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REACTIONS OF P-YLIDES WITH SULPHENES

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Abstract— The reactions of stable P-ylides with sulphonyl chlorides in the presence of triethylamine have been investigated. P-Ylides bearing an α-hydrogen such as carbethoxymethylene- and benzoylmethylene-triphenylphosphoranes react with methanesulphonyl chloride to yield α-sulphonated P-ylides (A). On the other hand, if P-ylides having no α-hydrogen are used, episulphones (B) or their decomposition compounds, olefins (C), *and* (alkanesulphonyl)methylene P-ylides (the sulphene insertion compounds) (D), are obtained. The ratio of B and D is 4:1 in the reaction with fluorenylidenetriphenylphosphorane, but D is usually the principal product in the reaction with a series of α-carboalkoxy(or carbophenoxy)ethylidenetriphenylphosphoranes.

ALTHOUGH the successful isolation of sulphenes has not been achieved, their transitory existence has been indicated in many reactions in which both sulphonyl halides and tertiary amines are involved. For example, in reactions with electron-rich olefins such as enamines, ketene acetals, or ketene aminals, the formation of four-membered ring sulphones (thiethane dioxides) could be understood as a result of cycloadditions of sulphenes to these olefins.[1] Moreover, recently two research groups have independently obtained strong evidence for intermediate sulphenes in the base-catalysed solvolysis of sulphonyl chlorides, namely through the appearance of nearly one and only one atom H—D exchange at the α-position to the sulphonyl group during the reaction in deuterated media.[2]

An electrophilic attack of halocarbenes (generated *in situ*) on P-ylides leading to halo-ölefins has been described.[3a,b,c] We now wish to report the results on an analogous reaction between sulphonyl chlorides, which would act as sulphene sources in basic media, and stable P-ylides.

Treatment of stable P-ylides bearing an α-hydrogen such as carbethoxymethylene- and benzoylmethylene-triphenylphosphoranes with methanesulphonyl chloride and triethylamine afforded α-sulphonyl P-ylides in which the α-hydrogen had been replaced by methanesulphonyl group. This sulphonation is similar to α-acylation of stable P-ylides with acyl halides.[4] *A priori*, two reasonable reaction paths can explain this sulphonation: (1) an electrophilic addition of sulphene initially formed to the

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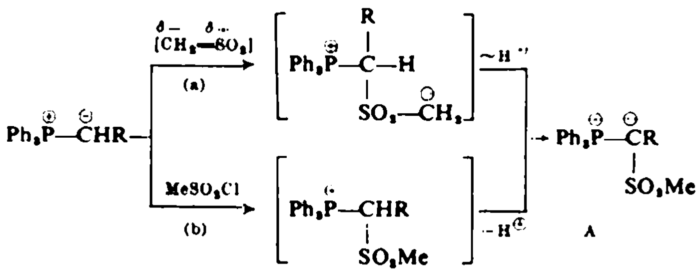
[1] R. H. Hasek and J. C. Martin, *J. Org. Chem.* **26**, 4775 (1961); G. Opitz, M. Klumann and F. Zimmerman, *Angew. Chem.* **74**, 32 (1962).

[2] J. F. King and T. Durst, *J. Am. Chem. Soc.* **86**, 287 (1964); **87**, 5684 (1965); W. E. Truce, R. W. Campbell and J. R. Norell, *ibid.* **86**, 288 (1964).

[3] Y. Ito, M. Okano and R. Oda, *a Tetrahedron Letters* 7 (1964); *b Bull. Inst. Chem. Research* Kyoto Univ. **42**, 217 (1964); *c Tetrahedron* **22**, 2615 (1966).

[4] H. J. Bestmann and B. Arnason, *Chem. Ber.* **95**, 1513 (1962).

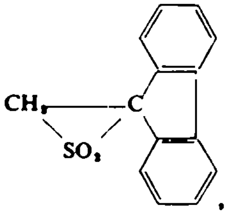
α-carbon of a P-ylide, followed by proton migration (probably through an intramolecular process) (path a), (2) an S_N2-like attack of a P-ylide on the sulphonyl chloride, followed by deprotonation (path b).



