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STABLE SULPHONIUM PHENACYLIDES

ISOLATION AND REACTIONS[1]

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Abstract—Methylphenylsulphonium phenacylide (II) was isolated as a stable solid upon treatment of methylphenacylphenylsulphonium bromide (I) with bases. No evidence supporting the proposed intermediacy of benzoylcarbene, which was postulated to be formed by thermal decomposition of II and then transformed into 1,2,3-tribenzoylcyclopropane (IV), was obtained, but the reaction of II with I or phenacyl bromide did give IV. The ylide II reacted with certain α,β-unsaturated or α-halogenated carbonyl compounds and yielded cyclopropane derivatives (IV, XI–XIII). Treatment of the ylide II with phenyl isocyanate or acid anhydrides resulted in C-acylation affording novel stabilized ylides (XIV–XVI, Table 1), while reaction with acyl halides yielded O-acylated products (XVII, XVIII). Attempted resolution of II and *p*-iodo derivative (VIII) failed.

IN CONTINUATION of the work on carbene chemistry,[2] the probable formation of benzoylcarbene (III) from the proposed sulphonium ylide (II) was investigated. Both were assumed as intermediates in the transformation of methylphenacylphenylsulphonium bromide (I)[3] into 1,2,3-tribenzoylcyclopropane (IV) upon treatment with hot bases.[4] Re-examination of this reaction at lower temp led to the isolation of the ylide II as a crystalline solid.[5–7] The present paper consists of the characterization and examination of reactions of the sulphonium ylide II.

Isolation of compound II

Treatment of I with triethylamine or sodium ethoxide in ethanol at 0–5° gave the crystalline sulphonium phenacylide II. No change occurred, however, on treatment

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[1] Communicated in part: H. Nozaki, K. Kondô and M. Takaku, *Tetrahedron Letters* 251 (1965).

[2a] H. Nozaki, R. Noyori and K. Sisido, *Tetrahedron* **20**, 1125 (1964); [b] H, Nozaki, M. Yamabe and R. Noyori, *Ibid.* **21**, 1657 (1965); [c] H. Nozaki, M. Nakano and K. Kondô, *Ibid.* **22**, 477 (1966).

[3] F. Krollpfeiffer, H. Hartmann and F. Schmidt, *Liebigs Ann.* **563**, 15 (1949).

[4a] F. Krollpfeiffer and H. Hartmann, *Chem. Ber.* **83**, 90 (1950); [b] V. Horák and L. Kohout, *Chem. & Ind.* 978 (1964).

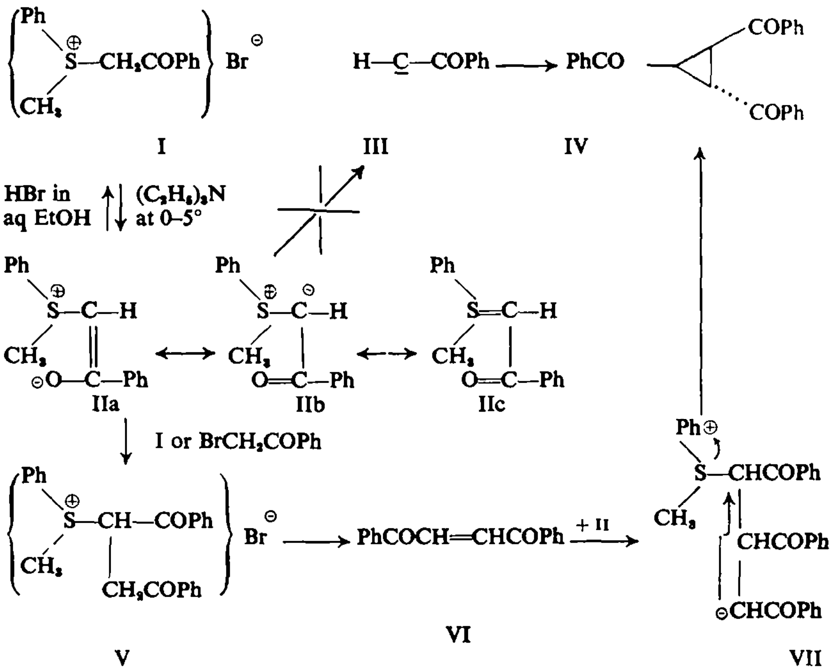
[5] Stable phosphorus ylides are well known, see [a] F. Ramirez and S. Dershowitz, *J. Org. Chem.* **22**, 41 (1957); [b] O. Isler, H. Gutmann, M. Montavon, R. Rüegg, G. Ryser and P. Zeller, *Helv. Chim. Acta* **40**, 1242 (1957).

