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FURANS FROM SULPHONIUM DIACYLMETHYLIDES AND ACETYLENES

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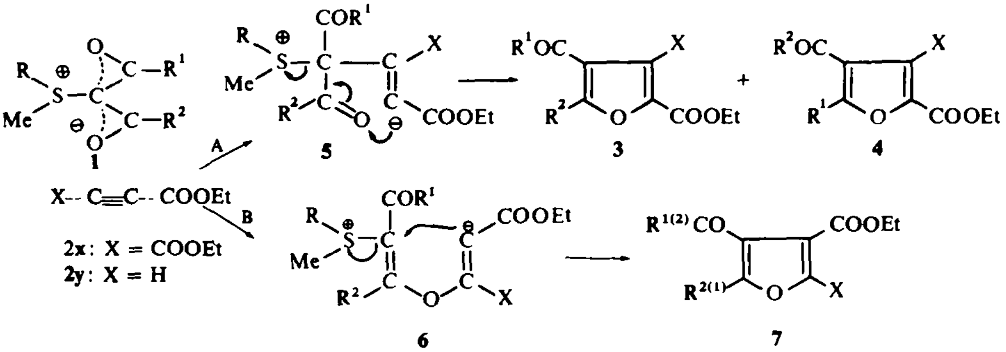
Abstract—Heating of a neat mixture of the title components **1a–1f** and **2x**, **2y** at 120–180° gives furan derivatives **3** and/or **4** with elimination of the corresponding sulphide. Cyclic diketo-type ylides **9a**, **9b** and **13** react with diethyl acetylenedicarboxylate to afford novel ylides **10a**, **10b** and **14**, respectively.

DOUBLY acylated sulphonium methylides (**1**) are readily accessible,[1] but the synthetic applications are limited due to the chemical inertness.[2] Herewith we report a furan synthesis which consists in the reaction of **1** with carbethoxy substituted acetylenes (**2x** and **2y**) proceeding *via* **5** to give **3** and/or **4** (Scheme 1).[3] Condensations of other sulphonium ylides with acetylenes have been recorded to afford different products.[4, 5] Table 1 lists present reaction conditions and yields of furans, whose spectral data and analyses are given in Tables 2 and 3, respectively.

SCHEME 1



Reaction of **1** (R = Me) with **2x** in the absence of a solvent proceeded at 120–170° in 5–15 minutes with evolution of dimethyl sulphide.[*] Methylphenylsulphonium ylides (**1**, R = Ph) react under similar conditions to afford inferior yields. Ylides with different acyl groups ($R^1 \neq R^2$) gave mixtures of **3** and **4** in ratios given in Table 1, which were determined by NMR and supported by IR spectra. The ester CO group in **1f** was found to be inert to the cyclization process to afford a single furan derivative

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[*] Attempted reaction of **1** with **2x** in chloroform at room temperature resulted in nearly quantitative recovery of the starting materials.

TABLE 1. YIELDS OF FURANS 3 and 4

No.	R	Ylide R¹	R²	Acetylene No.	Reaction temp.[a] (°C)	Furan No.	Yield (%)
1a	Me	Me	Me	**2x**	120	**3ax**	97
				2y	160	**3ay**	70
1b	Me	Ph	Ph	**2x**	170	**3bx**	97
				2y	180	**3by**	42
1'b	Ph	Ph	Ph	**2x**	180	**3bx**	66
1c	Me	Me	Ph	**2x**	135	**3cx**	46[b]
						4cx	52
				2y	180	**3cx**	28[b]
						4cy	33
1'c	Ph	Me	Ph	**2x**	120	**3cx**	45[b]
						4cx	32
1d	Me	Et	Ph	**2x**	120	**3dx** **4dx**	98[c]
1e	Me	iso-Pr	Ph	**2x**	140	**3ex**	36[b]
						4ex	62
1f	Me	OEt	Me	**2x**	120	**3fx**	93
				2y	160	**3fy**	73

[a] At this temperature the evolution of sulphide occurred violently.

