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 τ 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.

(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.

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

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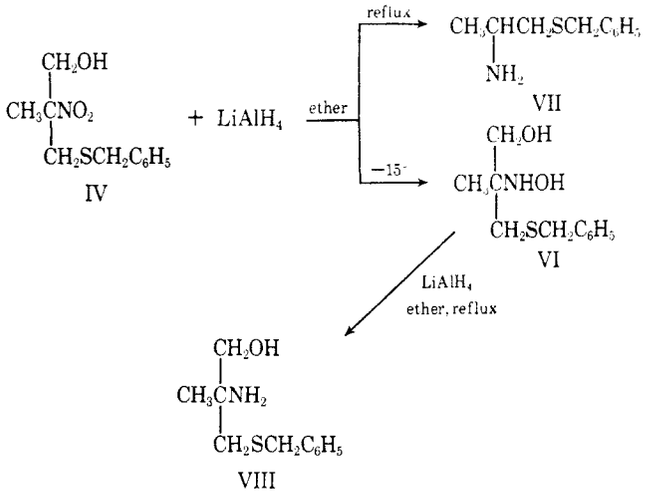
The normal product resulting from the treatment of an aliphatic nitro compound with lithium aluminum hydride is the corresponding amine.[2] However, the reduction of *t*-alkyl nitro compounds can give the corresponding hydroxylamine[3] and the reduction of aliphatic nitro compounds containing a β-hydroxyl 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 β-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.

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

SCHEME I



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 δ 1.02 ($CH_3C<$), an AB quartet at 2.60, J = 13 cps ($-CH_2OH$), an AB quartet

(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.

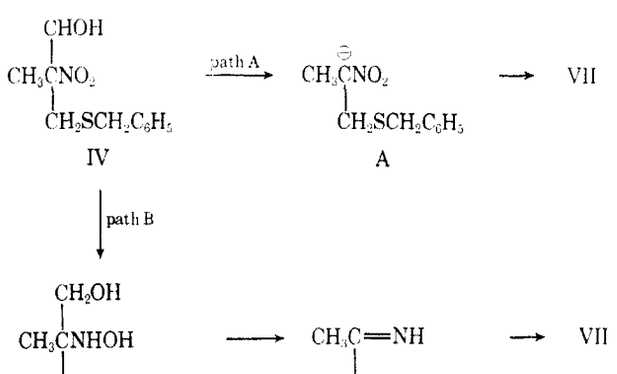
(3) H. J. Barber and E. Lunt, *J. Chem. Soc.*, 1187 (1960).

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

at 3.53 ($-CH_2S-$), a singlet at 3.75 ($-SCH_2Ar$), a broad singlet at 5.55 (OH + NH) and a singlet at 7.31 ppm (aromatic protons). Additional support for this structure results from the reduction of IV to VI with zinc and ammonium chloride, a reagent used specifically for the reduction of nitro groups to hydroxylamino groups.[3] If the reduction of IV with lithium aluminum hydride was carried out in refluxing ethyl ether using the normal mode of addition, very little if any of VI was formed. Instead, 41% of 1-benzylthio-2-propylamine (VII) resulting from the loss of a methylenehydroxy group and reduction of the nitro function was observed. The elemental analysis, the infrared spectrum which showed $-NH_2$ absorption at 3375 cm^{-1} and the absence of hydroxyl absorption, and the nmr spectrum, which showed a doublet at δ 1.03, J = 6 cps (CH_3 of CH_3CH group), a singlet at 1.37 ($-NH_2$), a multiplet at 2.35 (CH_2S), a multiplet at 2.88 (CHN<), a singlet at 3.67 ($-SCH_2Ar$) and a singlet at 7.23 ppm (aromatic protons) are in agreement with this assignment.

