CHEMISTRY LETTERS, pp. 1315-1318, 1973. Published by the Chemical Society of Japan

SYNTHESIS AND SOME REACTIONS OF DITHIOBIS(CARBONYL CHLORIDE)[1)]

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Dithiobis(carbonyl chloride) (I) was synthesized for the first time by the hydrolysis of bis(trichloromethyl) disulfide in concentrated sulfuric acid. Treatment of I with amines and phenols gave bis(carbamoyl) disulfides (III) and bis(oxycarbonyl) disulfides (IV), respectively.

We wish to report the synthesis and unequivocal characterization of dithiobis-(carbonyl chloride) (I), a potentially interesting precursor, especially in the synthesis of polymers. While dithiobis(carbonyl fluoride), the fluorine analog of I, has been prepared by the reductive coupling of fluorocarbonylsulfenyl chloride with mercury, similar treatment of chlorocarbonylsulfenyl chloride with mercury resulted in the formation of carbonyl sulfide instead of I[2)]. The present method consists of the hydrolysis of bis(trichloromethyl) disulfide, which can be prepared by the reaction of trichloromethanesulfenyl chloride with cyclohexane under the influence of ultraviolet light[3)].

$$Cl_3CSSCCl_3 \xrightarrow[-HCl]{H_2O} Cl_3CSSC(=O)Cl \xrightarrow[-HCl]{H_2O} ClC(=O)SSC(=O)Cl$$

(II) (I)

A heterogeneous solution of bis(trichloromethyl) disulfide and water (2 mole equivalents) in concentrated sulfuric acid[4)] was heated at 65-70°C with vigorous stirring. After about 5 hr, the organic layer was separated, and distilled under reduced pressure to give I (bp 82°C/19 mm), trichloromethyldithiocarbonyl chloride (II, bp 92°C/10 mm), and unreacted bis(trichloromethyl) disulfide. The yield of I

was in the range 20-40% and that of II was 5-15%. Since the hydrolysis of I sets in before completion of the transformation of bis(trichloromethyl) disulfide into I, it is practical to stop the reaction partway (70-75% conversion) and reuse the recovered starting disulfide.

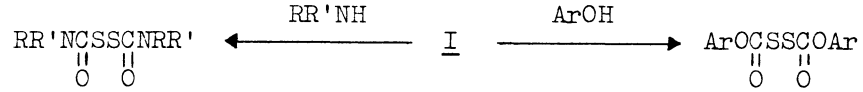
Attempts were made to synthesize I by heating a mixture of bis(trichloromethyl) disulfide and maleic anhydride at 175°C in the presence of zinc chloride or ferric chloride[5], but we were unable to find any evidence for the existence of I in the reaction mixture.

Compounds I and II are colorless liquids with an unpleasant odor, stable at ambient temperature for days if moisture is excluded. Their structures were established from elemental analyses and IR and mass spectra.

I: Anal. Found: C, 12.66; Cl, 37.03; S, 33.81%. Calcd for $C_2Cl_2O_2S_2$: C, 12.57; Cl, 37.11; S, 33.57%. IR (neat): 1780, 1000, 790, 580, 550 cm^{-1}. Mass: m/e (relative intensity) 190 (M^+, 5), 127 (7), 95 (50), 63 (100), 60 (44).

II: Anal. Found: C, 9.83; Cl, 57.99; S, 26.54%. Calcd for $C_2Cl_4OS_2$: C, 9.77; Cl, 57.66; S, 26.07%. IR (neat): 1800, 1000, 800, 750, 570, 560 cm^{-1}. Mass: m/e (relative intensity) 244 (M^+, 3), 209 (7), 181 (12), 149 (8), 117 (100).

Dithiobis(carbonyl chloride) I is a new bifunctional reagent capable of reacting with compounds having easily replaceable hydrogen atoms to provide a simple and general approach to otherwise difficultly obtainable disulfides. Thus bis(carbamoyl) disulfides (III) were readily obtained by stirring 1:4 mixtures of I and amines in dichloromethane for 1 hr below 10°C. The results are summarized in Table 1[6].

