

tion more complex than the assumed unimolecular decomposition of this dialkyl peroxide.

Experimental Section

Materials.—*t*-Amyl peroxide was prepared by the method described by Milas and Surgenor.⁵ The crude peroxide was distilled twice [bp 44–45° (10 mm)] through a 40-mm glass bead column and yielded a sample at least 98% pure by gas chromatographic analysis. Authentic samples of 1,1,2-trimethylethylene oxide (IV) and 1-ethyl-1-methylethylene oxide (V) for gas chromatographic analysis were prepared from the appropriate alkenes by reaction with peracetic acid as described by Sorenson and Campbell.⁶ The nmr spectrum of 1,1,2-trimethylethylene oxide (bp 74–74°) showed a multiplet at 1.2 ppm and a quartet at 2.7 ppm in a ratio of 10:1. The 1-ethyl-1-methylethylene oxide (bp 80–81°) has an nmr spectra with a triplet at 0.9 ppm, a singlet at 1.2 ppm, a quartet at 1.5 ppm, and a singlet at 2.4 ppm.

Rate Determinations.—Samples approximately 1 ml in size of either the pure peroxide or solution were placed in several 9 mm × 9 in. Pyrex tubes. After sparging with nitrogen and cooling, the tubes were sealed and placed in a constant-temperature oil bath at the temperature indicated in Table II. The tubes were withdrawn at various time intervals; the amount of peroxide remaining was determined by gas chromatographic analysis of the contents of the tubes employing the method described previously for determination of *t*-butyl peroxide.³

Thermal Decomposition of Liquid *t*-Amyl Peroxide.—A small amount of peroxide was placed in a glass tube, sealed, and heated for 17 hr at 115°. A portion of the resulting mixture was subjected to gas chromatographic analysis on two different columns (0.25 in. × 13 ft column packed with 17% dodecyl phthalate on Chromosorb W and 1/8 in. × 19 ft column packed with 20% TCEP on Chromosorb W). The products of the reaction were identified by comparison of their retention times on both columns with authentic samples of the materials. The quantities were determined from the peak areas of each component as measured with a Disc Integrator. No attempt was made to analyze the gaseous products of the reaction.

Registry No.—III, 10508-09-5.

(5) N. A. Milas and D. N. Surgenor, *J. Amer. Chem. Soc.*, **68**, 643, (1946).

(6) W. R. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry," 2nd ed, Interscience, New York, N. Y., 1968, p 370.

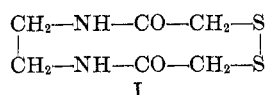
A Ten-Membered-Ring Cyclic Disulfide¹

TERENCE C. OWEN AND J. M. FAYADH

Department of Chemistry, University of South Florida,
Tampa, Florida 33620

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Reaction of ethylenediamine with methyl or butyl dithiodiglycollate in the absence of solvent affords the cyclic disulfide diamide N,N'-ethylenedithiodiglycollamide (perhydro-1,2,5,8-dithiadiazecine-4,9-dione, I) in excellent yield. The same product, rather than the



expected low polymer with amine end groups, results in fair yield even from reaction of the ester with a considerable excess (up to 1.6 mol) of the amine. Poorer yields result from reaction in solution in ethanol or dimethylformamide. The disulfide is quite stable at

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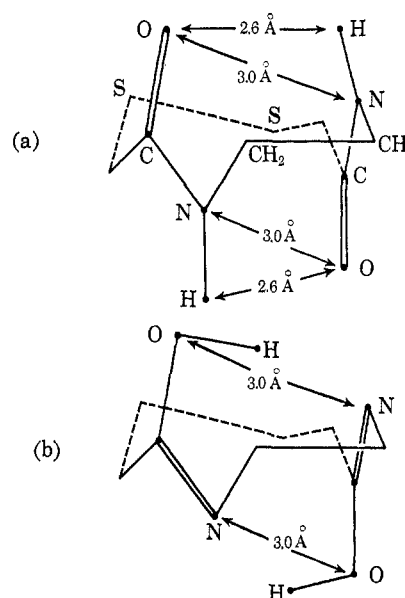


Figure 1.—Skeletal structures for N,N'-ethylenedithiodiglycollamide: (a) amide extreme, (b) isoamide extreme.

room temperature but undergoes some decomposition upon heating, in solution in dimethylformamide, and at temperatures above 100°.

