TABLE IV

PRODUCTS FROM THE ACETOLYSIS OF *t*-BUTYLCYCLOHEXYL METHANESULFONATES

| Product | % from *cis* | % from *trans* |
|---|---|---|
| 4-ene | 85.0 | 75.0 |
| 3-ene | 0.9 | 1.5 |
| *trans*-4-OAc | 8.1 | 0.1 |
| *cis*-4-OAc | 1.2 | 19.8 |
| *trans*-3-OAc | 4.6 | 0.3 |
| *cis*-3-OAc | 0.4 | 1.1 |

appropriate times aliquots were titrated with standardized perchloric acid in acetic acid to the bromophenol blue end point. Rate constants were calculated by a modified LSKIN2 computer program.[17]

**Registry No.**—*trans*-4-*t*-Butylcyclohexyl methanesulfonate, 18508-90-2; *cis*-4-*t*-butylcyclohexyl methanesulfonate, 18508-91-3; *trans*-4-methylcyclohexyl methanesulfonate, 18508-92-4; *cis*-4-methylcyclohexyl methanesulfonate, 18508-93-5; cyclohexyl methanesulfonate, 16156-56-2.

[17] D. F. DeTar and C. E. DeTar, Florida State University. We are grateful to Mr. Howell A. Hammond for his assistance in modifying these programs.

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# A Facile Synthesis of 1,4-Cyclooctadiene

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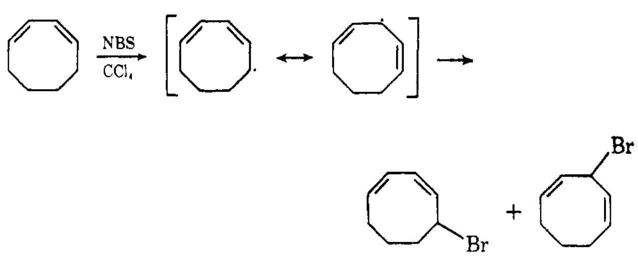
The chemical reactions of both 1,3- and 1,5-cyclooctadiene have been studied in some detail.[1] The chemistry of the corresponding 1,4 isomer, however, has been largely neglected, possibly due to the inaccessibility of this compound.

Although some preparations of 1,4-cyclooctadiene have been reported,[2-6] a facile synthesis which gives a substantial quantity of the pure compound is still lacking. In this paper, we wish to describe a simple synthetic procedure which utilizes a readily available and inexpensive starting material and which affords 1,4-cyclooctadiene of high purity.

The synthesis is based upon the partial rearrangement of 1,3-cyclooctadiene during bromination with N-bromosuccinimide (NBS). Treatment of the bromination product with lithium aluminum hydride affords approximately a 50:50 mixture of 1,3- and 1,4-cyclooctadiene. It therefore appears that the intermediate radical, formed in the NBS reaction, undergoes an allylic rearrangement in the manner illustrated.



On the basis of previous studies made by Jones,[4] we have found that, at room temperature, 1,3-cyclooctadiene is inert to silver nitrate while the 1,4 isomer readily forms a silver nitrate complex. 1,4-Cyclooctadiene can thus be conveniently and selectively separated from the lithium aluminum hydride reduction mixture by extraction with 50% silver nitrate at room temperature. Regeneration of the 1,4-diene from its silver nitrate complex is accomplished by treatment with cold concentrated ammonium hydroxide. Ether extraction of the resultant ammonium hydroxide solution followed by distillation affords pure (>99% by vpc analysis) 1,4-cyclooctadiene.

## Experimental Section[7]

**Bromination of 1,3-Cyclooctadiene.**—To 105.4 g of freshly distilled 1,3-cyclooctadiene[8] in 400 ml of carbon tetrachloride was added 175 g of NBS and 1.25 g of benzoyl peroxide. The mixture was refluxed, with stirring, for 17 hr, then cooled and the succinimide removed by filtration. The filtrate was washed with two 600 ml-portions of 10% $NaHCO_3$ and 600 ml of $H_2O$ and then dried ($MgSO_4$). The solvent was removed under reduced pressure (20 mm) through a Vigreux column. The residue was then distilled through a short-path distillation column to give 97.1 g (53% based on 1,3-cyclooctadiene) of a bromide mixture, bp 25–52° (0.3 mm). The nmr spectrum of the distillate suggested that it was a mixture of 2,4-cyclooctadien-1-yl bromide and 2,7-cyclooctadien-1-yl bromide.

