

Acid-induced Interaction of 2-Diazoacetophenones and Sulphides with Special Reference to the Cyclization of 2-Diazo-2'-(phenylthio)acetophenones and the Unusual Formation of a Diacylolefin in a Reaction between a β -Carbonylsulphonium Ylide and a Phenacylsulphonium Salt

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When treated with a molar excess of perchloric acid, 2-diazo-2'-(phenylthio)acetophenone provides 2,3-dihydro-3-oxo-1-phenylbenzo[*b*]thiophenium perchlorate, which may be deprotonated by triethylamine or, more slowly, by the diazo-ketone. When the latter is used, the first formed β -carbonylsulphonium ylide reacts with unconsumed salt to provide 1,2-bis-[*o*-(phenylthio)benzoyl]ethylene. Similar results are obtained with 2'-(*p*-chlorophenylthio)-2-diazoacetophenone. Previously, such reactions between sulphonium salts and ylides have always provided 1,2,3-triacylcyclopropanes. In the presence of perchloric acid, typical 2-diazoacetophenones react with dimethyl sulphide and with methyl phenyl sulphide to provide the corresponding phenacylsulphonium salts in high yield. With diphenyl sulphide the reaction fails, suggesting that the ready cyclization of 2-diazo-2'-(phenylthio)acetophenone is a consequence of the juxtaposition of the diazoacetyl and phenylthio-groups.

2-DIAZOACETOPHENONES with an *ortho*-substituent possessing lone-pair electrons (I; e.g. X-Y = OMe,¹ SMe,² or NH \cdot SO₂Ar³) readily undergo acid-promoted cyclization in the presence of water or an alcohol to give the heterocycle (IV), presumably *via* the 'onium salt (III). We now report what we believe to be the first example of such a reaction in which the intermediate 'onium salt (III) has been isolated. When 2-diazo-2'-(phenylthio)acetophenone (I; X = S, Y = Ph) was added to aqueous acetonitrile containing 2 molecular proportions of 71% perchloric acid, the diazo-nitrogen was rapidly evolved and the cyclic phenacylsulphonium salt (III; X = S, Y = Ph, A = ClO₄) was obtained in nearly quantitative yield. Its structure was confirmed by elemental analysis, i.r. and n.m.r. spectroscopy, and deprotonation with triethylamine to the ylide (V;

X = S, Y = Ph). Salts such as (III; X = S or O, Y = Me) readily lose a methyl group to a nucleophile such as water or an alcohol to provide the heterocycle (IV; X = O or S). Since aryl groups are not readily removed in this way, isolation of the salt (III; X = S, Y = Ph) is not surprising. We have previously shown that 2-diazo-2'-phenoxyacetophenone⁴ (I; X = O, Y = Ph) likewise fails to lose a phenyl group on treatment with acid but in this instance only acyclic products are obtained, presumably because under the conditions used, oxonium salts are less stable than their sulphonium counterparts.

When the diazo-ketone (I; X = S, Y = Ph) was treated with half a molecular proportion of perchloric acid, 50% of the nitrogen was evolved almost immediately; there followed a much slower gas evolution which continued until the balance of the diazo-nitrogen had

¹ A. K. Bose and P. Yates, *J. Amer. Chem. Soc.*, 1952, **74**, 4703.