The monomer structure, I, is indicated by the mass spectrum and elemental analysis. Chromatographic homogeneity and the expected retardation are observed upon gel filtration (Sephadex G 10 or G 15); by which means the material is readily separated from a putative dimer² which results from it upon exposure, in aqueous solution, to X-rays.

Such ready formation of a ten-membered ring is unusual.³ Several contributing restrictions are apparent, however. Substantial hindrance to free rotation about the disulfide bond⁴ and the necessary planarity of the amide group in the presumptive monoamide intermediate (NH₂CH₂CH₂NHCOCH₂SSCH₂COOR) restrict the conformations which this may adopt essentially to those available to apodeictically cyclizable six-centered systems such as δ -aminovaleric acid. The cyclic product can adopt a strain-free and uncrowded, though compact, conformation (Figure 1) in which all six centers of each amide unit are coplanar, the preferred (10–15 kcal mol⁻¹)⁴ dihedral angle of $\sim 90^\circ$ about the disulfide group is maintained and, indeed, even the diamidoethane moiety has the *gauche* conformation. It is noteworthy that the length of the disulfide bond (2.04 Å) contributes significantly to the lack of both crowding and strain. The internuclear distance between each carbonyl oxygen and the juxtaposed nitrogen of the antipodal amide group is 2.9–3.0 Å, approximately the sum of the respective van der Waals' radii. The probability of duple, strong intramolecular hydrogen bonding seems considerable. The formal

(2) T. C. Owen and A. C. Wilbraham, *J. Amer. Chem. Soc.*, **91**, 3365 (1969).

(3) H. Stetter and J. Marx, *Justus Liebigs Ann. Chem.*, **607**, 59 (1957), have prepared a number of simple macrocyclic diamides. The yields of larger rings (12 centers and above) were good but the 10-membered rings, ethylene-adipamide and tetramethylenesuccinamide, were obtained only in yields of 24 and 34%, respectively, even under high-dilution conditions and with carefully purified reactants.

(4) O. Foss, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961.

diamide structure (Figure 1a) requires an O---H-N angle of $\sim 90^\circ$ and an O---H internuclear distance of 2.6–2.8 Å whereas the diisoamide extreme (Figure 1b) offers the more attractive O-H---N angle of $\sim 152^\circ$. The two structures are interconvertible by concerted electromeric shifts and simultaneous intramolecular transfer of both protons. Spectroscopic studies of the C-O and N-C bond orders are in progress.

Experimental Section

Analyses were by Galbraith Laboratories. Mass spectra were by Morgan-Schaeffer Corp.

Equimolar quantities of ethylenediamine and methyl dithiodiglycollate are admixed. Reaction is moderately exothermic and cooling is desirable for large-scale reactions. The mixture becomes viscous and sets to a yellow crystalline solid within 30 min. The solid, allowed to stand overnight or heated briefly on a steam bath and then washed with ethanol, affords the disulfide diamide (I) as pale yellow crystals, mp 205° , in 90–100% yield. Crystallization from hot dimethylformamide (20–40 ml/g), a process attended by some decomposition, removes the yellow color but does not raise the melting point.

Anal. Calcd for $C_6H_{10}N_2O_2S_2$: C, 34.95; H, 4.85; N, 13.59; S, 31.12; Found, C, 34.77; H, 5.16; N, 13.68; S, 30.88.

Spectra follow: ir (Nujol) 3290, 3250, 1640, and 1530 cm^{-1} ; mass spectrum (50 eV) *m/e* (rel intensity), 208 (S^{34} molecular ion, 3), 206 (S^{32} molecular ion, 37), 177 (2), 173 (2), 164 (9), 160 (23), 142 (90), 133 (21), 106 (13), 104 (22), 87 (56), 84 (56), and 72 (100), no fragments above mass 208; solubility, very slowly soluble in H_2O (150 mg l^{-1} at 25°), dilute HCl, MeOH, EtOH, $CHCl_3$, and other common solvents, moderately soluble in hot dimethylformamide (some decomposition), soluble in concentrated HCl (36%) from which it precipitated essentially quantitatively, and chloride free after washing, upon dilution.

