

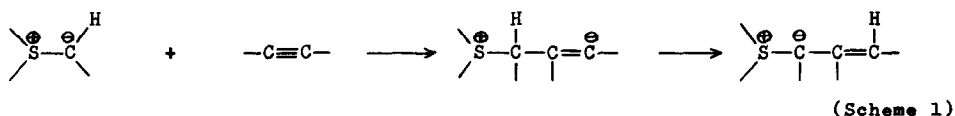
A NEW SYNTHESIS OF FURANS BY THE REACTION OF SULPHONIUM DIACYLMETHYLIDES
WITH DIETHYL ACETYLENEDICARBOXYLATE

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Reactions of sulphonium methylide (1) and sulphonium phenacylide (2) with electrophilic reagents have often been reported. These ylides react with electrophilic acetylenes under proton transfer to afford new stable ylides (Scheme 1) (3). In contrast, little is known with respect to the reaction of sulphonium diacylmethylides because



of their poor nucleophilicity (4). We wish to report a reaction of sulphonium diacylmethylides with diethyl acetylenedicarboxylate at high temperature which provides a new route to substituted furans (5).

This reaction is illustrated by the following specific case: A mixture of dimethylsulphonium dibenzoylmethylide (6) (Ia, 1.42 g, 5.0 mmoles) and diethyl acetylenedicarboxylate (II, 4 ml) was heated at 170° for 5 min. After excess diethyl acetylenedicarboxylate was removed under reduced pressure, the residue was purified by column chromatography (Florisil, benzene) to afford 3-benzoyl-4,5-bis(ethoxycarbonyl)-2-phenylfuran (IVa, 1.90 g) in a 97% yield. Other disubstituted ylides Ib (7), Ic (8) and Id (7) also reacted with the acetylene II to yield furan derivatives IV (Table 1). The structural assignments were made on the basis of the elemental analyses and spectral data (Table 2). The reaction of an asymmetric ylide Ic gave a ca. 1:1 mixture of isomeric furans IVc and IVc'. The structures of IVc and IVc' were assigned on the basis of infrared spectra. The spectrum of IVc showed an absorption at 1689 cm⁻¹ which was assigned to the acetylfuran function, whereas IVc' at 1640 cm⁻¹ due to the benzoylfuran. In contrast, Id reacted exclusively at the acetyl site to afford a single product which showed no

Table 1

Yields and m.p.s of furans IV from ylides I and diethyl acetylenedicarboxylate II

Compd. I No.	Reaction		temp. ^a (°C)	Compd. IV			Yield (%)	m.p. (or b.p.) (°C)
	R	R'		No.	R	R'		
Ia	Ph	Ph	170	IVa	Ph	Ph	97	87 - 88.5
Ib	Me	Me	120	IVb	Me	Me	97	(140 - 142/0.35)
Ic	Me	Ph	135	IVc	Me	Ph	46	(200/0.22) ^b
				IVc'	Ph	Me	52	92 - 93
Id	OEt	Me	120	IVd	OEt	Me	93	(167 - 167.5/0.90)

^a At this temperature the evolution of dimethyl sulphide occurred greatly.

^b Bath temperature.

Table 2

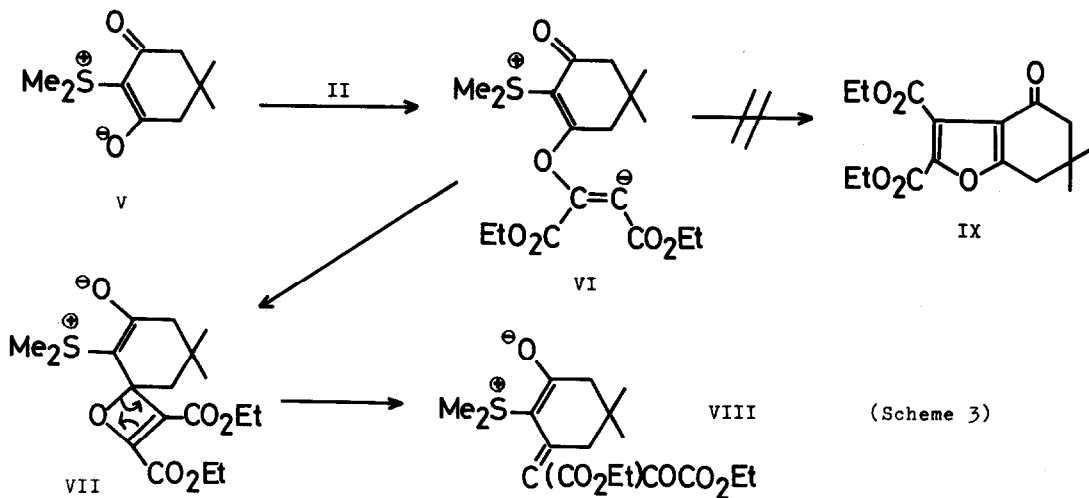
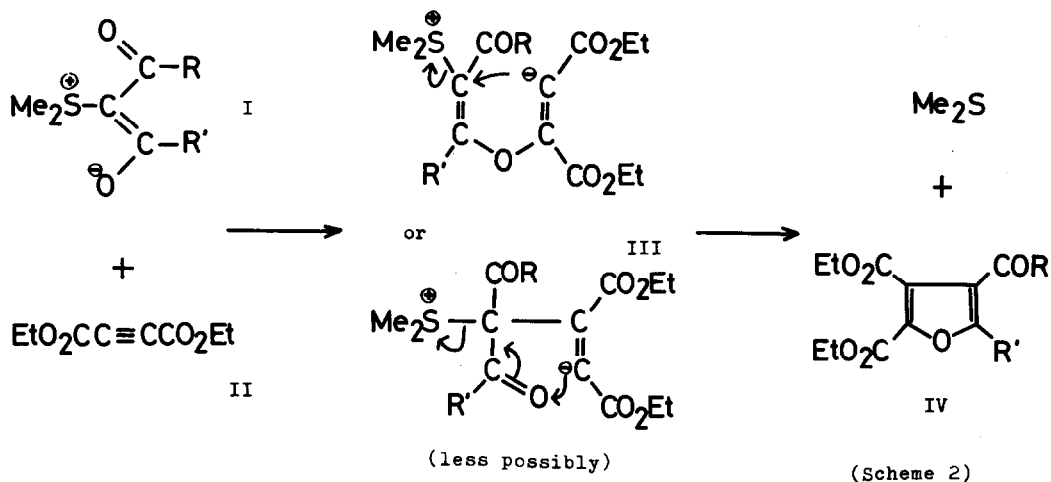
Spectral data of furans IV^a

