

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  $205^\circ$ , 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  $1530\text{ cm}^{-1}$ ; 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  $25^\circ$ ), 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.

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### A Safe and Convenient Synthesis of Dichloroacetylene

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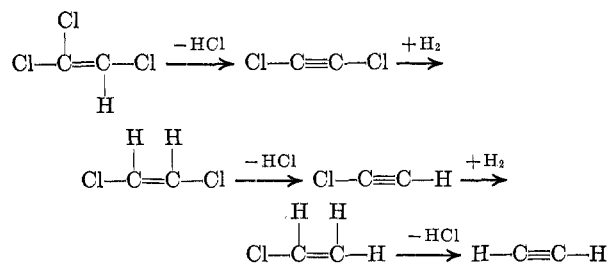
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During the course of our investigation of the toxicology of dichloroacetylene (DCA), the necessity of producing substantial quantities of this compound under safer conditions became quite evident. In 1942, Ott<sup>1</sup> reported that in the presence of ether the autoxidation of dichloroacetylene is retarded and the hazard of explosion is greatly reduced. However, Riemschneider and Brendel<sup>2</sup> 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  $50^\circ$ . Helium flow was 50 ml/min and FID detector temperature was  $200^\circ$ . 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  $-10^\circ$ . 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  $140^\circ$ .

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.

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(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).