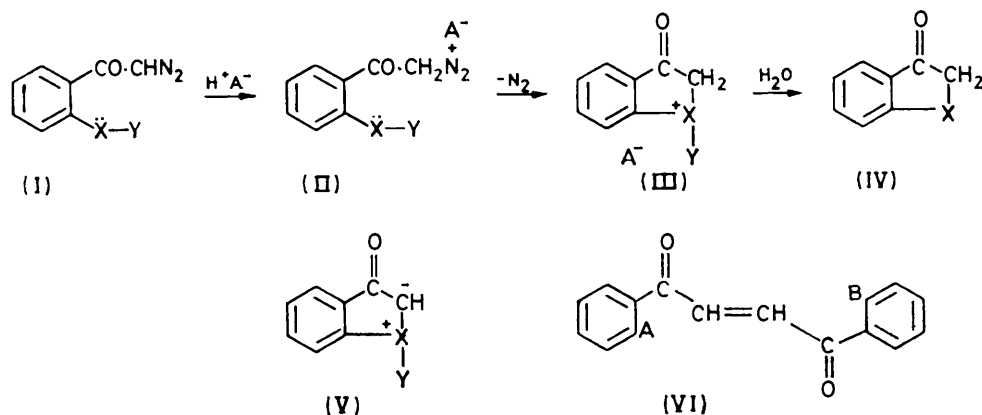
² W. Hampel and J. Friedrich, *Z. Chem.*, 1970, **10**, 343.

³ W. Hampel, *J. prakt. Chem.*, 1969, **311**, 78.

⁴ P. McC. Duggleby and G. Holt, *J. Chem. Soc.*, 1962, 3579.

been liberated (*ca.* 24 h). The major product then proved to be not the sulphonium salt (III; X = S, Y = Ph) but a compound which, on the basis of analytical and spectroscopic evidence (see later) was shown to be the diacylolefin (VI; A = B = SPh); the latter was also obtained in small quantities when aqueous perchloric

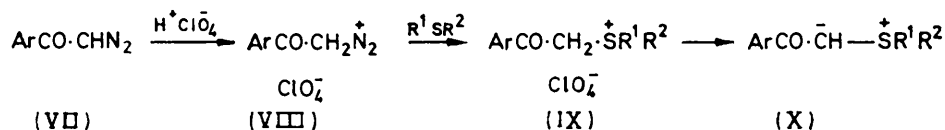
(VI; A = B = SPh); it therefore appears that this failure is a consequence of some structural feature of the ylide (V; X = S, Y = Ph) rather than of the fact that our experiments were carried out under essentially acidic conditions in which ylide concentration is presumably low. Cyclopropane derivatives have usually been



acid was slowly added to the diazo-ketone in acetonitrile. In the same way, 2'-(*p*-chlorophenylthio)-2-diazoacetophenone (I; X = S, Y = *p*-ClC₆H₄) provided the corresponding sulphonium salt (III; X = S, Y = *p*-ClC₆H₄, A = ClO₄), ylide (V; X = S, Y = *p*-ClC₆H₄), and diacylolefin (VI; A = B = *p*-ClC₆H₄S). These results may be rationalized by postulating rapid formation of the sulphonium salt [(I) → (II) → (III)], which in the presence of diazo-ketone slowly undergoes deprotonation to provide the acyldiazonium ion (II) and the ylide (V; X = S, Y = Ph). The former cyclizes to the sulphonium salt (III; X = S, Y = Ph), which apparently reacts with the ylide to provide the protonated form of the diacylolefin (VI; A = B = SPh). In keeping with this view, treatment of the diazo-ketone with a catalytic quantity of sulphonium salt slowly brings about quantitative liberation of the diazo-nitrogen and the formation of the diacylolefin in high yield. Further interaction of equimolecular proportions of the salt (III; X = S, Y = Ph) and the ylide (V; X = S, Y = Ph) also provided the diacylolefin (VI; A = B = SPh) in similar yield. This result is surprising since in no instance has the interaction of a β-carbonylsulphonium ylide and the corresponding sulphonium salt been reported to provide a diacylolefin.⁵ The observed product has always been a 1,2,3-triacylcyclopropane

obtained under basic or other conditions which guarantee a high ylide concentration.