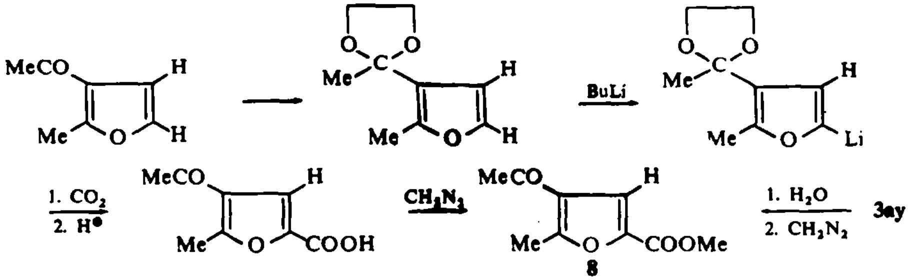
[b] The relative yields are based on integrated areas of NMR signals.

[c] The relative yields were not determined.

3fx or **3fy** in each reaction. All these furan derivatives are formed by path A *via* intermediary adducts **5**. Alternative route B leading to **7** can not be excluded, if X is carbethoxy.[*],[†] However, the reaction with ethyl propiolate (**2y**) proceeded to afford **3** and/or **4** and the presence of **7** was disproved. Ethyl phenylpropiolate was inactive toward ylides **1a–f** under the present conditions.

The product **3ay** was converted to the corresponding methyl ester **8** which was prepared independently as outlined in Scheme 2. The resulting authentic sample was identical with **8** on mixed m.p. and spectral comparison. Hydrolysis of furan **3fy** gave 5-methylfuran-2,4-dicarboxylic acid. The ester and the acid were different from the known isomer, 2-methyl-furan-3,4-dicarboxylic acid and its ethyl ester,[8] which is expected to be produced according to path B from the isomer **7**.

SCHEME 2



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[*] Winterfeldt recorded an instance of furan formation in the reaction of methyl phenylpropiolate and an ylide obtained by the addition of dimethyl acetylenedicarboxylate on dimethyl sulphoxide. The product is explained on the basis of path B rather than path A. See ref. 6.

[†] For reaction of an azomethine ylide and acetylenes, see ref. 7.

TABLE 2. SPECTRAL DATA OF FURAN 3, 4 AND 8

Compd. No.	λ_{max}^{EtOH} nm (log ε)	IR (KBr or neat)[a] cm^{-1}	NMR δppm (relative intensity, multiplicity)[b]
3ax	274 (4·09)	1740, 1720, 1688	1·32 (t, 3H), 1·36 (t, 3H), 2·39 (s, 3H), 2·66 (s, 3H), 4·25 (q, 2H), 4·31 (q, 2H)
3ay	258 (4·17)	1725, 1675	1·41 (t, 3H), 2·42 (s, 3H), 2·70 (s, 3H), 4·33 (q, 2H), 7·27 (s, 1H)
3bx	266 (4·23), 316 (4·22)	1727, 1650, 1639	1·28 (t, 3H), 1·31 (t, 3H), 4·23 (q, 2H), 4·29 (q, 2H), 7·0–8·2 (m, 10H)
3by	268 (4·09), 320 (4·34)	1730, 1652	1·39 (t, 3H), 4·33 (q, 2H), 7·2–8·5 (m, 11H)
3cx	218 (4·08), 296 (4·24)	1740–1720, 1689	1·29 (t, 3H), 1·38 (t, 3H), 2·46 (s, 3H), 4·23 (q, 4H), 7·2–8·1 (m, 5H)
4cx	218 (4·04), 264 (4·02), 294 (4·24)	1742, 1726, 1640	1·32 (t, 3H), 1·34 (t, 3H), 2·68 (s, 3H), 4·31 (q, 4H), 7·2–8·2 (m, 5H)
3cy	[c]	1723, 1683	1·36 (t, 3H), 2·47 (s, 3H), 4·30 (q, 2H), 7·2–8·2 (m, 6H)
4cy	[c]	1723, 1649	1·36 (t, 3H), 2·71 (s, 3H), 4·30 (q, 2H), 7·2–8·2 (m, 6H)
3dx	[c]	1739, 1723, 1687	1·34 (t, 6H), 1·36 (t, 3H), 3·00 (q, 2H), 4·27 (q, 4H), 7·2–8·1 (m, 5H)
4dx	[c]	1739, 1723, 1650	1·34 (t, 6H), 1·42 (t, 3H), 31·2 (q, 2H), 4·27 (q, 4H), 7·2–8·1 (m, 5H)
3ex	[c]	1740, 1727, 1688	1·25 (d, 6H), 1·34 (t, 6H), 3·38 (septet, 1H), 4·29 (q, 4H), 7·2–8·2 (m, 5H)
4ex	[c]	1740, 1727, 1658	1·34 (t, 6H), 1·48 (d, 6H), 3·86 (septet, 1H), 4·29 (q, 4H), 7·2–8·2 (m, 5H)
3fx	256 (4·09)	1745–1714	1·33 (t, 3H), 1·36 (t, 6H), 2·68 (s, 3H), 4·25 (q, 2H), 4·30 (q, 4H)
3fy	252 (4·05)	1725	1·36 (t, 3H), 1·37 (t, 3H), 2·65 (s, 3H), 4·25 (q, 2H), 4·28 (q, 2H), 7·24 (s, 1H)
8	258 (4·16)	1728, 1678	2·47 (s, 3H), 2·70 (s, 3H), 3·93 (s, 3H), 7·40 (s, 1H)

