# Preparation and Reaction of Sulphonium Ylides stabilized by a Phosphinyl Substituent

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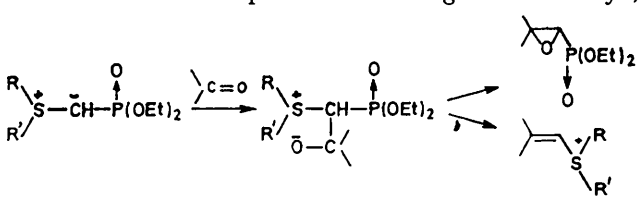
Sulphonium methylides with a dialkoxyphosphinyl substituent were prepared by the treatment of the corresponding sulphonium salts with sodium hydride. The reaction of these ylides with phenyl isocyanate, acid chlorides, or acid anhydrides gave new stabilized ylides. While the reaction of these ylides with benzaldehyde afforded vinyl sulphonium salts, that with αβ-unsaturated esters resulted in the formation of phosphono-substituted cyclopropanes.

SULPHUR ylides are well known to be stabilized by electron-withdrawing substituents and thus can be isolated in most cases.[1] Earlier we reported preliminary results on a new class of sulphur ylide stabilized by a phosphinyl substituent.[2] We studied this ylide because an intermediate betaine resulting from the nucleophilic attack of the ylide on an electron deficient centre should be capable of reacting in two ways;



[1] See for an example, A. W. Johnson, 'Ylide Chemistry,' Academic Press, New York, 1966.

[2] K. Kondo and D. Tunemoto, *J.C.S. Chem. Comm.*, 1972, 952.

elimination of the sulphonium group (path *a*) or of the phosphinyl group (path *b*). This paper provides a full account of our research on this subject.

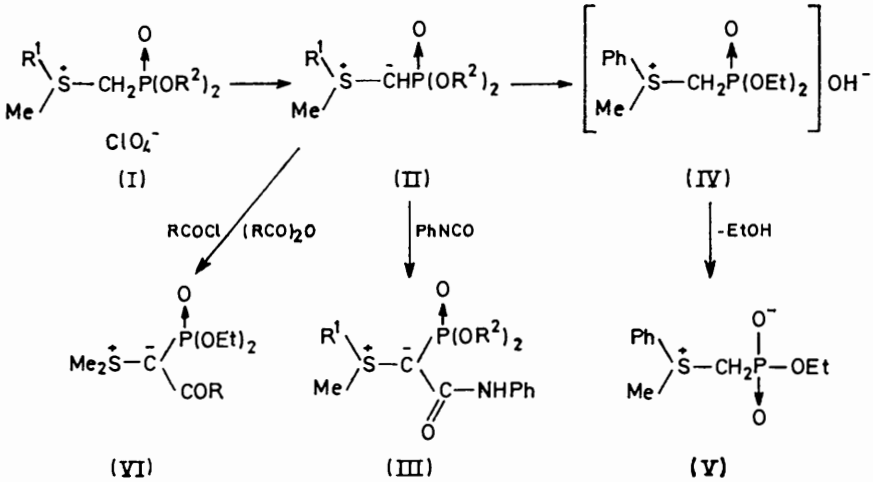
## RESULTS AND DISCUSSION

(Diethoxyphosphinylmethyl)methylphenylsulphonium perchlorate (Ia) was obtained as a viscous oil in quantitative yield by alkylation of the corresponding phenylthiomethylphosphonate with methyl iodide in the presence of an equimolar amount of silver perchlorate. Other sulphonium salts (Ib) and (Ic) were prepared similarly. Treatment of the sulphonium salt (Ia) with sodium hydride in tetrahydrofuran (THF) at −20° afforded methylphenylsulphonium diethoxyphosphinylmethylide (IIa) in quantitative yield. The ylide (IIa) was a hygroscopic, viscous oil and was identified by spectra and chemical reactions (see below). One of the characteristics of the ylide (IIa) is the i.r. stretching absorption of P=O at 1215 $cm^{-1}$, which is appreciably shifted to longer wavelength as compared with that of the parent sulphonium salt (Ia) (1265 $cm^{-1}$), owing to the delocalization of the negative charge on the ylide carbanion.