Previous failures to isolate diacylolefins from reactions between sulphonium salts and β-carbonylsulphonium ylides led us to investigate the possibility that in our experiments they were produced in some other way. Thus deprotonation of a sulphonium salt by diazo-ketone presumably leaves the resulting ylide and acyldiazonium ion in intimate contact. In principle, the negative carbon atom of the ylide could act as nucleophile to displace nitrogen from the acyldiazonium ion to yield the protonated form of the diacylolefin [(II; X = S, Y = Ph) + (V; X = S, Y = Ph) → (VI; A = B = SPh)]. To test this hypothesis, we treated the cyclic sulphonium salt (III; X = S, Y = Ph) with 2-diazoacetophenone (VII; Ar = Ph) in aqueous acetonitrile. When all the diazo-nitrogen had been evolved, there remained much unconsumed sulphonium salt; the unsymmetrical diacylolefin (VI; A = SPh, B = H), the expected product from interaction of the ylide (V; X = S, Y = Ph) and phenacyldiazonium ion (VIII; Ar = Ph) could not be detected. Apparently here too, deprotonation of the sulphonium salt (III; X = S, Y = Ph) by the diazo-ketone yields (V; X = S, Y = Ph), which reacts with as yet undeprotonated salt to yield the symmetrical diacylolefin (VI; A = B = SPh) rather



arising possibly by Michael addition of a second molecule of ylide to the first formed diacylolefin. In our hands, the cyclic ylide (V; X = S, Y = Ph) fails to provide the expected cyclopropane derivative with either *trans*-dibenzoyl ethylene or its bis-(*o*-phenylthio)-derivative

than with phenacyldiazonium ion (VIII; Ar = Ph) to provide the unsymmetrical olefin (VI; A = SPh, B =

⁵ See The Chemical Society, Specialist Periodical Report, Organic Compounds of Sulphur, Selenium and Tellurium, vol. I, 1970, p. 248, for compilation of references.

H). Doubtless, the phenacyldiazonium ion is diverted by reaction with water to provide the corresponding ketol, nitrogen, and a proton. This process is known to be rapid⁶ and the slowness of our reactions leading to diacylolefin indicates that deprotonation of the salt by diazo-ketone is the rate-determining step. In the absence of water, 2-diazoacetophenone (VII; Ar = Ph) failed to react with the sulphonium salt (III; X = S, Y = Ph), presumably because protonation of diazo-ketones is reversible and the decomposition of the resulting acyldiazonium ion (VIII) is dependant upon nucleophilic intervention⁷ which the ylide is apparently unable to provide.

The acid-promoted conversion of 2-diazo-2'-(phenylthio)acetophenone (I; X = S, Y = Ph) into the sulphonium salt (III; X = S, Y = Ph) is, we believe, the first recorded example of such a process and we were therefore led to investigate its generality. It then proved that in the presence of perchloric acid, 2-diazoacetophenone (VII; Ar = Ph) and its 4'-nitro- and 4'-methoxy-derivatives (VII; Ar = *p*-NO₂C₆H₄ or *p*-MeOC₆H₄) reacted readily with dimethyl sulphide and phenyl methyl sulphide to provide the acyclic sulphonium perchlorates (IX) in excellent yield. Dialkylphenacylsulphonium salts (IX; R¹ = R² = alkyl) have previously been prepared from phenacyl halides and dialkyl sulphides⁸ but the reaction fails with methyl phenyl sulphide and with diphenyl sulphide.⁹ Our procedure, therefore, represents a novel synthesis of alkylarylphenacylsulphonium salts (IX; R¹ = alkyl, R² = Ar). The interaction of 2-diazoacetophenone and diphenyl sulphide under conditions which gave a high yield of a sulphonium salt from 2-diazo-2'-(phenylthio)acetophenone (I; X = S, Y = Ph) gave a complex mixture which appeared to contain little of the expected salt (IX; R¹ = R² = Ar = Ph). It therefore appears that in the diazo-ketone (I; X = S, Y = Ph) the interaction of aryl sulphide and diazoacetyl groups under the influence of acid is a consequence of their juxtaposition. A similar effect has previously been reported between ester and diazoacetyl groups in 2'-alkoxycarbonyl-2-diazoacetophenones (I; X = CO, Y = OR).⁴

