a quartz vessel a solution of stilbene, 7.5 g (0.03 mol), in 200 ml of 3,4-dihydropyran was irradiated at 2537 Å in a Rayonet photochemical reactor for 48 hr. After removal of the unreacted dihydropyran under reduced pressure, the crude reaction mixture was heated with petroleum ether and then cooled. A white crystalline product (2.45 g, 24% based on reacted stilbene) was isolated by filtration and characterized as a mixture of *cis,trans,-cis*-1,2,3,4-tetraphenylcyclobutane (II) and *trans,trans,trans*-1,2,3,4-tetraphenylcyclobutane (III): nmr ($CDCl_3$), τ 2.71, 2.91 (20 H, singlets, aromatic protons), 5.54, 6.33 (4 H, singlets, methine protons).[5] The filtrate was subjected to column chromatography on alumina (80–200 mesh). Elution with benzene–petroleum ether (bp 30–60°) (5:95) gave two products: 7,8-*cis-exo*-diphenyl-2-oxabicyclo[4.2.0]octane (IV) [3.65 g (43.3%); mp 48–50°; parent peak, 264.1495 ($C_{19}H_{20}O$); ir (thin film) 3040 (aromatic CH), 2900 (aliphatic CH), 1610, 1500 (aromatic C═C), 1053 (COC) and 740, 700 cm^{-1} (monosubstituted phenyl); nmr ($CDCl_3$) τ 2.75–2.83 (10 H, multiplet, aromatic protons), 5.75–5.87 (2 H, multiplet, H_7 and H_8), 6.13–6.38 (2 H, multiplet, H_3 and $H_{3'}$) 6.60–6.80 (1 H, multiplet, H_1), 7.10–7.35 (1 H, multiplet, H_6) and 8.36–8.70 (4 H, multiplet, H_4, $H_{4'}$, H_5 and $H_{5'}$), $J_{1-6} = 4.5$ cps, $J_{1-8} = 6.5$, $J_{6-7} = 6.5$, $J_{7-8} = 6.5$]; 7-*exo*,8-*endo*-diphenyl-2-oxabicyclo[4.2.0]octane (V) [1.92 g (23.6%); mp 36–38°; parent peak, 264.1525 ($C_{19}H_{20}O$); ir (thin film) 3030 (aromatic CH), 2890 (aliphatic CH), 1600, 1490 (aromatic C═C), 1110 (COC) and 750, 740, 700 cm^{-1} (monosubstituted phenyl); nmr ($CDCl_3$) τ 2.72–2.90 (10 H, aromatic protons), 5.7 (1 H, multiplet, H_7), 6.0 (1 H, multiplet, H_1), 6.6 (1 H, multiplet, H_8), 6.20–6.32 (2 H, multiplet, H_3, $H_{3'}$), 7.0 (1 H, multiplet, H_6) and 8.25–8.50 (4 H, multiplet, H_4, $H_{4'}$, H_5, $H_{5'}$), $J_{1,6} = 11$ cps, $J_{1,8} = 10$ cps, $J_{7,8} = 5$ cps, $J_{6,7} = 3.5$ cps].

The Hydrogenation of 7,8-Diphenyl-2-oxabicyclo[4.2.0]oct-7-ene (I).[1]—In a Paar hydrogenation vessel 0.2 g of 5% Pt on charcoal was added to a solution of I, 1.0 g in 35 ml of absolute ethanol. The solution was then subjected to hydrogenation at 50 lb pressure for 24 hr. The reaction mixture was filtered and evaporated to a volume of 10 ml. The solution was then analyzed by glpc. The chromatogram showed the presence of two peaks with areas in the ratio of 1:4. The retention time of the smaller peak was identical with that of I and the larger peak corresponded to IV. The solvent was removed under vacuum and the products were separated by column chromatography on alumina. The ir spectrum of the reduction product was identical with that of IV.

Isomerization of 7,8-*cis-exo*-Diphenyl-2-oxabicyclo[4.2.0]-octane (IV).—A mixture of 7,8-*cis-exo*-diphenyl-2-oxabicyclo-[4.2.0]octane 0.1 and 0.2 g of potassium *t*-butoxide in 25 ml of ethanol was refluxed for 12 hr. The solvent was evaporated under vacuum and the residue was taken up in ether which was than washed with water and dried over anhydrous $MgSO_4$. The ether solution was analyzed by glpc. The chromatogram showed two new peaks with approximately equal areas. The retention times of one of these components on two different columns was identical with those of V.

Registry No.—*cis*-Stilbene, 645-49-8; *trans*-stilbene, 103-30-0; 2,3-dihydropyran, 110-87-2; IV, 18521-18-1; V, 18521-19-2.

[5] Values reported in ref 2 are the following: τ 2.95 and 5.60 for II and 2.79 and 6.37 for III.

