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DIMETHYLSULPHONIUM (PHENYLTHIO)METHYLIDE

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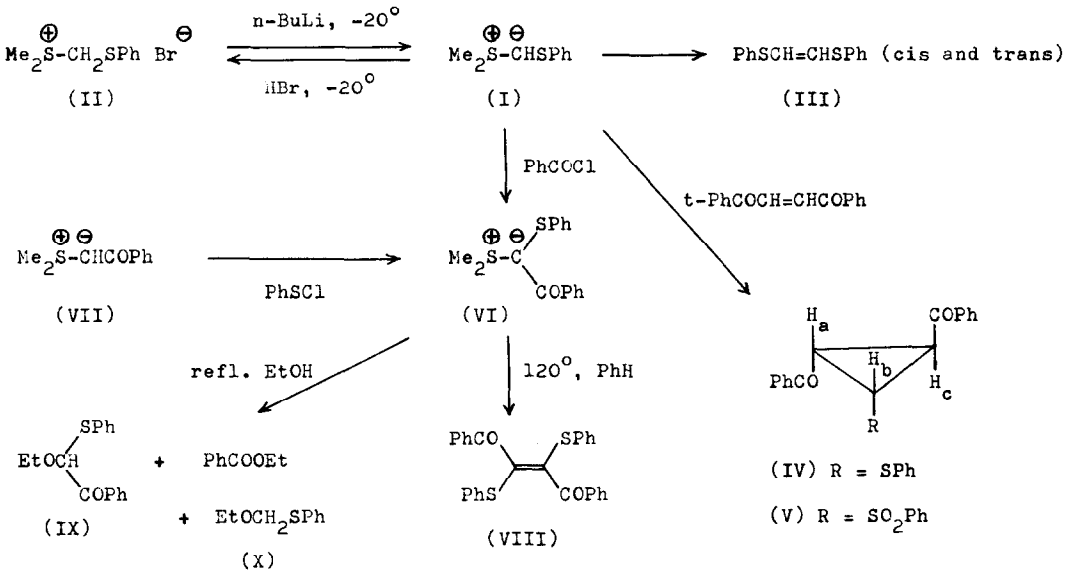
Sulphonium ylides are stabilized by substitution on the ylide carbon with electron-attracting group(s), such as COR, COOR, SO_2R (1). We now wish to report the synthesis and reactions of dimethylsulphonium (phenylthio)methylide (I) and related ylides, as no precedent of this class seems to have been described previously.

Addition of n-butyllithium to a suspension of dimethyl(phenylthiomethyl)sulphonium bromide (II) (2) in THF at -20° under nitrogen produced a pale yellow solution containing the ylide I, which was reconverted into II by the addition of HBr at the same temperature. Evaporation of the solution of I gave a cis-trans mixture of 1,2-bis(phenylthio)ethylene (III), which was subjected to column chromatography (Alumina, hexane) to afford cis-III (27%, oil) and trans-III (43%, mp. 60-61°) (lit. cis-III: mp. 31.5°; trans-III: 62°) (3). When the solution of I was treated with trans-1,2-dibenzoylethylene at -20°, the single



product isolated was found to be 1,2-dibenzoyl-3-(phenylthio)cyclopropane (IV) (27%, mp. 113.5-114° (from PhH-hexane), IR(KBr) 1660 cm^{-1}). The configuration of IV was determined by the oxidation to V (mp. 188-189° (from PhH)). The NMR of V showed two quartets at δ 3.47 (H_a) and 3.81 (H_b), and a triplet at 4.42 ppm (H_c) (J_{ac} and J_{bc} = 6.0 Hz, J_{ab} = 10.2 Hz). The nonequivalency of H_a, H_c protons excludes the alternative cis-dibenzoyl structures of V and therefore of IV.

Treatment of I with benzoyl chloride gave a new ylide, dimethylsulphonium benzoyl-(phenylthio)methylide (VI) (mp. 135-136° (from PhH), IR (KBr) 1530 cm^{-1}, NMR ($CDCl_3$) δ 2.64 (s, 6H), 7.1-7.9 ppm (m, 10H), λ_{max}^{EtOH} 247 nm (log ε 4.07), 282 (3.84)) in a 64% yield. VI was also prepared from dimethylsulphonium phenacylide (VII) and benzenesulphenyl chloride in a 98% yield. The ylide VI was stable in benzene at reflux temperature, but it was converted to trans-1,2-dibenzoyl-1,2-bis(phenylthio)ethylene (VIII) (10%, mp. 173.5-174°, IR (KBr) 1665 cm^{-1}) by heating in a sealed glass tube at 120° for 3 hr. In contrast, the alcoholic solution of VI at reflux gave IX (oil, 25%), ethyl benzoate (19%) and X (oil, 12%). Ylides I and VI can be considered to be the precursors of "thiocarbenes", on which further investigation is in progress.

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REFERENCES AND NOTES

1. H. Nozaki, M. Takaku, Y. Hayasi and K. Kondo, Tetrahedron 24, 6563 (1968) and references cited therein.
2. II was prepared from dimethyl sulphide and bromometnyl phenyl sulphide in an 68% yield, mp. 69-70° (dec) (very hygroscopic crystals), NMR (DMSO-d6) δ 3.12 (s, 6H), 5.41 (s, 2H) and 7.2-7.9 ppm (m, 5H).
3. W. E. Truce and R. J. McManimie, J. Am. Chem. Soc. 76, 5745 (1954).
4. All new compounds II, IV, V, VI, VIII, IX and X gave satisfactory elemental analyses.