All the foregoing sulphonium salts were, by treatment with triethylamine, converted into the corresponding ylides (X), some of which have not been reported previously. In general, the yields appear to be superior to those obtained by the photolysis, thermolysis, or copper-catalysed decomposition of diazo-ketones in the presence of sulphides.¹⁰

Bis(aroyl)ethylenes.—Identification of 1,4-bis[*o*-phenylthio]phenyl]but-2-ene-1,4-dione (VI; A = B = SPh) was hampered by there being no C=C absorption in the i.r. spectrum, and by the ¹H n.m.r. spectrum having

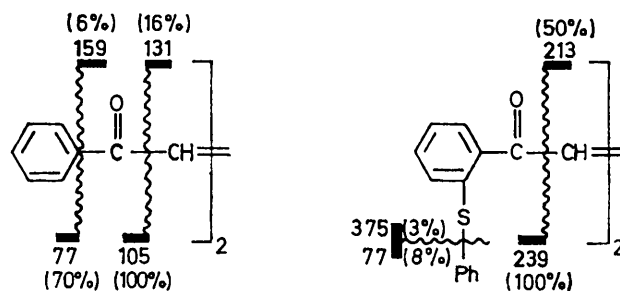
† For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1973, Index issue.

⁶ See B. Eistert, 'Newer Methods of Preparative Organic Chemistry,' Interscience, vol. I, p. 513, for compilation of references.

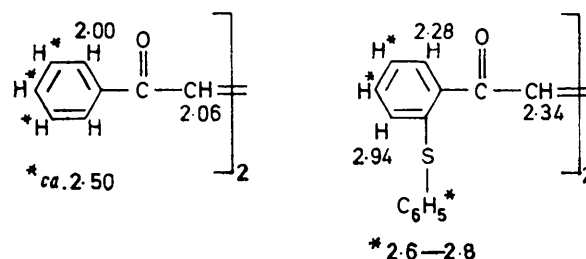
⁷ C. Wentrup and H. Dahn, *Helv. Chim. Acta*, 1970, **53**, 1637.

⁸ K. W. Ratts and A. N. Yao, *J. Org. Chem.*, 1966, **31**, 1185.

absorptions only in the 'aromatic' regions; proof of the structure was achieved by a comparison of the spectra with those of bis(benzoyl)ethylene (VI; A = B = H).



Mass spectra of bis(aroyl)ethylenes



¹H N.m.r. spectra of bis(aroyl)ethylenes (τ values)

The i.r. carbonyl absorption of each compound occurred at 1643 cm⁻¹. The chemical shifts of the vinylic protons were very similar to those of the protons *ortho* to the carbonyl, but were distinguishable by virtue of being singlets; the introduction of an SPh group into the *ortho*-position leads to an upfield shift of 0.28 p.p.m. for both the vinylic and the *ortho*-protons. The mass spectrum of 1,2-bis(benzoyl)ethylene (VI; A = B = H) shows prominent ions due to all four possible cleavages α to the C=O group; in the sulphur derivative (VI; A = B = SPh) only those α both to the C=O and C=C groups were observed; each compound had one prominent fragment radical ion: (VI; A = B = H) at *m/e* 208 (20%) due to expulsion of CO from the molecular ion, and (VI; A = B = SPh) at 184 (44%) due to the formation of the dibenzothiophen radical ion.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 instrument, ¹H n.m.r. spectra on Perkin-Elmer R10 and Varian HA100 spectrometers and mass spectra on an A.E.I. MS902 spectrometer. Gas volumes have been reduced to S.T.P. All the known compounds gave satisfactory analytical and spectroscopic data. For products marked with an asterisk, further spectral data are available in Supplementary Publication No. SUP 20938 (3 pp.).†

Diazo-ketones.—Prepared from diazomethane and 2-(phenylthio)benzoyl chloride¹¹ or 2-(*p*-chlorophenylthio)-

⁹ Von F. Krollpfeiffer, H. Hartmann, and F. Schmidt, *Annalen*, 1949, **563**, 15.