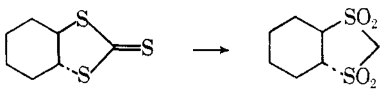
The Hydrogenolysis of Trithiocarbonates

D. J. MARTIN

Stauffer Chemical Company, Eastern Research Center,
Dobbs Ferry, New York

Received July 15, 1968

The hydrogenolysis of carbon–sulfur bonds has found extensive use in both structure determination and synthesis.[1] However, relatively little attention has been focused on the hydrogenolysis of trithiocarbonates. Gibson[2] reported an unsuccessful attempt to convert ethylene trithiocarbonate into 1,3-dithiolane, while McSweeney and Wiggins[3] reported the reductive desulfurization of the trithiocarbonate derivatives of carbohydrates with Raney nickel to the corresponding dideoxy compound. In 1960, Iqbab and Owen[4] found cyclic trithiocarbonates, upon treatment with lithium aluminum hydride, undergo smooth reductive fission to vicinal dithiols. More recently, Owen and coworkers[5,6] described the oxidation of *trans*-1,2-cyclohexane trithiocarbonate (I) with excess per acid in which the thiocarbonyl is converted into a methylene group affording the corresponding methylenedisulfonyl compound II. We now wish to report the results of our studies in which the direct catalytic hydrogenolysis of trithiocarbonates yield the corresponding 1,3 disulfides (see Table I).



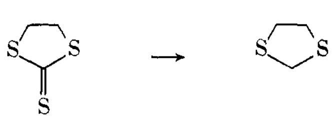
I II

TABLE I

CATALYTIC HYDROGENOLYSIS OF TRITHIOCARBONATES

	Reaction conditions		Product			
Trithio-carbonate	Time, hr	Temp, °C	1,3-Di-sulfide	Yield, %	Bp, °C (mm)	n_D
I	12	150	V	50	53–55 (0.01)	1.5706 (31°)
III	16	150	IV	88	75 (25)	1.5980 (23°)
VI	12	160	VII	12	70–72 (20)	1.5331 (21°)

Contrary to Gibson's observation[2] we have found hydrogenolysis (2000 psi) of ethylene trithiocarbonate (III) in benzene containing a catalytic amount of molybdenum trisulfide at 150° afforded 1,3-dithiolane (IV) as a colorless liquid in 88% yield. The infrared (1415 cm^{-1}) and pmr spectrum [δ 3.83 (singlet, 2 H, $-SCH_2S-$), 3.13 (singlet, 4 H, $-CH_2S-$)] are in complete agreement with IV; both spectra were identical with the spectra of an authentic sample[2] of IV. The reaction is clean with the only other product observed (*via* glpc) being ethylene dimercaptan in ~2% yield. Since current synthetic routes[7] to 1,3-dithiolane suffer from either low yield and/or polymer formation this method offers a



III IV

---

[1] G. R. Pettit and E. E. van Tamelen, *Org. Reactions*, **12**, 356 (1962); H. Hauptmann and W. F. Walter, *Chem. Rev.*, **62**, 347 (1962); R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, Inc., New York, N. Y., 1965.

[2] D. T. Gibson, *J. Chem. Soc.*, 12 (1930).

[3] G. P. McSweeney and L. F. Wiggins, *Nature*, **168**, 874 (1951).

[4] S. M. Iqbab and L. N. Owen, *J. Chem. Soc.*, 1030 (1960).

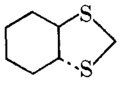
[5] A. K. M. Anisuzzaman and L. N. Owen, *Chem. Commun.*, 16 (1966).

[6] T. J. Adley, A. K. M. Anisuzzaman, and L. N. Owen, *J. Chem. Soc.*, 807 (1967).

[7] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., Inc., New York, N. Y., 1958.

direct, high yield synthesis of IV from readily available starting material.

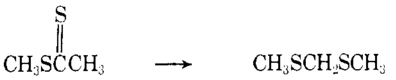
To determine whether this hydrogenolysis reaction was general for a variety of trithiocarbonates, we prepared *trans*-1,2-cyclohexane trithiocarbonate (I) using the method of Culvenor, Davies, and Pausacker.[8] Hydrogenation of I under similar conditions (MoS_3, 160°, 1900 psi) afforded *trans*-methylenedithiocyclohexane (V)[5] in 50% yield. The infrared (1439 cm^{-1}) pmr



V

[δ (CCl_4) 3.78 (singlet, 2 H, $-SCH_2S-$), 2.86 (multiplet, 2 H, $>CHS$), 1.16–2.36), multiplet (8 H, $-CH_2-$)], and mass spectrum [m/e 160 (M^+)] are consistent with our structural assignment.

In addition, we have found noncyclic trithiocarbonates can also be converted into the corresponding 1,3-disulfides. Thus dimethyl trithiocarbonate (VI), pre-



$$CH_3SC(=S)CH_3 \longrightarrow CH_3SCH_2SCH_3$$

VI VII

pared from methyl chloride and sodium trithiocarbonate, was reduced using cobalt sulfide and molybdenum disulfide as catalyst at 2500 psi and 150°. In addition to recovered starting material, 2,4-dithiapentane (VII)[9] [infrared spectrum 1435, 1421 cm^{-1}; δ (neat) 3.65 (singlet, 2 H, $-SCH_2S-$), 2.13 (singlet, 6 H, $-SCH_3$)] was isolated in ~10–15% yield.