Under conditions where a considerable excess of triethylamine (3 ~ 10 fold excess) is used, deuterium incorporation in solvolysis (in D_2O) of methanesulphonyl chloride is somewhat low[2] (0·72 atom per molecule), as compared with that of phenylmethanesulphonyl and ethanesulphonyl chlorides (0·977 and 0·93 atoms per molecule, respectively). This seems to imply that in the case of methanesulphonyl chloride an S_N2 process accounts for approximately 25% of the solvolysis. This is probably due to the fact that no conjugation or hyperconjugation stabilization is expected in the sulphene derived from this sulphonyl chloride.

In the experiment using the benzoylmethylene ylide, it was also found that a variation in quantity of excess amine had little effect on the yield of the product. This might be related to the considerable basicity of the ylide[5] present in the reaction mixture. At any rate, a favourable contribution of path (a) beyond (b) in the present reaction would be reasonable in so far as the reaction conditions are kept sufficiently basic. Further, support is obtained from the reaction with carbethoxymethylene P-ylide in the absence of triethylamine forming only traces of the sulphonated product along with good recovery of the starting ylide. On this point, however, more conclusive evidence is desirable.

When P-ylides having no α-hydrogen were treated with sulphonyl chlorides in the



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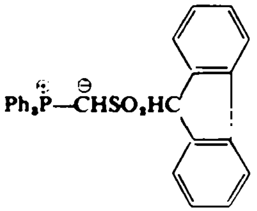

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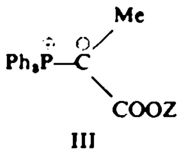
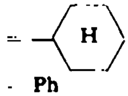


III

a: z = Et
b: z = $CH_2C_6H_5$
c: z = $CH_2CH_2C_6H_5$
d: z =



e: z = Ph

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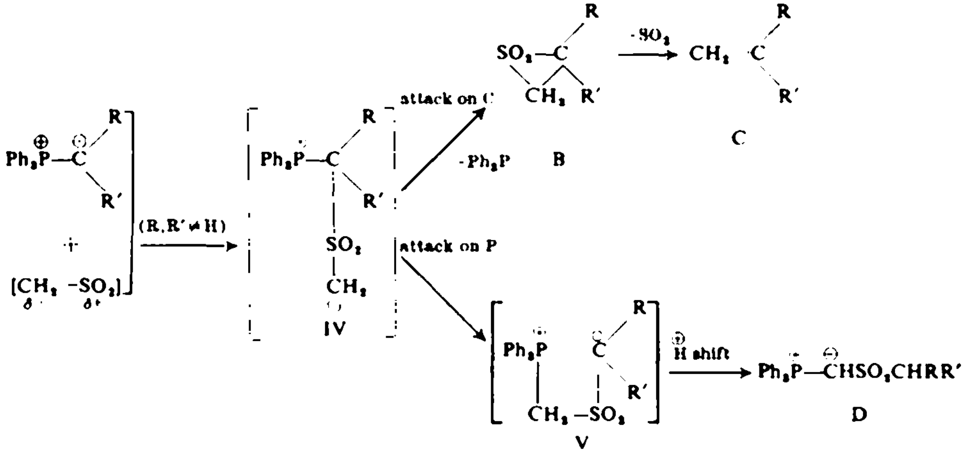
[5] The known p*K*b values of stable P-ylides having α-hydrogen are as follows: benzoylmethylenetriphenylphosphorane; 8·0; carbethoxymethylenetriphenylphosphorane; 4·8 [A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.* **85**, 2760 (1963)].

presence of 10 mole % excess of triethylamine, two products were generally obtained. Thus, fluorenylidenetriphenylphosphorane afforded the episulphone (thiirane dioxide) I and the sulphonylmethylene P-ylide II in 40 and 10% yields, respectively. On the other hand, in the reaction with a series of α-carboalkoxy(or carbophenoxy)-ethylidenetriphenylphosphoranes (III), the principal product was generally the corresponding sulphonylmethylene ylides of the type II and, though the direct isolation of the expected episulphone had failed, the methacrylate corresponding to its decomposition product could be obtained in a low yield on distillation after heating the reaction product. The thermal instability of the episulphones has been known as their general behaviour; the episulphone I, however, is found to be rather stable, that is, it gradually decomposes on heating above its m.p. (184°) with evolution of SO_2.