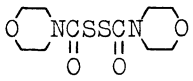
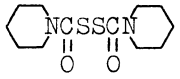
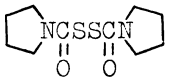
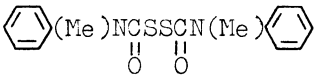
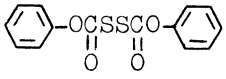
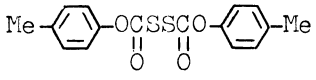
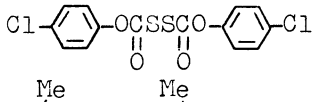
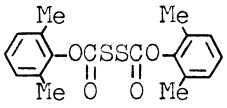


(III) (IV)

Compounds IIIa-IIIc decomposed on standing for a long time, as observed for bis-(dimethylcarbamoyl) disulfide[7], whereas compound IIId can be stored indefinitely without change. Phenols reacted smoothly with I in chloroform-water, sodium hydroxide being used as an acid acceptor, to give stable bis(oxycarbonyl) disulfides (IV)[8] (Table 1). Furthermore, the thiol-induced fragmentation reaction[9] of I provides a new route to symmetrical disulfides. For example, poly(decamethylene disulfide) was obtained in 93% yield by the reaction of I with 1,10-decanedithiol in the presence of

$$\text{I} + \text{HS}(\text{CH}_2)_{10}\text{SH} \xrightarrow{\text{Et}_3\text{N}} \{(\text{CH}_2)_{10}\text{SS}\}_n + 2\text{COS} + 2\text{HCl}$$

Table 1. Bis(carbamoyl) disulfides III and bis(oxycarbonyl) disulfides IV[a)]

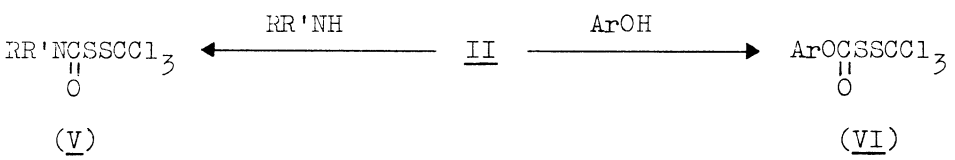
No.	Disulfide	Yield (%)	Mp (°C)	Analysis (%) Found (Calcd) C	H	N	S
IIIa		90	125-126	41.31 (41.08)	5.41 (5.52)	9.58 (9.58)	21.91 (21.93)
IIIb		95	104-105	50.03 (49.97)	7.01 (6.99)	9.67 (9.71)	22.28 (22.23)
IIIc		81	116-117	46.05 (46.13)	6.34 (6.19)	10.80 (10.76)	24.71 (24.63)
IIId		96	241-242	57.79 (57.81)	4.92 (4.85)	8.26 (8.43)	19.31 (19.29)
IVa		87	76- 77	54.66 (54.89)	3.28 (3.29)		21.08 (20.93)
IVb		79	73- 75	57.41 (57.47)	4.28 (4.22)		19.29 (19.18)
IVc		86	130-131	44.61 (44.81)	2.19 (2.15)	18.80[b)] (18.90)	17.16 (17.09)
IVd		88	121-122	59.73 (59.76)	4.77 (5.01)		17.71 (17.69)

a) The optimum conditions have not been explored.

b) Chlorine analysis.

triethylamine (2 mole equivalents)[10)].

It should be noted that the reaction intermediate II is a new example of perhalomethyldithiocarbonyl halides whose derivatives are of interest both as herbicides and for further syntheses[11)]. The chlorocarbonyl group of II is available for nucleophilic substitutions. The action of amines and phenols on II leads to trichloromethyl carbamoyl disulfides (V)[12)] and trichloromethyl oxycarbonyl disulfides (VI), respectively (Table 2).



(V) (VI)

Table 2. Unsymmetrical disulfides V and VI[a)]

No.	Disulfide	Yield (%)	Mp or (Bp) (°C)	Analysis (%) Found (Calcd) C	H	N	S	Cl
Va	Cl_3CSSCN(O)=O	90	87-88	24.50 (24.30)	2.82 (2.72)	4.77 (4.72)	21.75 (21.62)	35.77 (35.86)
Vb	Cl_3CSSCN(C=O)(C=C)	72	79-80	28.52 (28.53)	3.55 (3.42)	4.80 (4.75)	21.87 (21.76)	36.10 (36.10)
Vc	Cl_3CSSCN(C=O)(CH=CH)	82	89-90	25.73 (25.68)	2.93 (2.87)	5.03 (4.99)	23.02 (22.85)	37.79 (37.90)
VIa	Cl_3CSSCO-C$_6$H$_4$	88	(110-112/0.05)	31.16 (31.65)	1.66 (1.66)		21.32 (21.12)	34.81 (35.03)
VIb	Cl_3CSSCO-C$_6$H$_3$(Me)	95	(124-125/0.09)	36.11 (36.21)	2.53 (2.74)		19.36 (19.33)	32.19 (32.07)

a) The optimum conditions have not been explored.

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(Received November 1, 1973)