[6] For stable oxosulphonium ylides previously recorded, see [a] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.* **86**, 1640 (1964); [b] H. König and H. Metzger, *Tetrahedron Letters* 3003 (1964).

[7] The sulphonium ylides known prior to our publication (ref. 1) were dimethylsulphonium fluorenylide and its derivatives. See [a] C. K. Ingold and J. A. Jessop, *J. Chem. Soc.* 713 (1930); [b] E. D. Hughes and K. I. Kuriyan, *Ibid.* 1609 (1935). Thereafter, several research groups have recorded stable sulphonium ylides of various kinds: [c] A. Hochrainer and F. Wessely, *Tetrahedron Letters* 721 (1965); [d] E. Winterfeldt, *Chem. Ber.* **98**, 1581 (1965); [e] H. Behringer and F. Scheidl, *Tetrahedron Letters* 1757 (1965); [f] W. J. Middleton, E. L. Buhle, J. G. McNally, Jr. and M. Zanger, *J. Org. Chem.* **30**, 2384 (1965); [g] J. Diekmann, *Ibid.* **30**, 2272 (1965); [h] A. J. Speziale, C. C. Tung, K. W. Ratts and A. Yao, *J. Amer. Chem. Soc.* **87**, 3460 (1965).

of I with triethylamine in benzene solution even at room temp, but decomposition of I to phenacyl bromide and thioanisole was observed at the b.p. of the solution. When I was treated with triethylamine in boiling ethanol only IV was produced.

The structure of this stable ylide II was consistent with analysis, cryoscopic mol. wt, mass spectrum[8] and other spectroscopic data as summarized in Table 1. This was further confirmed chemically by the action of hydrogen bromide in aqueous ethanol, which yielded the sulphonium bromide (I).



Obviously, the ylide II must be represented as a resonance hybride of the formulas IIa, IIb and IIc. The formula IIa would possible be of maximum importance in view of the recent report of Speziale and Ratts on analogous phosphorus ylides.[9]

Iodine-containing ylide VIII (Table 1) was obtained analogously as a crystalline solid.

Attempted resolution of compounds II *and* VIII

Attempted preparation of the sulphonium phenacylides (II and VIII) in optically active form has failed.[10] Thus, the reaction of VIII with (+)-2-bromo-π-camphorsulphonic acid[11] afforded a sulphonium salt IX. After recrystallization, this salt was

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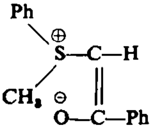
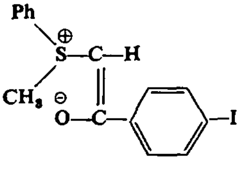
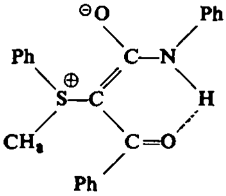
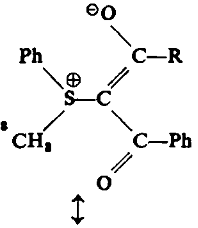
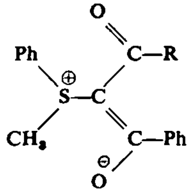
[8] Mass spectral isotope abundances: (P + 1) 17·1% and (P + 2) 7·2% of the parent peak at m/e 242. Fragment peaks were observed at *m/e* 124 (the base peak assigned to $[Ph—S—CH_3]^{\oplus}$), 109, 105, 91, 78, 77, 69, 65, 51, 50, 45 and at 39. With exception of the peaks at 105, 77 and 51, each possibly originating from benzoyl cation, the fragmentation pattern was in accord with that of the mass spectrum of thioanisole itself.

[9] A. J. Speziale and K. W. Ratts, Abstr. of papers, ACS meeting p. 57S. Atlantic City, New Jersey, September 13–17 (1965). These authors have found the maximum contribution of the betaine structure with the geometry of *cis* hetero atoms as proposed by E. Winterfeldt (ref. 7[4]).

