SYNTHESIS OF A SYMMETRICAL DITHIIRANE

M. A. Allakhverdiev, V. M. Farzaliev,
and Ch. I. Mamedov

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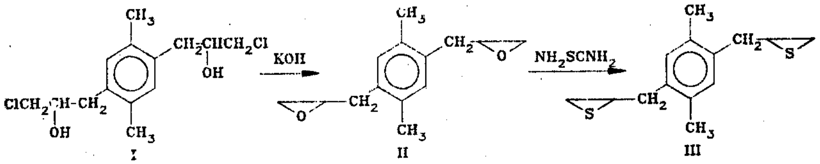
The reaction of p-xylene with epichlorohydrin in the presence of aluminum chloride gave 1,4-dimethyl-2,5-bis(1-chloro-2-hydroxypropyl)benzene, which serves as the starting compound for the synthesis of the corresponding symmetrical dithiirane.

Thiiranes are the least-studied organosulfur compounds [1], and dithiiranes have not been studied adequately. Only a few studies have been devoted to this class of compounds [2-5].

The aim of the present research was to develop a method for the synthesis of a new representative of symmetrical dithiiranes, viz., 1,4-dimethylbis(2,3-epithiopropyl)benzene (III). The product of the reaction of p-xylene with epichlorohydrin in the presence of aluminum chloride was used as the starting compound. The reaction of p-xylene with epichlorohydrin in the presence of aluminum chloride in a ratio of 24:1:1 at 0°C, which leads to 3-chloro-1-(2,5-dimethylphenyl)-2-propanol in 47% yield, was studied in [6].

We investigated this reaction in the case of p-xylene:epichlorohydrin:aluminum chloride ratio of 3:1:0.5 at 5-10°C and obtained 1,4-dimethyl-2,5-bis(1-chloro-2-hydroxypropyl)benzene (I) in 35% yield. These results show that increasing the amounts of epichlorohydrin and aluminum chloride leads to the formation of dichlorohydrin I. In our case we did not observe the formation of 3-chloro-1-(2,5-dimethylphenyl)-2-propanol. Dichlorohydrin I in dry ether and in the presence of potassium hydroxide was converted to the corresponding dioxirane II in 72% yield, which reacts with thiourea at 0°C to give III in 55% yield.



It should be noted that an attempt to obtain dithiirane III by the method in [7] was unsuccessful. Only a polymeric product is always formed as a result of the reaction.

A broad absorption band at 3430-3450 cm^{-1}, which is retained upon dilution of a solution in CCl_4 to 0.005 mole/liter, is observed in the IR spectrum of dichlorohydrin I; this excludes the possibility of intermolecular association but is characteristic for an intramolecular OH...Cl bond [8]. In addition to this, the IR spectrum of I contains intense bands at 890 and 1725 cm^{-1}, which correspond to a 1,2,4,5-tetrasubstituted benzene ring [9, 10].

The IR spectrum of epoxide II does not contain an absorption band characteristic for the OH group, but bands at 830 and 1240 cm^{-1}, which correspond to asymmetrical, symmetrical, and pulsation vibrations of the epoxide ring, are observed; an intense characteristic band at 645 cm^{-1}, which corresponds to the thiirane ring in the symmetrical dithiirane molecule, was identified in the spectrum of thiirane III.

In the PMR spectra of I-III the signals of the protons of two methyl groups bonded to the automatic ring in the 1 and 4 positions are observed in the form of a singlet at 2.1-2.25 ppm, and singlets of two protons of the aromatic ring appear at 6.8-6.9 ppm, which corresponds to a 1,2,4,5-tetrasubstituted benzene ring. In the PMR spectrum of dichlorhydrin I the signals of the protons of CH_2 groups bonded with an aromatic ring and chlorine atom are observed in the form of doublets at, respectively, 2.62 and 3.45 ppm. Signals of a methylidyne proton

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were identified at 3-4 ppm in the form of a multiplet and were superimposed on the signals of the protons of the CH_2Cl group. The signals of the proton of the OH group at 3.35 ppm are also superimposed on the signals of the CH_2Cl group; this was determined by recording the spectrum in the presence of D_2O.

The signals of the protons of the CH group in the PMR spectra of II and III are shifted to stronger field.