[a] Only the carbonyl absorptions are recorded.

[b] All spectra were obtained in CCl_4 with TMS ref. Chemical shifts are given in δppm and abbreviations s, d, t, q and m refer to singlet, doublet, triplet, quartet and multiplet, respectively.

[c] The spectra were not obtained due to the failure in isolating analytically pure samples.

In contrast to these open chain diacylmethylides, the diketo-type ylides **9a** and **9b** of cyclic structure reacted with the acetylene **2x** in a different way (Scheme 3) affording novel ylides **10a** and **10b**. No evolution of dimethyl sulphide was observed during the reaction at 180° (15 min) and 145° (20 min), respectively. The ylide structures **10a**, **10b** were based on the IR absorptions (KBr) at 1510 and 1496 cm^{-1} (ylide CO) as well as on NMR and mass spectra. Intermediates **11**, **12** explain the formation of **10a**, **10b**, and this wlll be discussed below in further detail. A similar type of ylide **14** was found to be produced from 5-membered cyclic ylide **13** as shown in Scheme 4. Notably, the intermediates such as **11** in Scheme 3 should be formed by the path B in Scheme 1. The contradictory behaviour of open chain and cyclic diacylmethylides may be explained as shown in Scheme 5.

TABLE 3. M.PS (B.PS) AND ANALYTICAL DATA OF NOVEL FURANS

Compd. No.	m.p. (b.p.) °C	Formula	Anal. (%) Found C	H	Req. C	H
3ax	(140–142/0·35)	$C_{13}H_{16}O_6$	58·5	5·8	58·2	6·0
3ay	75–77	$C_{10}H_{12}O_4$	61·4	6·2	61·2	6·2
3bx	87–88·5	$C_{23}H_{20}O_6$	70·5	5·1	70·4	5·1
3by	85–86	$C_{20}H_{16}O_4$	75·3	4·8	75·0	5·0
3cx	(200/0·22)[a]	$C_{18}H_{18}O_6$	65·4	5·6	65·4	5·5
4cx	92–93	$C_{18}H_{18}O_6$	65·2	5·3	65·4	5·5
3cy	[b]	$C_{15}H_{14}O_4$	69·5	5·8	69·8	5·5
4cy	[b]	$C_{15}H_{14}O_4$	69·5	5·8	69·8	5·5
3dx	[c]	$C_{19}H_{20}O_6$	66·0	5·7	66·3	5·9
4dx	[c]	$C_{19}H_{20}O_6$	66·0	5·7	66·3	5·9
3ex	[d]	$C_{20}H_{22}O_6$	66·9	6·1	67·0	6·2
4ex	[d]	$C_{20}H_{22}O_6$	66·9	6·1	67·0	6·2
3fx	(167–167·5/0·90)	$C_{14}H_{18}O_7$	56·5	6·0	56·4	6·1
3fy	(108/0·05)	$C_{11}H_{14}O_5$	58·7	6·4	58·4	6·2
8	147·148	$C_9H_{10}O_4$	59·5	5·6	59·3	5·5

