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REACTION OF SULPHONIUM YLIDES WITH DIPHENYLCYCLOPROPENONE

A NEW SYNTHESIS OF 2-PYRONES

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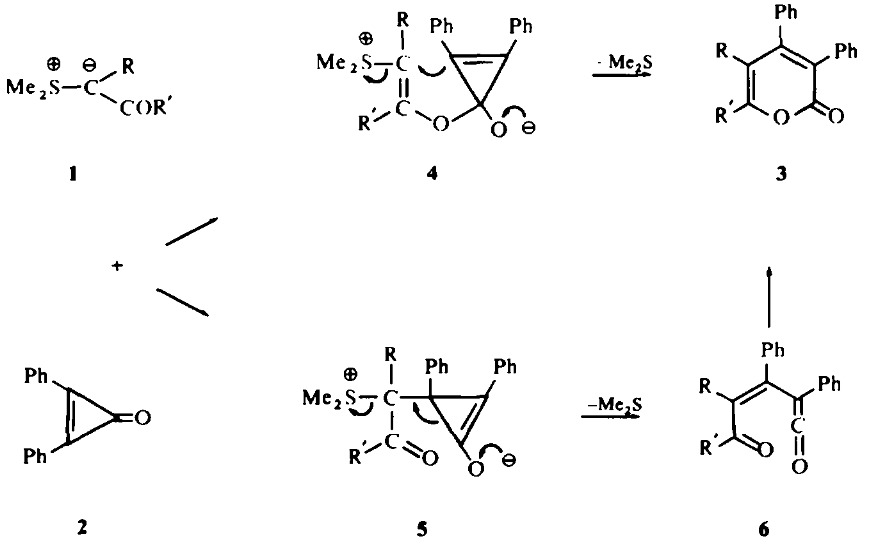
Abstract—The title reaction of carbonyl-stabilized sulphonium ylides **1a–1g** with diphenylcyclopropenone (**2**) gives 2-pyrone derivatives **3a–3g** under elimination of the sulphide at room temperature. Diacylmethylide **1i** reacts with **2** at 145° to yield **3i**. Reaction of unstable dimethyloxosulphonium methylide (**7**) takes another course affording a novel ylide **8**.

MANY authors have described syntheses of heterocyclic compounds by means of thermally labile ylides such as dimethylsulphonium and dimethyloxosulphonium methylide,[1] but little is known on similar preparative applications of much less reactive, stable ylides such as carbonyl-stabilized types (**1**). Previously, we reported that dimethylsulphonium diacylmethylides reacted with carbethoxy-substituted acetylenes to yield furans.[2] In extension of this work, we have examined the reaction of inactive sulphur ylides (**1**) with diphenylcyclopropenone (**2**), also a good electrophile, and demonstrated that the reaction constitutes a novel route to 2-pyrones (Scheme 1).*

SCHEME 1



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* For the reaction of phosphonium and pyridinium ylides with cyclopropenones, see Ref. 3. The present sulphonium ylides react in a completely different sense.

Reaction with carbonyl-stabilized sulphonium ylides

Table 1 lists present reaction conditions and yields of 2-pyrones (**3**), whose spectral data and analyses are given in Table 2 and 3.

TABLE 1. REACTION CONDITIONS[a] AND YIELDS OF 2-PYRONES (3)

Ylide				Reaction		2-Pyrone	
No.	R	R'	Ref.	Solvent	temp	No.	Yield (%)
1a	H	C_6H_5	6*a*, *b*, *c*	PhH	r.t.	**3a**	99
1a	H	C_6H_5		THF	r.t.	**3a'**[b]	95
1b	H	$p\text{-}CH_3C_6H_4$	7	PhH	r.t.	**3b**	99
1c	H	$p\text{-}BrC_6H_4$	6*a*	PhH	r.t.	**3c**	99
1d	H	OCH_3	8	THF	r.t.	**3d**	72
1e	CH_3	C_6H_5	9	PhH	r.t.	**3e**	56
1f	C_6H_5	C_6H_5	[a, c]	THF	r.t.	**3f**	58
1g	Br	C_6H_5	6*a*	THF	r.t.	**3g**	75
1h'[d]	H	CH_3	10	THF	66	**3h**	97
1i	CH_3CO	CH_3	11	neat	145	**3i**	43

[a] For details, see Experimental.

