Preparation of Diepoxides from Diketones and a Sulfur Ylide

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A method for preparing diepoxides involves the reaction of diketones with dimethylsulfoxonium methylide. Syntheses of diepoxides from two diketones provide examples of the method.

DIEPOXIDES, useful polymer precursors, can be conveniently prepared from diketones and dimethylsulfoxonium methylide. The synthetic method appears to be general for all diketones except α-diketones, which do not react, and β-diketones, which react with the ylide by acid-base neutralization. Examples are described below.

2,5-Hexanedione and dimethylsulfoxonium methylide reacted to give 1,2,5,6-diepoxy-2,5-dimethylhexane. That only 31% of pure product was isolated may be attributed to partial hydrolysis of the slightly water-soluble compound during its isolation, as well as to some monoepoxidation. Higher boiling products, not isolated, were shown by infrared spectra to contain hydroxyl, ketone, and epoxide groups. In similar manner, 1,4-diacetylbenzene and dimethylsulfoxonium methylide reacted to give *p*-bis(1,2-epoxy-1-methylethyl)benzene in 33% yield. In an attempted reaction between benzil and dimethylsulfoxonium methylide, only the starting diketone, benzil, could be obtained from the reaction mixture.

Dimethylsulfoxonium methylide was introduced in 1962 (*1*) as a reagent for producing oxiranes from carbonyl compounds, but syntheses from substrates with more than one carbonyl group have never before been studied (*3*).

EXPERIMENTAL

1,2,5,6-Diepoxy-2,5-dimethylhexane. A solution of dimethylsulfoxonium methylide was prepared from 5.76 grams of sodium hydride, 52.8 grams of trimethylsulfoxonium iodide (*4*), and 160 ml. of dimethyl sulfoxide. 2,5-Hexanedione (11.4 grams) was added dropwise over a 15-minute period, during which time the temperature rose from 21° to 40° C. The mixture was heated at 50° for one hour. Then ice water was added and the mixture was extracted with ether. The ether solution was dried and the ether was removed to give 5.7 grams of pale yellow liquid. This was fractionated through a short Vigreux column to give 4.42 grams of colorless diepoxide, b.p. 78 to 80°/13 mm. [reported (*2*) b.p. 88°/20 mm.].

ANALYSIS. Calculated for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 66.77; H, 10.03.

The infrared spectrum of a liquid film showed only C – H absorption in the 3-micron region, no 6-micron absorption, and two medium intensity epoxide bands at 898 cm.$^{-1}$ (sharp) and 804 cm.$^{-1}$ (broad). The pot residue showed strong absorption at 3460 cm.$^{-1}$ and medium bands at 1715, 900, and 803 cm.$^{-1}$.

***p*-Bis(1,2-epoxy-1-methylethyl)-benzene.** The reaction described above was repeated with 1.38 grams of sodium hydride, 13.3 grams of trimethylsulfoxonium iodide, and 3.24 grams of 1,4-diacetylbenzene. After the reaction, water was added and the solid product was removed by filtration, washed with water, and dried. The mixture of diastereo isomers weighed 1.2 grams and melted at 48° to 80° C. The infrared spectrum showed no carbonyl or hydroxyl bands. A sample of the diepoxide, recrystallized from hexane, melted at 50° to 80° C.

ANALYSIS. Calculated for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.62; H, 7.61.

LITERATURE CITED

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Hydrazine Derivatives

1,1′-Azobisformamides and Biureas

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The reaction between dialkyl azodiformates and amines was exploited to prepare a series of 1,1′-azobis(*N*-substituted formamides). Yields were higher for unhindered than for branched or cyclic primary amines. Competitive experiments involving amine mixtures or different dialkyl azodiformates are described. 1,6-Disubstituted biureas were isolated as by-products of the 1,1′-azobisformamide synthesis.

IN PREPARING a series of 1,1′-azobis(*N*-substituted formamides) for a spectroscopic study (*4*), the reaction between dialkyl azodiformates and amines was a convenient laboratory synthesis (*1*).

EXPERIMENTAL

Microanalyses were performed on a Fisher micro combustion apparatus. Melting points were determined in capillaries and are uncorrected. The NMR spectra were obtained on a Varian A-60 instrument with tetramethylsilane as internal standard. The amines used in this study were the highest quality materials available from laboratory supply houses and were used without further purification.

1,1′-Azobis(*N*-*n*-propylformamide). *n*-Propylamine (172 ml., 2.1 moles) in 250 ml. of ether was added to a stirred solution of 1 (174 grams, 1.0 mole) in 250 ml. of ether over 1.5 hours at room temperature. Stirring was continued for 0.5 hour, after which the slurry was diluted with 250 ml. of ether, filtered with suction, and washed with ether until the washings were nearly colorless.