Compd. No.	NMR δ ppm (in CCl ₄) ^b	IR (KBr or neat) ^c cm ⁻¹	$\lambda_{\max}^{\text{EtOH}}$ nm(log ϵ)
IVa	1.28 (t, 3H), 1.31 (t, 3H)	1727, 1650, 1639, 1576	266 (4.23)
	4.23 (q, 2H), 4.29 (q, 2H)	1540, 1234, 1110, 1075	316 (4.22)
	7.0 - 8.2 (m, 10H)	920	
IVb	1.32 (t, 3H), 1.36 (t, 3H)	1740, 1720, 1688, 1600	274 (4.09)
	2.39 (s, 3H), 2.66 (s, 3H)	1555, 1245, 1210, 1094	
	4.25 (q, 2H), 4.31 (q, 2H)	1050, 949	
IVc	1.29 (t, 3H), 1.38 (t, 3H)	1740 - 1720, 1689, 1592	218 (4.08)
	2.46 (s, 3H), 4.23 (q, 4H)	1580, 1540, 1220, 1112	296 (4.24)
	7.2 - 8.1 (m, 5H)	1065, 1020, 945	
IVc'	1.32 (t, 3H), 1.34 (t, 3H)	1742, 1726, 1640, 1597	218 (4.04)
	2.68 (s, 3H), 4.31 (q, 4H)	1589, 1540, 1270, 1245	264 (4.02)
	7.2 - 8.2 (m, 5H)	1210, 1098, 1078, 947	294 (4.24)
IVd	1.33 (t, 3H), 1.36 (t, 6H)	1745 - 1714, 1610, 1565	256 (4.09)
	2.68 (s, 3H), 4.25 (q, 2H)	1280, 1240, 1210, 1160	
	4.30 (q, 4H)	1090, 1050, 1015, 850	

^a All new compounds had satisfactory elemental analyses.

^b Abbreviations: s = singlet; t = triplet; q = quartet; m = multiplet.

^c Solid spectra were obtained with KBr tablets, whereas liquid ones with liquid films.



discernible infrared bands in the $1700-1620\text{ cm}^{-1}$.

The formation of furans IV may be accounted for by assuming nucleophilic addition of the enolate site of I to the acetylenic bond of II and the following ring closure under elimination of dimethyl sulphide (Scheme 2).

2-Dimethylsulphuranylidene-5,5-dimethylcyclohexane-1,3-dione (V) (8) and II gave under similar condition (180° , 15 min.) a new sulphonium ylide VIII (Scheme 3) (yield: 83%, m.p. $148-149.5^\circ$ from benzene, NMR (in CDCl_3): δ 1.08 (s, 6H), 1.31 (t, 3H), 1.35

(t, 3H), 2.36 (broad s, 2H), 2.56 (broad s, 2H), 3.17 (s, 6H), 4.20 (q, 2H) and 4.26 ppm (q, 2H). IR (KBr): 1712, 1700, 1621, 1575, 1510, 1235, 1087 and 994 cm^{-1} , UV: $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ) 222 (4.07), 274 (3.93) and 392 (4.17)). The configuration about the exocyclic olefinic bond of VIII is still an open problem. Poorly satisfied stereo-electronic requirement of VI for ring closure to IX may account for the formation of unexpected ylide VIII.

The scope and utility of this reaction are being investigated with several other ylides and acetylenes.

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