Attempted purification of the ylide (IIa) by column chromatography on silica gel using 99% ethanol as eluant resulted in the formation of a new crystalline betaine (V). The transformation of (IIa) to (V) can be explained by assuming the intermediacy of the sulphonium hydroxide (IV) followed by partial hydrolysis of the phosphinyl function. An analogous betaine has already been reported as thetin, which was obtained by hydrolysis of the ylide bearing an ester or amide function.[3] Treatment of the ylide (IIa) with an equimolar amount of phenyl isocyanate in THF at room temperature produced a new stable ylide (IIIa). Analogously, ylides (IIIb) and (IIIc) were prepared directly from the corresponding sulphonium salts (Ib) and (Ic) by successive treatment with sodium hydride and phenyl isocyanate in THF. In the case of *C*-carbamoylated ylides (III), the i.r. absorption of the P=O stretch was at 1250 and that of C=O at 1640 $cm^{-1}$, indicating extensive delocalization of the negative charge into both stabilizing substituents.

The reaction of the ylide (II) with acylating reagents such as acid chlorides or acid anhydrides produced the normal *C*-acylated stable ylides. Thus, treatment of (IIc) with acetyl or benzoyl chloride afforded the new ylides (VIa) and (VIb) in 79 and 38% yields, respectively.

When the ylide (IIa) generated *in situ* was treated with benzaldehyde at room temperature, the vinylsulphonium salt (VIIa) was obtained as a viscous oil in 66% yield. The i.r. and n.m.r. spectra of the salt were in good agreement with those of the authentic sulphonium salt prepared from phenyl *trans*-styryl sulphide[4] and methyl iodide in the presence of silver perchlorate. It was, however, impossible to rule out completely the presence of the *cis*-isomer in the product, because the n.m.r. absorption of the vinylic protons overlapped that of the phenyl protons. A similar reaction of the ylide (IIc) with benzaldehyde gave a mixture of *cis*- and *trans*-isomers of the sulphonium salt (VIIc) as crystals in 64% yield. In this case, the ratio of the isomers could readily be determined to be *cis* : *trans* = 33 : 67 from the n.m.r. spectrum ($J_{cis}$ 10, $J_{trans}$ 16 Hz[5]). The exclusive formation of these vinylsulphonium salts indicates that the leaving power of diethyl sodium phosphate is superior to that of sulphide in the intermediate betaine, *i.e.*, path *b* appears




(I), (II), (III) a; $R^1$ = Ph, $R^2$ = Et; b; $R^1$ = Me, $R^2$ = Me; c; $R^1$ = Me, $R^2$ = Et

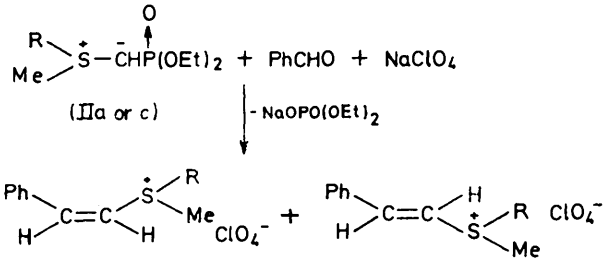
(VI) a; R = Me; b; R = Ph

[3] J. Adams, L. Hoffmann, jun., and B. M. Trost, *J. Org. Chem.*, 1970, **35**, 1600; K. W. Ratts and A. N. Yao, *ibid.*, 1968, **33**, 70.

[4] A. A. Oswald, K. Griesbaum, B. E. Hudson, jun., and J. M. Bregman, *J. Amer. Chem. Soc.*, 1964, **86**, 2877.

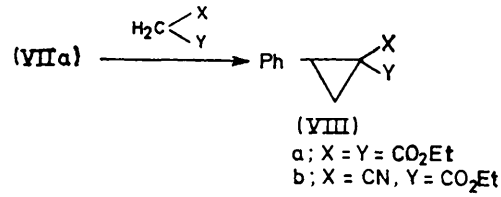
[5] M. C. Caserio, R. E. Pratt, and R. J. Holland, *J. Amer. Chem. Soc.*, 1966, **88**, 5747.

