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CLEAVAGE OF A CARBON-SULFUR BOND IN A DISULFIDE BY A CARBENE

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Although the disulfide linkage is readily cleaved by a variety of reagents,[1] selective cleavage of a carbon-sulfur bond of a disulfide does not seem to have been observed previously, except as a mode of decomposition of disulfides in the mass spectrometer.[2, 3]

The reaction of a disulfide with a carbene, which has not been previously reported, has been found in the present work to give selective carbon-sulfur cleavage, with the disulfide linkage remaining intact. In the case of the reaction of t-butyl disulfide (I) with dichlorocarbene, the product, t-butyl dichloromethyl disulfide (II), was isolated in 80% yield.

$$\underset{\text{(I)}}{(CH_3)_3C\text{-}S\text{-}S\text{-}C(CH_3)_3} + Cl_2C{:} \rightarrow \underset{\text{(II)}}{(CH_3)_3C\text{-}S\text{-}S\text{-}CHCl_2} + (CH_3)_2C{=}CH_2$$

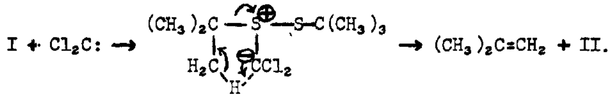
The reaction was carried out by heating a solution of (I) and sodium trichloroacetate in 1,2-dimethoxyethane under reflux.[4] The gas evolved was identified as isobutylene by its infrared and mass spectra and its b.p. of -6°. The t-butyl dichloromethyl disulfide (II), which was isolated by distillation, b.p. 114° (32 mm.), was identified by its elemental analysis, infrared and p.m.r. spectra, and independent synthesis. (Anal. Calcd.

for $C_5H_{10}Cl_2S_2$: C, 29.26; H, 4.91; S, 31.26; Cl, 34.56. Found: C, 29.13; H, 5.05; S, 31.40; Cl, 34.65).

The infrared spectrum of II shows typical S-S absorption at 475-500 cm.$^{-1}$[5] but no C=S absorption. The p.m.r. spectrum has a sharp, singlet band at 6.54 δ (for 25% carbon tetrachloride solution), in addition to the singlet band expected for the t-butyl group. The assignment of the down-field singlet band to the dichloromethyl proton is in agreement with its singlet nature, chemical shift and area of one-ninth that of the t-butyl band. The position is similar to the proton position of 7.03 δ in dichloromethanesulfenyl chloride[6] (Cl_2CH-S-Cl) in 25% carbon tetrachloride solution and the value of 6.92 δ calculated from Shoolery's rules.[7]

An independent synthesis of t-butyl dichloromethyl disulfide was achieved by the reaction of dichloromethanesulfenyl chloride with 2-methyl-2-propanethiol, which gave a product identical to II in all respects, including b.p., refractive index (n_D^{20} 1.5308), infrared and p.m.r. spectra.

It seems reasonable to formulate this carbene-disulfide reaction as formation of the ylide (III) by electrophilic attack of the carbene on a sulfur atom, followed by a cyclic, concerted β-elimination process, as follows:



(III)

Similar cleavage of carbon-oxygen and carbon-nitrogen bonds have been observed in the reactions of carbenes with ethyl ether,[8] n-butyl ether,[9] and triethylamine,[10, 11] but these were relatively minor side-reactions rather than the principal reaction. Such cleavage of carbon-sulfur bonds has not been previously reported.

Probable generality of the reaction for disulfides possessing β-hydrogen atoms is indicated by the fact that dichlorocarbene[4] reacted with ethyl disulfide and *n*-butyl disulfide to give the corresponding alkyl dichloromethyl disulfides, as shown by their b.p. and p.m.r. singlet band at about 6.7δ.[12] The purity of these compounds, however, was less than that of II, due no doubt to the possibility of α-CH insertion in these cases.[13]

It is anticipated that this method may have synthetic value for the preparation of unsymmetrical disulfides, and that it can be extended to other carbenes and other compounds having hetero-atoms with unshared electrons attached to groups too susceptible to β-elimination. Further work is in progress.

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