

THE REACTION OF CARBONYL-STABILIZED SULFUR YLIDES WITH SOME 1,3-DIPOLES

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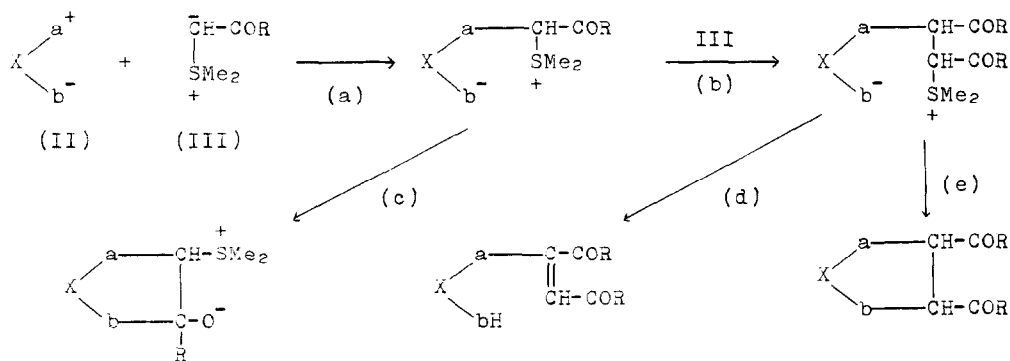
(Received in Japan 22 December 1969; received in UK for publication 19 January 1970)

The 1,3-dipolar addition to unsaturated compounds provides a useful method of preparation of heterocyclic compounds¹⁾. The reaction between 1,3-dipoles and dimethylloxosulfonium methylide(I) is also an useful alternative for the synthesis of these compounds²⁾.

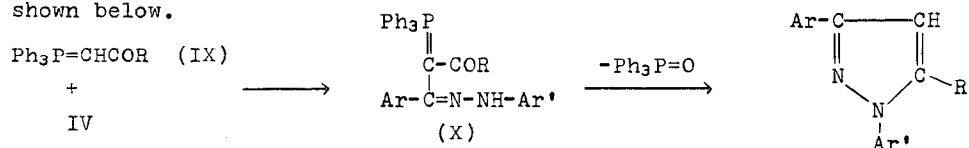
From a study of the recent publication³⁾ concerned with the reaction of dimethylsulfonium phenacylides with nitrile imines, we were anxious to determine how carbonyl-stabilized ylides would react with 1,3-dipoles and the recent publications on the reaction of phosphorous ylides with 1,3-dipoles⁴⁻⁷⁾ has prompted the publication of closely related findings on the reaction of carbonyl-stabilized ylides with some 1,3-dipoles leading to useful heterocyclic compounds.

The five principal reactions involved in the reaction of carbonyl-stabilized sulfur ylides with the dipoles are shown in Chart 1, while the course of the reaction depends upon the nature of the dipoles and the carbonyl group of the ylides.

Chart 1



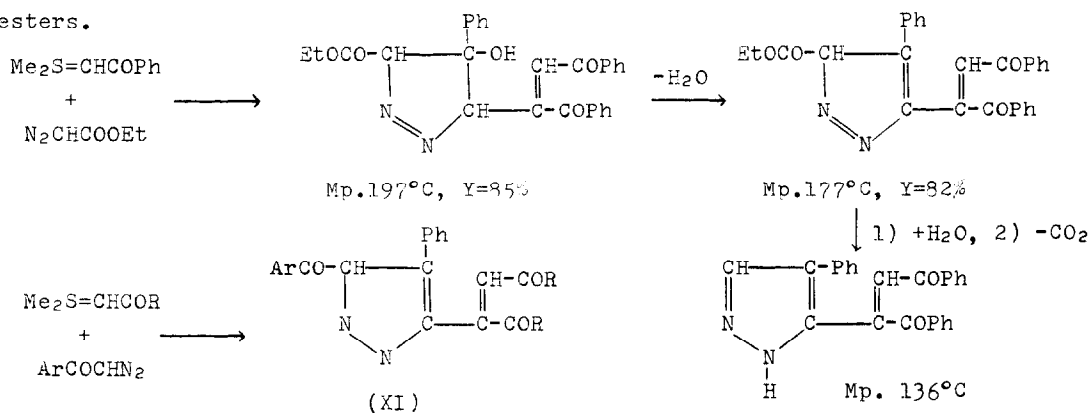
fumarate. Two examples of the reaction of phosphorous ylides with nitrile imines are reported recently⁷⁾. The authors have also found the same results³⁾ as shown below.