to be favoured in the reaction of the ylide (II) with these carbonyl compounds.*



(VIIIa or c) a ; R = Ph ; c ; R = Me

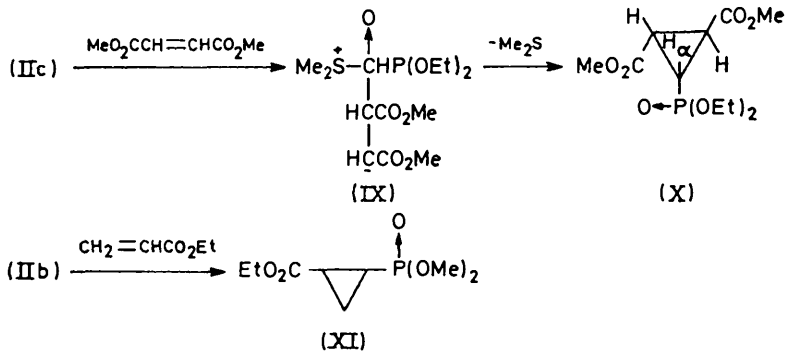
The nucleophilic addition of active methylene compounds to vinylsulphonium salts has been reported to give cyclopropane derivatives in excellent yields.[7] Thus, the vinylsulphonium salt (VIIa) generated *in situ* in THF was treated with the sodium salt of diethyl malonate to afford diethyl 2-phenylcyclopropane-1,1-dicarboxylate (VIIIa). The overall yield from the sulphonium salt (Ia) was 59%. Similar treatment of the salt (VIIa) with ethyl cyanoacetate afforded the cyclopropane (VIIIb) in 63% yield. In the latter case,



(VIII)
a; X = Y = $CO_2Et$
b; X = CN, Y = $CO_2Et$

two stereoisomers are the possible products. The n.m.r. spectrum of the product revealed the exclusive formation of only one isomer. However, the exact stereochemistry of the product is unknown. The foregoing reaction thus provides a convenient one-flask method of obtaining cyclopropanes by a three-carbon condensation.

The reaction of the ylide (IIc) with dimethyl maleate or dimethyl fumarate gave the same phosphono-substituted cyclopropane (X) in 20 and 46% yield, respectively. The structure of (X) was confirmed by its n.m.r. spectrum, in which the methine proton (δ 1·8) assignable to $H_\alpha$ was observed as a clear octet and the methyl protons of the ester group as two singlets. The other stereoisomer could not be detected in the product. The following conclusion can be drawn from the present results. Nucleophilic addition of the ylide (II) to the αβ-unsaturated system affords the relatively stable betaine (IX) as an intermediate in which free rotation is possible.[8] In the case of this intermediate, the leaving power of the sulphonium group is superior to that of the phosphinyl group and thus the intramolecular nucleophilic substitution produces the thermodynamically most stable cyclopropane as the final product. The reaction of the ylide (IIb) with ethyl acrylate in dimethyl sulphoxide (DMSO) gave the cyclopropane (XI) in 48% yield. The exact stereochemistry of (XI) was unknown, though the n.m.r. spectrum of the isolated product suggested the formation of only one isomer. In conclusion, the appropriate use of a sulphur ylide stabilized by a phosphinyl substituent may offer a novel method for the syntheses of certain cyclopropanes as well as cyclopropylphosphonate.[9]



(IX) (X)



(XI)

## EXPERIMENTAL

All reactions of ylides were carried out under an atmosphere of dry nitrogen. I.r. spectra were taken on a Hitachi-Perkin-Elmer model 337 Infracord or a Hitachi EPI-G3 Infracord spectrometer as neat liquids or powdered solids in potassium bromide discs. N.m.r. spectra were obtained on a Varian HA-100 or a Hitachi R20-B spectrometer. Elemental analyses were performed at the microanalytical laboratory of our research centre. The n.m.r. and i.r. spectra of new compounds are given in Table 1. The results of elemental analyses are listed in Table 2.

*Sulphonium Salts* (Ia, b, *and* c).—Treatment of diethyl phenylthiomethylphosphonate,[10] dimethyl methylthiomethylphosphonate,[11] and diethyl methylthiomethylphosphonate [10] with methyl iodide in the presence of silver

* Christensen *et al.*[6] have reported that the condensation of (IIc) with acetaldehyde gave diethyl (*cis*-1,2-epoxypropyl)-phosphonate in good yield. This behaviour is in sharp contrast with the result described here.

[6] B. G. Christensen, S. Plains, and R. A. Firestone, U.S.P. 3,632,691/1972.

[7] (*a*) J. Gosselck, H. Ahlbrecht, F. Dost, H. Schenk, and G. Schmidt, *Tetrahedron Letters*, 1968, 995; (*b*) J. Gosselck, L. Beress, and H. Schenk, *Angew. Chem.*, 1966, **78**, 606; (*c*) C. R. Johnson and J. P. Lockard, *Tetrahedron Letters*, 1971, 4589.