¹⁰ J. Quintana, M. Torres, and F. Serratosa, *Tetrahedron*, 1973, **29**, 2065.

¹¹ W. G. Bentrude and J. C. Martin, *J. Amer. Chem. Soc.*, 1962, **84**, 1561.

benzoyl chloride¹² by standard procedures,¹³ these were characterized as their triphenylphosphazenes¹⁴ and by the results of Wolff rearrangement with silver benzoate and triethylamine¹⁵ in ethanol.

(a) 2-Diazo-2'-(phenylthio)acetophenone* (I; X = S, Y = Ph) (75%) (Found: C, 66.2; H, 3.7; N, 10.7; S, 12.5. C₁₄H₁₀N₂OS requires C, 66.1; H, 3.9; N, 11.0; S, 12.6%) had m.p. 47.5–48.5°, ν_{\max} 2112s and 2092m (diazo) cm⁻¹, τ (CDCl₃) 2.3–3.1 (9H, m, aromatic) and 4.13 (1H, s, -CO-CHN₂). PPP-Triphenyl-N-(2-pnyhelthiophenacylidene)-phosphadiazene* (96%) (Found: C, 74.4; H, 5.1; N, 5.3; S, 6.5. C₃₂H₂₆N₂OPS requires C, 74.5; H, 4.8; N, 5.4; S, 6.2%) had m.p. 135–137° [from benzene-light petroleum (b.p. 60–80°)]. [2-(Phenylthio)phenyl]acetic acid (from hydrolysis of the crude ester) (80%) had m.p. 125–127° [from light petroleum (b.p. 60–80°)] [lit.,¹⁶ 123° (from benzene)].

(b) 2'-(p-Chlorophenylthio)-2-diazoacetophenone* (I; X = S, Y = p-ClC₆H₄) (96%) (Found: C, 58.5; H, 3.3; Cl, 12.5; N, 9.6; S, 11.1. C₁₄H₉ClN₂OS requires C, 58.3; H, 3.1; Cl, 12.3; N, 9.7; S, 11.1%) had m.p. 110–113° (from methanol), ν_{\max} 2110s cm⁻¹ (diazo), τ (CDCl₃) 2.4–3.2 (8H, m, aromatic) and 4.12 (1H, s, CO-CHN₂). N-[2-(p-chlorophenylthio)phenacylidene]-PPP-triphenylphosphadiazene* (83%) (Found: C, 70.3; H, 4.4; Cl, 6.4; N, 4.9. C₃₂H₂₄ClN₂OPS requires C, 69.8; H, 4.4; Cl, 6.4; N, 5.1%) had m.p. 113–115° [from benzene-light petroleum (b.p. 60–80°)]. Ethyl [2-(p-chlorophenylthio)phenyl]acetate* (49%) (Found: C, 62.6; H, 4.9; Cl, 11.2; S, 10.3. C₁₆H₁₅ClO₂S requires C, 62.7; H, 4.9; Cl, 11.6; S, 10.4%) had m.p. 42–43° (from ethanol), ν_{\max} 1744s (CO) cm⁻¹.