The formation of VII under the more stringent conditions could result from the action of lithium aluminum hydride as a strong base on IV to give the resonance stabilized anion A which on further reduction would give VII (Scheme II, path A). Alternatively,

SCHEME II



VII could result from the rearrangement of hydroxylamine VI to an intermediate B which on further reduction would yield VII (path B).[5,6] However, path B can be eliminated since treatment of VI with lithium aluminum hydride in refluxing ether gave a quantitative yield of 2-methyl-2-amino-3-benzylthiopropanol (VIII).[7] The correctness of the structural assignment was shown by the nmr spectrum which showed a singlet at δ 1.03 ($CH_3C<$), a singlet at 2.54 ($-CH_2S-$), a broad singlet at 2.70 (NH_2 and OH), a singlet at 3.33 ($-CH_2O$), a singlet at 3.73 ($-SCH_2Ar$) and a singlet at 7.33 ppm (aromatic protons).

(5) Barber and Lunt[3] have shown that 1-methylcyclohexylhydroxylamine undergoes rearrangement when treated with lithium aluminum hydride.

(6) It is realized that these explanations are oversimplifications since the intermediate reduction products would exist as complex negative ions. However they do give an over-all picture of the results obtained.

(7) 2-Methyl-2-amino-3-benzylthiopropanol was obtained as a viscous liquid and has analyzed as its tosylate salt which could be obtained in 94% yield from the free base.

Experimental Section[8]

Preparation of 2-Methyl-2-nitro-1,3-propanediol Monotosylate (II) and 2-Methyl-2-nitro-1,3-propanediol Ditosylate (III).—To an ice cold, stirred solution of 109 g (0.535 mol) of 2-methyl-2-nitro-1,3-propanediol in as little pyridine as possible was added dropwise 110 g (0.535 mol) of *p*-toluenesulfonyl chloride dissolved in as little pyridine as possible. The reaction mixture was allowed to warm to room temperature and remain for 15 hr. The mixture was then diluted with water and extracted with ether. The ether extracts were washed with a 4% hydrochloric acid solution, washed with water, dried and concentrated to give 132 g of a red-brown oil. The oil was dissolved in a small amount of ethanol and cooled to give 30 g of 2-methyl-2-nitro-1,3-propanediol ditosylate, mp 96–98°.[9] The analytical sample prepared by recrystallization from the same solvent had mp 99.5–100.5°; $\nu_{max}^{CH_2Cl_2}$ 1560 and 1368 (NO_2), and 1180 and 1015 cm^{-1} ($-SO_2O$). The nmr spectrum ($CDCl_3$) showed a singlet at δ 1.56 ($CH_3C<$), a singlet at 2.44 ($ArCH_3$), a singlet at 4.35 ($-CH_2OTos$) and an A_2B_2 pattern for the aromatic protons centered at 7.55 ppm, J = 8 cps.

Anal. Calcd for $C_{18}H_{21}NO_8S_2$: C, 48.29; H, 4.77. Found: C, 48.42; H, 4.81.

The filtrate was concentrated to afford 102 g of an oil. Crystallization from an ether and petroleum ether mixture gave 98 g (68%) of 2-methyl-2-nitro-1,3-propanediol monotosylate, mp 59–61°. The analytical sample prepared by recrystallization from the same solvent had mp 60–62°; $\nu_{max}^{CH_2Cl_2}$ 3600 (OH), 1550 and 1360 (NO_2), and 1275 and 1000 cm^{-1} ($-SO_2O$). The nmr spectrum ($CHCl_3$) showed a singlet at δ 1.55 ($CH_3C<$), a singlet at 2.46 ($ArCH_3$), a singlet at 2.87 (–OH), a singlet at 3.93 ($-CH_2OH$), a singlet at 4.45 ($-CH_2OTos$) and an A_2B_2 pattern at 7.57 ppm for the aromatic protons, J = 8 cps.

Anal. Calcd for $C_{11}H_{15}NO_6S$: C, 45.66; H, 5.23. Found: C, 45.51; N, 5.30.