[b] Ylide **1a** was allowed to react with diphenylthiocyclopropenone (**2'**) under similar condition as **2**. The product **3a'** is therefore 3,4,6-triphenylpyran-2-thione.

[c] This novel ylide was not isolated.

[d] Ylide **1h'** stands for dimethyloxosulphonium acetylmethylide (see Text).

Dimethylsulphonium phenacylides **1a**, **1b** and **1c** reacted with equimolar diphenylcyclopropenone (**2**) in C_6H_6 at room temp with smooth evolution of dimethyl sulphide to yield 2-pyrones **3a**, **3b** and **3c**, respectively, in nearly quantitative yields. The Scheme 1 gives some explanations for the formation of **3**. The first route consists of nucleophilic addition of the enolate anion site of **1** to the carbonyl bond of **2** giving intermediate **4** and the subsequent ring closure with elimination of dimethyl sulphide. The second involves a ketene **6** as possible intermediate.[3b]* The alkoxycarbonylmethylide **1d** reacted similarly as acylmethylides **1a**–**1c** to afford **3d**.

Pyrone formation is not affected by the presence or absence of a hydrogen on the ylide carbon: disubstituted phenacylides **1e**, **1f** and **1g** reacted with **2** at room temperature to afford **3e**, **3f** and **3g**, respectively. The behaviour is in contrast to the reaction of the ylides with acetylenes affording furans, where the presence of a hydrogen atom attached to ylide carbon in **1** causes the reaction to proceed differently, producing no furans.[4]

A solution of dimethyloxosulphonium acetylmethylide (**1h'**) and **2** in THF remained unchanged at room temperature, but gave **3h** in a 97% yield upon refluxing for 64 hr. Dimethylsulphonium diacetylmethylide (**1i**) as a poor nucleophile required higher reaction temperature.[2] Thus, heating of a neat mixture of **1i** and **z** at 145° for 30 min yielded 5-acetyl-6-methyl-3,4-diphenyl-2-pyrone (**3i**) in a 43% yield. However, the highly stable dimethylsulphonium acetylcarbethoxy- (**1**, R = COMe, R' = OEt), dibenzoyl- (**1**, R = COPh, R' = Ph) and acetylbenzoylmethylide (**1**, R = COMe, R' = Ph) were inactive toward **2** under similar extreme conditions.

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* The postulated intermediacy of ketenes **6** and **12** (Scheme 2) is due to the suggestion of a referee. The authors are grateful for this valuable contribution.

The structural assignment of **3** was based on spectral data (Table 2) and elemental analyses (Table 3). Particularly, the mass spectrum showed an intense (M − CO) peak characteristic of 2-pyrones.[5] An example is found in the spectrum of 3,4-diphenyl-6-methyl-2-pyrone (**3h**) (Fig 1) and a possible fragmentation route is given in Fig 2.

TABLE 2. SPECTRAL DATA OF 2-PYRONES (3)

Compd No.	λ_{max}^{EtOH} nm (log ε)	ν_{max}^{KBr} cm^{-1}	NMR δ ppm (relative intensity, multiplicity)[a]
3a	253 (4·19) 358 (4·16)	1705, 1627, 1532	6·79 (s, 1H), 6·9–8·0 (m, 15H)
3a′	291 (4·46) 435 (4·09)	1619, 1510, 1480 1345, 1255, 1115	7·07 (s, 1H), 6·9–8·1 (m, 15H)
3b	261 (4·32) 362 (4·27)	1709, 1628, 1534	2·41 (s, 3H), 6·77 (s, 1H), 6·9–7·9 (m, 14H)
3c	263 (4·35) 360 (4·29)	1705, 1630, 1532	6·81 (s, 1H), 6·8–7·9 (m, 14H)
3d	240 (4·29)	1738, 1715, 1631 1534	3·99 (s, 3H), 5·55 (s, 1H), 6·9–7·4 (m, 10H)
3e	239 (4·37) 286 (3·87) 329 (4·09)	1703, 1620, 1530	1·89 (s, 3H), 6·9–7·8 (m, 15H)
3f	237 (4·24) 253 (4·23) 346 (4·12)	1729, 1600, 1520	6·5–7·5 (m)
3g	250 (4·23) 344 (4·13)	1720, 1590, 1530	6·9–8·1 (m)
3h	238 (4·06) 286 (3·71) 328 (3·93)	1715, 1640, 1545	2·34 (coalesced d, 3H, J = 0·9 Hz), 6·17 (coalesced q, 1H, J = 0·9 Hz), 7·0–7·4 (m, 10H)
3i	254 (3·92) 335 (4·04)	1728, 1696	2·14 (s, 3H), 2·66 (s, 3H), 6·8–7·5 (m, 10H)