Cyclic Phenylsulphonium Salts, Ylides, and Diacylolefin. —(a) When 2-diazo-2'-(phenylthio)acetophenone (2.54 g, 0.01 mol) in acetonitrile (20 ml) was added with stirring during 20 min to 71% w/w perchloric acid (2.85 g, 0.02 mol) in acetonitrile (10 ml), nitrogen (224 ml, 100%) was evolved. The solvent was removed under reduced pressure, water (50 ml) was added, and after 12 h at 0° the crude product (2.85 g, 87%) was separated; recrystallization from ethanol provided 2,3-dihydro-3-oxo-1-phenylbenzo[b]thiophenium perchlorate* (III; X = S, Y = Ph, A = ClO₄) (Found: C, 51.8; H, 3.7; Cl, 10.4; S, 10.2. C₁₄H₁₁ClO₅S requires C, 51.8; H, 3.4; Cl, 10.8; S, 9.8%), m.p. 177–180°, ν_{\max} 1729s (CO) and 1080s,br (ClO₄⁻) cm⁻¹, τ [(CD₃)₂SO] 1.6–2.4 (9H, m, aromatic) and 5.02 (2H, s, CH₂). The salt with triethylamine under standard conditions¹⁷ provided 3-oxo-1-phenylbenzo[b]thiophenium-2-ylide* (V; X = S, Y = Ph) in quantitative yield (Found: C, 74.2; H, 4.5; S, 14.5. C₁₄H₁₀OS requires C, 74.3; H, 4.5; S, 14.2%), m.p. 135–137° [from benzene-light petroleum (b.p. 60–80°)], ν_{\max} 1594 (CO) cm⁻¹, τ (CDCl₃) 1.9–3.0 (9H, m, aromatic) and 5.57 (1H, s, CH), *m/e* 226 (M⁺, 52%). In the same way 2'-(p-chlorophenylthio)-2-diazoacetophenone (I; X = S, Y = p-ClC₆H₄) with perchloric acid provided 1-(p-chlorophenyl)-2,3-dihydro-3-oxobenzo[b]thiophenium perchlorate* (70%) (Found: C, 47.0; H, 2.6; Cl, 19.9; S, 9.4. C₁₄H₁₀Cl₂O₅S requires C, 46.6; H, 2.8; Cl, 19.7; S, 8.9%), m.p. 157–160° (from ethanol), ν_{\max} 1733s (CO) and 1083s,br (ClO₄⁻) cm⁻¹, τ [(CD₃)₂SO] (solubility was low) 1.7–2.9 (8H, unresolved m, aromatic) and 5.2br (2H, s, CH₂).

¹² D. L. Tuleen, W. G. Bentrude, and J. C. Martin, *J. Amer. Chem. Soc.*, 1963, **85**, 1938.

¹³ See *Org. Reactions*, 1942, **1**, 38, for compilation of references.

¹⁴ H. J. Bestmann, H. Buckshewski, and H. Leube, *Chem. Ber.*, 1959, **92**, 1345.

(b) To 2-diazo-2'-(phenylthio)acetophenone (0.64 g, 2.5 mmol) in acetonitrile (10 ml) 0.464M-perchloric acid (2.7 ml, 1.25 mmol) was added in one portion. There was a brisk evolution of nitrogen (27 ml, 48%) which subsided after 1 min, followed by a much slower reaction during which nitrogen (23 ml, 41%) was liberated over 24 h. Water (7.3 ml) was added; the bright yellow product (0.41 g, 72%) was separated and recrystallized from benzene-light petroleum (b.p. 60–80°) to provide 1,4-bis-[o-(phenylthio)phenyl]but-2-ene-1,4-dione* (VI; A = B = SPh) (Found: C, 74.3; H, 4.6; S, 14.0. C₂₈H₂₀O₂S₂ requires C, 74.3; H, 4.5; S, 14.2%), m.p. 151–153°, ν_{\max} 1643s (CO) cm⁻¹, τ (CDCl₃) 2.28 (2H, aromatic proton *ortho* to the COR, *Jortho* 7.5, *Jmeta* 2.0 Hz), 2.34 (2H, s, -COCH=), and 2.6–3.0 (16H, m, aromatic), *m/e* 452.0890 (M⁺, 1.8%. C₂₈H₂₀O₂S₂ requires 452.0904) and 239 (C₁₆H₁₁OS⁺, 100%). When the above experiment was repeated except that the perchlorate acid was added in small portions until the whole of the diazo-nitrogen had been evolved, 87% of the theoretical quantity of acid was consumed during 2 h and there resulted the diacylolefin (VI; A = B = SPh) (12%) and the sulphonium salt (III; X = S, Y = Ph) (70%), identical (mixed m.p. and spectra) with those described above.