Treatment of II with *p*-toluenesulfonyl chloride in methylene chloride catalyzed by triethylamine gave a 66% yield of III, mp 99.5–100.5°.

Preparation of 2-Methyl-2-nitro-3-benzylthiopropanol (IV).—To a solution of sodium benzyl mercaptide in 100 ml of absolute ethanol [prepared from 1.15 g (0.065 g-atom) of sodium and 8.1 g (0.065 mol) of benzyl mercaptan] under a dry nitrogen atmosphere was added 18.9 g (0.065 mol) of 2-methyl-2-nitro-1,3-propanediol monotosylate. The stirred reaction mixture was refluxed overnight. The cooled reaction mixture was filtered, and the filtrate was concentrated under vacuum. The residue was dissolved in ether and washed with water. The ether layer was dried (Na_2SO_4) and then concentrated to give 11.5 g of a red-brown oil. This oil was chromatographed on 60 g of Florisil using benzene as the eluent to give 9 g (57%) of 2-methyl-2-nitro-3-benzylthiopropanol as a colorless oil, $\nu_{max}^{CH_2Cl_2}$ 3590 (OH), and 1545 and 1345 cm^{-1} (NO_2). The nmr spectrum ($CDCl_3$) showed a singlet at δ 1.54 ($CH_3C<$), a broad peak at 2.77 (–OH), a singlet at 2.98 ($-CH_2S$), a singlet at 3.70 ($-CH_2OH$), a broad singlet at 3.88 ($-SCH_2Ar$) and a singlet at 4.76 ppm (aromatic protons). This compound could not be crystallized. It was characterized as its tosylate derivative (V) as described in the following experiment.

The Preparation of 2-Methyl-2-nitro-3-benzylthiopropanol Tosylate (V) from 2-Methyl-2-nitro-3-benzylthiopropanol (IV).—A mixture of 5 g (0.02 mol) of 2-methyl-2-nitro-3-benzylthiopropanol, 3.94 g (0.02 mol) of *p*-toluenesulfonyl chloride and 10 ml of pyridine was stirred at room temperature overnight. The reaction mixture was diluted with water and extracted with ether. The ether extracts were washed with 4% hydrochloric acid solution, washed with water, dried ($MgSO_4$) and concentrated under vacuum to give 6.5 g of a red oil. The oil was chromatographed on 100 g of Florisil using a 1:1 mixture of benzene and ethyl acetate as the eluent to give 4.2 g of crystals. Recrystallization of the product from ethanol afforded 3.1 g

(8) Melting points were determined on a Kofler hot-stage microscope using a calibrated thermometer. Nmr spectra were recorded on a Varian Model A-60, using tetramethylsilane as an internal standard. Infrared spectra were measured with a Perkin-Elmer 221 spectrophotometer. Microanalyses were carried out by Micro-Tech Laboratories, Skokie, Ill.

(9) Treatment of 2-methyl-2-nitro-1,3-propanediol with 2 equiv of *p*-toluenesulfonyl chloride in pyridine gave an 87% yield of III.

(42%) of crystals, mp 54.5–56°. The infrared spectrum showed absorption at 1550 and 1365 ($-NO_2$), 1175 and 1005 cm^{-1} ($-SO_2O$) and the absence of hydroxyl absorption. The nmr spectrum ($CHCl_3$) showed a singlet at δ 1.53 (CH_3C), a singlet at 2.40 ($ArCH_3$), a singlet at 2.93 ($-CH_2S$), a singlet at 3.65 ($-CH_2OTos$) a broad singlet at 4.37 ($-SCH_2Ar$), a singlet at 7.25 ($-SCH_2C_6H_5$) and an A_2B_2 pattern centered at 7.54 ppm for the tosylate aromatic proton resonances, J = 8 cps.

Anal. Calcd for $C_{18}H_{21}NO_5S_2$: C, 54.66; H, 5.35. Found: C, 54.47; H, 5.46.