EXPERIMENTAL

The IR spectra of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions in CCl_4 were recorded with a Varian T-60 spectrometer with tetramethylsilane (TMS) as the internal standard. The purity of the substances isolated was verified by thin-layer chromatography (TLC) on Brockmann activity II Al_2O_3 in a hexane–ethanol system (5:1).

1,4-Dimethyl-2,5-bis(1-chloro-2-hydroxypropyl)benzene (I). A 92.5-g (1 mole) sample of epichlorohydin was added dropwise with vigorous stirring in the course of 2 h to a cooled (to 5-10°C) suspension of 318 g (3 moles) of p-xylene and 66 g (0.5 mole) of aluminum chloride, after which the temperature of the reaction mixture was raised to room temperature, and the mixture was stirred for another 8 h. It was then decomposed with water acidified with HCl, and the resulting mixture was washed several times with water until the wash water was neutral and dried with calcined $MgSO_4$. The unchanged components were removed by distillation, and the residue was distilled in vacuo to give 24 g (35%) of dichlorohydrin I with bp 102-103°C (0.8 mm), n_D^{20} 1.5282, and d_4^{20} 1.1727. IR spectrum (thin layer): 755 (CH_2Cl); 890, 1725, 1620 (C=C); 2915 (C–H); 3445 cm^{-1} (OH). PMR spectrum: 2.1 (6H, s, CH_3), 2.62 (4H, d, 2-CH_2, 5-CH_2), 3.45 (4H, d, CH_2Cl), 3-4 (2H, m, CH), 3.35 (2H, s, OH), and 6.8 ppm (2H, s, Ar). Found: C 57.9; H 7.1; Cl 24.5%. $C_{14}H_{20}Cl_2O_2$. Calculated: C 57.7; H 6.9; Cl 24.3%.

1,4-Dimethyl-2,5-bis(1,2-epoxypropyl)benzene (II). An 11.2-g (0.2 mole) sample of finely ground KOH was added to a solution of 29.0 g (0.1 mole) of chlorhydrin I in 50 ml of dry ether, and the mixture was heated on a water bath for 1 h. It was then cooled, and the ether layer was decanted and washed three times with water until the wash water was neutral. After drying over $MgSO_4$, the ether was removed by distillation, and the product was distilled in vacuo to give 16 g (72%) of II with bp 79-80°C (1.3 mm), n_D^{20} 1.5120, and d_4^{20} 1.0612. IR spectrum: (thin layer); 890, 1720 (1,2,4,5-tetrasubstituted benzene ring); 830, 1240 (epoxide ring); 1460, 1505, 1620 (C=C) 2940 cm^{-1} (CH). PMR spectrum: 2.2 (6H, s, CH_3), 2.7 (4H, m, 2-CH_2, 5-CH_2), 3.55 (4H, d, CH_2O), 2.8-3.7 (2H, m, CH), and 6.85 ppm (2H, s, Ar). Found: C 77.2; H 8.1%. $C_{14}H_{18}O_2$. Calculated: C 77.0; H 8.3%.

1,4-Dimethyl-2,5-bis(1,2-epithiopropyl)benzene (III). A 15.2-g (0.2 mole) sample of thiourea was added to a solution of 22 g (0.1 mole) of epoxide II in 50 ml of methanol, after which the mixture was stirred slowly for 1 h at 0°C and then for 3 h at 20°C. The organic layer was washed with water and extracted with carbon tetrachloride, and the extract was dried over $MgSO_4$. The solvent was removed by distillation, and the residue was distilled in vacuo to give 14 g (55%) of dithiirane III with bp 90-92°C (0.7 mm), n_D^{20} 1.550, and d_4^{20} 1.0856. IR spectrum (thin layer): 600 (C–S); 645 (thiirane); 890, 1725 (1,2,4,5-tetrasubstituted ring); 1455, 1510, 1620 (C=C); 2935 cm^{-1} (CH). PMR spectrum: 2.25 (6H, s, CH_3), 2.75 (4H, s, 2-CH_2, 5-CH_2), 3.7 (4H, s, CH_2S), 2.7-3.6 (2H, m, CH), and 6.9 ppm (2H, s, Ar). Found: C 66.9; H 7.4; S 25.4%. $C_{14}C_{18}S_2$. Calculated: C 67.2; H 7.2; S 25.6%.

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