(c) 2-Diazo-2'-(phenylthio)acetophenone (1.27 g, 5.0 mmol) and 2,3-dihydro-3-oxo-1-phenylbenzo[b]thiophenium perchlorate (0.165 g, 0.5 mmol) were stirred in acetonitrile (25 ml) and water (6.8 ml) until nitrogen evolution (112 ml, 100%) was complete (72 h). The bright yellow solid (1.12 g, 99%) was separated and after recrystallization proved to be identical (mixed m.p. and spectra) with the diacylolefin (VI; A = B = SPh). In the same way 2'-(p-chlorophenylthio)-2-diazoacetophenone (I; X = S, Y = p-ClC₆H₄) (1.44 g, 5.0 mmol) and 1-(p-chlorophenyl)-2,3-dihydro-3-oxobenzo[b]thiophenium perchlorate (III; X = S, Y = p-ClC₆H₄, A = ClO₄) (0.18 g, 0.5 mmol) provided (VI; A = B = p-ClC₆H₄S), 1,4-bis-[o-(p-chlorophenylthio)phenyl]but-2-ene-1,4-dione* (99%) (Found: C, 64.4; H, 3.8; Cl, 13.3; S, 12.8. C₂₈H₁₈Cl₂O₂S₂ requires C, 64.5; H, 3.5; Cl, 13.6; S, 12.3%), m.p. 219–222° [from benzene-light petroleum (b.p. 60–80°)], ν_{\max} 1645s (CO) cm⁻¹.

(d) When the sulphonium perchlorate (III; X = S, Y = Ph) (0.33 g, 1.0 mmol) and the ylide (V; X = S, Y = Ph) (0.23 g, 1.0 mmol) in acetonitrile (10 ml) and water (2.7 ml) were stirred for 24 h, there resulted the diacylolefin (VI; A = B = SPh) (0.30 g, 66%), identical with that described above.

(e) 2-Diazoacetophenone (0.73 g, 5.0 mmol) and 2,3-dihydro-3-oxo-1-phenylbenzo[b]thiophenium perchlorate (1.63 g, 5.0 mmol) were stirred in acetonitrile (25 ml) and water (6.8 ml) until nitrogen evolution (110 ml, 98%) was complete (48 h). The yellow solid (0.21 g, 19%) was filtered off and shown to be identical with the diacylolefin (VI; A = B = SPh). The solution from which it had separated was evaporated to dryness under reduced pressure and the residue was stirred with water (15 ml) and chloroform (50 ml); there separated the sulphonium perchlorate (III; X = S, Y = Ph 0.93 g, 57%), identical with that described above. After separation of the sulphonium salt, the water was removed from the filtrate and the residual chloroform layer was washed with water (1 × 20 ml),

¹⁵ M. S. Newman and P. F. Beal, *J. Amer. Chem. Soc.*, 1950, **72**, 5163.

¹⁶ J. O. Jilek, V. Seidlova, E. Svatek, and M. Protiva, *Monatsh.*, 1965, **96**, 182.

¹⁷ H. Nozaki, M. Takaku, and K. Kondo, *Tetrahedron*, 1966, **22**, 2145.

dried (MgSO_4), and concentrated to provide an oil (1.04 g) which slowly solidified. Recrystallization from benzene-light petroleum (b.p. 80—100°) gave 2-hydroxyacetophenone (0.53 g, 78%), m.p. 87—89° (lit.,¹⁸ 89.5—90.5°).