[8] *Cf.* G. B. Payne, *J. Org. Chem.*, 1967, **32**, 3351.

[9] D. Seyferth, R. S. Marmor, and P. Hilbert, *J. Org. Chem.*, 1971, **36**, 1379.

[10] M. Green, *J. Chem. Soc.*, 1963, 1324.

[11] E. B. Pedersen and S. O. Lawesson, *Synthesis*, 1969, 170.

TABLE 1

N.m.r. and i.r. spectral data of new compounds

| Compound | N.m.r. (solvent) δ | I.r. (medium) $\nu_{max.}$/cm$^{-1}$ |
|---|---|---|
| (Ia) | [$(CD_3)_2SO$] 1·13 (6H, t, *J* 7 Hz, $CH_2CH_3$), 3·43 (3H, s, SMe), 3·72—4·30 (4H, m, $CH_2CH_3$), 4·52 (2H, d, *J* 14 Hz, $SCH_2$), 7·70—8·30 (5H, m, Ph) | (Neat) 1265 |
| (Ib) | [$(CD_3)_2SO$] 3·03 (6H, s, SMe), 3·80, (6H, d, *J* 12 Hz, OMe), 4·09 (2H, d, *J* 14 Hz, $SCH_2P$) | (Neat) 1250 |
| (Ic) | [$CD_3)_2SO$] 1·30 (6H, t, *J* 7 Hz, $CH_2CH_3$), 3·03 (3H, s, SMe), 4·05 (2H, d, *J* 14 Hz, $SCH_2P$), 3·97—4·45 (4H, m, $CH_2CH_3$) | (Neat) 1250 |
| (IIa) | ($CDCl_3$) 1·28 (6H, t, *J* 7 Hz, $CH_2CH_3$), 2·80 (3H, s, SMe), 3·70—4·30 (5H, m, $CH_2CH_3$ + CH), 7·35—7·80 (5H, m, Ph) | (Neat) 1215 |
| (IIIa) | ($CDCl_3$) 1·25 and 1·37 (6H, 2t, *J* 7 Hz, $CH_2CH_3$), 3·35 (3H, s, SMe), 3·75—4·40 (4H, m, $CH_2CH_3$), 6·75—7·90 (10H, m, Ph), 9·90br (1H, s, NH) | (KBr) 1640, 1540, 1255 |
| (IIIb) | ($CDCl_3$) 3·30 (6H, s, SMe), 3·70 (2H, d, *J* 11 Hz, OMe), 6·78—7·64 (5H, m, Ph), 9·23br (1H, s, NH) | (KBr) 1635, 1532, 1255 |
| (IIIc) | ($CDCl_3$) 1·33 (6H, t, *J* 7 Hz, $CH_2CH_3$), 3·00 (6H, s, SMe), 3·80—4·25 (4H, m, $CH_2CH_3$), 7·10—7·60 (5H, m, Ph), 9·30br (1H, s, NH) | (KBr) 1640, 1535, 1250 |
| (V) | ($CDCl_3$) 1·20 (3H, t, *J* 4 Hz, $CH_2CH_3$), 3·60 (3H, s, SMe), 3·80—4·10 (2H, m, $CH_2CH_3$), 4·52 (2H, m, $SCH_2P$), 7·24—7·42 (5H, m, Ph) | (KBr) 1240, 1080, 1040 |
| (VIa) | ($CDCl_3$) 1·15 (6H, t, *J* 7 Hz, $CH_2CH_3$), 2·13 (3H, s, Ac), 2·97 (6H, s, SMe), 3·77—4·30 (4H, m, $CH_2CH_3$) | (Neat) 1565, 1220 |
| (VIb) | ($CDCl_3$) 1·13 (6H, t, *J* 7 Hz, $CH_2CH_3$), 3·07 (6H, s, SMe), 3·58—4·27 (4H, m, $CH_2CH_3$) 7·25—7·83 (5H m, Ph) | (KBr) 1540, 1210 |
| (VIIa) | ($CDCl_3$) 3·42 (3H, s, SMe), 6·75—8·15 (12H, m, Ph + CH=CH) | (Neat) 1605, 1575, 1495 |
| (VIIc) | [$(CD_3)_2SO$] 3·13 (3H, s, SMe), 6·68 and 7·82 (2d, *J* 10 H , CH=CH of *cis*-isomer), 7·18 and 7·76 (2d, *J* 16 Hz, CH=CH of *trans*-isomer), 7·40—7·85 (5H, m, Ph) | (KBr) 1610, 1570, 1490 |
| (X) | ($CCl_4$) 1·30 (6H, t, *J* 7 Hz, $CH_2CH_3$), 1·50—1·87 (1H, oct, CH), 2·10—2·87 (2H, m, CH), 3·67 (3H, s, OMe), 3·70 (3H, s, OMe), 3·80—4·33 (4H, m, $CH_2CH_3$) | (Neat) 1740, 1280 |
| (XI) | ($CCl_4$) 1·27 (3H, t, *J* 7 Hz, $CH_2CH_3$), 1·43—1·57 (2H, m, $CH_2$ or CH) 1·83—2·48 (2H, m, $CH_2$ or CH), 3·78 (6H, d, *J* 13 Hz, OMe 4·17 (2H, q, *J* 7 Hz, $CH_2CH_3$) | (Neat) 1740, 1250 |