The episulphone formation apparently resembles dichloroölefin formation from stable P-ylides and dichlorocarbene, which is believed to proceed through a betaine intermediate.[3c] Another reaction product, the sulphonylmethylene ylides, corresponds to the 1:1 adducts in which the sulphene insertion into the P—C bond of the starting ylides has taken place, similar to the insertion of dimethyl acetylenedicarboxylate into stable P-ylides.[6] The essential process in these insertion reactions would involve the initial formation of an adduct and subsequent rearrangement involving the P—C bond cleavage and another P—C bond formation, and the latter step probably proceeds through a cyclic (four-membered) transition state as shown below.



An internal nucleophilic substitution of the initially formed betaine IV on the carbon atom, which is sandwiched in between two different electron-attracting groups, would proceed by an S_N2 mechanism to yield an episulphone (B), which sometimes collapses to an olefin (C). If this is true, in the transition state, R, R' and SO_2 groups should become coplaner with the carbon atom at which the internal substitution took place. If a P-ylide having an ester group is used as substrate, an examination of the molecular models indicates that a considerable suppression of free rotation of alkyl or aryl group of the ester function exists owing to the interference by any one of the phenyl groups on the phosphorus atom (see VI). Such a disadvantage may favour

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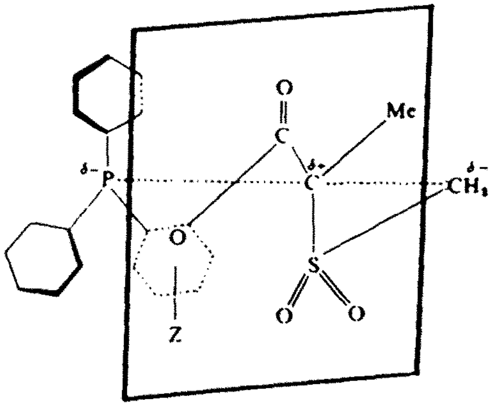
[6] J. B. Hendrickson, R. Rees and J. F. Templeton, *J. Am. Chem. Soc.* **86**, 107 (1964); G. W. Brown, R. C. Cookson and I. D. R. Stevens, *Tetrahedron Letters* 1263 (1964).

another intramolecular attack of the sulphonyl carbanion to the positive phosphorus atom leading to a sulphonylmethylene ylide (D) via a betaine V, because of the lack of appreciable steric interference of the substituents, R and R′ in IV, to this attack. The results obtained by using various P-ylides III, shown in Table 1, seem to be in accord with the above expectation. Yields of D from the ylides having a bulky ester group (e.g., IIId and IIIe) were somewhat high as compared with those for other ylides. Furthermore, the C:D ratio (in yields) for IIId was 0·07, while for IIIa 0·34.[7] A higher B:D ratio for fluorenylidene ylide would be noteworthy, and the predominant formation of I can be understood by considering that fluorenyl group is rather rigid and flat, though it has a broad structure.



Z = Alkyl or Aryl
VI

TABLE 1. REACTIONS OF P-YLIDES $(Ph)_3\overset{\ominus}{P}-\overset{\circ}{C}RR'$ WITH SULPHENES $R''CH=SO_2$[a]

Run No.	Ylide R	Ylide R′	Sulphene R″	Product (yield %) A	B	C	D	B or C:D
1	H	COPh	H	35				
2	H	COPh	H	39[b]				
3	H	COOEt	H	59				
4	$C_{13}H_8$[c]		H		40		10	4
5	Me	COOEt	H			19	56	0·34
6	Me	COOEt	Ph			15	41	0·37
7	Me	$COOCH_2Ph$	H			trace	60	
8	Me	$COOCH_2CH_2Ph$	H			trace	65	
9	Me	$COOC_6H_{11}$[d]	H			6	86	0·07
10	Me	COOPh	H			trace	72	
11	Ph	COOEt	H			Unreacted		

[a] Ten mole % excess (i.e., 1·1 equiv) of Et_3N were used unless otherwise indicated.
[b] Five equiv of Et_3N were used.
[c] $C_{13}H_8$: Fluorenylidene group.
[d] C_6H_{11}: Cyclohexyl group.