Some of X (for example, Ar=Ph, Ar'=p-NO₂C₆H₄) were rather unstable to isolate pure product and elimination of the phosphine oxide from X drives the reaction to completion. When the ylides are strongly basic as in IXa (R=CH₃), the product is hydrogen chloride salt of X in spite of the presence of excess triethylamine.

2). Diazomethanes

The reaction of diphenyldiazomethane with I did not give the expected heterocycle²⁾ and this was the case in the reaction of diphenyldiazomethane with III. On the other hand, pyrazolenine derivatives were isolated in high yield from the reaction mixture of III and benzoyldiazomethanes (Table 2) or diazoacetic acid esters.



3) Azides

Acylmethylenetriphenyl phosphoranes react with organic azides to furnish either 1,2,3-triazoles or α -diazocarbonyl compounds in high yield⁴⁾.

1-Arylamino-1,2-dibenzoylethylenes (XII) were isolated in excellent yield from the reaction mixture of III and aryl azides. The structure of XIIa (Ar=R=Ph) was established by comparison with the authentic specimen⁸⁾. Arylsulfonyl azides also gave analogous product to XII in poor yield, while the reaction was not suitable

for aliphatic azides. A small amount of XIII was isolated from the reaction of IIIa(R=OEt) with p-nitrophenyl azide. The results obtained are shown in Table 3.

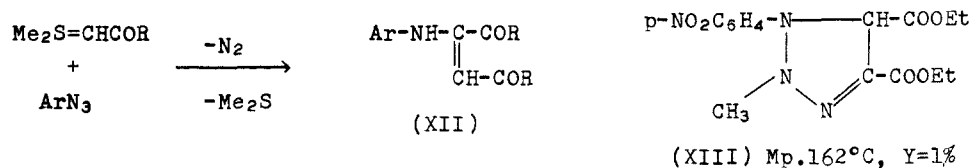


Table 2. Melting point and yield of XI. Table 3. Melting point and yield of XII.

R	Ar	Y.(%)	Mp.(°C)	Ar	R	Y.(%)	Mp.(°C)
Ph	Ph	84	192-193	Ph	Ph	89	126-128
Ph	p-ClC ₆ H ₄	92	203-204	p-NO ₂ C ₆ H ₄	Ph	100	167-168
Ph	m-BrC ₆ H ₄	90	178-179	p-CH ₃ C ₆ H ₄	Ph	29	153-155
Ph	p-CH ₃ C ₆ H ₄	82	158-160	Ph	p-CH ₃ C ₆ H ₄	100	142-143
p-ClC ₆ H ₄	Ph	85	118-119	p-NO ₂ C ₆ H ₄	p-CH ₃ C ₆ H ₄	99	204-205
p-CH ₃ C ₆ H ₄	m-BrC ₆ H ₄	89	190-191	Ph	p-BrC ₆ H ₄	100	169-170
p-BrC ₆ H ₄	p-CH ₃ C ₆ H ₄	68	189-190	p-CH ₃ C ₆ H ₄ SO ₂	p-BrC ₆ H ₄	12	231-232

4). Nitrile oxide

Extensive studies have been made on the reaction of phosphorous ylides with nitrile oxides^{5,6}). 3-Phenylisoxazoline was obtained from the reaction of phenyl nitrile oxide with the ylide I²). 4,5-Dibenzoyl-3-phenylisoxazoline(Mp. 147°C, yield 15%) was isolated from the reaction mixture of IIIb(R=Ph) and α-chloro-benzaldoxime in the presence of triethylamine.

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