TABLE 2

Elemental analyses

| Compound | M.p./°C | Formula | Found (%) C | Found (%) H | Required (%) C | Required (%) H |
|---|---|---|---|---|---|---|
| (Ia) † | 115—116 | $C_{36}H_{40}BO_3PS$ | 72·9 | 7·0 | 72·7 | 6·8 |
| (Ib) † | 163—164 | $C_{29}H_{34}BO_3PS$ | 69·1 | 7·3 | 69·1 | 6·8 |
| (Ic) † | 124—125 | $C_{31}H_{36}BO_3PS$ | 70·2 | 7·4 | 69·9 | 7·2 |
| (IIIa) | 89—90 | $C_{19}H_{24}NO_4PS$ | 57·9 | 6·1 | 58·0 | 6·2 |
| (IIIb) | 119—120 | $C_{12}H_{18}NO_4PS$ | 47·4 | 6·3 | 47·5 | 6·0 |
| (IIIc) | 99—100 | $C_{14}H_{22}NO_4PS$ | 50·6 | 6·7 | 50·8 | 6·7 |
| (V) ‡ | 148—149 | $C_{10}H_{15}O_3PS$ | 48·3 | 6·5 | 48·8 | 6·1 |
| (VIa) ‡ | Oil | $C_9H_{19}O_4PS$ | 41·3 | 7·9 | 42·5 | 7·5 |
| (VIb) | 98—99 | $C_{14}H_{21}O_4PS$ | 53·1 | 6·8 | 53·2 | 6·7 |
| (VIIa) † | 129—130 | $C_{39}H_{35}BS$ | 85·5 | 6·4 | 85·7 | 6·5 |
| (VIIc) | 118—122 | $C_{10}H_{13}ClO_4S$ | 45·6 | 4·9 | 45·4 | 5·0 |
| (X) | Oil | $C_{11}H_{19}O_7P$ | 45·1 | 6·7 | 44·9 | 6·5 |
| (XI) | Oil | $C_8H_{15}O_5P$ | 43·5 | 6·7 | 43·3 | 6·8 |

† Elemental analyses were carried out upon the corresponding tetraphenylborate. ‡ These compounds were hygroscopic.

perchlorate afforded (diethoxyphosphinylmethyl)methylphenyl- (Ia), (dimethoxyphosphinylmethyl)dimethyl- (Ib), and (diethoxyphosphinylmethyl)dimethyl- (Ic) sulphonium perchlorate, respectively, in quantitative yields. The oily sulphonium perchlorates were transformed into the corresponding tetraphenylborates by treating (Ia, b, and c) with sodium tetraphenylborate in acetone–water, and the resulting crystalline salts were submitted to elemental analyses.

*Methylphenylsulphonium Diethoxyphosphinylmethylide* (IIa).—To a suspension of the sulphonium salt (Ia) (750 mg, 2 mmol) in THF (20 ml), sodium hydride (96 mg, 2 mmol; 50% in mineral oil) was added with stirring at −20°. Evolution of hydrogen occurred. After stirring for 1 h at room temperature, the solvent was evaporated off under reduced pressure to give a viscous syrup. Dichloromethane (20 ml) was added to the residue and the resulting precipitated sodium perchlorate was filtered off through a Celite pad. The filtrate was evaporated and the residue washed three times with hexane (20 ml). Removal of the last trace of the solvent *in vacuo* gave crude (IIa) (570 mg) as a viscous oil, *m/e* 274 ($M^+$).