TABLE I. SPECTRAL PROPERTIES OF NOVEL SULPHONIUM YLIDES

No.	Compounds Formula	IR[a] cm^{-1} (state)	UV max mμ (log ε) solvent	NMR τ value	NMR wt.	NMR Assignment (multiplicity)[b]
II		1504–1470 (KBr) 1540 (0·2M PhH) 1535 (0·2 DMSO) 1525 (0·2 $CHCl_3$)	310(4·18) EtOH[c] 320(4.01) MeCN 320(3·95) $CHCl_3$ 326(4·06) THF	6·84 5.44 2·8–2·0	3 1 10	S-methyl (s) methine (s) aromatic (m)
VIII		1505 (KBr)	251(4·35), 315(4·30) EtOH	6·83 5·37 2·8–2·2	3 1 9	S-methyl (s) methine (s) aromatic (m)
XIV		1630, 1535 (KBr)	241(3·32), 286(4·25) EtOH	6·75 3·4–2·6 −1·33	3 15 1	S-methyl (s) aromatic (m) imide (m)
XV R = CH_3		1590, 1565 (KBr)	279(4·06) EtOH	7·82 6·67 2·8–2·1	3 3 10	acetyl (s) S-methyl (s) aromatic (m)
XVI R = Ph		1590, 1560 (KBr)	288(3·87), 317(3·80) EtOH	6·58 3·1–2·0	3 15	S-methyl (s) aromatic (m)

[a] Ylide carbonyl stretching frequencies are given.
[b] s for singlet and m for multiplet.
[c] EtOH for 100% ethanol.

converted into an optically active sulphonium picrate[10a] which showed $[\alpha]_D$ −11·0°,[12] but the subsequent basic treatment yielded the inactive ylide (VIII).

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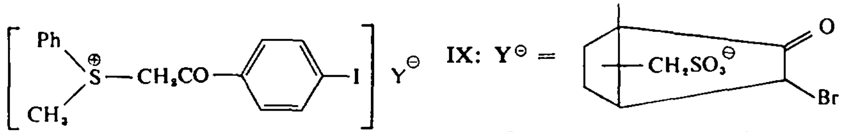
[10] Optically active trivalent sulphur compounds have been reported. For sulphonium salts, see [a] M. P. Balfe, J. Kenyon and H. Phillips, *J. Chem. Soc.* 2554 (1930). For sulphoxides, see [b] K. K. Andersen, W. Gaffield, N. E. Papanikolaou, J. W. Foley and R. I. Perkins, *J. Amer. Chem. Soc.* **86**, 5637 (1964); [c] K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons and A. L. Ternay, Jr, *Ibid.* **87**, 1958 (1965). For sulphilimines, see [d] G. Kresze and B. Wustrow, *Chem. Ber.* **95**, 2652 (1962); [e] J. Day and D. J. Cram, *J. Amer. Chem. Soc.* **87**, 4398 (1965).

[11] A. W. Ingersoll and S. H. Babcock, *J. Amer. Chem. Soc.* **55**, 341 (1933).

[12] The rotation of optically pure ethylmethylphenacylsulphonium picrate was reported[10a] as $[\alpha]_{5461}$ −11·2° in acetone.



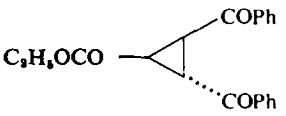
IX: $Y^{\ominus}$ =

X: $Y^{\ominus}$ = 2,4,6-trinitrophenoxide

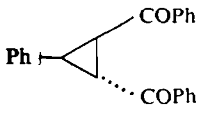
Reactions of compound II *leading to cyclopropane derivatives*

Regarding the formation of 1,2,3-tribenzoylcyclopropane (IV) from the sulphonium bromide (I), the isolated ylide II was found to be stable under conditions which were sufficient to effect the transformation of I to IV. The striking thermal stability of the ylide II does not support the benzoylcarbene hypothesis[4,13] in this particular case at least. The cyclopropane IV was, however, obtained by the reaction of II with I and by treating II with phenacyl bromide. The addition of II to both *cis* and *trans* isomers of 1,2-dibenzoylethylene (VI) proceeded quantitatively in ethanolic solutions at room temp and afforded IV in each case. Notably the *trans* VI reacted faster than its *cis* isomer, as treatment of a mixture of *cis* and *trans* VI and the ylide II (one molar each) similarly as above afforded a mixture of IV and the unchanged *cis* VI.[14] The thermal reaction of diazoacetophenone with VI[15] has been recorded to proceed only with the *cis* isomer, the *trans* VI here in this case being inactive towards diazoacetophenone. These facts may again be in contradiction to the carbene hypothesis. The series of reactions in the flow-sheet is analogous to that of triphenylphosphonium phenacylide with phenacyl bromide furnishing a mixture of VI and IV in 50 and 7% yields, respectively.[16] In contrast to the phosphorus ylide reaction, however, no 1,2-dibenzoylethylene (VI) could be isolated in the present reaction of I and/or II.