**Lithium Aluminum Hydride Reduction of the Bromination Product.**—To a suspension of 15 g of lithium aluminum hydride in 250 ml of anhydrous ether was added, dropwise and with stirring, 97.1 g of the bromide mixture in 25 ml of ether. Following complete addition, the solution was refluxed overnight. After cooling, 40 ml of $H_2O$ was cautiously added, dropwise and with stirring, to the externally cooled solution. Sulfuric acid (20%, 100 ml) was then added in a similar manner, followed by 400 ml more of the acid added at room temperature. Stirring was continued until all of the white precipitate, formed on $H_2O$ addition, had dissolved. The aqueous portion was separated and extracted with 250 ml of ether. The latter was added to the original organic layer and the combined extracts were washed with two 400 ml-portions of 10% $NaHCO_3$ and 400 ml of $H_2O$ and dried ($MgSO_4$). The ether was removed by distillation. The crude diene mixture (50.5 g, 90% based on the bromide mixture) was analyzed by vpc (TCEP, 65°) and found to be approximately a 50:50 mixture of two compounds with slightly different retention times. Each compound was isolated by

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[1] See, for example, A. C. Cope and P. E. Peterson, *J. Amer. Chem. Soc.*, **81**, 1643 (1959); R. S. H. Liu, *ibid.*, **89**, 112 (1967); I. Haller and R. Srinivasan, *ibid.*, **88**, 5084 (1966).

[2] K. Ziegler and H. Wilms, *Ann. Chem.*, **567**, 1 (1950).

[3] L. E. Craig, R. M. Elofson, and I. J. Ressa, *J. Amer. Chem. Soc.*, **75**, 480 (1953).

[4] W. O. Jones, *J. Chem. Soc.*, 312 (1954).

[5] W. Grimme, *Chem. Ber.*, **98**, 756 (1965).

[6] U. S. Rubber Co., Netherlands Patent 6,607,898 (1966); *Chem. Abstr.*, **67**, 11922 (1967).

[7] Nmr spectra were determined on a Varian A-60 spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 337 grating infrared spectrophotometer. Gas chromatography was performed on an F & M Model 720 thermal conductivity gas chromatograph using a 4-ft column containing 20% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on Chromosorb P. Boiling points are uncorrected.

[8] We are grateful to the Columbian Carbon Co. for a generous sample of this compound.

preparative gas chromatography. The ir and nmr spectra of the compound with shorter retention time were identical with those of 1,3-cyclooctadiene. The nmr spectrum ($CCl_4$) of the second compound showed absorptions centered at $\tau$ 4.54 (4 H, multiplet), 7.22 (2 H, multiplet), 7.73 (4 H, multiplet) and 8.58 (2 H, multiplet), while the ir spectrum (neat) exhibited bands at 3000 and 1645 $cm^{-1}$. Both of these spectra are compatible with those expected for 1,4-cyclooctadiene. In addition, the spectra are idential with those of an authentic sample.[9]

**Separation of 1,3- and 1,4-Cyclooctadiene.**—To 50.5 g of the diene mixture was added 140 ml of 50% aqueous[10] $AgNO_3$. The mixture was stirred, in the dark, overnight. The silver nitrate complex, a green solid, was isolated by filtration and washed with several small portions of ether which were then added to the filtrate. The complex was further washed with acetone and again with ether and then dried. The filtrate was separated into aqueous and organic portions and the latter reextracted with 100-, 75-, and 75-ml portions of 50% $AgNO_3$. The remaining organic layer, after washing with water, drying ($MgSO_4$) and concentration, gave 22.5 g of 1,3-cyclooctadiene found to be ~98% pure by vpc retention time. Each aqueous $AgNO_3$ extract, including that from the original filtrate, was washed with ether to remove any residual 1,3-cyclooctadiene. To the combined, ether-washed $AgNO_3$ extracts was added, with external cooling and stirring, 250 ml of cold concentrated $NH_4OH$. After stirring for 15 min, the resultant mixture was extracted with two 500-ml portions of ether. Similarly, the dried solid complex was dissolved in 350 ml of cold, concentrated $NH_4OH$ (a small amount of greyish residue remained insoluble) and carefully extracted with two 300-ml portions of ether (*caution*—vigorous ebullition of bubbles). The ether extracts from the solid complex and the aqueous $AgNO_3$ portions were combined, washed with water, dried ($MgSO_4$) and concentrated by distillation. The residue was further distilled through a microdistillation column to give 13.3 g (13% based upon 1,3-cyclooctadiene used; 16% based upon 1,3-cyclooctadiene consumed) of 1,4-cyclooctadiene (>99% pure by vpc), bp 57–58° (35 mm).