Preparation of 2-Methyl-2-nitro-3-benzylthiopropanol Tosylate (V) from 2-Methyl-2-nitro-1,3-propanediol Ditosylate (III).—To a solution of sodium benzyl mercaptide in 70 ml of absolute ethanol [prepared from 0.69 g (0.03 g-atom) of sodium and 3.72 g (0.03 mol) of benzyl mercaptan] under a dry nitrogen atmosphere was added 13.3 g (0.03 mol) of 2-methyl-2-nitro-1,3-propanediol ditosylate. The stirred reaction mixture was refluxed overnight under a nitrogen atmosphere. The cooled reaction mixture was concentrated, diluted with water and extracted with ether. The ether extracts were dried ($MgSO_4$) and concentrated to give a yellow oil. The oil was chromatograhed on 50 g of Florisil using a 1:1 mixture of benzene and ethyl acetate as the eluent to afford 7.5 g (63%) of 2-methyl-2-nitro-3-benzylthiopropanol tosylate, mp 50–53°. The infrared spectrum of this product was identical with the spectrum of 2-methyl-2-nitro-3-benzylthiopropanol tosylate prepared from 2-methyl-2-nitro-3-benzylthiopropanol. A mixture of the two products melted at 52–54°.

Reduction of 2-Methyl-2-nitro-3-benzylthiopropanol with Lithium Aluminum Hydride in Ethyl Ether at −15°.—To a solution of 6 g (0.025 mol) of IV in 100 ml of ether cooled by an ice–methanol bath (−15°) was added 2.85 g (0.075 mol) of lithium aluminum hydride in 200 ml of ether. The addition was dropwise over a 1-hr period. The excess lithium aluminum hydride was decomposed by the cautious addition of water and then 400 ml of a 20% potassium sodium tartrate solution was added. The organic layer was separated and the aqueous layer extracted with ether. The combined organic layers were dried over anhydrous sodium sulfate. Concentration of the solution afforded 4.34 g of an oil which was crystallized from an ether cyclohexane mixture to give 34. g (60%) of 2-methyl-2-hydroxylamino-3-benzylthiopropanol (VI), mp 77–82°. The analytical sample prepared by further recrystallization from the same solvent mixture had mp 82–83°.

Anal. Calcd for $C_{11}H_{17}O_2NS$: C, 58.13; H, 7.54. Found: C, 58.23; H, 7.61.

Reduction of 2-Methyl-2-nitro-3-benzylthiopropanol with Zinc and Ammonium Chloride.—To a suspension of 0.721 g (0.003 mol) of 2-methyl-2-nitro-3-benzylthiopropanol in 5 ml of water containing 0.161 g (0.003 mol) of ammonium chloride was added 0.392 g (0.006 mol) of zinc powder, and the mixture was stirred vigorously for 4 hr. The aqueous layer was separated by decantation and the remaining residue was washed with methanol. The methanol washings were concentrated to give a cloudy oil which was dissolved in ether and extracted with 5% hydrochloric acid solution. The acid extracts were made alkaline with sodium bicarbonate and extracted with ether. The ether extracts were dried (Na_2SO_4) and concentrated to give 0.250 g of an oil. Crystallization from cyclohexane afforded 0.200 g (30%) of 2-methyl-2-hydroxylamino-3-benzylthiopropanol, mp 78–81°.