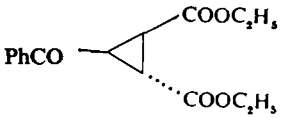
The cyclopropane formation of the ylide II was extended to α-halo and α,β-unsaturated carbonyl compounds. A mixture of II and ethyl bromoacetate (1:1 molar ratio) dissolved in chloroform was allowed to react at room temp. The products were IV and ethyl 2,3-dibenzoylcyclopropanecarboxylate (XI) in 45 and 4% yields, respectively. When an equimolar mixture of II and chalcone dissolved in chloroform was heated under reflux the lower melting, thermodynamically more stable isomer of 1,2-dibenzoyl-3-phenylcyclopropane (XII)[17] was obtained in 77% yield. The *trans* configuration of two benzoyl groups of XI and XII is tentatively assumed. An



XI



XII



XIII

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[13] The formation of carbenes by thermal decomposition of intermediary sulphonium ylides has been postulated in other kinds of reactions. [a] V. Franzen, H. Schmidt and C. Mertz, *Chem. Ber.* **94**, 2942 (1961); [b] A. W. Johnson, V. J. Hruby and J. L. Williams, *J. Amer. Chem. Soc.* **86**, 918 (1964); [c] I. Rothberg and E. R. Thornton, *Ibid.* **85**, 1704 (1963) **86**, 3296, 3302 (1964).

[14] Analogous selectivity of *cis* and *trans* isomers of 1,2-dibenzoylethylene has been recorded in the cases of 1,3-dipolar addition and Diels-Alder reactions. [a] R. Huisgen, H. J. Sturm and H. Wagenhofer, *Z.Naturforsch.* **17b**, 202 (1962); [b] J. Sauer, D. Lang and H. Wiest, *Ibid.* **17b**, 206 (1962).

[15] H. Strzelecka and M. Siemiatycki, *C.R. Acad. Sci., Paris* **252**, 3821 (1961).

[16] M. Siemiatycki and H. Strzelecka, *C.R. Acad. Sci., Paris* **250**, 3489 (1960).

[17] E. P. Kohler and W. N. Jones, *J. Amer. Chem. Soc.* **41**, 1249 (1919).

equimolar mixture of II and diethyl fumarate or diethyl maleate in hot tetrahydrofuran afforded diethyl 3-benzoylcyclopropane-*trans*-1,2-dicarboxylate (XIII).[18] The *trans* configuration of two ester carbonyl groups has been concluded from NMR analysis.[19]

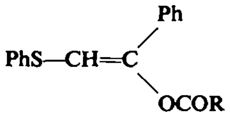
It should be added that irradiation of the ylide II in ethanol with a high pressure mercury lamp afforded the cyclopropane IV in 30% yield along with thioanisole and unidentified polymers. Compounds originating from the Wolff rearrangement of benzoylcarbene could not be isolated. This is in marked contrast with the reported behaviour of oxosulphonium ylides,[6a] as well as with the photochemical decomposition of diazoacetophenone in hydroxylic solvents.[20]

Other reactions of compound II

The ylide II reacted smoothly with phenyl isocyanate[21] in tetrahydrofuran at room temp and afforded another crystalline sulphonium ylide XIV (Table 1). The NMR spectrum indicated the presence of internal hydrogen bonding of the imide proton.

C-Acylation of the ylide II with acid anhydrides furnished crystalline ylides XV and XVI (Table 1) in 95 and 42% yields, respectively. IR and NMR spectra supported the resonance structure as indicated.

The action of acid chlorides resulted in O-acylation affording XVII in 66% yield and XVIII in 78% yield. The fate of S-methyl group is not clear yet.[22] Attempted condensation of the ylide II with benzaldehyde or *p*-nitrobenzaldehyde failed to afford the expected epoxy ketones.



$$\mathrm{PhS{-}CH{=}C(Ph)(OCOR)}$$

XVII (R = CH_3); XVIII (R = Ph)

EXPERIMENTAL

All temps are uncorrected. Microanalyses were performed at the Elemental Analyses Centre of Kyôto University. NMR spectra were obtained on 60 Mc machines in $CDCl_3$ solutions with TMS as an internal reference. Unless otherwise noted, the optical rotations were measured photoelectronically in EtOH with 1 dm cell, the smallest reading being to 0·005°.