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

TABLE 3. M.PS AND ANALYTICAL DATA OF NOVEL 2-PYRONES[a]

Compd No.	m.p.	Formula	Anal. (%) Found C	Found H	Req. C	Req. H
3b	185–187·5	$C_{24}H_{18}O_2$	84·0	5·4	85·2	5·4
3d	134–135	$C_{18}H_{14}O_3$	77·8	5·1	77·7	5·1
3e	189–190	$C_{24}H_{18}O_2$	85·0	5·3	85·2	5·4
3f	154–156	$C_{29}H_{20}O_2$	87·0	4·9	87·0	5·0
3g	150·5–152	$C_{23}H_{15}BrO_2$	68·8	3·8	68·5	3·8
3h	134–135	$C_{18}H_{14}O_2$	82·2	5·2	82·4	5·4
3i	162·5–163	$C_{20}H_{16}O_3$	79·1	5·3	78·9	5·3

[a] Compounds **3a** and **3c** are known, whose spectral data and melting points agreed with those in literature.[3b]

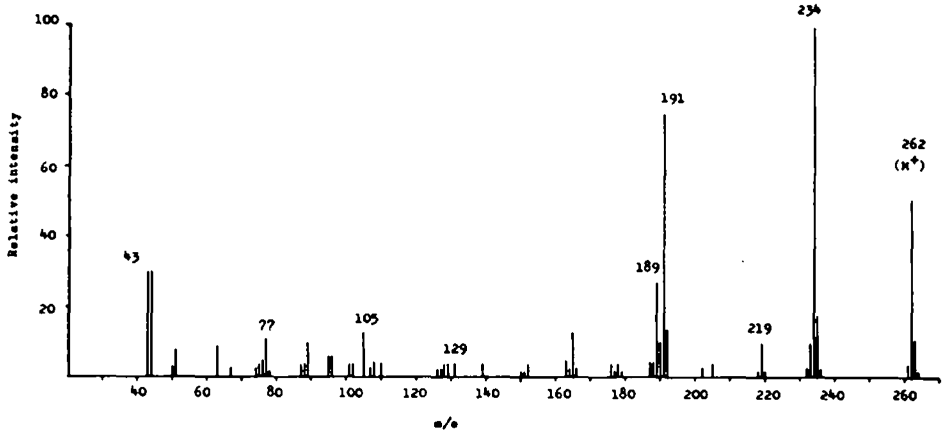


FIG 1. Mass spectrum of 3,4-diphenyl-6-methyl-2-pyrone (**3h**) (Metastable peaks at *m/e* 156 and 209 are not given).

