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SULPHONIUM AND OXOSULPHONIUM CARBALKOXYMETHYLIDES

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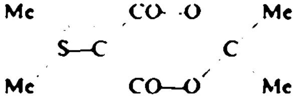
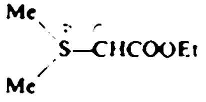
Abstract– Sulphur-ylides with carbalkoxy substituent on the ylide carbon have been prepared and identified. They are classified into monoester type (IV, X), β-keto ester type (V, XII), malonamide ester type (VI, XIII), malonic diester type (XIV, XV) and lactone type (VIII). The structure of each class of compounds is discussed on the basis of IR and NMR spectra and large contribution of the betaine formula (A) is concluded. Reactions of less stable monoester type ylides IVa and X with *trans*-1,2-dibenzoylethylene resulted in formation of a cyclopropane XVIa and a cyclic sulphoxide XVII, respectively.

Previous publications have been concerned with sulphonium ylides substituted with a benzoyl group at the ylide carbon.[1] Sulphur-ylides I[2] and II,[3] both stabilized by carbalkoxy group(s), are known, but interest in the structure and reactivity of this kind of compounds as compared with those of phosphorus-ylides[4] have motivated the present research, which comprises preparation and characterization of 15 novel ylides as well as examination of reactions.



I



II

Preparation of ylides. Treatment of sulphonium fluoroborates IIIa and IIIb with triethylamine yielded sulphonium carbethoxymethylides IVa and IVb. These oily ylides were stable below 0° but slowly decomposed at room temp into a mixture of diethyl maleate, fumarate and the respective sulphide.

Acylation of the ylides with either acid chlorides or anhydrides gave the corresponding C-acylated products Va–Vd each as a stable solid. No O-acylated product was obtained upon treatment with acid chlorides.[5] Carbamoylation with phenyl isocyanate yielded another type of crystalline stable ylides VIa and VIb.

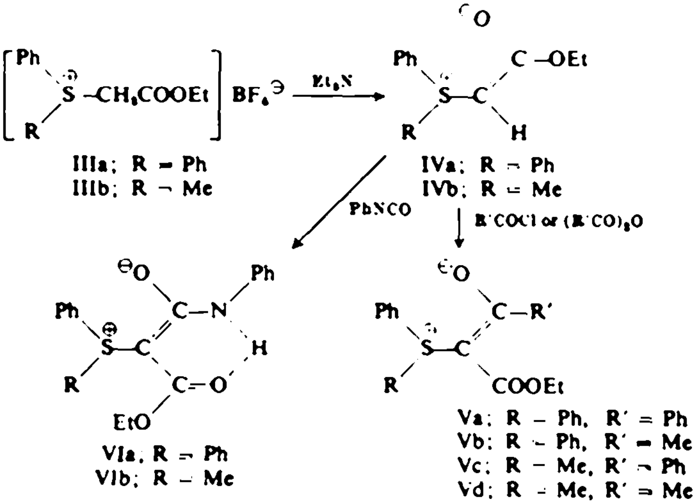
[1a] H. Nozaki, K. Kondo and M. Takaku, *Tetrahedron Letters* 251 (1965); [b] H. Nozaki, M. Takaku and K. Kondo, *Tetrahedron* **22**, 2145 (1966); See also [c] A. W. Johnson and R. T. Amel, *Tetrahedron Letters* 819 (1966); [d] B. M. Trost, *J. Amer. Chem. Soc.* **88**, 1587 (1966).

[2] A. Hochrainer and F. Wessely, *Tetrahedron Letters* 721 (1965).

