Dimethylsulphonium Methoxycarbonylmethylid

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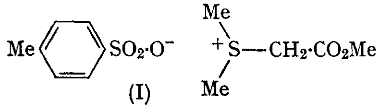
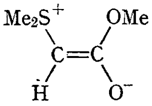
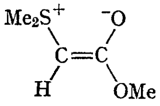
IN the course of investigating the hydrolysis of esters which bear a neighbouring sulphonium group,[1] we have prepared and studied the properties of dimethylsulphonium methoxycarbonylmethylid (II), by the reaction of methyl dimethylsulphonium acetate toluene-*p*-sulphonate (I) with potassium t-butoxide in t-butyl alcohol. The ylid can be obtained in a pure condition (77% yield) by extraction with methylene chloride from the alcohol-freed reaction mixture, followed by molecular distillation (< 50°/0·5 μ). The ylid thus obtained is a colourless oil which crystallizes slowly to a solid, m.p. 19—21°. It can be stored at $-20°$ in an inert atmosphere for an extended period, but decomposes slowly at room temperature. Significant contribution from the enolate structure (IIa,b) is suggested by the infrared spectrum, which shows a maximum at 1621 cm.$^{-1}$ (s; C=C stretch), and the ^{1}H n.m.r. spectrum, which consists of three singlets (2·77 p.p.m., 6H; 2·87 p.p.m., 1H, broad; 3·55 p.p.m., 3H) at room temperature. The *S*-methyl chemical shift of sulphonium salt (I) (3·10 p.p.m.), and that of the zwitterionic salt (III) (2·93 p.p.m.) indicate only a small increase in shielding at the *S*-methyl protons in the ylid—an observation which suggests that d_π–p_π carbon–sulphur bonding in the ylid does not lead to large electron donation to sulphur. This observation is supported by examination of the temperature dependence of the ^{1}H n.m.r. spectrum of (II). At +45° the methine proton becomes sharp. The methine proton signal is broad at 0°, but at $-45°$ the spectrum consists of 6 lines in two sets (2·65 p.p.m., 1H; 2·68 p.p.m., 6H; 3·58 p.p.m., 3H; and 2·81 p.p.m., 6H; 2·94 p.p.m., 1H: 5·53 p.p.m., 3H). The two sets are in the ratio of 17 : 83 to each other, respectively, and are attributed to isomers (IIa) and (IIb). The shielding changes which accompany the appearance of two isomers suggest that the major isomer is (IIb). Nozaki[2a] and Trost [2b] reported ^{1}H n.m.r. spectra of stable ylids and Trost assigned a similar structure to dimethylsulphonium phenacylid, which showed only a single isomer at $-20°$.



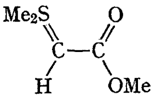
(I)



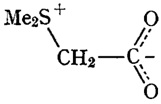
(IIa)



(IIb)

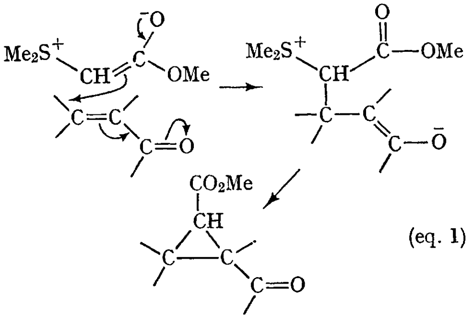


(IIc)



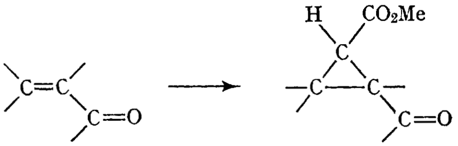
(III)

Ylid (II), generated from dimethylsulphoxonium methylide in dimethyl sulphoxide, decomposed slowly at 90° to give methyl *S*-methylmercaptoacetate (8%), *trans*-1,2-dimethoxycarbonylcyclopropane (43%), and *trans*-1,2,3-trimethoxycarbonylcyclopropane (2%). These products are easily rationalized by a Michael addition–elimination sequence of the ylid on $\alpha\beta$-unsaturated esters initially formed from the ylid (eq. 1). That this is a probable route of reaction is shown by the reaction of the ylid, generated in the same manner as described above, with methyl acrylate to give *trans*-1,2-dimethoxycarbonylcyclopropane (44%), with dimethyl maleate to give *trans*-1,2,3-trimethoxycarbonylcyclopropane (54%), and with dimethyl fumarate to give *trans*-1,2,3-trimethoxycarbonylcyclopropane (45%). However, ylid is a sufficiently strong base so that reaction of (I) with sodium methoxide in methanol, followed by fumarate, gave *trans*-trimethylaconitrate (83%), apparently due to the greater acidity of methanol in the early steps of the reaction sequence. The synthetic potential of a similar ylid has been carefully examined by Payne.[3] Together, the reactions of (II) in dimethyl sulphoxide and

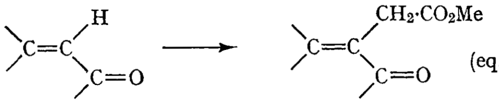


(eq. 1)

methanol provide excellent new methods to effect the useful transformation:



(eq. 2)



(eq. 3)

when the olefin is a Michael acceptor.

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[1] J. Casanova, jun., N. D. Werner, and H. R. Kiefer, *J. Amer. Chem. Soc.*, 1967, **89**, 2411.

[2] (a) H. Nozaki, K. Kondô, and M. Takaku, *Tetrahedron Letters*, 1965, 251; (b) B. M. Trost, *J. Amer. Chem. Soc.*, 1967, **89**, 138 (1967). Leading references may be found in this article.

[3] G. B. Payne, 154th National Meeting, American Chemical Society, Chicago, Ill., Sept. 11–15, 1967, Organic Section, paper No. 158, and private communication. We thank this author for making his results available to us prior to publication.