Methylphenylsulphonium phenacylide (II). To a suspension of I (6·5 g, 20 mmoles) in ethanol (30 ml) Et_3N (4 g, 40 mmoles) was added under vigorous stirring at 0–5°. The reaction mixture was stirred at the same temp for 2 hr, diluted with water (100 ml) and repeatedly extracted with chloroform. The combined extracts were washed with water, dried ($MgSO_4$) and concentrated *in vacuo*. Recrystallization of the yellow crystalline residue from benzene afforded the analytically pure ylide II (3·4 g,

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[18] Similar examples of the exclusive formation of thermodynamically more stable isomer have been recorded in the reaction of vinyl sulphones with dimethyloxosulphonium methylide. See W. E. Truce and V. V. Badiger, *J. Org. Chem.* **29**, 3277 (1964).

[19] The NMR spectrum of 2,4-dinitrophenylhydrazone of XIII in $CDCl_3$ indicated the presence of two non-equivalent ethoxy groups. An ethoxy group showed a methyl triplet at τ 9·12 and a methylene quartet at τ 6·29 (J 6·0 c/s), while another one had a methyl triplet at τ 8·68 and a methylene quartet at τ 5·74 (J 7·0 c/s).

[20] A. Padwa and R. Layton, *Tetrahedron Letters* 2167 (1965).

[21] For the reaction of oxosulphonium ylides with phenyl isocyanate, see Ref. 6*b*.

[22] Analogous difference in the reactivity of acid anhydrides and chlorides towards phosphorus ylides has recently been described: P. A. Chopard, R. J. G. Searle and F. H. Devitt, *J. Org. Chem.* **30**, 1015 (1965).

70%) as fine plates, m.p. 113–114°, $\nu_{\max}^{\text{KBr}}$ 1504–1470, 1365, 1195, 990, 860 and 700 cm^{-1}. (Found: C, 74·69; H, 6·05; MW 254 (cryoscopic in PhH). $C_{15}H_{14}OS$ requires: C, 74·34; H, 5·82%; MW 242.)

Similar treatment of I (3·2 g, 10 mmoles) with 1% ethanolic EtONa (10 ml) or with 8% NaOHaq (10 ml) at 0–5° afforded II in 63 and 75% yields, respectively. Reaction of I (8·0 g) with Et_3N (5·0 g) in EtOH (50 ml) at 20–30°, followed by chromatographic separation on a silica gel column, gave II (2·0 g, 33%) and IV (0·3 g, 10%), m.p. 212°[23], while reaction in refluxing EtOH yielded IV (0·7 g, 25%) as a sole product.

A solution of II (0·5 g, 2 mmoles) in 8% NaOHaq (3 ml) was heated under reflux for 10 min and then extracted with chloroform. Working up the product afforded unchanged II (0·46 g, 92% recovery). Similar treatment of II (0·5 g) with alkali in the presence of sodium bromide (0·2 g, 2 mmoles) resulted in 90% recovery.

To a solution of II (0·7 g, 3 mmoles) in EtOH (10 ml) 47% HBraq (0·33 ml) was added dropwise under stirring and cooling with an ice-bath and the mixture was stirred for 30 min at the same temp. The precipitating I (0·8 g, 86%) was collected by filtration. A sample melted at 92° (mixed m.p. 91°) and indicated exactly identical IR spectrum with that of an authentic I.

p-*Iodo-α-phenylmercaptoacetophenone.* A sodium thiophenoxide solution prepared from thiophenol (8·8 g, 80 mmoles) and Na (1·84 g, 80 mg-atoms) in EtOH (100 ml) was treated with a solution of *p*-iodophenacyl bromide (25 g, 77 mmoles) in MeOH (50 ml), whereupon colourless fine crystals of the sulphide (12·7 g, 48%) separated. An analytical sample had m.p. 75–76° (from MeOH). (Found: C, 47·27; H, 2·93. $C_{14}H_{11}IOS$ requires: C, 47·46; H, 3·11%.) The mass spectrum indicated peaks at *m/e* 354 (parent peak), 231, 203, 123, 109, 104, 76, 44 and 28 (base peak).