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[7] Even if a large loss in decomposition of B to C is assumed, the ratio would not exceed over 1 because yields of D are generally over 50%.

An attempted reaction of sulphene with carbethoxybenzylidenetriphenylphosphorane did not take place (Run No. 11 in Table 1). This lack of reactivity would not be due to the electronic effect of the phenyl group, since no significant difference in the yield of dichloroölefins from the reaction of ethylidene- (45%) and benzylidenetriphenylphosphorane (38%) with dichlorocarbene has been observed.[3b] Therefore, it may be attributable to the steric crowding in the transition state.

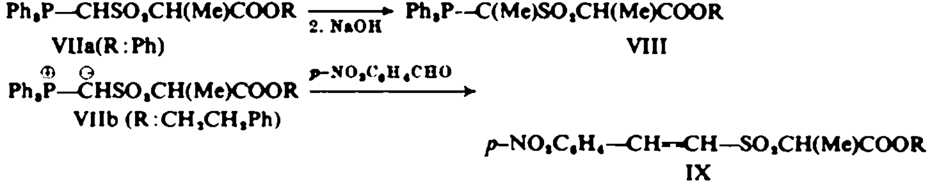
The reaction between IIIa and benzylsulphene derived from *β*-phenylethanesulphonyl chloride gave *trans*-*β*-benzylmethacrylate with a trace of the *cis*-isomer. This result evidently shows a selective formation of the *trans*-episulphone, because the stereospecific feature in decomposition of an episulphone has recently been established.[8] This stereochemical feature may be understood by supposing the base-catalysed *cis–trans* isomerization of the intermediate episulphone and/or by considering a preferred conformation of the betaine IV.

TABLE 2. α-SULPHONYL P-YLIDES $(Ph)_3\overset{\oplus}{P}-\overset{\ominus}{C}(R)SO_2R'$

Sulphonyl P-ylide			Analysis							
			Found				Requires			
R	R′	M.p.	C	H	S	P	C	H	S	P
COPh	Me	193–194°	70·60	5·21	—	7·25	70·73	5·06	—	6·77
COOEt	Me	175–177°	65·57	5·69	—	7·61	64·78	5·44	—	7·28
H	$C_{13}H_9$[a]	208–210°	76·63	5·04	6·56	—	76·17	4·99	6·35	—
H	CH(Me)COOEt	129–130°	65·71	5·95	7·55	—	65·44	5·72	7·28	—
CH_2Ph	CH(Me)COOEt	65–68°[c]	69·79	6·28	6·25	—	70·03	6·07	6·03	—
H	$CH(Me)COOCH_2Ph$	60–62°[c]	69·04	5·10	6·30	—	69·32	5·38	6·37	—
H	$CH(Me)COOCH_2CH_2Ph$	154–155°	70·24	5·83	6·90	—	69·76	5·66	6·20	—
H	$CH(Me)COOC_6H_{11}$[b]	154–155°	68·72	6·34	6·67	—	68·00	6·32	6·48	—
H	CH(Me)COOPh	153°	68·87	5·12	6·74	—	68·85	5·29	6·56	—

[a] $C_{13}H_9$: Fluorenyl group.
[b] C_6H_{11}: Cyclohexyl group.
[c] Though these values seemed to be lower than the expected values (may be due to unavoidable contamination with the starting ylides), they did not rise even after repeated recrystallisations.