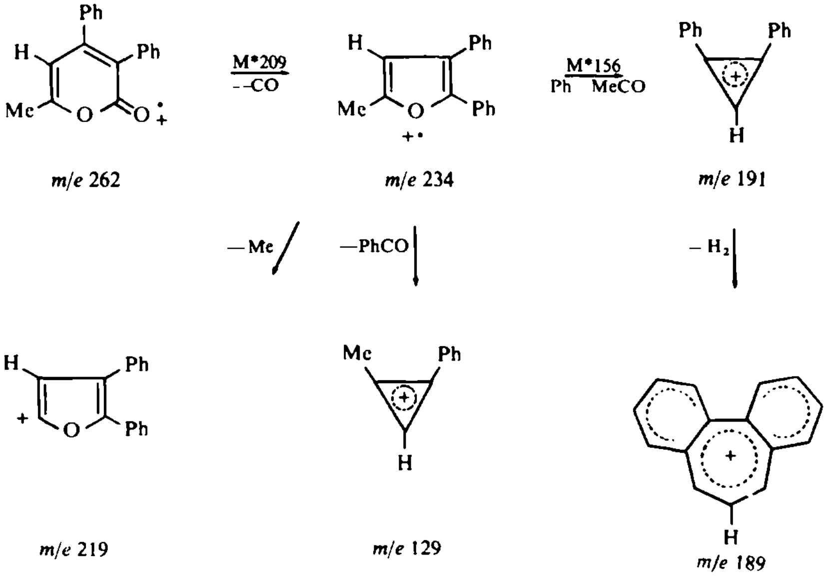


FIG 2. Fragmentation of 3,4-diphenyl-6-methyl-2-pyrone (**3h**).

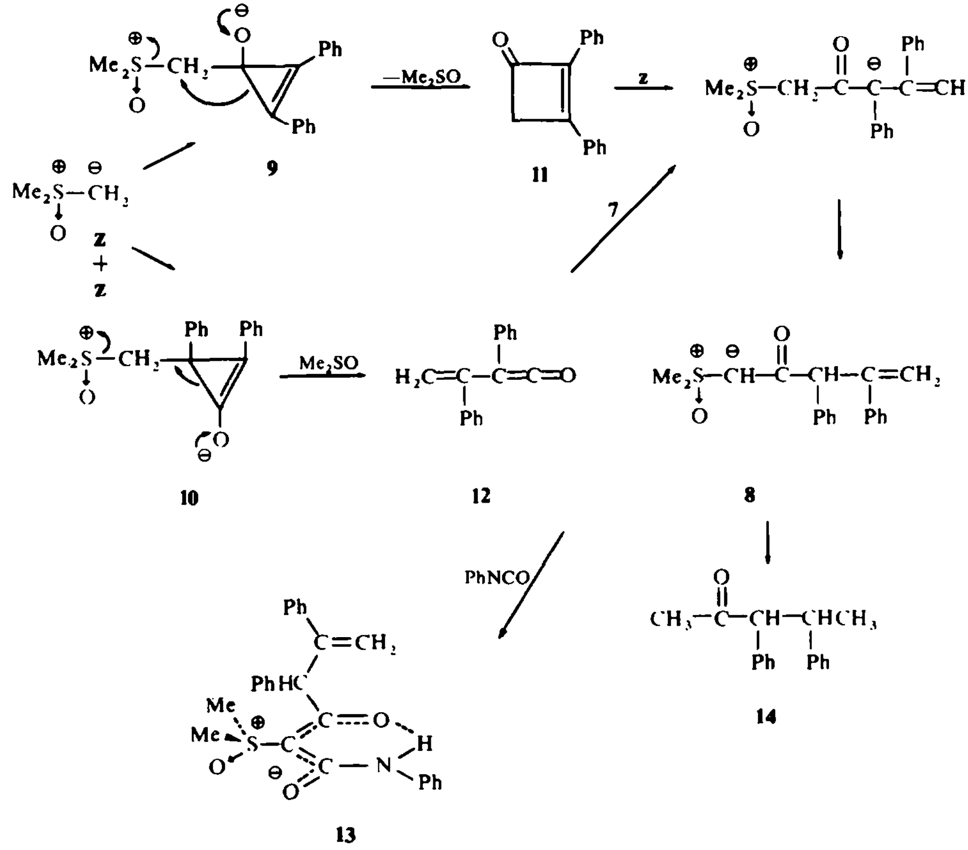
These data reject the possibility of isomeric structures such as 4-pyrone and cyclobutenone.

Dimethylthiocyclopropenone (**2'**) reacted with **1a** under similar conditions to afford 3,4,6-triphenylpyran-2-thione (**3a'**), whose characteristic fragmentation pathways were again the expulsion of thiocarbonyl from the molecular ion affording a furan derivative (Experimental).

Reaction with dimethyloxosulphonium methylide

The reaction of ylides with cyclopropenones involves the key cyclization step, in which the original ylide-carbonyl oxygen is transformed to pyrone ring oxygen. Thus, it seemed of interest to investigate the reaction of **2** with a labile ylide having no ylide carbonyl group.

