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DICHLOROSULFINE (THIOPHOSGENE-S-OXIDE) (1)

B. Zwanenburg, L. Thijs and J. Strating,
Department of Organic Chemistry, The University
Bloemsingel 10, Groningen, The Netherlands

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Oxidation of thiocarbonyl compounds such as aromatic thiones (2), dithiocarboxylic esters (3) and thioacid chlorides (4) with peracid produces the corresponding sulfines (>C=S=O) in good yields. In the course of this study we attempted the oxidation of thiophosgene. Treatment of thiophosgene in pentane/ether with slightly less than one equivalent of m-chloroperbenzoic acid (MCPBA) for 1.5 hr at 35° afforded the dichlorosulfine II in 32% yield.

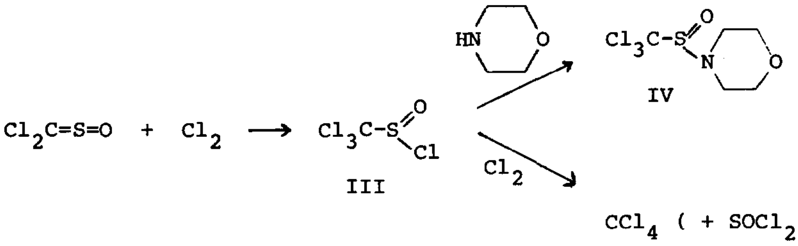
$$\underset{\text{I}}{Cl_2C{=}S} \xrightarrow{\text{MCPBA}} \underset{\text{II}}{Cl_2C{=}S{=}O}$$

The sulfine II could be isolated, after removal of m-chlorobenzoic acid and solvents, by distillation of the remaining oil; b.p. 34-36°/25 mm (5), n_D^{20} 1.5593. The i.r. spectrum displays three strong absorptions of about equal intensity at 1155, 1055 and 955 cm^{-1}. A similar arrangement of bands is present in phenylchlorosulfine (4,6) and phenylsulfenylchlorosulfine (4). The u.v. spectrum of II in hexane exhibits maxima at 252 mμ (log ε 3.07) and 288 mμ (log ε 3.30). Dichlorosulfine (II) is a pale yellow liquid with a pungent, disagreeable, suffocating odor. Its vapor is very lachrymatory and strongly irritating to skin and mucous membranes. Dichlorosulfine can be stored at -20° for at least one month without noticeable deterioration.

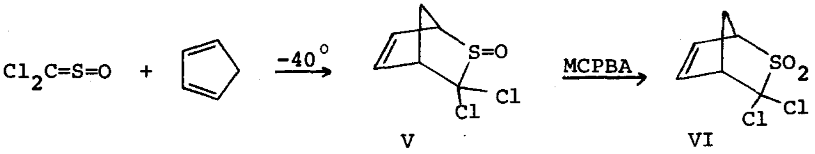
Recently Silhânek and Zbirovský (7) prepared the same compound, which they named dichloromethylene sulfoxide, by hydrolysis of trichloromethanesulfenyl chloride.

The sulfine II reacts sluggishly with methanol and water, vigorously with pyridine or triethylamine and violently with thiophenol. Iodine was liberated when II was added to an aqueous solution of potassium iodide, demonstrating that dichlorosulfine has strong oxidizing power.

Treatment of II with an excess of chlorine at -70° for 2 hr and subsequent raising of the temperature to -10° gave, after removal of volatile materials, an oil which displays a strong band in the i.r. spectrum at 1200 cm^{-1}. The unstable product was characterized (8) as trichloromethanesulfinyl chloride III by conversion into the morpholide IV (9) (yield 26%). Prolonged treatment with chlorine lowered the yield of III, owing to its subsequent reaction (10) with chlorine. Indeed, carbon tetrachloride could be detected (by v.p.c.) in the reaction mixture when the reaction was carried out in a sealed tube at 20°.



Dichlorosulfine reacted rapidly with cyclopentadiene in pentane at -40°. The reaction proceeds explosively in the absence of solvent. The precipitated cyclo-addition product V was rather unstable. However, upon oxidation with MCPBA the stable sulfone VI (11) (yield 50%) was obtained.

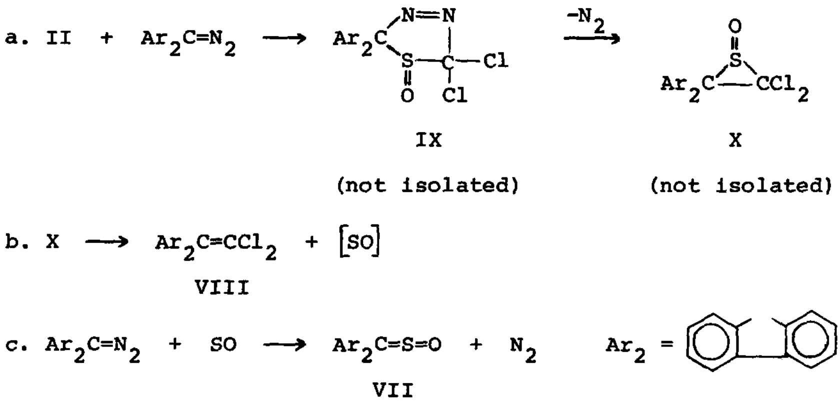


This cyclo-addition reaction (12) as well as the addition of chlorine (13) provide chemical confirmation of the sulfine entity in II.

A very interesting reaction of II takes place with diazofluorene. As main products were isolated thiofluorenone-S-oxide (VII, yield 50% (14)) and 9-dichloromethylene fluorene (15) (VIII, yield 70%).

$$\underset{}{Cl_2C{=}S{=}O} + Ar_2C{=}N_2 \longrightarrow \underset{\text{VII}}{Ar_2C{=}S{=}O} + \underset{\text{VIII}}{Ar_2C{=}Cl_2}$$

Tentatively, we propose that the apparent transfer of the sulfinyl group proceeds *via* the following steps:



Step a represents a 1,3-cyclo-addition to IX which loses nitrogen to give the episulfoxide (16) X. The latter type of compound is known (17) to decompose easily furnishing in this case VIII and sulfur monoxide (step b). Capture of SO with diazofluorene as shown in step c was first observed by Van Tamelen (18) who found that when cyclohexene episulfoxide was heated with diazofluorene, thiofluorenone-S-oxide was produced in 3% yield. The sulfine formation as shown in step c resembles the reaction of diazo compounds with SO_2 which yields sulfenes (19) as the initial reaction product.

We are currently exploring the chemistry of dichlorosulfine, the simplest stable sulfine known sofar, in our laboratory.

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