#### THE REACTION OF CARBONYL-STABILIZED SULFUR YLIDES WITH SOME 1.3-DIPOLES

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The 1,3-dipolar addition to unsaturated compounds provides a useful method of preparation of heterocyclic compounds<sup>1)</sup>. The reaction between 1,3-dipoles and dimethyloxosulfonium methylide(I) is also an useful alternative for the synthesis of these compounds<sup>2)</sup>.

From a study of the recent publication<sup>3</sup> 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-dipoles<sup>4-7</sup> 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

Some examples obtained are reported briefly and more complete details will be reported later. The structural assignment of the new compounds obtained was substantiated by elemental analysis, molecular weight, IR and NMR.

# 1). Nitrile imines

In previous paper<sup>3</sup>) we reported the reaction of phenacylsulfonium ylides, yielding pyrazoles in excellent yield. Carboalkoxymethylenesulfonium ylides were also reacted with nitrile imines to give interesting products (Table 1). The yield of the products was dependent on the molar ratio of the reagents used and the maximum yield is shown in Table 1.

Table 1. Melting point(°C) and yield(%) of the products

Δ					VI				
R	Ř	" R	Mp.	Yield	R	Ř	" R	Mp. (dec.)	Yield
00 <sub>2</sub> H <sub>5</sub>	H	Н	121-122	62	OC <sub>2</sub> H <sub>5</sub>	Ħ	Н	135-136	36
OCH3	H	H	99-101	53	OCH3	Н	H	138-139	74
OC <sub>2</sub> H <sub>5</sub>	H	Cl	170-171	54	OCH3	СНз	Н	141-142	56
осн₃	H	Cl	132-133	13	C <sub>6</sub> H <sub>5</sub>	Н	H	152-154	5

A variation of the reaction was observed as shown below.

The product VIII can also be prepared from the reaction of IVa with diethyl

fumarate. Two examples of the reaction of phosphorous ylides with nitrile imines are reported recently<sup>7</sup>). The authors have also found the same results<sup>3</sup>) as shown below.

shown below.

$$Ph_{3}P$$

$$C-COR$$

$$+$$

$$Ar-C=N-NH-Ar$$

$$(X)$$

$$Ar-C$$

$$N$$

$$N$$

$$Ar^{C}$$

Some of X(for example, Ar=Ph, Ar'=p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) 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  $IXa(R=CH_3)$ , 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 heterocycle<sup>2</sup>) 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 a-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 specimen<sup>8</sup>). Arylsulfonyl azides also gave analogous product to XII in poor yield, while the reaction was not suitable

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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.

Me<sub>2</sub>S=CHCOR 
$$\xrightarrow{-N_2}$$
  $\xrightarrow{-Me_2S}$  Ar-NH-C-COR  $\xrightarrow{p-NO_2C_6H_4-N}$  CH-COOEt  $\xrightarrow{CH-COOEt}$   $\xrightarrow{CH-COO$ 

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 <sub>6</sub> H <sub>4</sub>	92	203-204	$p-NO_2C_6H_4$	Ph	100	167-168
Ph	m-BrC <sub>6</sub> H <sub>4</sub>	90	178-179	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	Ph	29	153-155
Ph	$p-CH_3C_6H_4$	82	158-160	Ph	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	100	142-143
p-ClC <sub>6</sub> H <sub>4</sub>	Ph	85	118-119	p-NO2C6H4	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	99	204-205
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	m-BrC <sub>6</sub> H <sub>4</sub>	89	190-191	Ph	p-BrC <sub>6</sub> H <sub>4</sub>	100	169-170
p-BrC <sub>6</sub> H <sub>4</sub>	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	68	189-190	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO	2 p-BrC <sub>6</sub> H <sub>4</sub>	12	231-232

4). Nitrile oxide

Extensive studies have been made on the reaction of phosphorous ylides with nitrile oxides<sup>5,6)</sup>. 3-Phenylisoxazoline was obtained from the reaction of phenyl nitrile oxide with the ylide  $I^{2)}$ . 4,5-Dibenzoyl-3-phenylisoxazoline(Mp. 147°C, yield 15%) was isolated from the reaction mixture of IIIb(R=Ph) and  $\alpha$ -chlorobenzaldoxime in the presence of triethylamine.

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