

NOTES

Oxidation of 1,4-Cyclohexadiene Dioxide with Dimethyl Sulfoxide

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The oxidation of 1,4-cyclohexadiene dioxide with dimethyl sulfoxide and boron trifluoride etherate catalysis yields catechol in 70-75% yield.

L'oxydation du dioxyde du cyclohexanediène-1,4 par le diméthyl sulfoxyde, catalysée par l'éthérate de trifluorure de bore, conduit au cathécol avec un rendement de 70-75%.

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The use of dimethyl sulfoxide as an oxidizing agent in organic chemistry has recently been reviewed (1). The boron trifluoride etherate catalyzed oxidation of epoxides with dimethyl sulfoxide provides a useful synthesis of  $\alpha$ -hydroxyaldehydes and  $\alpha$ -hydroxyketones and the oxidation of cyclohexene oxide gives 2-hydroxycyclohexanone in good yield (2, 3). The reaction has been demonstrated as proceeding through an intermediate alkoxysulfonium salt which decomposes to the hydroxyketone and dimethyl sulfide (4).

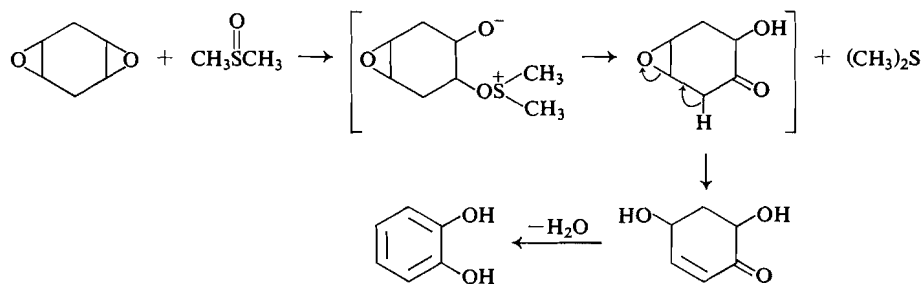
The boron trifluoride etherate catalyzed oxidation of 1,4-cyclohexadiene dioxide (5, 6) with dimethyl sulfoxide yields catechol in 70-75% yield. Presumably after the oxidation of one epoxide ring the reaction intermediates decompose as shown in Scheme 1, dimethyl sulfide being a readily identifiable product.

The decomposition of the intermediate epoxyketol to catechol rather than resorcinol or hydroquinone would appear reasonable on the basis of the known severity of conditions usually required to eliminate hydroxyl groups next to

ketone functions (7, 8) and the expected ease of epoxide opening due to the adjacent active methylene group (9).

The reaction was carried out using dimethyl sulfoxide as solvent, 0.025 to 0.1 mol of boron trifluoride etherate per mol of diepoxide, and a temperature of 90 to 130 °C. Under these conditions the time required for reaction was 3 to 12 h depending on the aforementioned variables. The reaction was also performed with tetramethylene sulfoxide, tetramethylene sulfide being isolated and identified.

The reaction was generally performed on the *trans*-diepoxide (5, 6) since the favored method of preparation was the *t*-butyl hydroperoxide - molybdenum trioxide method (10) which gave nearly exclusively the highly crystalline *trans*-isomer. However, when the diepoxide is prepared by an extension of the halohydrin method for cyclohexene oxide (11) a nearly equal mixture of both isomers is obtained which can also be used. Separation of the *cis*-isomer (6) by column chromatography on alumina and reaction separately also gave catechol in similar yield. Various



per-acids may also be used to prepare the diepoxides (6).

### Experimental

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. The i.r. spectra were run on a Perkin-Elmer Model 521 Grating Infrared Spectrophotometer. Gas chromatography was carried out on a Varian Aerograph Model 1200. The n.m.r. spectra were determined in deuteriochloroform at 60 MHz on a Varian T-60 spectrometer. Column chromatography was performed on standard silica gel and neutral activity II alumina.