Finally, some properties of the sulphonylmethylene ylides concerning their structural confirmation are given below. Hydrogen chloride added reversibly to a 1:1 adduct obtained from sulphene and IIIe. Treatment of this adduct with methyl bromide, followed by dehydrobromination afforded the methylated product. Furthermore, the adduct derived from IIIc reacted with *p*-nitrobenzaldehyde to give a vinyl sulphone derivative having characteristic IR absorption bands of ester (1732 cm^{-1}), conjugated C=C (1620 cm^{-1}), and SO_2 (1300 and 1130 cm^{-1}). All these transformations confirm that these 1:1 adducts should have the sulphonylmethylene P-ylide structure (see VIIa and VIIb).



$$Ph_3\overset{\oplus}{P}-\overset{\ominus}{C}HSO_2CH(Me)COOR \xrightarrow[2.\ NaOH]{1.\ MeBr} Ph_3\overset{\oplus}{P}-\overset{\ominus}{C}(Me)SO_2CH(Me)COOR$$

VIIa(R : Ph) VIII

$$Ph_3\overset{\oplus}{P}-\overset{\ominus}{C}HSO_2CH(Me)COOR \xrightarrow{p\text{-}NO_2C_6H_4CHO} p\text{-}NO_2C_6H_4-CH=CH-SO_2CH(Me)COOR$$

VIIb (R : CH_2CH_2Ph) IX

Further evidence for the proposed structure was obtained by NMR spectroscopy. The NMR spectrum of VIIa in $CDCl_3$ shows 4 types of protons in the ratio 20:1:1:3

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[8] N. Tokura, T. Nagai and S. Matsumura, *J. Org. Chem.* 31, 349 (1966).

with the peaks at τ 2·42, 6·31 ($J = 7$ c/s, quartet), 7·10 and 8·60 ($J = 7$ c/s, doublet), respectively. Here, a group of closely packed signals at the lowest field can be assigned to the aromatic protons. Addition of D_2O resulted in disappearance of the middle two peaks and in becoming the peak at τ 8·60 due to C—Me (singlet). This clearly implies the presence of two methinyl protons, i.e., $SO_2—\overset{|}{C}H—COO$ and $P—\overset{|}{C}H—SO_2$. The NMR spectrum of VIII has characteristic doublet at τ 8·19 ($J_{PH} = 13$ c/s) which would be ascribed to P—C—Me. Similar couplings between phosphorus atom and Me group are known.[9]

EXPERIMENTAL

All temps were uncorrected.

The starting P-ylides were prepared by the usual method.[10] Analytical data for new α-carboalkoxyethylidene ylides (III) are shown below. The m.p. of other ylides were in good agreement with those in literatures.

		Analysis			
		Found		Requires	
Z in III	M.p.	C	H	C	H
CH_2Ph	105–106°	79·51	6·13	79·23	5·94
CH_2CH_2Ph	130–132°	79·38	6·26	79·43	6·21
cyclo—C_6H_{11}	133·5–134·5°	77·69	7·03	77·86	7·02

Several illustrative examples of the reactions are given below.

(a) *Reaction of benzoylmethylenetriphenylphosphorane with methanesulphonyl chloride.* To a stirred soln of benzoylmethylenetriphenylphosphorane (13 g, 0·0342 mole) and Et_3N (3·79 g, 0·0375 mole) in dry dioxan (250 ml), methane-sulphonyl chloride (3·92 g, 0·0342 mole) was added dropwise at 15°. After completion of addition, stirring was continued for 5 hrs, and then the mixture was allowed to stand overnight. The reaction mixture was concentrated to ca. one-half of its volume, and diluted with a large excess of ice water. The ppt was collected, washed with water, and dried. It was recrystallized from EtOH to give pure benzoyl(methanesulphonyl)methylenetriphenylphosphorane, m.p. 193–194°, yield 35% (5·5 g). The IR spectrum of this compound showed characteristic bands at 1545 (CO), 1290 and 1120 cm^{-1} (SO_2).