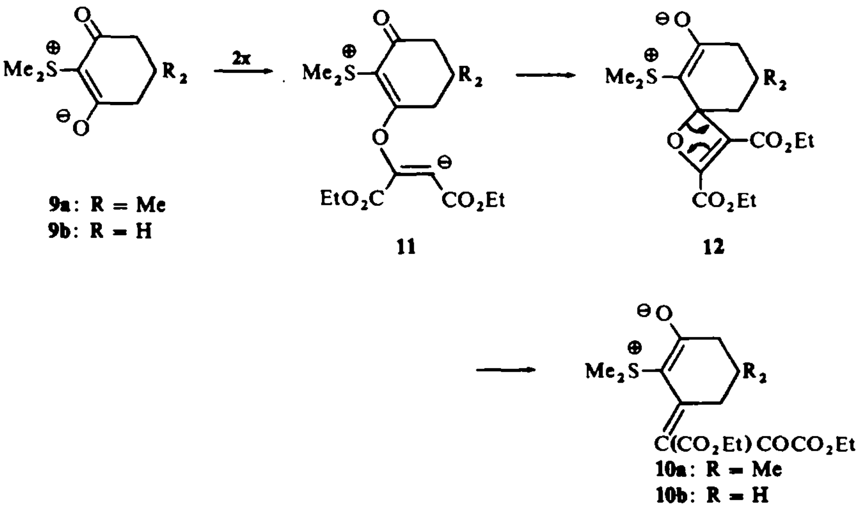
[a] Bath temperature.

[b] A mixture of **3cy** and **4cy** boiled at 160–165°/0·2 mmHg.

[c] A mixture of **3dx** and **4dx** boiled at 173–181°/0·04 mmHg.

[d] A mixture of **3ex** and **4ex** boiled at 185–192°/0·05 mmHg.