Acyclic Phenacylsulphonium Salts.—When the 2-diazoacetophenone (0.01 mol) and dimethyl or methyl phenyl sulphide (0.02 mol) in acetonitrile (15 ml) was added dropwise over 20 min with stirring to 71% w/w perchloric acid (2.85 g, 0.02 mol) in acetonitrile (10 ml), nitrogen evolution was quantitative. The residue obtained on removal of the solvent under reduced pressure was stirred with water (50 ml), the mixture was set aside for 12 h at 0°, and the sulphonium salt was separated. In each instance the crude salt was purified by crystallization from ethanol and by a standard procedure¹⁷ converted into the corresponding ylide, which was recrystallized from benzene-light petroleum. *Dimethylphenacylsulphonium perchlorate* (87%) (Found: C, 42.8; H, 4.9; Cl, 12.4; S, 11.5. $\text{C}_{10}\text{H}_{13}\text{ClO}_5\text{S}$ requires C, 42.8; H, 4.6; Cl, 12.6; S, 11.4%) had m.p. 184—185°; dimethylsulphonium phenacylide (98%) had m.p. 56—58° (lit.,⁹ 56—57°). *Methylphenacylphenylsulphonium perchlorate* (90%) (Found: C, 52.6; H, 4.5; Cl, 10.2; S, 9.8. $\text{C}_{15}\text{H}_{15}\text{ClO}_5\text{S}$ requires C, 52.6; H, 4.4; Cl, 10.2; S, 9.4%) had m.p. 153—154°; methylphenylsulphonium phenacylide (84%) had m.p. 110—112° (lit.,¹⁷ 114°). *p-Methoxyphenacyldimethylsulphonium perchlorate* (87%)

(Found: C, 42.5; H, 4.9; Cl, 11.2; S, 10.6. $\text{C}_{11}\text{H}_{15}\text{ClO}_6\text{S}$ requires C, 42.5; H, 4.8; Cl, 11.4; S, 10.3%) had m.p. 199—201°; *dimethylsulphonium p-methoxyphenacylide* (48%) (Found: C, 62.5; H, 6.8; S, 14.9. $\text{C}_{11}\text{H}_{14}\text{O}_2\text{S}$ requires C, 62.8; H, 6.7; S, 15.2%) had m.p. 110—112°. *p-Methoxyphenacylmethylphenylsulphonium perchlorate* (86%) (Found: C, 51.3; H, 4.7; Cl, 9.2; S, 8.8. $\text{C}_{16}\text{H}_{17}\text{ClO}_6\text{S}$ requires C, 51.5; H, 4.6; Cl, 9.5; S, 8.6%) had m.p. 146—148°; methylphenylsulphonium *p*-methoxyphenacylide (95%) was obtained as an oil. *Dimethyl-p-nitrophenacylsulphonium perchlorate* (91%) (Found: C, 36.9; H, 3.7; Cl, 11.3; N, 4.3; S, 9.6. $\text{C}_{10}\text{H}_{12}\text{ClNO}_7\text{S}$ requires C, 36.8; H, 3.7; Cl, 10.9; N, 4.3; S, 9.8%) had m.p. 182—184°; dimethylsulphonium *p*-nitrophenacylide (92%) had m.p. 109—111° (lit.,⁸ 110—111°). *Methyl-p-nitrophenacylphenylsulphonium perchlorate* (100%) (Found: C, 46.6; H, 3.7; Cl, 9.4; N, 3.6; S, 8.2. $\text{C}_{15}\text{H}_{14}\text{ClNO}_7\text{S}$ requires C, 46.4; H, 3.6; Cl, 9.2; N, 3.6; S, 8.3%) had m.p. 166—168°; *methylphenylsulphonium p-nitrophenacylide* (99%) (Found: N, 4.6; S, 11.6. $\text{C}_{16}\text{H}_{13}\text{NO}_3\text{S}$ requires N, 4.9; S, 11.1%) had m.p. 91—93°.

All the sulphonium salts and ylides gave spectral details consistent with those previously reported.

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¹⁸ L. Wolff and R. Greulich, *Annalen*, 1912, **394**, 36.