Experimental Section

All boiling points are uncorrected. Infrared spectra were recorded with a Perkin-Elmer Infrared or Model 21 spectrophotometer. Pmr spectra were determined at 27° (probe temperature) with a Varian Associates Model A-60A spectrometer using tetramethylsilane (TMS) as an internal standard. For each compound, chemical shifts cited are the centers of the multiplet. Numbers in parentheses refer to the multiplicity of the observed resonance.

Reagents.—Ethylene trithiocarbonate, molybdenum di- and trisulfide, cobalt sulfide and hydrogen (CP grade) were obtained from commercial sources and used without further purification. *trans*-1,2-Cyclohexane trithiocarbonate[8] and dimethyl trithiocarbonate[10] were prepared by known literature methods.

General Procedure.—The experimental conditions for the hydrogenations are recorded in Table II. A typical laboratory procedure for the preparation of 1,3-dithiolane follows.

TABLE II

Compd	Amt, mol	Catalyst (g)	Benzene, ml	H_2, psi
I	0.37	MoS_3 (5)	200	2000
III	0.11	MoS_3 (3)	50	1900
VI	0.36	MoS_2 (5) CoS (5)	100	2500

1,3-Dithiolane.—Ethylene trithiocarbonate (50 g, 0.37 mol) dissolved in 200 ml of benzene and 5.0 g of molybdenum trisulfide were placed in a 300-ml stainless steel autoclave. The autoclave was pressured to 2000 psi with hydrogen and heated to 150° for 12 hr while maintaining a constant hydrogen pressure of 2000 psi. After cooling to 25°, the autoclave was vented through a 20% sodium hydroxide solution; filtration of the clear solution followed by removal of the solvent at 15 mm afforded 37.0 g of 1,3-dithiolane (93% purity). Distillation yielded a malodorous, colorless liquid: bp 75° (25 mm); $n^{23}D$ 1.5980 [lit.[2] bp 61° (11 mm), $n^{16}D$ 1.5975]; infrared 2960, 2919, 1415, 1270, 858, 728, 680 cm^{-1}; pmr (CS_2) δ 3.83 (SCH_2S, 1), 3.13 (CH_2S, 1).

Registry No.—I, 16166-42-0; III, 822-38-8; IV, 4829-04-3; V, 5673-01-8; VI, 2168-84-5; VII, 1618-26-4.

Acknowledgment.—The technical assistance of Mr. Richard Eletto is gratefully acknowledged.

---

[8] C. C. J. Culvenor, W. Davies, and K. H. Pausacker, *J. Chem. Soc.*, 1050 (1946).

[9] H. Bohme and R. Marx, *Ber.*, **74**, 1667 (1941).

[10] E. Wertheim, *J. Amer. Chem. Soc.*, **48**, 826 (1926); **53**, 4037 (1931). This compound was kindly provided by Professor N. Remes.

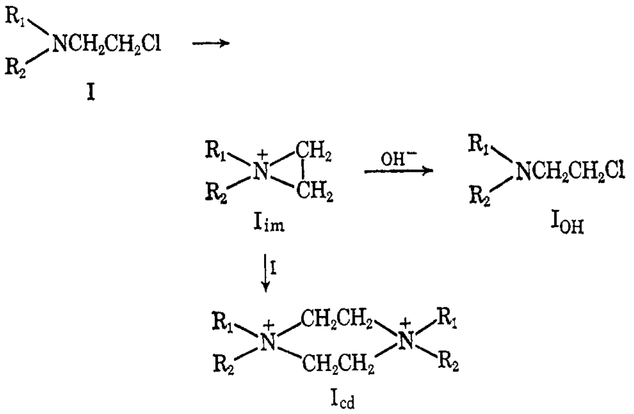
Nitrogen Mustard Reactions by Nuclear Magnetic Resonance Spectroscopy[1]

JOHN R. SOWA[2] AND CHARLES C. PRICE

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Received June 4, 1968

Classical chemical studies have shown that the reactions of many 2-chloroethylamines in aqueous solvent systems proceed through the formation of reactive ethyleneimonium ion intermediates.[3,4]



I, $R_1 = R_2 = C_2H_5$

II, $R_1 = R_2 = CH_3$

III, $R_1 = CH_3$; $R_2 = ClCH_2CH_2$

Levins and Papanastassiou[5] have recently shown that, for a number of primary and secondary 2-haloethylamines and for one tertiary amine, methylbis(2-chloroethyl)amine (HN-2), nmr studies in ^2H_2O can be useful for studying the rate of formation and

---

[1] Supported in part by U. S. Public Health Service Grant No. Ca-08485.

[2] From the Ph.D. Dissertation of J. R. Sowa, University of Pennsylvania, 1964.

[3] C. Golumbic, J. S. Fruton, and M. Bergman, *J. Org. Chem.*, **11**, 578 (1946).

[4] P. D. Bartlett, S. D. Ross, and C. G. Swain, *J. Amer. Chem. Soc.*, **71**, 1415 (1949).

[5] P. L. Levins and Z. B. Papanastassiou, *ibid.*, **87**, 826 (1965).