SCHEME 2



Reaction of dimethyloxosulphonium methylide (**7**)[12] with equimolar **2** in DMSO or THF afforded a novel ylide **8** (m.p. 128–129·5°) in 25% and 36% yield, respectively. The use of twice as much **7** exactly doubled the yield of **8**, (72%, under the same reaction conditions). The structure was based on the following.

The IR spectrum showed an ylide carbonyl absorption band at 1540 cm^{-1}, and the NMR spectrum (Fig 3) was consistent with the structure given. The results of C, H analysis were in good agreement with the values calculated for $C_{19}H_{20}O_2S$, and the mass spectrum showed an intense peak at *m/e* 234, which indicated loss of Me_2SO (78) from the molecular ion (312), besides a base peak at *m/e* 78. Furthermore, desulphurization of **8** with Raney Ni gave 3,4-diphenyl-2-pentanone (**14**) in 77% yield. These results clearly point to the structure **8** with a terminal methylene.

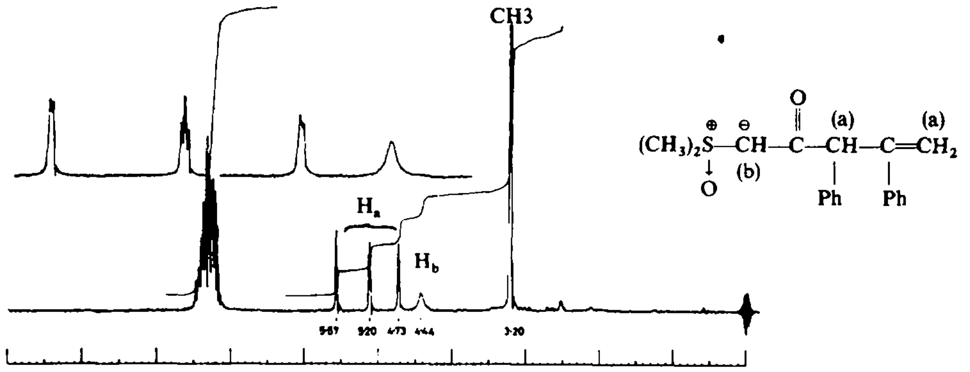


FIG 3. 100-MHz NMR Spectrum of **8** in $CDCl_3$ at 31·5°.

Scheme 2 gives possible courses for this reaction. The first consists of initial formation of cyclobutenone **11** *via* **9**. The carbonyl group of **11** is then attacked by another molecule of methylide **7**, followed by ring opening to afford **8**. The second route involves an intermediary ketene **12** and subsequent reaction with **7**.

Dimethyloxosulphonium methanesulphonylmethylide[13] was found to be inactive toward **2**.

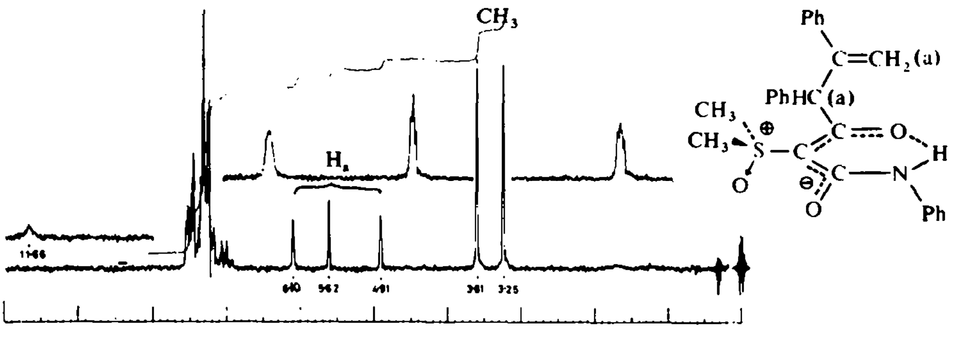


FIG 4. 100-MHz NMR Spectrum of **13** in $CDCl_3$ at 31·5°.