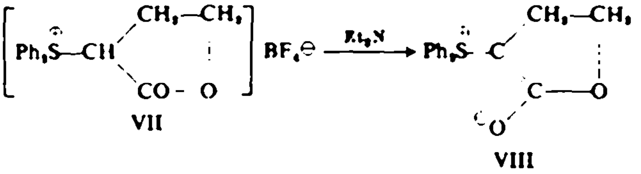
[3a] A. J. Speziale, C. C. Tung, K. W. Ratts and A. Yao, *J. Amer. Chem. Soc.* **87**, 3460 (1965); [b] K. W. Ratts and A. N. Yao, *J. Org. Chem.* **31**, 1185 (1966).

[4a] O. Isler, H. Gutmann, M. Montavon, Rüegg, G. Ryser and P. Zeller, *Helv. Chim. Acta* **40**, 1242 (1957); See also [b] A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.* **87**, 5603 (1965).

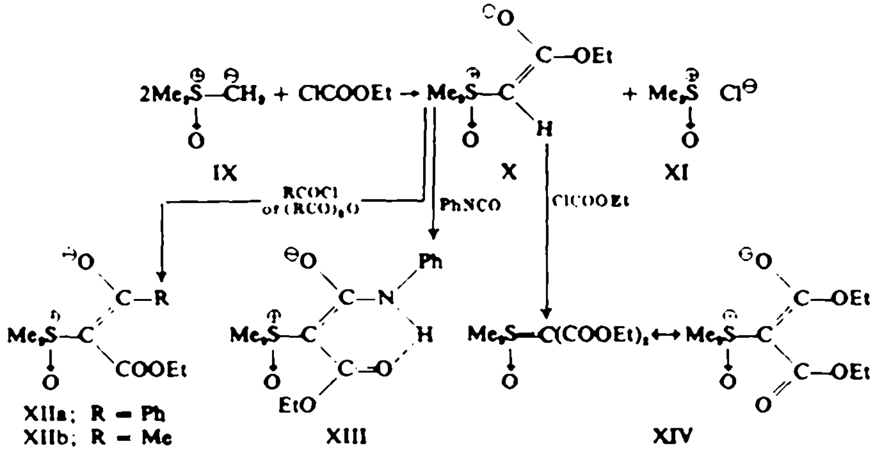
[5] Acylation of sulphonium acylmethylide with acid chloride results in exclusive formation of O-acylated products, see Ref. 1. For similar behaviour of phosphorus-ylide, see P. A. Chopard R. J. G. Searle and F. H. Devitt, *J. Org. Chem.* **30**, 1015 (1965).



A lactone sulphonium fluoroborate VII was obtained from α-bromo-γ-butyrolactone and diphenyl sulphide. Treatment with triethylamine yielded a lactone type sulphonium ylide VIII as a solid. This represents the first example of isolating a crystalline sulphur-ylide stabilized by a single carbalkoxy group.



Acylation of dimethyloxosulsulphonium methylide IX has been described.[*] Reaction with ethyl chloroformate has now been found to yield a metastable ylide X



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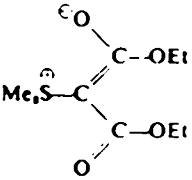
[*] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.* 86, 1640 (1964).

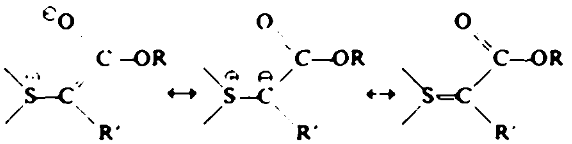
of another monoester type. Attempted purification of X failed, but treatment of its tetrahydrofuran solution with acid chlorides or acid anhydrides afforded C-acylated ylides XIIa and XIIb in low yields. The action of phenyl isocyanate yielded carbamoylated ylideXIII,[7] while further reaction with ethyl chloroformate produced a malonic diester type ylide XIV.

Sulphonium ylide XV of another malonic diester type was obtained by the action of ethyl chloroformate on dimethylsulphonium methylide[8] in dimethyl sulphoxide solution. No monoester type sulphonium ylide, which corresponds to the ylide X has been isolated.