(b) *Reaction of fluorenylidenetriphenylphosphorane with methanesulphonyl chloride.* A mixture of fluorenylidenetriphenylphosphorane (7 g, 0·0164 mole) and Et_3N (3·64 g, 0·0360 mole) in dry dioxan (250 ml) was stirred vigorously at 15° and to this soln methanesulphonyl chloride (3·72 g, 0·0328 mole) was added slowly. After stirring had been continued for 5 hrs, the mixture was allowed to stand overnight. The yellow colour of the starting ylide faded almost completely. After the separation of Et_3NHCl, the filtrate was evaporated *in vacuo* to dryness. The resulting solid was collected by filtration, washed with a small amount of cold EtOH, and treated with hot AcOEt. The solid insoluble in AcOEt was dissolved in hot EtOH and the soln made alkaline with NH_4OHaq. The ppt was recrystallized from EtOH to give II, m.p. 208–210°, in 10% (0·8 g) yield. The IR spectrum of II showed characteristic SO_2 absorptions at 1260 and 1080 cm^{-1}. On the other hand, evaporation of the solvent from the AcOEt extract afforded crude I. Recrystallization from AcOEt gave the pure episulphone, m.p. 183·5–184·5°, in 40% (1·6 g) yield. (Found: C, 69·19; H, 4·63; S, 13·31. $C_{14}H_{10}SO_2$ requires: C, 69·40; H, 4·16; S, 13·22%.) This compound had characteristic bands at 1305 and 1110 cm^{-1}, probably due to SO_2 function. The NMR spectrum (in $CDCl_3$) of I showed signals at τ 2·25 (m, 8H aromatic protons), 10·50 (s, 2H methylene protons).

(c) *Reaction of α-carbethoxyethylidenetriphenylphosphorane with β-phenylethanesulphonyl chloride.* β-Phenylethanesulphonyl chloride (6·13 g, 0·03 mole) was added dropwise into a stirred mixture of

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[9] For example, C. E. Griffin and T. D. Mitchell, *J. Org. Chem.* **30**, 2829 (1965).

[10] O. Isler, H. Gutman, M. Montavan, R. Puezy, G. Reysen, and P. Zeller, *Helv. Chim. Acta* **40**, 1242 (1957).

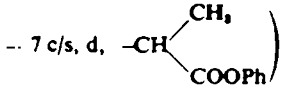
α-carbethoxyethylidenetriphenylphosphorane (10·9 g, 0·03 mole) and Et_3N(3·33 g, 0·033 mole) in dry dioxan (150 ml). The reaction temp was maintained at 15°. Stirring was continued for an additional 5 hrs, and the reaction mixture was allowed to stand overnight. After the ppt of Et_3NHCl had been removed, the filtrate was concentrated *in vacuo*. One half of its concentrate was diluted with aq. dioxan containing HCl, and then treated with NaOHaq. The crude ppt was filtered and washed with water. This was dissolved in HClaq and treatment with NaOHaq afforded a 41% yield of pure α-(α′-carbethoxyethanesulphonyl)-β-phenethylidenetriphenylphosphorane, m.p. 65–68°. Another half of the concentrate was decomposed at 140° for 3 hr under N_2 into a viscous liquid having an ester-like odour with evolution of SO_2 gas. This liquid was extracted with Chf-pet. ether (1:5), and distilled *in vacuo* to give a 15% yield of ethyl *trans*-β-benzylmethacrylate, b.p. 125°/5 mm. The identification of this compound and determination of its purity were carried out by GLC analysis. Authentic material (Found: C, 76·39; H, 8·11. $C_{13}H_{16}O_2$ requires: C, 76·44; H, 7·90%) was prepared by the Wittig reaction of α-carbethoxyethylidenetriphenylphosphorane with phenylacetaldehyde.