Methylphenylsulphonium p-*iodophenacylide* (VIII). A mixture of p-iodo-α-phenylmercaptoacetophenone (8 g, 22 mmoles) and dimethyl sulphate (2·8 g, 22 mmoles) was heated at 100° under exclusion of moisture for 1 hr. The sulphonium methylsulphate (10·6 g) obtained as a semi-solid was dissolved in EtOH (50 ml) and treated with Et_3N (2·3 g, 22 mmoles) at 0–5°. Working up the product afforded VIII (5·7 g, 70% based on the sulphide) as pale yellow needles. An analytical sample showed m.p. 140–141° (from PhH). (Found: C, 48·94; H, 3·81. $C_{15}H_{13}IOS$ requires: C, 48·92; H, 3·53%.) The mass spectrum showed peaks at *m/e* 368 (parent peak), 354, 246, 231, 203, 124 (base peak), 109, 91, 78, 65, 51, 45 and 39.

Attempted resolution of methylphenylsulphonium phenacylide (II). Methylphenylsulphonium phenacylide (3·5 g, 14 mmoles) and (+)-10-camphorsulphonic acid (3·4 g, 14 mmoles) were dissolved in chloroform (100 ml) and the solution was allowed to stand overnight at room temp. The evaporation residue was yellow oil which crystallized gradually on standing. Single recrystallization from benzene afforded *methylphenacylphenylsulphonium* (+)-10-*camphorsulphonate* (5·5 g, 80%), m.p. 146–147°. (Found: C, 63·30; H, 6·55. $C_{25}H_{30}O_5S_2$ requires: C, 63·28; H, 6·37%.) Fractional recrystallizations from EtOH, AcOEt, $CHCl_3$, AcMe or various mixtures of these solvents did not change appreciably the observed optical rotation, $[\alpha]_D$ +20·4° (α_D +0·250°, $c = 1{\cdot}22$).

Treatment of the salt (0·15 g, 0·3 mmole) with sodium picrate (0·07 g, 0·3 mmole) in MeOH (5 ml) at 0° yielded the *methylphenacylphenylsulphonium picrate* (0·12 g, 85%), which was found to be optically inactive (α_D 0·00 in AcMe), m.p. 129–130°. (Found: C, 53·33; H, 3·87. $C_{21}H_{17}N_3O_8S$ requires: C, 53·50; H, 3·61%.)

Attempted resolution of methylphenylsulphonium p-*iodophenacylide* (VIII). Treatment of VIII (2·0 g, 5·4 mmoles) with (+)-10-camphorsulphonic acid (1·25 g, 5·4 mmoles) similarly as above gave analytically pure p-*iodophenacylmethylphenylsulphonium* (+)-10-*camphorsulphonate* (2·6 g, 80%), m.p. 158–159°, $[\alpha]_D$ +16·9° (α_D+0·200°, $c = 1{\cdot}19$). (Found: C, 50·14; H, 4·66. $C_{25}H_{29}IO_5S_2$ requires: C, 50·16; H, 4·85%.) Fractional recrystallization from EtOH did not change the observed rotation. Treatment of the product (0·5 g, 0·83 mmole) with Et_3N in EtOH afforded the optically inactive VIII (0·25 g, 81%, α_D 0·00).

The ylide VIII (4·0 g, 11 mmoles) and 2-bromo-π-camphor-sulphonic acid (3·4 g, 11 mmoles) were dissolved in tetrahydrofuran (200 ml) and the mixture was allowed to stand overnight at room temp. The pale yellow evaporation residue was dissolved in AcMe and cautious addition of AcOEt to the solution resulted in precipitation of the pure p-*iodophenacylmethylphenylsulphonium* 2-*bromo-π-camphorsulphonate* (IX; 3·95 g, 53%), m.p. 149°, $[\alpha]_D$ +46·5° (α_D +0·551°, $c = 1{\cdot}19$). (Found: C, 43·85; H, 4·07. $C_{25}H_{28}BrIO_5S_2$ requires: C, 44·19; H, 4·15%.)

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[23] G. Maier, *Chem. Ber.* **95**, 611 (1962).

