Tetrahedron Letters No.56, pp. 4937-4940, 1969. Pergamon Press. Printed in Great Britain.

REACTION OF β-DIKETONES WITH DIMETHYLOXOSULPHONIUM METHYLIDE

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(Received in UK 22 October 1969; accepted for publication 4 November 1969)

We have reported$^{(1)}$ that dimethyloxosulphonium methylide (I) reacts with salicylaldehyde to yield 2,3-dihydro-3-hydroxybenzofuran, which readily dehydrates to benzofuran, whereas o-hydroxyacetophenone is converted into 3-methylbenzofuran directly, no intermediate hydroxy-compound being detected. In order to extend this work, we reacted (I) with some β-diketones (II), on the assumption that, as these compounds contain high proportions of the enol forms, the probable reaction products would be substituted furans (III). Higher temperatures and longer reaction times were required than previously and no furan derivatives were isolated. The main products were the C-methyl compound (IV) (R = R' = Me; R = Me, R' = Ph; R = R' = Ph), in 25-74% yield. Ethyl acetoacetate also gave the corresponding C-methyl compound in 60% yield, as also did acetoacetanilide (32%). Reeder$^{(2)}$ recently described the formation of diepoxides from reaction of the diketones 2,5-hexanedione and 1,4-diacetylbenzene with the ylide (I), but not from α- and β-diketones.

Reaction of the β-diketone (V) (R = H, R' = Me) with the ylide (I) yielded a crystalline solid (42%) to which we assigned structure (VI) (R = H, R' = Me) based on spectral data. Its infrared spectrum contains no carbonyl bands, the principal absorption being at $1130 cm^{-1}$ (S=O). Its n.m.r. spectrum (in $CDCl_3$) shows singlets at 6.55τ and 7.9τ (two Me groups), two multiplets at 7.5τ and 8.3τ (four CH_2 - groups) and two doublets at 3.5τ and 3.85τ (J = 5.5 Hz) which disappear on addition of $D_2O/CF_3{\cdot}CO_2D$ (aromatic H's). Its mass spectrum corresponds to $C_{11}H_{16}OS$, in agreement with elemental analysis. The mass spectrum shows a base peak at m/e 111 (C_6H_7S) to which we ascribed structure (VII). Two metastable peaks at m/e 129.5 and m/e 80.5 are due to fragmentations 181 $(C_{10}H_{13}OS) \longrightarrow 153(C_9H_{13}S)$ and $153 \longrightarrow 111$.

The compound (VIII) was obtained by Hortmann(3) from the reaction of ylide (I) with 3-phenylpropiolophenone, and a similar thiabenzene-1-oxide derivative (IX) has been described(4). In our hands the reaction of (I) with (II) (R = R' = Ph) did not give any of the compound (VIII).

The Table shows the results from reaction of the ylide (I) and various 2-acylcyclohexanones.

Table (a,b)

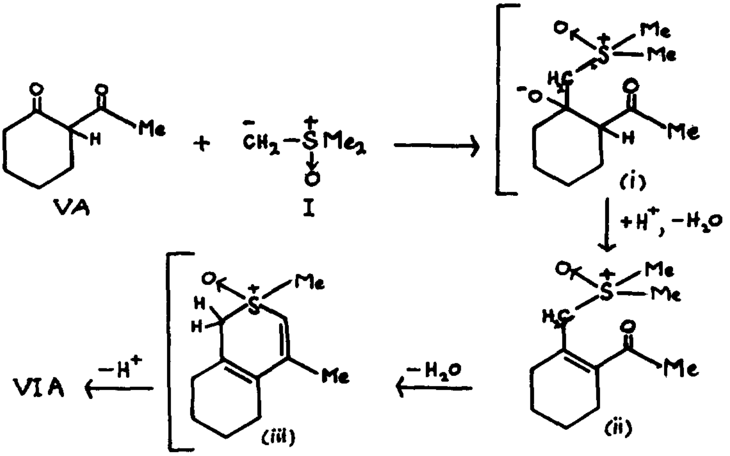
	V		VI (R,R' as in V)
	R	R'	Yields (%)
A	H	Me	42
B	H	CH_2Me	39
C	H	$CH\begin{smallmatrix}\diagup Me\\ \diagdown Me\end{smallmatrix}$	26
D	H	$C\begin{smallmatrix}\diagup Me\\ - Me\\ \diagdown Me\end{smallmatrix}$	58
E	H	$CH_2\text{-}CH\begin{smallmatrix}\diagup Me\\ \diagdown Me\end{smallmatrix}$	18
F	Me	Me	36(c)
G	H	Ph	15
H	H	CH_2Ph	6

(a) The structures were determined by i.r., n.m.r. and mass spectrometry.

(b) The reactions of the ylide (I) (1.1 mole) and the ß-diketones (V) (1 mole) were performed at 20° or 60° in D.M.S.O.

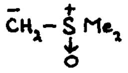
(c) (VII F) is a mixture of two stereoisomers, the n.m.r. spectrum showing two R-methyl doublets and two R'-methyl singlets, both sets in a ratio of 60:40.

The mechanism leading to the product (VIA) can be visualised as follows:-



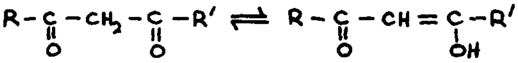
Addition of a proton to the intermediate betaine (i) followed by elimination of water produces (ii) in which the active methyl group on the positively charged S atom condenses with the acetyl carbonyl group to give the heterocycle (iii); subsequent proton loss yields (VlA). The products may be looked upon as cyclic ylides stabilised by conjugation within the ring.

Further investigation into the reaction of ylide (I) with β-diketones is in progress.



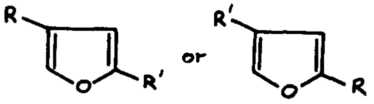
$\overset{-}{\mathrm{C}}\mathrm{H}_2-\underset{\overset{\downarrow}{\mathrm{O}}}{\overset{+}{\mathrm{S}}}\mathrm{Me}_2$

I

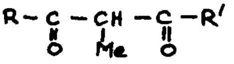


$R-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-R' \rightleftharpoons R-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{OH}{|}}{C}-R'$

II

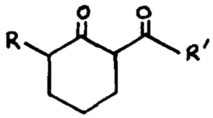


III

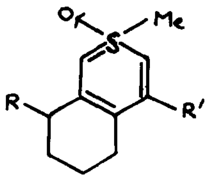


$R-\underset{\underset{O}{\|}}{C}-\underset{\underset{Me}{|}}{CH}-\underset{\underset{O}{\|}}{C}-R'$

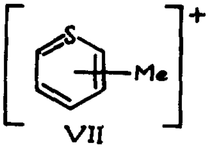
IV



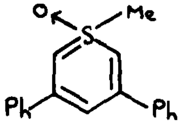
V



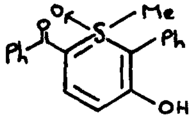
VI



VII



VIII



IX

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We are indebted to Mr. A. Hart of A.E.I. Instrument Division, Manchester, for the accurate mass analyses.