Reduction of 2-Methyl-2-nitro-3-benzylthiopropanol with Lithium Aluminum Hydride in Refluxing Ethyl Ether.—A solution of 12 g (0.05 mol) of 2-methyl-2-nitro-3-benzylthiopropanol in 50 ml of ether (dried over sodium metal) was added dropwise to an ice-cooled stirred solution–suspension of 5.7 g (0.15 mol) of lithium aluminum hydride in 200 ml of anhydrous ether. After the addition was completed, the reaction mixture was refluxed for 3 hr. The excess lithium aluminum hydride was decomposed with water and 1 l. of a 20% sodium potassium tartrate solution was added. The ether layer was separated and the remaining aqueous layer was extracted with ether. The organic layers were combined and dried ($MgSO_4$). Concentration of the ether afforded 9.9 g of light yellow liquid. Distillation of the liquid under reduced pressure afforded 3.7 g (41%) of colorless product, bp 95° (0.08 mm), $n^{25}D$ 1.5564. The 1-benzylthio-2-propylamine formed a carbonate salt rapidly on exposure to the atmosphere and was thus analyzed as the hydrochloride salt, mp 149–151°. The nmr spectrum (D_2O) showed a doublet at δ 1.44, CH_3 of ($CH_3{}^aCH^b$, $J_{a,b}$ = 7 cps), a doublet at 2.81 , $J_{b,c}$ = 7 cps (slightly perturbed due to the nonequivalence of the methylene protons, $-CH_2$ of $CH^bCH_2{}^cS$), a sextet at 3.57 (CH of $CHCH_2S$ group), a singlet at 3.85 ($-SCH_2Ar$) and a singlet at 7.37 ppm (aromatic protons).

Anal. Calcd for $C_{10}H_{16}ClNS$: C, 55.15; H, 7.41. Found: C, 55.28; H, 7.11.

In a separate experiment the product was isolated in 49% yield as the hydrochloride.

Reduction of 2-Methyl-2-hydroxylamino-3-benzylthiopropanol with Lithium Aluminum Hydride in Refluxing Ethyl Ether.—To a solution–suspension of 0.57 g (0.015 mol) of lithium aluminum hydride in 20 ml of anhydrous ether was added dropwise a solution of 1.14 g (0.005 mol) of VI in 50 ml of ether. After the addition was completed, the mixture was refluxed for 8 hr. The mixture was worked up as in the previous reductions to give 1.07 g of a viscous liquid. This liquid was dissolved in ether and treated with an ethereal solution of *p*-toluenesulfonic acid to give 1.8 g (94%) of 2-methyl-2-amino-3-benzylthiopropanol *p*-toluenesulfonate, mp 133–137°. The analytical sample prepared by recrystallization from an ethanol and ether mixture had mp 134–137°.

Anal. Calcd for $C_{18}H_{25}NS_2O_4$: C, 56.37; H, 6.57; N, 3.65; S, 16.72. Found: C, 56.49; H, 6.58; N, 3.81; S, 16.52.

Registry No.—II, 18386-49-7; III, 18386-50-0; IV, 18386-51-1; V, 18386-52-2; VI, 18354-31-9; VII·HCl, 18354-32-0; VIII·*p*-toluenesulfonate, 18386-53-3.

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Phenylethynylpentafluorobenzene and Phenylethynylpentachlorobenzene

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During the course of some current studies concerned with the reductive dimerization of arylacetylenes to dilithium reagents[2] and the conversion of arylacetylenes to aryl-substituted cyclobutadiene–cobalt complexes,[3] we developed a need for several diarylacetylenes in which one of the aryl groups was perhalogenated. Very recently, Filler and Heffern[4] have described a multistep, phosphorane-type route to one of these acetylenes, *viz.*, phenylethynylpentafluorobenzene (**1**). Other at-

$ArC{\equiv}CC_6H_5$	$ArC{\equiv}CC{\equiv}CAr$
1, Ar = C_6F_5	**3**, Ar = C_6H_5
2, Ar = C_6Cl_5	**4**, Ar = C_6F_5

(1) National Science Foundation Graduate Trainee, 1965–1968.

(2) M. D. Rausch and L. P. Klemann, *J. Amer. Chem. Soc.*, **89**, 5732 (1967); unpublished studied by these authors.

(3) M. D. Rausch and R. A. Genetti, *ibid.*, **89**, 5502 (1967); F. Higbie, A. Siegel, and M. D. Rausch, unpublished studies.

(4) R. Filler and E. W. Heffern, *J. Org. Chem.*, **32**, 3249 (1967).