#### Mixture of *cis*- and *trans*-1,4-Cyclohexadiene Dioxide

Calcium hypochlorite (19.0 g, 0.13 mol) was added to water (250 ml), and treated with glacial acetic acid (15.8 g, 0.26 mol). The resultant solution was added dropwise with stirring to 1,4-cyclohexadiene (8.4 g, 0.105 mol) over 45 min maintaining the temperature at 15–20 °C by cooling in a cold water bath. After the addition was complete the solution was stirred 10 min, then saturated with salt, and extracted with five 50-ml portions of ether. The combined extracts were washed with saturated salt solution, dried over anhydrous sodium sulfate, and evaporated to give a crude mixture of colorless solid chlorohydrins (17.3 g). This mixture was crushed and suspended in water (20 ml) then added to a solution of sodium hydroxide (8.0 g, 0.2 mol) in water (30 ml). The resultant mixture was stirred for 1½ h then saturated with salt and extracted with five 50-ml portions of dichloromethane. The combined extracts were washed with saturated salt solution and dried over anhydrous sodium sulfate. The solvent removed by distillation through a 40-cm Vigreux column at slightly reduced pressure to yield a crude residual mixture of *trans*- and *cis*-1,4-cyclohexadiene dioxides (10.9 g, 93% yield). Gas chromatography on 5% SE 30, 1/8" × 5', at 90 °C indicated the *trans*:*cis* ratio was about 6:4. This procedure could easily be scaled up to large quantities.

Column chromatography of a small amount of this mixture on alumina allowed an easy separation of the two isomers. Elution with benzene gave the pure *trans*-isomer, recrystallized from ether-hexane, m.p. 107.5–108.5 °C (lit. (6) 106.5–107.5 °C) and elution with benzene-ether (9:1) gave the *cis*-isomer, recrystallized from ether-hexane, m.p. 58–60 °C (lit. (6) 60–61 °C). The n.m.r. spectra of each isomer agreed with the reported data (6).

#### *trans*-1,4-Cyclohexadiene Dioxide

A solution of 1,4-cyclohexadiene (10 g, 0.125 mol) in benzene (20 ml) was refluxed with 90% *t*-butyl hydroperoxide (37.5 g, 0.375 mol) and molybdenum trioxide (1.0 g) for 12 h. The catalyst was filtered and the solution concentrated to a small volume by vacuum distillation through a 10-cm Vigreux column. The semi-solid crude diepoxide was triturated with hexane, filtered, and crystallized from ether-hexane to give long needles of the pure *trans*-diepoxide (7.5 g) m.p. 107.5–108.5 °C. This procedure could also be scaled up to larger quantities.

#### Oxidation of *trans*-1,4-Cyclohexadiene Dioxide with Dimethyl Sulfoxide

A solution of *trans*-1,4-cyclohexadiene dioxide (1.0 g,

8.93 mmol) in dry dimethyl sulfoxide (10 ml) containing boron trifluoride etherate (0.028 ml) was heated in an oil bath at 125 °C for 3 h. Dimethyl sulfide and most of the excess dimethyl sulfoxide were distilled under reduced pressure, the dimethyl sulfide being collected in a Dry Ice-acetone trap and identified by i.r. comparison with an authentic sample. The dark residue was extracted with five 10-ml portions of ether. The combined extracts were washed twice with a small amount of water, then the washes were back-extracted twice with ether. The combined ether extracts were dried over anhydrous sodium sulfate and evaporated to give crude yellow crystalline catechol (920 mg). This was chromatographed on silica gel (20 g) and elution with chloroform-ethyl acetate (5:1) gave pure catechol (740 mg, 75% yield) identical in all respects with an authentic sample.

A number of variations in quantities of the reactants were tried and a similar yield obtained. For example heating the *trans*-diepoxide (1.0 g), dimethyl sulfoxide (15 ml), and boron trifluoride etherate (0.057 ml) at 100–105 °C for 7 h gave catechol in 73% yield. Temperatures lower than 90 °C or smaller amounts of catalyst lowered the yield or made the reaction time unduly long. A mixture of *cis*- and *trans*-diepoxides, as obtained by the chlorohydrin route, or the pure *cis*-isomers could also be used with similar results.

#### Oxidation of *trans*-1,4-Cyclohexadiene Dioxide with Tetramethylene Sulfoxide

A solution of the *trans*-diepoxide (1.0 g, 8.93 mmol) in dry tetramethylene sulfoxide (15 ml) containing boron trifluoride etherate (0.028 ml) was heated at 125 °C for 5½ h. Work-up as described above gave tetramethylene sulfide identified by i.r. comparison with an authentic sample and catechol in 50–60% yield.

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