Registry No.—I, 25286-76-4.

A Safe and Convenient Synthesis of Dichloroacetylene

J. SIEGEL, R. A. JONES, AND L. KURLANSIK

U. S. Navy Toxicology Unit,
National Naval Medical Center,
Bethesda, Maryland 20014

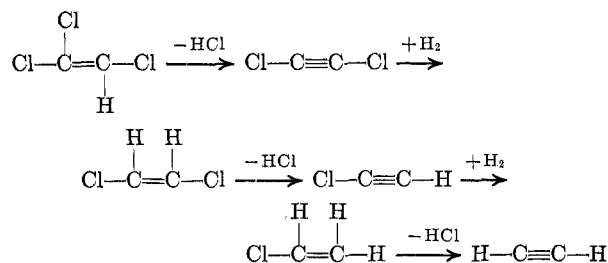
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During the course of our investigation of the toxicology of dichloroacetylene (DCA), the necessity of producing substantial quantities of this compound under safer conditions became quite evident. In 1942, Ott¹ reported that in the presence of ether the autoxidation of dichloroacetylene is retarded and the hazard of explosion is greatly reduced. However, Riemschneider and Brendel² found the preparation, as reported by Ott, to be extremely dangerous, and there were frequent explosions.

The important advantages of the synthesis presented here is that the preparation is carried out in a liquid

medium (ethylene glycol) instead of in a dry combustion tube filled with NaOH; excess ether is present in the system at all times thus reducing the hazards of explosions, and side reactions of DCA with ether are kept minimal. The by-products of the reaction have been identified as being acetylene, monochloroacetylene, dichloroethylene, and acetaldehyde.

The reaction apparently proceeds by a dehydrohalogenation and reduction, which are not unknown in strongly basic solutions. The reactions may be illustrated as follows.



The acetaldehyde present in the crude product may arise from either the ether or ethylene glycol present in the reaction mixture.

From a 1:1 mol solution of trichloroethylene and ether according to the subsequent procedure, we obtained a product containing 55% w/w of DCA in ether.

Identification of the product was made by mass spectrometry, ir spectrometry, and retention time indices on glc using the following conditions: a 12 ft \times $\frac{1}{8}$ in. stainless steel column packed with 30% diisodecyl phthalate on Chromosorb W 60–80 mesh at an oven temperature of 50° . Helium flow was 50 ml/min and FID detector temperature was 200° . Analysis was made using a Dohrmann microcoulometer connected to a glc system as previously described.

Experimental Section

To a 2-l. three-necked round bottom flask equipped with an efficient mercury-sealed stirrer, thermometer, gas inlet and dropper tube, and a tube to an upright Liebig condenser having a 1-l. receiver flask at its base to collect the reaction products, was added 400 g of technical flake KOH and 350 ml of ethylene glycol. The top of the condenser was connected to a 500-ml trap flask immersed in a Dry Ice bath and the condenser cooled to -10° . All connections were ground glass. A 1:1 mol mixture of trichloroethylene and ether was added dropwise at 3–5 ml/min while nitrogen was passed through the system at 100 ml/min, and the reaction mixture was maintained at 140° .

The contents of the receiver and trap were mixed together and the water layer was decanted. The ether solution was dried over magnesium sulfate for 12 hr. The dried solution was distilled through a 550-mm Widmer column and the fraction between $31\text{--}33^\circ$ was collected. The still pot residue was reusable as starting material; yield, 90% (based on TCE lost).

Registry No.—DCA, 7572-29-4.

Acknowledgment.—The Chemical Dynamics Branch and the Physical Chemical Branch of the Chemistry Division, Naval Research Laboratory, conducted the mass spectrographic and ir analyses and their assistance is gratefully acknowledged.

(1) E. Ott, W. Ottmeyer, and K. Paekendorff, *Chem. Ber.*, **63**, 1941 (1930); E. Ott and K. Paekendorff, *ibid.*, **64**, 1324 (1931); E. Ott, *ibid.*, **75**, 1517 (1942); E. Ott, G. Dittus, and H. Wissenburger, *ibid.*, **76**, 87 (1943).

(2) R. Riemschneider and K. Brendel, *Justus Liebigs Ann. Chem.*, **640**, 5 (1961).