*Methylphenylsulphonium Diethoxyphosphinyl-(N-phenylcarbamoyl)methylide* (IIIa).—To a THF solution of the ylide (IIa) (2 mmol), phenyl isocyanate (240 mg, 2 mmol) in THF was added at room temperature and the mixture was stirred overnight. After evaporation of the solvent, the residue was purified by column chromatography (silica gel; chloroform) to give (IIIa) as *crystals*. Recrystallization from ethanol gave a pure sample of (IIIa) (570 mg, 72%), m.p. 89—90°. Similarly, (IIc) (2 mmol) generated *in situ* in THF was treated with phenyl isocyanate to give *dimethylsulphonium diethoxyphosphinyl-(N-phenylcarbamoyl)-methylide* (IIIc) (470 mg, 71%) as *crystals*, m.p. 99—100°.

*Dimethylsulphonium Dimethoxyphosphinyl-(N-phenylcarbamoyl)methylide* (IIIb).—To a solution of the sulphonium salt (Ib) (854 mg, 3 mmol) in DMSO (10 ml), a solution of methylsulphinylmethanide (3 mmol) in DMSO (10 ml) [12] was added slowly under cooling at 0—5°. After 1 h at the same temperature, phenyl isocyanate (360 mg, 3 mmol) in DMSO (5 ml) was added. The mixture was stirred overnight at room temperature. The usual work-up of the reaction mixture afforded an oil, which was purified by column chromatography (silica gel; chloroform) to yield the *ylide* (IIIb) as crystals. Recrystallization from ethyl acetate gave a pure sample of (IIIb) (480 mg, 53%), m.p. 119—120°.

*Betaine* (V).—The crude ylide (IIa) (600 mg) [prepared from (Ia) (750 mg, 2 mmol) and sodium hydride (2 mmol)] was chromatographed through a 30 cm column of silica gel (50 g) using 99% ethanol as an eluant. The eluted substance solidified on standing to crystals, and recrystallization of the crude product from acetone gave *ethyl [(methylphenylsulphonio)methyl]phosphonate* (V) (210 mg, 43%), *m/e* 246 ($M^+$), m.p. 148—149°.

*Reaction of the Ylide* (IIc) *with Acetyl Chloride or Acetic Anhydride.*—The ylide (IIc) (3 mmol) generated *in situ* in THF was treated with acetyl chloride (118 mg, 1·5 mmol) at room temperature. After standing overnight at room temperature, the mixture was poured into water (100 ml) and extracted with chloroform. Evaporation of the solvent followed by purification of the residual oil by chromatography [silica gel; 99% ethanol–ethyl acetate (1 : 1)] afforded

[12] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, **87**, 1345.

dimethylsulphonium acetyl(diethoxyphosphinyl)methylide (VIa) (300 mg, 79%) as a viscous oil. Similar treatment of (IIc) (3 mmol) with acetic anhydride (306 mg, 3 mmol) gave the same product (90 mg, 12%).

*Reaction of the Ylide* (IIc) *with Benzoyl Chloride or Benzoic Anhydride.*—In a similar manner as described above, the ylide (IIc) (3 mmol) was treated with benzoyl chloride (210 mg, 1·5 mmol) to give *dimethylsulphonium benzoyl(diethoxyphosphinyl)methylide* (VIb) (180 mg, 38%) as crystals, m.p. 98—99° (from ethyl acetate). Similar reaction of the ylide (IIc) (3 mmol) with benzoic anhydride (679 mg, 3 mmol) afforded the same ylide (VIb) (120 mg, 13%).

*Reaction of the Ylide* (IIa) *with Benzaldehyde.*—To a solution of (IIa) (2 mmol) in THF (20 ml), benzaldehyde (212 mg, 2 mmol) in THF (10 ml) was added at −20°. The mixture was stirred for 1 h at room temperature and evaporated under reduced pressure. Water (20 ml) was added to the residue and the mixture was extracted with ether in order to remove the organic substance. The aqueous layer was evaporatively dried *in vacuo* to give a viscous oil which was dissolved in hot dichloromethane (50 ml) and dried ($MgSO_4$). Removal of the solvent under reduced pressure afforded methylphenylstyrylsulphonium perchlorate (VIIa) (560 mg, 66%) as a viscous oil. The i.r. and n.m.r. spectra of (VIIa) were identical with those of the sulphonium salt prepared from phenyl *trans*-styryl sulphide [4] and methyl iodide in the presence of an equimolar amount of silver perchlorate. Treatment of an aqueous solution of (VIIa) with sodium tetraphenylborate produced the corresponding tetraphenylborate salt, m.p. 129—130° (from acetone).