Phenylcarbamoylation of **8** with phenyl isocyanate gave **13** in 51% yield. Its NMR spectrum is given in Fig 4, in which S-Me signals were observed as two distinct singlets with a chemical shift difference of 0·36 ppm. This shows the S-Me groups are diastereotopic, which is ascribed to the pyramidal structure of the sulphur atom and to the presence of asymmetric carbon. Therefore, they are intrinsically nonequivalent.* The chemical shift difference of this kind is usually decreased by increasing the number of intervening bonds between the inducing centre and the observed protons.[15] The reasonable interpretation may be the fixing of the sickle conformation of the mesomeric system consisting of the ylide carbon and both ylide carbonyl groups. This is supported by the appearance of the NH proton at δ 11·66 ppm.†

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* We have reported similar observations on the sulphonium ylides.[14]

† In contrast to **13**, the S-Me protons of **8** were observed as a singlet.

EXPERIMENTAL

All m.ps are uncorrected. Micronalyses were performed at the Elemental Analyses Centre of Kyoto University by Mrs. K. Fujimoto at Prof. K. Sisido's Laboratory. NMR spectra were taken with JEOL C-60-H and Varian HA-100D spectrometers with $CDCl_3$ or CCl_4 as solvent, chemical shifts are reported in δ values relative to TMS internal standard. Mass spectra were obtained on a Hitachi RMU-6L instrument (70 ev) and UV spectra were taken in 95% EtOH on a Shimadzu MPS-50L spectrometer.

Reaction of dimethylsulphonium phenacylide (**1a**) *with diphenylcyclopropenone* (**2**). A soln of **1a** (1·0 g, 5·6 mmoles) and **2** (1·2 g, 5·6 mmoles) in C_6H_6 (70 ml) was stirred at room temp for 1 hr. After the solvent was removed at reduced pressure, the residual solids were purified by column chromatography (Florisil, C_6H_6) and following recrystallization from C_6H_6 afforded **3a** (1·8 g, 99%), m.p. 182·5–184° (lit.[3a] m.p. 183–184°); mass spectrum *m/e* (relative intensity) P + 2 = 326 (3), P + 1 = 325 (16), P = 324 (63), 297 (25), 296 (100), 191 (27), 189 (11), 105 (29), 77 (20). (Found: C, 85·4; H, 5·1. Calc. for $C_{23}H_{16}O_2$: C, 85·2; H, 5·0%).

Reaction of **1a** *with diphenylthiocyclopropenone* (**2'**). A soln of **1a** (0·72 g, 4·0 mmoles) and **2'** (0·89 g, 4·0 mmoles) in THF (50 ml) was stirred at room temp for 3 hr. After the solvent was removed, the crystalline residue was recrystallized from cyclohexane to afford **3a'** (1·30 g, 95%), m.p. 164·5–166° (lit.[3a] m.p. 165–166°); mass spectrum *m/e* (relative intensity) P + 1 = 341 (8), P = 340 (21), 339 (21), 324 (37), 297 (31), 296 (100), 192 (12), 191 (44), 189 (23), 106 (16), 105 (93), 78 (81), 77 (95). (Found: C, 81·2; H, 4·9. Calc. for $C_{23}H_{16}OS$: C, 81·2; H, 4·7%).

Reaction of dimethylsulphonium p-*methylphenacylide* (**1b**) *with* **2**. A soln of **1b** (0·97 g, 5·0 mmoles) and **2** (1·0 g, 5·0 mmoles) in C_6H_6 was stirred at room temp for 1 hr. Work up afforded **3b** (1·7 g, 99%), m.p. 185–187·5° (CCl_4–C_6H_6). Mass spectrum *m/e* (relative intensity) P + 2 = 340 (3), P + 1 = 339 (16), P = 338 (57), 311 (26), 310 (100), 205 (9), 191 (14), 189 (8), 119 (16), 105 (13), 91 (16), 77 (6).

Reaction of dimethylsulphonium p-*bromophenacylide* (**1c**) *with* **2**. A soln of **1c** (1·3 g, 5·0 mmoles) and **2** (1·0 g, 5·0 mmoles) in C_6H_6 was stirred at room temp for 1 hr to yield **3c** (2·0 g, 99%), m.p. 170–173° (CCl_4–C_6H_6). Mass spectrum *m/e* (relative intensity) P + 2 = 404 (2), P = 402 (2), 376 (3), 374 (3), 191 (4), 189 (3), 182 (5), 142 (10), 117 (11), 115 (11), 106 (10), 105 (100), 103 (18), 100 (30), 83 (28), 82 (26), 81 (23), 79 (45), 78 (20), 77 (41).