SCHEME 3



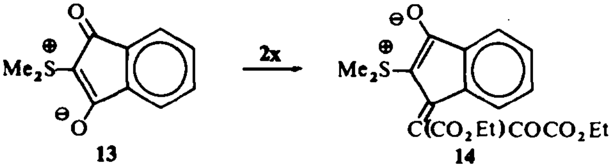
9a: R = Me
9b: R = H

11

12

10a: R = Me
10b: R = H

SCHEME 4



SCHEME 5

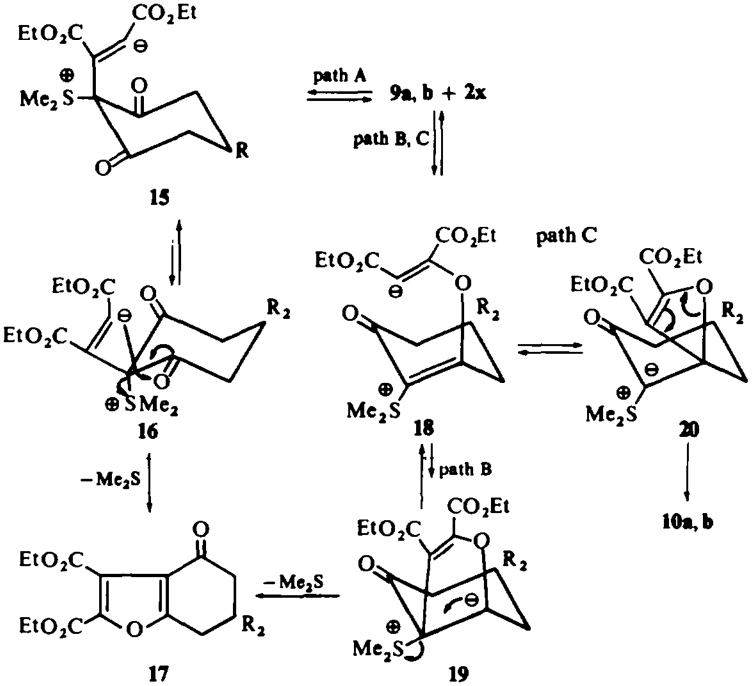


TABLE 4. M.PS AND SPECTRAL DATA OF NOVEL YLIDES

Compd. No.	m.p. (°C)	λ_{max}^{EtOH} nm(log ε)	IR (KBr)[a] (cm^{-1})	NMR[b] (δ ppm)
10a	148–149·5	222 (4·07) 274 (3·93), 392 (4·17)	1712, 1700, 1621, 1575, 1510	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), 4·26 (q, 2H)
10b	177–178	247 (3·69), 275 (3·76), 395 (4·17)	1727, 1702, 1615, 1579, 1496	1·31 (t, 3H), 1·36 (t, 3H), 1·9–3·0 (m, 6H), 3·14 (s, 6H), 4·19 (q, 2H), 4·26 (q, 2H)
14	142–144	244 (4·48), 296 (3·36), 303 (3·36) 423 (4·44)	1726, 1682, 1663, 1630, 1585, 1452	1·31 (t, 3H), 1·37 (t, 3H), 3·21 (s, 6H), 4·25 (q, 2H), 4·37 (q, 2H), 7·5–8·4 (m, 4H)

[a] Only the carbonyl absorptions are recorded.

[b] All NMR spectra were obtained in $CDCl_3$ with TMS ref. Chemical shifts are given in δ ppm and abbreviations s, t, q and m refer to singlet, triplet, quartet and multiplet, respectively.

The reaction of **9a, b** with **2x** gives a zwitterion **15** as in path A, but cyclization to furan requires the conformational change to **16**, which is less favoured because of the bulky dimethylsulphonium group in the axial position. If the adduct **15** can reversibly be dissociated into **9a, b** and **2x**, there should be a change of **18** being formed by path B. The zwitterion **18** can by cyclized to **17** *via* **19***, but isomerization to an ylide **20** with oxetene ring (path C) would probably be more favoured. Final isomerization of **20** gives **10a, b**.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. Microanalyses were performed at the Elemental Analyses Centre of Kyôto University and by Mrs. K. Fujimoto at Prof. K. Sisido's Laboratory. NMR spectra were taken with a JEOL C-60-H spectrometer with CCl_4 or $CDCl_3$ as a solvent and chemical shifts are reported in δ values relative to TMS internal standard. Mass spectra were obtained on a Hitachi RMS-4 spectrometer and UV absorption spectra were taken in 95% EtOH on a Shimadzu MPS-50L spectrometer. Most of the yields, spectral data and analyses are in Tables 2, 3 and 4, respectively.

Reactions of sulphonium ylides (**1**) *with diethyl acetylenedicarboxylate* (**2x**). A stirred mixture of **1** (10 mmoles) and **2x** (neat, 4·0 ml) was heated at the temp given in Table 1 for 5–15 min. The reaction of **1** (R = Me) proceeded with evolution of dimethyl sulphide. After removal of the sulphide and excess acetylene under reduced press, the residual products were purified by distillation, chromatography and recrystallization.

Furans **3ax** and **3fx** were obtained in an analytically pure state after distillation, whereas **3bx** was isolated by chromatography on a Florisil column with benzene as eluant. A mixture of **3cx** and **4cx** was separated by chromatography on a Florisil column with hexane and benzene. The furan **3cx** was purified by distillation and the isomer **4cx** by recrystallization from benzene and hexane (1:1). Separation of mixtures of **3dx** and **4dx** or **3ex** and **4ex** was unsuccessful either by distillation or by chromatography, but each mixture afforded satisfactory C, H analyses.