Fractional recrystallization of IX (3·8 g) from AcMe–AcOEt afforded a sample (0·45 g) with $[\alpha]_D$ +36·5° (α_D +0·349°, $c = 0·95$), which was converted to the p-*iodophenacylmethylphenylsulphonium picrate* (X; 0·20 g, 51 %), m.p. 144–145°, $[\alpha]_D$ −11·0° (α_D −0·050°, $c = 0·46$ in AcMe). (Found: C, 42·18; H, 2·78. $C_{21}H_{16}IN_3O_8S$ requires: C, 42·21; H, 2·68 %.) Treatment of the active picrate X with equimolar KOH in MeOH at 0° afforded the optically inactive ylide VIII (0·10 g, 81 %),

trans-1,2,3-*Tribenzoylcyclopropane* (IV). A solution of I (0·16 g, 0·5 mmole) and II (0·5 g. 2 mmoles) in benzene (20 ml) was heated under reflux for 2 hr. The pale yellow evaporation residue was washed with pet. ether (b.p. 35–40°) and recrystallized from benzene to afford IV (0·10 g, 45 % yield based on II) as colourless needles, m.p. 212–213°.

An ethanolic (20 ml) solution of phenacyl bromide (1·0 g, 5 mmoles) and II (1·2 g, 5 mmoles) was stirred at room temp for 2 hr and yielded the cyclopropane IV (0·48 g, 82 % yield based on II).

A solution of II (0·5 g, 2 mmoles) and *trans*-dibenzoyl-ethylene (0·5g, 2 mmoles) in EtOH (20 ml) was stirred at room temp for 30 min and yielded IV (0·65 g, 87 %). The ylide II (0·5 g) also reacted with *cis*-dibenzoylethylene (0·5 g)[24] to afford IV (0·62 g, 83 %).

Competitive reaction of II and dibenzoylethylenes. A mixture of *trans*-dibenzoylethylene (0·30 g, 1·2 mmoles), *cis*-dibenzoylethylene (0·30 g, 1·2 mmoles) and II (0·30 g, 1·2 mmoles) in EtOH (20 ml) was stirred for 1·5 hr at 5–10°. The evaporation residue was triturated with chloroform (5 ml). The insoluble part was IV (0·43 g, 95 %), while the soluble one recovered from the filtrate was almost pure *cis*-dibenzoylethylene (0·28 g, 93 %). Its purity was ascertained by m.m.p. (134°) and by IR.

Ethyl 2,3-dibenzoylcyclopropanecarobxylate (XI). A solution of II (6·6 g, 27 mmoles) and ethyl bromoacetate (2·3 g, 14 mmoles) in chloroform (50 ml) was stirred for 1·5 hr at room temp. Concentration of the reaction mixture *in vacuo* and dilution of the residue with hexane (50 ml) resulted in separation of IV (1·4 g, 45 %). Thioanisole was distilled off from the filtrate and the residue was recrystallized from pet. ether (b,p. 35–40°)–hexane (1 : 1) to afford an analytically pure sample of XI (0·18 g, 4·1 %), m.p. 92–93°, ν_{max}^{Nujol} 1725, 1670, 1195, 1020 and 705 cm^{-1}. (Found: C, 74.78; H, 5·77. $C_{20}H_{18}O_4$ requires: C, 74·52; H, 5·63 %.)

trans-1,2-*Dibenzoyl-3-phenylcyclopropane* (XII). A solution of II (1·0 g, 4·1 mmoles) and chalcone (0·86 g, 4·1 mmoles) in chloroform (20 ml) was heated under reflux for 6 hr. The evaporation residue solidified and this was washed with cold pet. ether (b.p. 35–40°) and recrystallized from EtOH to afford XII (1·02 g, 77 %), m.p. 119–120° (lit.[17] m.p. 116°).

Diethyl 3-benzoylcyclopropane-trans-1,2-*dicarboxylate* (XIII). A solution of the ylide II (1·4 g, 5·8 mmoles) and diethyl fumarate (1·0 g, 5·8 mmoles) in tetrahydrofuran (30 ml) was heated under reflux for 30 hr. IR spectrometry indicated complete disappearance of the ylide carbonyl (1500 cm^{-1}) and appearance of a benzoyl carbonyl (1690 cm^{-1}). The evaporation residue was dissolved in EtOH (10 ml) and treated with excess 2,4-dinitrophenylhydrazine.[25] Recrystallization of the product from AcOEt afforded 2,4-*dinitrophenylhydrazone of* XIII (1·9 g, 70 %). An analytical sample had m.p. 185·5–186·5° (from AcOEt). (Found: C, 55·90; H, 4·90. $C_{22}H_{22}O_8N_4$ requires: C, 56·17; H, 4·71 %.)

