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REACTION OF SULPHONIUM YLIDES WITH SULPHONYL CHLORIDES

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We wish to report that the reaction of sulphonium ylides I (1, 2) with substituted methanesulphonyl chlorides proceeds according to the courses as summarized in Fig. 1 in the presence of excess triethylamine in THF solution at room temperature. Yields of various types of products (II - IV) have been given in Table 1.

The C-sulphonylated ylides (II) (3) were obtained as stable crystals, whose properties have been shown in Table 2. All new compounds in this paper gave correct analyses. Remarkably, the sulphonylation has resulted in bathochromic IR shift of ca. 60 cm^{-1} with respect to the "ylide carbonyl" absorption of phenacylides (1, 4) and ca. 25 cm^{-1} in carbethoxymethylides (Y = OEt) (2). The S-O absorptions appeared in normal region. The intermediates for C-sulphonylation may be either V or VI or both.

In certain cases the major products were found to be not II but trans-olefins III. Yields as high as 75% have been obtained. The reaction would probably involve the initial formation of sulphenes ($RCH=SO_2$) and their adducts VI. Intramolecular S_N reaction on the original ylide carbon should give episulphones VII, which are supposed to be thermally decomposed to III (5). The stereospecific trans-configuration may partly be ascribed to the intermediacy of rather stable species VI, although the possibility of cis-trans isomerization of the α,β-unsaturated carbonyl system can not be excluded. This novel olefin-synthesis furnishes a method of transforming an alcohol RCH_2OH into R-CH=CH-CO- compounds without resource to the corresponding aldehyde RCHO.

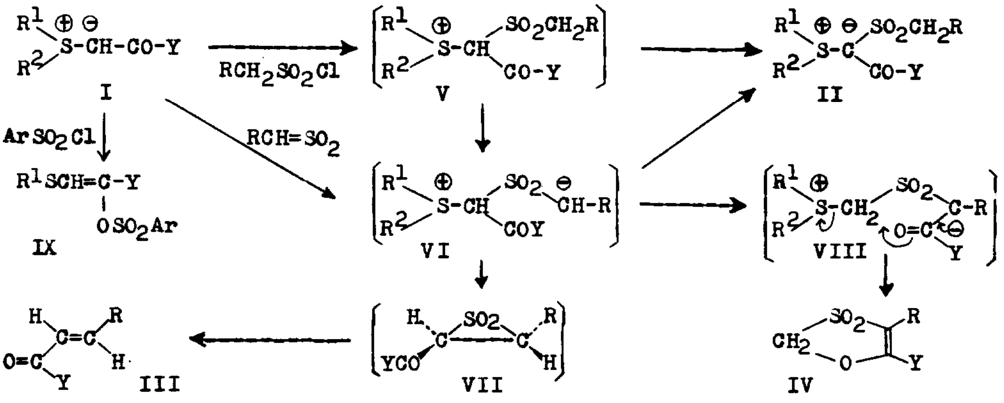

FIG. 1. Summary of the Observed Reactions

TABLE 1.

Product Distribution in the Sulphonylation of Ylides I

I					Yield (%)		
R^1	R^2	Y	Ref.	R	II	III	IV
Ph	Me	Ph	1	Ph	—	75	—
Ph	Me	Ph	1	Me	7	15	36
Ph	Ph	OEt	2	Ph	21	78	—
Me	Me	Ph	4	Ph	52	—	—
Me	Me	Ph	4	Me	—	—	25

Neither II nor III was isolated in the reaction of dimethylsulphonium phenacylide (I, R^1, R^2 = CH_3, Y = Ph) with ethanesulphonyl chloride. The only product isolated in 25% yield was found to be 4-methyl-5-phenyl-1,3-oxathiole-3,3-dioxide (IV), m.p. 112°. The assigned structure was consistent with NMR spectrum (6) (2.17 (s), C-methyl; 4.96 (s), methylene; 7.50 (s), aromatic) and IR absorptions (KBr) at 1650, 1308 and 1125 cm^{-1}. The UV absorption (ethanol was observed at 261 mμ (log ε 4.06) (7

TABLE 2.

Properties of C-Sulphonylated Ylides II

R^1	R^2	Y	R	m.p. (°C)	IR (cm^{-1})	NMR[a]
Ph	Me	Ph	Me	181	1565, 1305, 1125	
Ph	Ph	OEt	Ph	142	1664, 1300, 1123	b
Ph	Ph	OEt	Me	110	1665, 1300, 1120	c
Me	Me	Ph	Ph	171	1570, 1325, 1110	d

a) See ref. 6.

b) 1.22 (t), 4.18 (q) (J 7.2 c/s), COOEt; 4.65 (s), SO_2CH_2; 7.1-7.5 (m), aromatic.

c) 1.25 (t), 4.11 (q) (J 7.0 c/s), COOEt; 1.16 (t), 3.36 (q) (J 6.8 c/s), SO_2Et; 7.3-7.8 (m), aromatic.

d) 2.34 (s), $S-CH_3$; 4.56 (s), SO_2CH_2; 7.32 (m), aromatic.

TABLE 3.

Properties of Enol Sulphonates IX

R^1	Yield (%)	m.p. (°C)	IR (cm^{-1})	NMR[a]
Ph	47	85	1600, 1355, 1170	2.37 (s), $C-CH_3$; 6.45 (s), olefinic; 7.2-7.9 (m), aromatic
Me	30	oil	1600, 1370, 1175	2.30 (s), $S-CH_3$; 2.38 (s), $C-CH_3$; 6.23 (s), olefinic; 7.0-7.8 (m), aromatic

a) See ref. 6.

Treatment of methylphenylsulphonium phenacylide (I, R^1 = Ph, R^2 = CH_3, Y = Ph) with ethanesulphonyl chloride yielded the same compound IV.

Finally, it was found that the action of tosyl chloride on I resulted in O-sulphonylation to afford IX. Properties of these enol sulphonates IX have been summarized in Table 3. The fate of S-methyl group of I is still obscure, as this has been the case with O-acylation of I (1).

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5. The proposed mechanism is analogous to the one of the reaction of diazoalkanes with alkanesulphonyl chlorides. See G. Opitz and K. Fisher, Angew. Chem. 77, 41 (1965).
6. The NMR data (taken in $CDCl_3$ solutions on JEOLCO JNM-C-60H machine) are given in the order of chemical shift in p.p.m. from TMS ref., multiplicity in parentheses and assignment. Each signal showed correct integrated area.
7. In literature (K. Dichore, Ann. 671, 135 (1964)), 5-phenyl-1,3-oxathiole-3,3-dioxide (IV, R = H, Y = Ph) has been described.