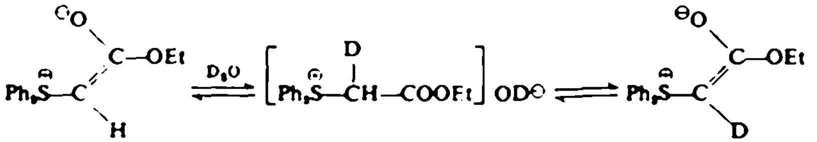

XV

Yields and properties of these 15 novel sulphur-ylides are presented in Table 1.

Structural problems. Based on the IR and NMR data listed in Table 1 several points of structural interest are discussed. The monoester type ylides (IVa, IVb, X) showed the "ylide-carbonyl" absorptions[1] shifted to a lower wave number region (ca. 100–110 cm^{-1}) as compared with that of the respective sulphonium salts (IIIa, IIIb, VII).[9] As pointed out previously,[1] this is ascribed to the contribution of the betaine formula (A) in the resonance stabilization of the carbalkoxymethylides.


A B C

A shift of the same magnitude was observed with the lactone type ylide VIII. This supports the suggestion that the open chain ylides IVa, IVb and X also have the *cis* configuration of the hetero atoms around the C=C bond as indicated in the formula A. The methine signal of the ylide IVa at τ 6·53 immediately disappears upon addition of deuterium oxide, thus indicating facile exchange with deuterium as shown below.



Ylides of β-keto ester type (V and XII) show two peaks at 1680–1660 cm^{-1} and at 1580–1550 cm^{-1}, respectively. As the carbonyl absorption of enols of β-keto esters

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[7] For similar carbamoylation to oxosulphonium ylides, see [a] H. König and H. Metzger, *Chem. Ber.* 98, 3733 (1965); [b] C. Kaiser, B. M. Trost, J. Beeson and J. Weinstock, *J. Org. Chem.* 30, 3972 (1965).

[8] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.* 87, 1353 (1965).

[9] Carbonyl absorption (Nujol) of the salts IIIa and IIIb was observed at 1740 cm^{-1} and the one of VII at 1770 cm^{-1}.

TABLE 1. NOVEL SULPHONIUM AND OXOSULPHONIUM CARBALKOXYMETHYLIDES[a]

Ylide	M.p.	Yield[b] (%)	IR (cm^{-1}) KBr CHCl$_3$	UV λ_{max}^{EtOH} mμ (log ϵ)	Formula	Analyses (%) Found C	H	Calc. C	H
				Monoester type ylides					
IVa	oil	95	1640[c]	279 (3·80)	$C_{16}H_{16}O_2S$	70·3	6·1	70·6	5·9
IVb	oil	47	1630[c]	264 (3·78)	$C_{11}H_{14}O_2S$	61·3[d]	7·2[d]	62·8	6·7
VIII	117°[d]	30	1670 1635	294 (3·69)	$C_{16}H_{14}O_2S$	70·8	5·3	71·1	5·2
X	unstable	70	1625[e]	—					
				β-Keto ester type ylides					
Va	152–153°	58	1675 1670 1565 1556	268 (4·02) 275 (4·02)	$C_{23}H_{20}O_3S$	73·7	5·4	73·4	5·4
Vb	96–97°	44	1660 1655 1580 1578	235 (4·33)	$C_{18}H_{18}O_3S$	68·9	5·9	68·8	5·8
Vc	91–92°	46	1655 1645 1560 1555	274 (4·09)	$C_{18}H_{18}O_3S$	68·9	5·8	68·8	5·8
Vd	60–61°	41	1660 1665 1585 1575	223 (4·29) 247 (4·13)	$C_{13}H_{16}O_3S$	61·6	6·6	61·9	6·4
XIIa	134–135°	2	1660 1640 1570 1570	274 (3·82)	$C_{13}H_{16}O_4S$	58·0	6·2	58·2	6·0
XIIb	oil	15	1665[c] 1590	247 (4·08)	$C_8H_{14}O_4S$	46·3	7·1	46·6	6·8
				Malonamide ester type ylides					
VIa′	141–142°	80	1640 1645 1535 1538	227 (4·45) 264 (4·44)	$C_{23}H_{21}NO_3S$	70·8	5·6	70·6	5·4
VIb	135–136°	24	1645 1640 1540 1540	265 (4·48)	$C_{18}H_{19}NO_3S$	65·3	5·8	65·6	5·8
XIII[g]	123–124°	66	1630 1655 1530 1540	230 (4·25) 260 (4·43)	$C_{13}H_{17}NO_4S$	55·4	6·3	55·1	6·1
				Malonic diester type ylides					
XIV	111–112°	27	1710 1635	225 (4·49)	$C_9H_{16}O_5S$	45·8	7·0	45·8	6·8
XV	135–137°	24	1655 1670 1625 1615	232 (4·18)	$C_9H_{16}O_4S$	49·3	7·4	49·1	7·3