Reaction of **1a** *with ethyl propiolate* (**2y**). A soln of **1a** (10 mmoles) and **2y** (15 mmoles) in anhyd dioxan (25 ml) was heated in a sealed glass tube at 160° for 15 hr. After the solvent and excess acetylene were removed, the residue was subjected to chromatography (Silicagel, hexane and benzene) and recrystallization from CCl_4 and hexane (1:1) to yield **3ay**.

Reaction of **1b** *with* **2y**. A soln of **1b** (5 mmoles) and **2y** (7·5 mmoles) in dioxan (25 ml) was heated at 180° for 66 hr. Chromatography (Silicagel, PhH) and following recrystallization from benzene and CCl_4 (1:1) afforded **3by**.

Reaction of 1c *with* **2y**. A soln of **1c** (20 mmoles) and **2y** (30 mmoles) in dioxan (30 ml) was heated at 180° for 53 hr. Distillation *in vacuo* and subsequent preparative GC (Silicone SE 30, 180°) gave a mixture of 3cy and 4cy. The yields and distributions were determined by IR and NMR analyses.

Reaction of **1f** *with* **2y**. A soln of **1f** (5 mmoles) and **2y** (7·5 mmoles) in dioxan (15 ml) was heated at 160° for 24 hr and the product was separated by vacuum distillation. An analytically pure sample was obtained by preparative GC (High Vacuum Silicone Grease 30% Celite 535, 200°).

3-*Acetyl*-2-*methylfuran ethylene acetal.* A mixture of 3-acetyl-2-methylfuran[9] (6·1 g, 49 mmoles) with ethylene glycol (6·2 g, 100 mmoles), benzene (*ca* 1 l) and *p*-toluenesulphonic acid (0·09 g) was heated for 32 hr under reflux and continuous removal of water. Distillation followed by chromatography (alumina, PhH) afforded a pure acetal (7·6 g, 92%), b.p. 92–95°/30 mmHg; NMR: δ ppm (CCl_4), 1·55 (s, 3H), 2·34 (s, 3H), 3·79 (2H), 3·86 (2H), 6·20 (d, 1H, $J = 2{\cdot}4$ Hz), 7·09 (d, 1H, $J = 2{\cdot}4$ Hz). (Found: C, 64·6; H, 7·3. $C_9H_{12}O_3$ requires: C, 64·3; H, 7·2%).

Preparation of methyl 4-*acetyl*-5-*methylfuran*-2-*carboxylate* (**8**).

(a) A soln of n-BuLi (30 mmoles) in 33·3 ml n-hexane was added dropwise during several min to a stirred soln of 3-acetyl-2-methylfuran ethylene acetal (5·0 g, 30 mmoles) in dry ether (200 ml) under N_2 at room temp. Further stirring for 0·5 hr produced a deep red soln. After cooling in an ice-salt bath, dry CO_2 was bubbled through the soln. The ppt was filtered off, washed with dry ether and then dissolved in water (*ca* 100 ml). The soln was acidified with HCl, extracted with EtOAc, and dried ($MgSO_4$). Concentration

* Remarkably, the Winterfeldt's case (Ref. 6) should involve an intermediate in which the negative charge is delocalized by an attached carbethoxy group instead of methylene in **19**.

in vacuo gave 4-acetyl-5-methylfuran-2-carboxylic acid which was esterified with diazomethane without further purification. The reaction products were chromatographed on a Silicagel column. Elution with hexane and benzene afforded **8** (1·80 g, 33%, m.p. 147–148°). (Found: C, 59·5; H, 5·6. $C_9H_{10}O_4$ requires: C, 59·3; H, 5·5%).

(b) A soln of **3ay** (4·85 g, 25 mmoles) and KOH (1·68 g, 30 mmoles) in MeOH was heated under reflux for 30 min and the resulting acid was methylated with diazomethane. Chromatography (Silicagel, benzene) and recrystallization from CCl_4 afforded **8** (2·10 g, 46%), m.p. 147–148°.

Both specimens showed no depression upon mixed m.p. and the IR spectra were completely superimposable.