*Reaction of the Ylide* (IIc) *and Benzaldehyde.*—In a similar way as described above, (IIc) (2 mmol) and benzaldehyde (2 mmol) gave dimethylstyrylsulphonium perchlorate (VIIc) (340 mg, 64%) as crystals, m.p. 118—122° (from ethanol). The sulphonium salt (VIIc) was a mixture of two geometrical isomers *cis* : *trans* ratio 33 : 67 (determined by n.m.r. spectrum).

*Reaction of the Sulphonium Salt* (VIIa) *with Active Methylene Compounds.*—To a solution of the ylide (IIa) (2 mmol) in THF (20 ml), a solution of benzaldehyde (212 mg, 2 mmol) in THF (5 ml) was added at −20°. After 30 min stirring at room temperature, diethyl malonate (320 mg, 2 mmol) in THF (5 ml) and then sodium hydride (2 mmol) were added slowly to the solution. The mixture was gradually warmed to room temperature and finally refluxed for 1 h. The mixture was poured in water and extracted with ether. The solvent was evaporated off and the residue was purified by column chromatography (silica gel; hexane–chloroform) to give diethyl 2-phenylcyclopropane-1,1-dicarboxylate (VIIIa) (310 mg, 59%) as a liquid, $\nu_{max.}$ (neat) 1720, 1600, 1580, 1495, 1270, 745, and 695 $cm^{-1}$, *m/e* 262 ($M^+$). The n.m.r. spectrum of the product was identical with that reported.[7a] Similar treatment of (VIIa) (3 mmol) with the carbanion derived from ethyl cyanoacetate (520 mg, 3 mmol) afforded ethyl 1-cyano-2-phenylcyclopropanecarboxylate (VIIIb) (610 mg, 63%) as a liquid, $\nu_{max.}$ (neat) 2220, 1730, 1600, 1500, 1260, 765, and 695 $cm^{-1}$, *m/e* 215 ($M^+$), δ ($CCl_4$) 1·36 (3H, t, *J* 7 Hz, $OCH_2CH_3$), 1·83—2·10 (2H, m, $J_{vic}$ 9, $J_{gem}$ 6 Hz, methylene), 3·00 (1H, t, $J_{vic}$ 9 Hz, CH), 4·20 (2H, q, *J* 7 Hz, $OCH_2CH_3$), and 7·10—7·40 (5H, m, Ph).[7b,c]

*Reaction of the Ylide* (IIc) *with Dimethyl Maleate or Dimethyl Fumarate.*—To a solution of the ylide (IIc) (3 mmol) in THF (30 ml), dimethyl maleate (432 mg, 3 mmol) in THF (5 ml) was added at room temperature. The mixture was stirred for 1 h at the same temperature and heated under reflux overnight. The solvent was evaporated off *in vacuo* at room temperature. Dichloromethane (50 ml) was added to the residue and the precipitate was filtered off. The filtrate was freed from the solvent and the residual oil was purified by column chromatography (silica gel; chloroform) to give *diethyl* (c-2,t-3-*bismethoxycarbonylcyclopropyl*)*phosphonate* (X) (180 mg, 20%) as a liquid. Similarly the reaction of (IIc) (3 mmol) with dimethyl fumarate (432 mg, 3 mmol) afforded the same product (X) (410 mg, 46%).

*Reaction of the Ylide* (IIb) *with Ethyl Acrylate.*—To a DMSO solution of the ylide (IIb) prepared from (Ib) (854 mg, 3 mmol) and sodium hydride (3 mmol) in DMSO (20 ml), ethyl acrylate (450 mg, 4·5 mmol) was added dropwise. After stirring overnight at room temperature, the mixture was poured into water (100 ml) and extracted with chloroform. The extract was washed with water and dried ($MgSO_4$). Evaporation of the solvent and purification of the product by column chromatography (silica gel; chloroform) gave *dimethyl* (2-*ethoxycarbonylcyclopropyl*)*phosphonate* (XI) (320 mg, 48%) as a liquid.

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