[a] Eminent signals in NMR are as follows (τ value, wt., multiplicity and assignment), the multiplicity being shown in abbreviated form, thus s for singlet, m for multiplet and t for triplet.

IVa 6·53, 1H, s, methine

Vb 7·50, 3H, s, acetyl Me

VIa −0·10, 1H, m, amide N—H

VIb −0·90, 1H, m, amide N—H 6·67, 3H, s, S-methyl

VIII 7·36, 2H, t, β-methylene in the lactone ring 5·17, 2H, t, γ-methylene in the lactone ring (J 8·0 c/s)

XIII −0·34, 1H, m, amide N—H; 6·31, 6H, s, S-methyl

XIV 6·28, 6H, s, S-methyl

XV 7·12, 6H, s, S-methyl

[b] Yields of monoester type ylides are based on their corresponding sulphonium salts, those of other sulphonium ylides on their parent ylides IV and that of oxosulphonium ylides on metastable IX.

[c] Measured on liquid film.

[d] Those dissatisfactory data are attributed to partial decomposition at room temp.

[e] Measured in THF solution.

[f] The cryoscopic mol. wt. found in PhH was 366 (Calc. 391).

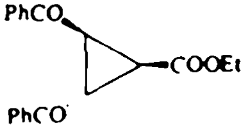
[g] The cryoscopic mol. wt. found in PhH was 264 (Calc. 283).

have been observed at ca. 1650 cm^{-1},[10] the higher wave number absorption is ascribed to the ester carbonyl, which is presumably outside the betaine ylide resonance. The "ylide-carbonyl" absorption at 1580–1550 cm^{-1} should, therefore, originate from the keto group which stabilizes the ylide system by a large contribution of the betaine structure as shown in the formulae.

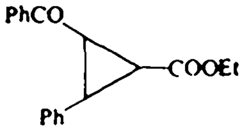
Ylides of malonamide ester type (VI and XIII) all exhibit the NMR signal of a hydrogen-bonded N—H proton. The chemical shift of this proton remains unchanged upon dilution and the ylides were found to be monomeric in benzene by mol. wt determination. The ester carbonyl was observed at 1640–1630 cm^{-1}, *viz.*, in a slightly lower wave number region as compared with that of the β-keto ester type ylides Va–d or XIIa,b. The shift should be ascribed to the hydrogen bond as indicated in the formulae given above. The carbamoyl group, to which the "ylide-carbonyl" band at 1530 cm^{-1} is ascribed, apparently acts as the ylide-stabilizing substituent.

Finally, the stable oxosulphonium ylides of malonic diester type (XIV) show carbonyl absorption in a higher wave number region (1710 cm^{-1}) in the solid state, which in this case, might imply a large contribution of the ylene structure. The spectrum of XIV in solution as well as that of XV both in the solid state and in solution is devoid of the anomalous blue shift and shows the presence of a regular "ylide-carbonyl".

