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STABLE SULPHUR-YLIDES FROM SULPHOXIDES AND ACTIVE METHYLENE COMPOUNDS

H. Nozaki, Z. Morita and K. Kondô
Department of Industrial Chemistry, Kyôto University
Kyôto, Japan

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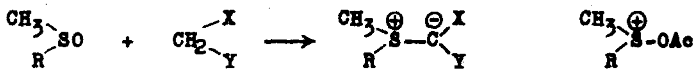
A recent paper of Gompper and Euchner (1) on the reaction of dialkyl sulphoxides with barbituric acids, 2-hydroxy-1,4-naphthoquinone and methylene-bisphenylsulphone has prompted the publication of closely related findings on the reaction of sulphoxides I and II with other classes of active methylene compounds leading similarly to stable sulphur-ylides III and IV (2,3).



I ($R = CH_3$) III ($R = CH_3$) V

II ($R = Ph$) IV ($R = Ph$)

The substituents X and Y are keto, ester or nitrile groups and the reaction is effected by either (A) heating the reaction components in acetic anhydride solution under reflux for 20 hr. or (B) treating a triethylamine solution of both

TABLE 1. Yields and Properties of Stable Sulphur-Ylides [a]

Substituents		Method of Conden-sation	Ylide III			Ylide IV		
X	Y		Yield %	M.p. °C	IR[b] cm.$^{-1}$	Yield %	M.p. °C	IR[b] cm.$^{-1}$
Ac	Ac	A[c]	5.0	168	1570	44	140	1582
		B[d]	13			12		
Ac	Bz	A	40	109	1572	27	138[e]	1590 1567
Cyclohexane-1,3-dione		A	nil	—	—	20	124	1565
Dimedone		A	24	172	1539	27	138	1572
Ac	COOEt	A	7.0	64	1668 1548	21	60	1665 1595
CN	COOEt	A	2.0	131	2160 1625	nil	—	—
		B[f]	14			11	oil	2180[g] 1660
CN	CN	B[f]	11	99[h]	2200	15	77[h]	2190

[a] With exception of the indicated ones, all sulphur-ylides in this Table are new. They gave correct C,H-analyses.

[b] Unless otherwise stated, wave numbers of characteristically shifted carbonyl and/or cyano group absorptions (Nujol) are given.

[c] In the method A, a mixture of I (or II), CH_2XY and acetic anhydride (1:1:30 mole ratio) was heated under reflux for 20 hr, treated with dil. aq. alkali and extracted with chloroform.

[d] A mixture of the reactants (12 mmoles each) was dissolved in 20 ml. of triethylamine and 3 g. of phosphorus pentoxide was added and the whole mixture was heated at 100° for 5 hr.

[e] See ref. 2.

[f] The reaction mixture was vigorously stirred at room temperature for 24 hr. At higher temperature only black tar was produced.

[g] IR was taken with a liquid film.

[h] See ref. 1.

reactants with phosphorus pentoxide. The respective sulphur-ylides were obtained as stable crystalline solids, which showed characteristic frequencies of carbonyl or cyano group shifted ca. 100 cm.$^{-1}$ to lower wave number region. These results are presented in Table 1. Obviously the two methods A and B are complementary and the yields recorded do not necessarily represent those under optimum conditions.

In the presence of acetic anhydride (method A) the principal side reaction is the formation of thiols, as this has been first observed by Pummerer (4). Another related reaction is the highly selective oxidation of alcohols by means of a mixture of dimethyl sulphoxide and acetic anhydride (5). The mechanisms of these two reactions point to the initial formation of acetoxysulphonium cation V. The presently observed sulphur-ylide formation also would presumably proceed via the attack of V on the active methylene compounds or the respective carbanions followed by the loss of acetic acid.

Attempted condensation of diphenyl sulphoxide did not produce any appreciable amounts of sulphur-ylides. Acid-catalyzed reaction of dimethyl sulphoxide and active methylene compounds in the presence of dicyclohexylcarbodiimide (6) also failed to occur in the expected way (7).

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