Reaction of dimethylsulphonium carbomethoxymethylide (**1d**) with **2**. A soln of **1d** was prepared by treatment of dimethyl(carbomethoxymethyl)sulphonium bromide (2·2 g, 10 mmoles) with NaH (0·48 g, 50% mineral oil dispersion, 10 mmoles). To this soln, **2** (1·0 g, 5·0 mmoles) was added at room temp and stirring continued for 1 hr. The mixture was diluted with H_2O and extracted with C_6H_6. After drying, the solvent was removed to afford **3d** (1·0 g, 72%), m.p. 134–135° (C_6H_6). Mass spectrum *m/e* (relative intensity) P + 2 = 280 (1), P + 1 = 279 (9), P = 278 (38), 251 (14), 250 (61), 236 (18), 235 (67), 191 (46), 189 (38), 179 (31), 178 (24), 105 (100), 77 (45).

Reaction of dimethylsulphonium α-methylphenacylide (**1e**) *with* **2**. A soln of **1e** (1·0 g, 5·0 mmoles) and **2** (1·0 g, 5·0 mmoles) in C_6H_6 (70 ml) was stirred at room temp for 10 hr. Work up afforded **3e** (0·95 g, 56%), m.p. 189–190° (C_6H_6). Mass spectrum *m/e* (relative intensity) P + 1 = 339 (4), P = 338 (10), 310 (6), 205 (33), 105 (100), 78 (86), 77 (96).

Reaction of dimethylsulphonium α-phenylphenacylide (**1f**) *with* **2**. A suspension of dimethyl(α-phenylphenacyl)sulphonium bromide (2·0 g, 6·0 mmoles) in THF was treated with NaH (0·29 g, 50% mineral oil dispersion, 6·0 mmoles) at room temp. After evolution of H_2 had ceased, **2** (1·0 g, 5·0 mmoles) was added to the reaction and stirring continued for 24 hr. Work up afforded **3f** (1·2 g, 58%), m.p. 154–156° (hexane–C_6H_6).

Reaction of dimethylsulphonium α-bromophenacylide (**1g**) *with* **2**. A soln of **1g** (1·3 g, 5·0 mmoles) and **2** (1·0 g, 5·0 mmoles) in THF was stirred at room temp for 24 hr. Work up afforded **3g** (1·5 g, 75%), m.p. 150·5–152° (CCl_4). Mass spectrum *m/e* (relative intensity) P + 2 = 404 (3), P = 402 (3), 376 (6), 374 (6), 295 (7), 223 (7), 205 (7), 189 (7), 179 (7), 178 (10), 155 (16), 141 (25), 134 (16), 105 (100), 101 (22), 81 (20), 79 (14), 78 (33), 77 (63).

Reaction of dimethyloxosulphonium acetylmethylide (**1h'**) *with* **2**. A soln of **1h'** (1·3 g, 10 mmoles) and **2** (2·1 g, 10 mmoles) in THF (100 ml) was heated under reflux for 64 hr. After evaporation of the solvent, the residual oil was chromatographed (Florisil, C_6H_6 as eluent) and recrystallized from 1:1 C_6H_6 and CCl_4 to give **3h** (2·5 g, 97%), m.p. 134–135°.

Reaction of dimethylsulphonium diacetylmethylide (**1i**) *with* **2**. A stirred mixture of **1i** (0·80 g, 5·0 mmoles) and **2** (1·0 g, 5·0 mmoles) was heated at 145° for 30 min. Chromatography (Silica gel, C_6H_6) and following recrystallization from C_6H_6 afforded **3i** (0·65 g, 43%), m.p. 162·5–163°. Mass spectrum *m/e* (relative intensity)

P + 2 = 306 (2). P + 1 = 305 (13). P = 304 (56). 262 (14). 261 (63). 233 (14). 206 (19). 205 (100). 204 (5). 203 (10). 202 (10). 189 (5). 78 (8). 77 (10).