Diethyl 2-methylfuran-3,4-dicarboxylate was prepared by the method similar to the report;[8] IR (neat): 3250, 1745, 1617, 1562, 1280, 1180, 1080 cm^{-1}; NMR (CCl_4): δ 1·45 (t, 6H), 2·51 (s, 3H), 4·26 (q, 4H), 7·68 (s, 1H). (Found: C, 58·7; H, 6·4. Calc. for $C_{11}H_{14}O_5$: C, 58·4; H, 6·2%).

Hydrolysis of **3fy**. A soln of **3fy** (1·0 g, 4·4 mmoles) in alcoholic KOHaq was heated under reflux for 3 hr. Work up afforded 5-methylfuran-2,4-dicarboxylic acid (0·6 g, 80%). A sample did not melt up to 250°. The isomer, 2-methylfuran-3,4-dicarboxylic acid has m.p. 230–231°.[8]

Attempted reaction of **1** *with ethyl phenylpropiolate*. Attempts were made to react ethyl phenylpropiolate with **1a**, **1b** and **1f** at 180° (2 hr), 180° (5 hr) and 150° (24 hr), respectively. In each case the starting ylide **1** was recovered almost quantitatively.

Reaction of **9a** *with* **2x**. A mixture of **9a** (4·00 g, 20 mmoles) and **2x** (7 ml) was heated at 180° for 15 min with stirring. After cooling, the resulting viscous oil was triturated with ether to give a yellow solid. Recrystallization from benzene afforded **10a** (6·15 g, 83%), m.p. 148–149·5°. (Found: C, 58·2; H, 7·0. $C_{18}H_{26}O_6S$ requires: V, 58·4; H, 7·1%).

Reaction of **9b** *with* **2x**. A mixture of **9b** (0·26 g, 1·5 mmoles) and **2x** (0·46 g, 2·7 mmoles) was heated at 140° for 20 min with stirring. Working up followed by recrystallization from benzene afforded a yellow crystalline solid **10b** (0·44 g, 86%), m.p. 177–178°. (Found: C, 55·8; H, 6·2. $C_{16}H_{22}O_6S$ requires: C, 56·1; H, 6·5%).

Reaction of **13** *with* **2x**. A mixture of **13** (1·00 g, 4·9 mmoles) and **2x** (1·50 g, 8·8 mmoles) was heated at 125° for 10 min. Chromatography (Florisil, AcOEt) and recrystallization from CCl_4 gave **14** (0·90 g, 49%), m.p. 142–144°. (Found: C, 60·3; H, 5·3. $C_{19}H_{20}O_6S$ requires: C, 60·6; H, 5·4%).

Preparation of dimethylsulphonium (benzoyl)-propionylmethylide (**1d**). A soln of dimethylsulphonium phenacylide[10] (12·6 g, 70 mmoles) and propionic anhydride (9·1 g, 70 mmoles) in anhyd THF (200 ml) was stirred for 6 hr at room temp. The mixture was diluted with water and extracted with $CHCl_3$. Recrystallization of the residue after evaporation from benzene yielded **1d** (4·5 g, 27%), m.p. 112–113°; IR (Nujol): 1600, 1565, 1330 cm^{-1}; NMR δ ($CDCl_3$), 1·04 (t, 3H), 2·61 (q, 2H), 2·96 (s, 6H), 7·40 (s, 5H). (Found: C, 66·2; H, 6·8. $C_{13}H_{16}O_2S$ requires: C, 66·1; H, 6·8%).

Preparation of dimethylsulphonium (benzoyl)-isobutyrylmethylide (**1e**). A soln of dimethylsulphonium phenacylide (7·6 g, 42 mmoles) and isobutyric anhydride (6·7 g, 42 mmoles) in THF was stirred for 24 hr at room temp. Work up followed by recrystallization from benzene afforded **1e** (3·6 g, 34%), m.p. 120–121°; IR (Nujol): 1578, 1545, 1370 cm^{-1}; NMR: δ ($CDCl_3$), 1·04 (d, 6H), 2·96 (s, 6H), 3·32 (septet, 1H), 7·40 (s, 5H). (Found: C, 67·4; H, 7·4. $C_{14}H_{18}O_2S$ requires: C, 67·2; H, 7·3%).

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