(d) *Reaction of α-(1)carbocyclohexyloxy(1)ethylidenetriphenylphosphorane with methanesulphonyl chloride.* According to the same procedure, a soln of α-(1)carbocyclohexyloxy-(1)ethylidenetriphenylphosphorane (8·32 g, 0·02 mole) and Et_3N (3·33 g, 0·033 mole) in dioxan was treated with methanesulphonyl chloride (3·44 g, 0·03 mole). The ppt was collected, washed with water to remove Et_3NHCl. Recrystallization from pet. ether–AcOEt gave pure α-(carbocyclohexyloxy)ethanesulphonylmethylenetriphenylphosphorane, m.p. 154–155° in 86% (8·5 g) yield. The filtrate was evaporated *in vacuo* by heating in a stream of N_2 at 100° for 1 hr, and then distilled *in vacuo* to give a 6% yield of cyclohexyl methacrylate. The characterisation and estimation of yield were carried out by GLC analysis. An authentic sample was prepared by ester exchange reaction of ethyl methacrylate with cyclohexanol.

Some physical and chemical properties of the two representative sulphonylmethylene P-ylides are summarized below.

IR and NMR spectra. Compound VIIa had characteristic bands at 1730 (ester), 1280 and 1095 cm^{-1} (SO_2). The NMR spectrum (in $CDCl_3$) showed signals at τ 2·42 (m, aromatic protons), 6·31 (J → 7 c/s, qu, $SO_2{-}\overset{|}{C}H{-}COOPh$), 7·10 (s, $P{-}\overset{|}{C}H$) and 8·60 (J = 7 c/s, d, $-\overset{|}{C}H{-}CH_3$). Their relative intensities were 20, 1·1, and 3, respectively. After addition of D_2O, two peaks at τ 6·31 and 7·10 disappeared and the signal at τ 8·60 appeared as a singlet instead of a doublet.

Reactions with HCl *or methyl bromide.* When an alcoholic soln of the ylide VIIa was treated with dry HCl gas, the corresponding phosphonium chloride separated in good yield. (Found: C, 63·79; H, 5·36; S, 6·01; Cl, 7·41. $C_{28}H_{26}O_4SPCl$ requires: C, 64·06; H, 4·99; S, 6·11; Cl, 6·75%.) Neutralization with NaOH precipitated the original ylide VIIa.

An analogous reaction with excess MeBr was carried out in a sealed tube. An aq. soln of the product was made alkaline with NaOH, and the solid which separated was collected, washed with water and dried. Recrystallization from pet. ether–AcOEt gave pure VIII, m.p. 150–151°. (Found: C, 69·23; H, 5·65. $C_{29}H_{27}O_4PS$ requires: C, 69·32; H, 5·38%.) The IR spectrum of VIII was almost the same (1730, 1270 and 1100 cm^{-1}) as that of VIIa. The NMR spectrum of VIII (in $CDCl_3$) showed the peaks at τ 2·42 (m, aromatic protons), 6·31 (J = 7 c/s, qu, $-SO_2{-}\overset{|}{C}H{-}COOPh$), 8·19 ($J_{PH}$ = 13 c/s, d, $P{-}\overset{|}{C}{-}CH_3$), and 8·60 (J = 7 c/s, d,  $-CH(CH_3)(COOPh)$).

The Wittig reaction with p-*nitrobenzaldehyde.* Compound VIIb (1·7 g, 0·0033 mole) and *p*-nitrobenzaldehyde (0·5 g, 0·0033 mole) were dissolved in chf (50 ml) and the reaction mixture was allowed to stand at room temp for 3 days. The soln was concentrated *in vacuo*, and a benzene soln of the residue was successively washed with 5% HBraq, 5% NaOHaq, $NaHSO_3$ aq, and water. Evaporation of the solvent gave a liquid which solidified on standing. Pure IX, m.p. 92–93°, was obtained in 76% yield after a recrystallization from EtOH—heptane. (Found: C, 58·88; H, 4·99; N, 3·40. $C_{19}H_{19}NSO_6$ requires: C, 58·61; H, 4·92; N, 3·60%.) IX had characteristic bands at 1720 (ester), 1620 (conj. C=C) 1300 and 1130 cm^{-1} (SO_2).

Acknowledgement—The authors are indebted to Dr. T. Singu, Faculty of Pharmacy of this University for determining NMR spectra.