**Registry No.**—1,4-Cyclooctadiene, 1,073-07-0.

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[9] We wish to extend our thanks to Dr. E. Ciganek for kindly supplying us with the spectra of 1,4-cyclooctadiene.

[10] Use of undistilled water was found to cause clouding of the $AgNO_3$ solution due to the formation of AgCl. This may have an adverse affect on the extraction.

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# The Preparation and Reduction of 2-Methyl-2-nitro-3-benzylthiopropanol[1]

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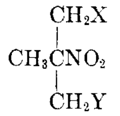
The normal product resulting from the treatment of an aliphatic nitro compound with lithium aluminum hydride is the corresponding amine.[2] However, the reduction of *t*-alkyl nitro compounds can give the corresponding hydroxylamine[3] and the reduction of aliphatic nitro compounds containing a $\beta$-hydroxyl group can give cleavage of the carbon–carbon bond between the nitro and hydroxyl group in addition to reduction of the nitro group.[4] In this paper we wish to report the preparation and the lithium aluminum hydride reduction of a *t*-alkyl nitro compound which contains a $\beta$-hydroxyl function and to discuss the mechanistic implications of the results.

Treatment of 2-methyl-2-nitro-1,3-propanediol (I) with 1 equiv of *p*-toluenesulfonyl chloride in pyridine at 0° gave a 68% yield of monotosylate II. If the reaction was carried out at room temperature using 2 equiv of *p*-toluenesulfonyl chloride, ditosylate III was obtained. The ditosylate could also be prepared by the treatment of II with 1 equiv of *p*-toluenesulfonyl chloride. The reaction of II with sodium benzyl mercaptide gave 57% of 2-methyl-2-nitro-3-benzylthiopropanol (IV). Treatment of IV with *p*-toluenesulfonyl chloride gave tosylate V which was identical with the product obtained by treating III with 1 equiv of sodium benzyl mercaptide. Although the reaction of II and III with sodium benzyl mercaptide proceeded quite smoothly, treatment of II or III with weaker nucelophiles such as thiourea or sodium thiocyanate gave no reaction.

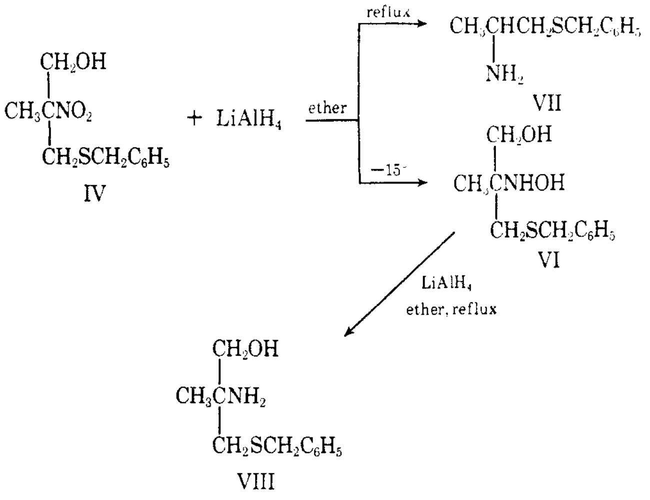


$$\begin{array}{c}CH_2X\\|\\CH_3CNO_2\\|\\CH_2Y\end{array}$$

I, X = Y = OH
II, X = OH; Y = 1,4-$CH_3C_6H_4SO_3$
III, X = Y = 1,4-$CH_3C_6H_4SO_3$
IV, X = OH; Y = $C_6H_5CH_2S$
V, X = 1,4-$CH_3C_6H_4SO_3$; Y = $C_6H_5CH_2S$

The reduction of IV with lithium aluminum hydride proved to be quite interesting. The results obtained are summarized in Scheme I. If the reduction was carried out in ethyl ether at −15° using the method of inverse addition, a 60% yield of 2-methyl-2-hydroxylamino-3-benzylthiopropanol (VI) was obtained. The structural assignment was based on the elemental analysis, a positive Tollens test and the nmr spectrum which showed a singlet at $\delta$ 1.02 ($CH_3C<$), an AB quartet at 2.60, $J$ = 13 cps ($-CH_2OH$), an AB quartet

SCHEME I



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[1] This investigation was supported by the Department of the Army and the U. S. Army Medical Research and Development Command, Contract No. DA-49-193-MD-2164.

[2] N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, p 672.

[3] H. J. Barber and E. Lunt, *J. Chem. Soc.*, 1187 (1960).

[4] A. Dornow and M. Gilbrich, *Ann.*, **594**, 177 (1955).