Attempted reaction of doubly acylated dimethylsulphonium methylide with **2**. Attempts were made to effect reaction of **2** with dimethylsulphonium acetylcarbethoxymethylide, dibenzoylmethylide and acetylbenzoylmethylide at 150° (1 hr), 110–145° (24 hr) and 110–130° (19 hr), respectively, in the absence of solvent. In each case starting ylide was recovered almost quantitatively.

Reaction of dimethyloxosulphonium methylide (**7**) *with* **2**. (a) *Reaction in DMSO*. A soln of ylide **7** in DMSO was prepared by treating trimethyloxosulphonium iodide (6·3 g, 29 mmoles) with NaH (1·4 g, 50% mineral oil dispersion, 29 mmoles) in DMSO (100 ml). A soln of **2** (2·7 g, 13 mmoles) in DMSO (50 ml) was added, stirring at room temp. After 24 hr the reaction mixture diluted with H_2O, extracted with $CHCl_3$ and dried ($MgSO_4$). After solvent was removed, the residual viscous oil solidified upon addition of dry ether. These solids were recrystallized from C_6H_6 to yield **8** (3·0 g, 72%), m.p. 128–129·5°, λ_{max}^{EtOH} 255 nm (log ε 4·27), ν_{max}^{KBr}: 1540, 1375, 1180 cm^{-1}. (Found: C, 72·9; H, 6·5. $C_{19}H_{20}O_2S$ requires: C, 73·1; H, 6·5%). Analogous treatment of **2** with an equimolar quantity of **7** afforded **8** in 25% yield.

(b) *Reaction in THF*. To a soln of **7** in THF prepared by treating trimethyloxosulphonium chloride (1·3 g, 10 mmoles) with NaH (0·5 g, 50% mineral oil dispersion, 10 mmoles) in THF (100 ml), a soln of **2** (1·6 g, 8 mmoles) in THF (50 ml) was added at 0° and stirred at room temp for 15 hr. Work up afforded 0·85 g (36%) of **8**, m.p. 128–129·5° (C_6H_6).

Desulphurization of **8**. Raney Ni catalyst (W-2) was added in one portion to a soln of **8** (1·43 g, 4·5 mmoles) in EtOH (100 ml). The mixture was stirred at room temp for 42 hr, and the filtrate concentrated. Recrystallization of residue from petroleum ether (b.p. 35–40°) afforded 3,4-diphenyl-2-pentanone (**14**) (0·84 g, 77%), m.p. 128–128·5°, ν_{max}^{KBr}: 1710, 1350, 1153 cm^{-1}; NMR: δ (CCl_4) 0·96 (d, 3H, J = 6·6 Hz), 1·77 (s, 3H), 3·20–3·95 (m, 2H), 7·1–7·4 (m, 10H). Mass spectrum: parent peak at m/e 238, base peak at m/e 105. (Found: C, 85·6; H, 7·6. $C_{17}H_{18}O$ requires: C, 85·6; H, 7·6%).

Reaction of **8** *with phenyl isocyanate*. A soln of **8** (0·23 g, 0·7 mmoles) in THF was treated with PhNCO (0·09 g, 0·8 mmoles) for 24 hr at room temp. Recrystallization of the evaporation residue from a 2:1 mixture of EtOH and hexane gave ylide **13** (0·17 g, 51%), m.p. 158·5–160°, λ_{max}^{EtOH} 240·5 nm (log ε 4·44), 269 (4·27), 278 (4·29); ν_{max}^{KBr}: 1630, 1530, 1350, 1210, 905 cm^{-1}. (Found: C, 72·5; H, 5·9. $C_{26}H_{25}NO_3S$ requires: C, 72·4; H, 5·8%).

Attempted reaction of dimethyloxosulphonium methanesulphonylmethylide with **2**. A soln of dimethyloxosulphonium methanesulphonylmethylide (1·0 g, 6·0 mmoles) and **2** (1·0 g, 5·0 mmoles) in THF (100 ml) was heated under reflux for 76 hr. Work up resulted in complete recovery of the starting ylide.

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