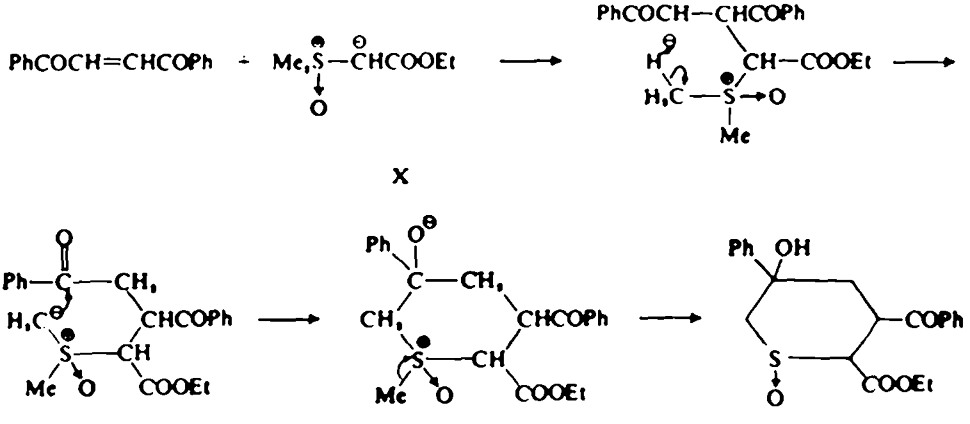
Reaction of ylides with α,β-unsaturated carbonyl compounds. Attempted condensation of these carbalkoxymethylides with benzaldehyde[11] did not proceed under the



XVIa



XVIb



X

XVII

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[10] L. J. Bellamy, *The Infrared Spectra of Complex Molecules* p. 184. Wiley, New York (1958).

[11] Interaction of unstable sulphur-ylide with carbonyl compounds forms epoxides in good yield. [a] E. J. Corey and W. Oppolzer, *J. Amer. Chem. Soc.* **86**, 1899 (1964); [b] A. W. Johnson, V. J. Hruby and J. L. Williams, *Ibid.* **86**, 918 (1964).

conditions examined. The Michael condensation of ylide IVa with *trans*- and *cis*-1,2-dibenzoylethylene, respectively, gave the same cyclopropane derivative XVIa[16] and the reaction of IVa with chalcone yielded another cyclopropane derivative XVIb in low yield. The stereochemistry of XVIb is not known yet. The reaction of dimethyloxosulphonium carbethoxymethylide X with *trans*-1,2-dibenzoylethylene yielded a cyclic sulphoxide XVII, instead of the cyclopropane derivative XVIa. This structure was tentatively assigned on the basis of elemental analyses, IR spectrum and an analogous reaction of oxosulphonium methylide.[18] No reaction was observed between X and chalcone. Other sulphur-ylides stabilized by two carbonyl groups attached to the ylide carbon failed to react with the α,β-unsaturated compounds.

EXPERIMENTAL

All temps are uncorrected. Microanalyses were performed at the Elemental Analyses Centre of Kyôto University. NMR spectra: 60 Mc machines in $CDCl_3$ sol with TMS as an internal reference. Physical properties, analyses and yields of novel S-ylides as in Table 1 were not repeated.

Sulphonium salts. According to the reported method,[19] *(carbethoxymethyl)diphenylsulphonium fluoroborate* (IIIa) and *diphenyl(2-oxotetrahydro-3-furyl)sulphonium fluoroborate* (VII) were obtained from diphenyl sulphide and ethyl bromoacetate or α-bromo-γ-butyrolactone, respectively. The analytically pure samples were recrystallized 3 times from EtOH. Similar treatment of ethyl phenylmercaptoacetate with silver fluoroborate in excess MeI and repeated recrystallizations of the resulting syrup from EtOH below −10° afforded pure *(carbethoxymethyl)methylphenylsulphonium fluoroborate* (IIIb). Yields, m.p. and analyses of these salts are given in Table 2.

