## REACTIONS OF AZIDES WITH CARBONYL-STABILIZED SULFONIUM YLIDS.

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Carbonyl-stabilized sulfonium ylids have only been synthesized in the last few years and hence little is known about their chemical reactivity.<sup>1</sup> We have now found that they react with azides in a completely different manner than the structurally analogous phosphonium ylids. Whereas the P-ylids react as dipolarophiles,<sup>2</sup> the following reactions show that the corresponding S-ylids react with azides as typical nucleophiles.

Ethyl azidoformate (2) reacts with two equivalents of the phenacylidenesulfuranes <u>la</u> and <u>lb</u> in benzene solution at room temperature to give the triazene <u>3</u> (m.p. 135-137°) which partially precipitates from the reaction mixture. Its structure follows from IR (N-H at 3420, C=O at 1744, 1660 and 1620 cm<sup>-1</sup>), NMR (N-H at  $\delta 6.80$ , olefinic proton singlet at  $\delta 6.66$ ), elemental analysis and mass spectrometry (molecular ion at 351). Of the two possible structures, 3 is favored over 4 on the

 $RMeS=CH-CO-Ph + EtOOC-N_3 + [EtOOC-N-N=N-CH-SMeR] \xrightarrow{- + + + 1}_{- - + + + 1} \xrightarrow{- + + + 1}_{- - + + + 1} [EtOOC-N-N=N-CH-CH-SMeR]$ Ph Ph Ρh 2 la R=Me b R=Ph -RMeS EtOOC-N=N-NH-C=CH-CO-Ph EtOOC-NH-N=N-C=CH-CO-Ph ċο çο 3 65% from la 4 50% from 1b scheme 1

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basis of the lack of a carbamate absorption in the region  $1530-1540 \text{ cm}^{-1}$ . A reasonable mechanism involves two nucleophilic attacks of the ylid (scheme 1) as in the case of triazene formation from non-stabilized oxosulfonium and sulfonium ylids.<sup>3</sup> Methyl phenyl sulfide formed in the reaction of <u>1b</u> with <u>2</u> could be isolated by distillation in 60% yield.

The reactions of the phenacylidenesulfuranes <u>la</u> and <u>lb</u> with the aryl azides <u>5a-c</u> in benzene at room temperature resulted in nitrogen evolution and formation of the enamines 6a-c. The weak N-H absorptions in the IR spectra at 3150-3180 cm<sup>-1</sup>

2 RMeS=CH-CO-Ph + Ar-N<sub>3</sub> -2RMeS, -N<sub>2</sub> Ar-N ar-N C = CH C = CHC = CH

and the very high NMR  $\delta$ -values ( $\delta$ 12.6-12.8) for the N-H protons indicate hydrogen bonding in the molecules. The enamines <u>6</u>a-c were obtained in ca 80-90% yield except in the reaction of <u>1</u>b with <u>5</u>c where <u>6</u>c was formed in only 30-40% yield. A side product of the latter reaction is trans-1,2,3-tribenzoylcyclopropane <u>7</u> (m.p. 221°), isolated in ca 20% yield. Its formation has previously been observed by several authors in the thermal and photochemical decomposition of the phenacyl ylid.<sup>4</sup> A mechanism analogous to scheme 1 can be invoked for the formation of the enamines <u>6</u>a-c, with this difference, however, that nitrogen is eliminated in some stage of the reaction.



No nitrogen evolution occurs when carbethoxymethylenedimethylsulfurane  $\underline{8}$  is allowed to react with the aryl azides  $\underline{5}a$  and  $\underline{5}b$  in benzene at room temperature, and the triazenes 9a and  $\underline{9}b$  are isolated in 75-80% yield.



Another typical example of the S-ylid reacting as a nucleophile is the exothermic reaction of carbethoxymethylenedimethylsulfurane 8 with p-nitrobenzoyl azide 10 which results in the formation of the amide 11 (m.p. 202-203°), together with the new stabilized S-ylid 12 (m.p. 169.5-170°). The structure of 12 was established from IR, NMR, elemental analysis, mass spectrometry, and by the failure to depress the melting point of an authentical specimen prepared according to the method of Payne.<sup>5</sup> Its formation can be rationalized by a nucleophilic attack of the ylid on the carbonyl function of the acyl azide, displacing N<sub>3</sub><sup>-</sup>. The origin of the amide 11 is tentatively assigned to fragmentation of a triazene formed initially.

 $2 \text{ Me}_{2}\text{S}=\text{CH-COOEt} + \text{p-NO}_{2}-\text{C}_{6}\text{H}_{4}-\text{CON}_{3} \xrightarrow{20^{\circ}}_{\text{benzene}}$   $\frac{8}{10}$   $\begin{pmatrix} \text{[} \text{p-NO}_{2}-\text{C}_{6}\text{H}_{4}-\text{CO-NH-N}=\text{N-C}=\text{CH-COOEt}] + \text{p-NO}_{2}-\text{C}_{6}\text{H}_{4}-\text{CO-NH}_{2} \\ \text{COOEt} & 1 \\ 11 : 35-40^{\circ} \\ 11 : 35-40^{\circ} \\ \text{COOEt} & 1 \\ 11 : 35-40^{\circ} \\ 12 : 30-35^{\circ} \\ \end{pmatrix}$ 

Butyl azide does not react with the phenacyl ylids <u>la</u> and <u>lb</u>, even after several weeks at room temperature. When the reaction mixtures are refluxed in benzene, decomposition of the ylids to trans-tribenzoylcyclopropane <u>7</u> occurs instead of reaction with the azide.

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