The reaction of the ylide II (1·4 g, 5·8 mmoles) and diethyl maleate (1·0 g, 5·8 mmoles) yielded the same 2,4-dinitrophenylhydrazone of XIII (1·4 g, 50 %). The identity of these two samples was ascertained by m.m.p., IR spectra and by TLC.

Photolysis of the ylide II. A solution of II (1·0 g, 4·1 mmoles) in EtOH (30 ml) was sealed in a Pyrex test tube and irradiated with a 200W high pressure Hg lamp for 10 hr. Crystalline precipitates were collected and found to be IV (0·14 g, 30 %). Evaporation of the solvent afforded an intractable oil (0·36 g). The presence of thioanisole in this oil was shown by TLC on alumina.

Methylphenylsulphonium benzoyl(N-*phenylcarbamoyl*)*methylide* (XIV). A solution of II (1·0 g, 4·1 mmoles) in anhydrous tetrahydrofuran (30 ml) was treated with phenyl isocyanate (0·5 g, 4·1 mmoles) for 2 hr at 0–5°. Recrystallization of the evaporation residue from AcOEt gave colourless fine needles of XIV (1·43 g, 95 %), m.p. 198–199°. (Found: C, 72·92; H, 5·58. $C_{22}H_{19}NO_2S$ requires: C, 73·11; H, 5·30 %.)

Methylphenylsulphonium acetylbenzoylmethylide (XV). A solution of II (2·0 g, 8·2 mmoles) and Ac_2O (0·84 g, 8·2 mmoles) in anhydrous dioxan (30 ml) was stirred for 2 hr at room temp. The evaporation residue was recrystallized from benzene to afford an analytically pure sample of XV (2·3 g, 95 %), m.p. 138–139°. (Found: C, 72·09; H, 5·90. $C_{17}H_{16}O_2S$ requires: C, 71·82; H, 5·67 %.)

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Methylphenylsulphonium dibenzoylmethylide (XVI). A solution of II (1·5 g, 6·2 mmoles), benzoic anhydride (1·4 g, 6·2 mmoles) and AcOH (0·37 g, 6·2 mmoles) in dioxan (30 ml) was stirred overnight at room temp. The reaction mixture was diluted with water (150 ml) and extracted with chloroform. Recrystallization of the evaporation residue from benzene–pet ether (b.p. 35–40°) (6:1) yielded XVI (0·9 g, 42%) as colourless fine plates, m.p. 178–179°. (Found: C, 76·58; H, 5·49. $C_{22}H_{18}O_2S$ requires C, 76·28; H, 5·24%.)

Enol acetate of α-phenylmercaptoacetophenone (XVII). The ylide II (2·5 g, 11 mmoles) in chloroform (40 ml) was treated with AcCl (0·81 g, 11 mmoles) for 2 hr at room temp. Evaporation of the solvent yielded a viscous oil (2·7 g) which crystallized on standing. Recrystallization from hexane afforded an analytically pure sample of XVII (1·73 g, 66%), m.p. 65–66°, ν_{max}^{Nujol} 1765, 1200 and 1040 cm^{-1}. (Found: C, 71·14; H, 5·30. $C_{16}H_{14}O_2S$ requires: C, 71·10; H, 5·22%.) The NMR spectrum exhibited a methyl singlet (acetyl) at τ 7·68 (3H), a vinylic singlet at τ 3·40 (1H) and an aromatic multiplet at τ 2·8–2·3 (10H).

Enol benzoate of α-phenylmercaptoacetophenone (XVIII). The ylide II (3·15 g, 13 mmoles) in tetrahydrofuran (40 ml) was treated with benzoyl chloride (1·8 g, 13 mmoles) for 2 hr at room temp. The solid residue (4·1 g) obtained by solvent removal was recrystallized from hexane to afford an analytically pure sample of XVIII (3·3 g, 78%), m.p. 94–95°, ν_{max}^{Nujol} 1735 and 1245 cm^{-1}. (Found: C, 75·88; H, 5·01. $C_{21}H_{16}O_2S$ requires: C, 75·89; H, 4·85%.) The NMR spectrum in CCl_4 exhibited a vinylic singlet at τ 3·84 (1H) and an aromatic multiplet at τ 2·9–2·4 (15H). Hydrolysis of XVIII (0·8 g, 3·0 mmoles) with an excess of alcoholic KOH afforded α-phenylmercaptoacetophenone (0·33 g, 50%), m.p. 51–52°.

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