINOPHENYLQUINOXALINES

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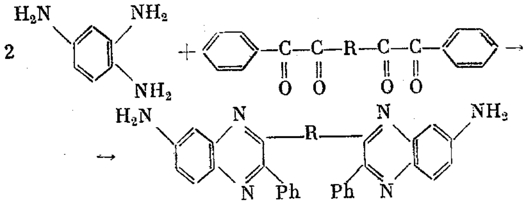
Aromatic diamines are widely used as the starting compounds in polycondensation reactions and, in particular, in the synthesis of high-molecular-weight polyamides [1] and polyimides [2].

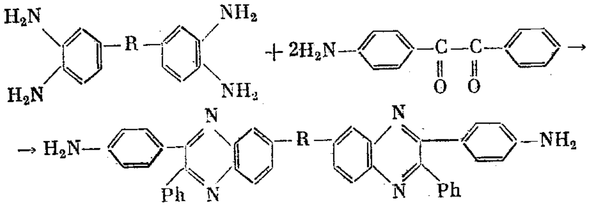
The present paper is devoted to developing methods for the preparation of some new aromatic diamines, and specifically the bisaminophenylquinoxalines, which are used in the synthesis of heat-resistant polyimidophenylquinoxalines [3].

The synthesis of the type A bisaminophenylquinoxalines was based on the reaction of 1,2,4-triaminobenzene hydrochloride with bis(α-diketones) in either dioxane — water or DMF — water mixture [4].



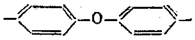
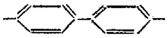
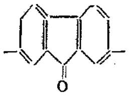
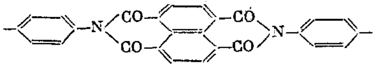
(A)

The type B bisaminophenylquinoxalines were obtained by the reaction of aromatic tetraamines with 4-aminobenzil in refluxing ethanol [5]



(B)

TABLE 1. Type A Bisaminophenylquinoxalines

| Compound | R | Yield, % | mp., °C | Found/Calculated, % C | H | N |
|---|---|---|---|---|---|---|
| (I) |  | 93 | 333–335 | 78,11<br>79,05 | 4,50<br>4,68 | 16,03<br>16,27 |
| (II) |  | 95 | 205–207 | 78,07<br>78,02 | 4,79<br>4,64 | 13,32<br>13,81 |
| (III) |  | 94 | 256–258 | 80,13<br>81,06 | 4,49<br>4,76 | 13,67<br>14,18 |
| (IV) |  | 90 | 308–310 | 78,81<br>79,59 | 4,12<br>4,24 | 13,00<br>13,58 |
| (V) |  | 87 | 460 | 74,92<br>75,69 | 3,94<br>3,75 | 12,92<br>13,08 |

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