TABLE 2. NOVEL SULPHONIUM FLUOROBORATES

Sulphonium fluoroborate	Yield (%)	M.p.	Formula	Analyses (%) Found C	H	Calc. C	H
IIIa	67	115°	$C_{16}H_{17}BF_4O_2S$	53·5	4·7	53·4	4·7
IIIb	60	oil*	$C_{11}H_{15}BF_4O_2S$	44·1	5·2	44·3	5·1
VII	28	150°	$C_{16}H_{15}BF_4O_2S$	53·6	4·4	53·7	4·2

Diphenylsulphonium carbethoxymethylide (IVa). Triethylamine (0·81 g) in EtOH (50 ml) was gradually added to a suspension of finely pulverized IIIa (1·46 g) in EtOH (250 ml) under stirring and cooling at 0°. After additional stirring for 1 hr at the same temp, the reaction mixture was diluted with H_2O (700 ml) and extracted with chf. Evaporation of the solvent *in vacuo* afforded a viscous oil (1·09 g), which solidified at −25°. Recrystallization of the product from ether-hexane at −80° gave an analytically pure sample of IVa, which was stable for a week at −10° but decomposed gradually at room temp to give a syrup. The decomposition occurred rapidly in the evaporation chamber of GLC apparatus at 200° to afford diphenyl sulphide and an equimolar mixture of diethyl fumarate and maleate.

Methylphenylsulphonium carbethoxymethylide IVb. Similar treatment of IIIb (0·55 g) with Et_3N and purification of the product at −80° yielded pure IVb (0·18 g) as a heavy viscous oil, which was also stable at −10° and decomposed at room temp.

Diphenylsulphonium 2-oxotetrahydrofuran-3-ylide (VIII). The crude syrup (0·47 g) obtained by a similar treatment of VII (0·58 g) with Et_3N was chromatographed (silica gel-Celite (3:7) column, chf). Recrystallization of the recovered syrup (0·32 g) from chf-Et_2O at −80° gave crystalline VIII (0·13 g).

Sulphonium acylcarbethoxymethylides (V). Acetyl chloride, Ac_2O or BzCl (5 mmoles each) in THF (100 ml) was added to a sol of crude IV (5 mmoles) dissolved in THF (100 ml) under stirring at room temp. The reaction mixture was concentrated to ca. 20 ml under red. press. diluted with H_2O and extracted with chf. Evaporation of the solvent afforded a pale yellow oil, which crystallized slowly on treatment with hexane at −10°. Recrystallization of the products from hexane–benzene gave analytically pure samples, yields, m.p. and other data are given in Table 1.

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[18] A. G. Hortmann, *J. Amer. Chem. Soc.* **87**, 4972 (1965).

[19] V. Franzen, H. Schmidt and C. Mertz, *Chem. Ber.* **94**, 2942 (1961).

Sulphonium carbethoxy(N-phenylcarbonyl)methylide (VI). A solution of IV (3 mmoles) in THF (100 ml) was treated with phenyl isocyanate (0·35 g) at room temp. Evaporation of the solvent and recrystallization of the resulting solid from EtOH afforded VI as plates.

Stable oxosulphonium ylides. When ethyl chloroformate (2·4 g) was added to a sol of IX (44 mmoles)[8] in THF, separation of XI occurred instantaneously. This was removed by filtration under exclusion of moisture, the filtrate was concentrated *in vacuo* and the residual liquid (X) was directly submitted to IR analyses. Complete removal of the solvent failed to afford X: IR spectrum of the decomposition product indicated the presence of dimethyl sulphoxide and unidentified esters.

Treatment of a solution of X (35 mmoles based on IX) in THF with Ac_2O, BzCl or phenyl isocyanate (35 mmoles) at room temp, followed by similar work-up of the reaction product as in the case of sulphonium ylides, afforded the corresponding stable oxosulphonium ylides. Compounds XIIa and XIII were purified by recrystallization from AcOEt, while XIIb was purified by column chromatography (basic alumina, benzene).

A mixture of IX (30 mmoles) and ethyl chloroformate (2·2 g) in THF (20 ml) was stirred overnight at room temp. The reaction mixture was treated with H_2O and extracted with chf. Evaporation of the solvent afforded crystalline XIV (0·64 g), which was recrystallized from EtOH.

Dimethylsulphonium dicarbethoxymethylide (XV). Ethyl chloroformate (2·7 g) in THF (20 ml) was added at 0° to a sol of dimethylsulphonium methylide[8] prepared from the corresponding sulphonium iodide (7·7 g) and NaH (0·9 g) in DMSO–THF (1:1) and the reaction mixture was stirred overnight at room temp. Usual work-up of the reaction product yielded XV (1·1 g), which was purified by repeated recrystallizations from hexane.

Ethyl 2,3-dibenzoylcyclopropanecarboxylate (XVIa). The ylide IVa (0·38 g) was treated with *cis*- or *trans*-1,2-dibenzoylethylene (0·33 g) in THF (100 ml) at room temp for 1·5 hr and the reaction mixture heated under reflux for 20 min. Evaporation of the solvent and treatment of the residual solid with hot pet. ether (b.p. 35–40°) yielded crude products free from the unchanged ethylene. Further purification of pet. ether soluble fraction was performed by dry column chromatography (alumina, pet. ether (b.p. 35–40°)-hexane–chf (3:5:2)). Extraction of the middle parts of the column with hot chf, followed by recrystallization from pet. ether (b.p. 40–50°), yielded pure XVIa (20 mg, 5%) as needles, m.p. 95–96° (lit.[10] m.p. 93°).

Ethyl 2-benzoyl-3-phenylcyclopropanecarboxylate (XVIb). The ylide IVa (0·7 g) was treated with chalcone (0·54 g) in THF (100 ml) at room temp for 5 hr and then at reflux temp for 5 hr. Elution chromatography (silica gel, benzene) of the reaction product (1·3 g) gave XVIb (0·15 g, 20%) as an oil, ν_{max}^{liq} 1740 and 1680 cm^{-1}. (Found: C, 77·7; H, 6·3. $C_{19}H_{18}O_3$ requires: C, 77·5; H, 6·2%.)

The oily product was converted to its 2,4-dinitrophenylhydrazone, m.p. 220–223°(d). (Found: C, 63·5; H, 4·7. $C_{25}H_{22}N_4O_6$ requires: C, 63·3; H, 4·7%.)

2-Carbethoxy-3-benzoyl-5-hydroxy-5-phenylthiane 1-oxide (XVII). To a sol of X prepared from dimethyloxosulphonium methylide (21 mmoles) and ethyl chloroformate (1·2 g) in THF (80 ml), *trans*-1,2-dibenzoylethylene (2·5 g) in THF (20 ml) was added at room temp. The reaction mixture was stirred at the same temp for 1 hr and then heated under reflux for 3 hr. Separation of the more soluble XVII from the less soluble, unchanged ethylene was effected by two fractional recrystallizations from EtOH. The soluble fraction was further washed with a small volume of acetone and then recrystallized from EtOH–chf to afford analytically pure XVII (1·1 g, 27%), m.p. 206–208°(d), ν_{max}^{Nujol} 3310(OH), 1740(COOEt), 1685(PhCO) and 1020($>$S$\rightarrow$O) cm^{-1}. (Found: C, 65·5; H, 5·9. $C_{21}H_{22}O_5S$ requires: C, 65·3; H, 5·7%.) Due to the low solubility of XVII in $CDCl_3$, the NMR spectrum did not serve to give any useful structural information. The mass spectrum gave no appreciable peak at region higher than *m/e* 160.

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