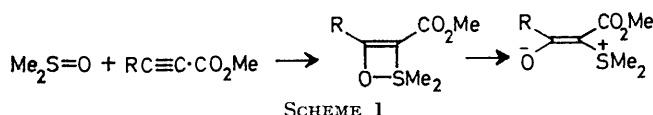


Reaction of Sulphimides with Electrophilic Acetylenes

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Stable sulphonium imidoylides (2) have been isolated from the reaction of *N*-aryl-*SS*-dimethylsulphimides (1) with electrophilic acetylenes at room temperature. Similar ylides (2) are also formed from *SS*-dimethyl-*N*-phthalimidodisulphimide. The ylides (2a, c, and e) give the pyrroles (3) when heated with a further mol. equiv. of dimethyl acetylenedicarboxylate or dibenzoylacetylene. The ylide (2c) reacts with other electrophiles, including hydrogen chloride, iodomethane, benzoyl chloride, and cyanogen bromide; these reactions (Scheme 5) involve electrophilic attack at the nitrogen atom of the ylide followed by nucleophilic attack at sulphur or at an *S*-methyl group.

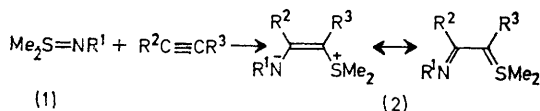
SULPHONIUM acylides have proved versatile synthetic intermediates, particularly in the preparation of furans and of pyrones.^{1,2} In order to develop similar routes to nitrogen heterocyclic systems we have investigated various methods of preparing sulphonium imidoylides. Winterfeldt discovered one preparation of sulphonium acylides which involves the reaction of acetylenic esters with dimethyl sulphoxide (Scheme 1).^{2a} We find that



SCHEME 1

analogous reactions take place between some sulphimides (1) and electrophilic acetylenes; the reaction has been used to prepare a series of sulphonium imidoylides (2), and some reactions of these with electrophiles have been investigated.

The ylides (2) were readily prepared by mixing the sulphimide and the acetylene in a dry solvent at room temperature. With the highly electrophilic acetylenes dimethyl acetylenedicarboxylate and dibenzoylacetylene, and with phenylprop-2-ynal compounds (2) were isolated in good yields from their reaction with *N*-arylsulphimides and with *SS*-dimethyl-*N*-phthalimidodisulphimide (Scheme 2). Pure products could not be obtained with



(1)

(2)

- a; $\text{R}^1 = p\text{-ClC}_6\text{H}_4$, $\text{R}^2 = \text{R}^3 = \text{CO}_2\text{Me}$ f; $\text{R}^1 = \text{N}\cdot\overline{\text{CO}\cdot\text{C}_6\text{H}_4\text{CO}}$, $\text{R}^2 = \text{R}^3 = \text{COPh}$
 b; $\text{R}^1 = \text{N}\cdot\overline{\text{CO}\cdot\text{C}_6\text{H}_4\text{CO}}$, $\text{R}^2 = \text{R}^3 = \text{CO}_2\text{Me}$ g; $\text{R}^1 = o\text{-C}_5\text{H}_4\text{N}$, $\text{R}^2 = \text{R}^3 = \text{COPh}$
 c; $\text{R}^1 = p\text{-ClC}_6\text{H}_4$, $\text{R}^2 = \text{R}^3 = \text{COPh}$ h; $\text{R}^1 = p\text{-ClC}_6\text{H}_4$, $\text{R}^2 = \text{Ph}$, $\text{R}^3 = \text{CHO}$
 d; $\text{R}^1 = p\text{-NO}_2\text{C}_6\text{H}_4$, $\text{R}^2 = \text{R}^3 = \text{COPh}$ j; $\text{R}^1 = \text{N}\cdot\overline{\text{CO}\cdot\text{C}_6\text{H}_4\text{CO}}$, $\text{R}^2 = \text{Ph}$, $\text{R}^3 = \text{CHO}$
 e; $\text{R}^1 = m\text{-ClC}_6\text{H}_4$, $\text{R}^2 = \text{R}^3 = \text{COPh}$

SCHEME 2

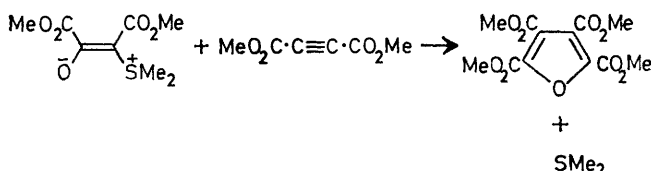
methyl propiolate; less activated acetylenes, including ethyl phenylpropiolate and phenylacetylene, failed to react. It was unnecessary to isolate the *N*-arylsulphimides before reaction with the acetylenes: an

¹ For reviews of the chemistry of sulphonium acylides see A. W. Johnson, 'Ylid Chemistry,' Academic Press, New York, 1966, p. 310; A. W. Johnson, in 'Organic Compounds of Sulphur, Selenium, and Tellurium,' senior reporter D. H. Reid, The Chemical Society, London, vol. 1, 1970, p. 248; vol. 2, 1973, p. 288.

alternative method of preparation of the ylides was investigated in which the sulphimides were generated *in situ* from the corresponding anilines. The sulphimides were then treated directly with the acetylenes; this also gave good yields. The products (2) are all air-stable crystalline solids.

Hayashi and his co-workers have reported briefly the preparation of two ylides of this type by the same method as we employed.³

Sulphonium acylides are known to react further with electrophilic acetylenes: such a reaction was observed by Winterfeldt, who found that the ylide from dimethyl sulphoxide and dimethyl acetylenedicarboxylate reacted when heated with another mol. equiv. of the acetylene to give tetramethyl furantetracarboxylate (Scheme 3).^{2a}



SCHEME 3

Several other furan syntheses of this type have since been reported, although the reaction is by no means universally observed: other types of reaction may involve proton transfer or acyl transfer to give new, extended ylides, and the nature of the products is solvent-dependent.¹ We investigated the further reaction of the sulphonium imidoylides (2) with acetylenes in order to discover whether it would be a useful route to pyrroles. The imidoylides (2) reacted readily with dimethyl acetylenedicarboxylate or with dibenzoylacetylene, but not with less activated acetylenes, when heated under reflux in benzene or toluene. Pyrroles (3) were isolated in good yields from the reactions of the ylides (2a, c, and e) with these acetylenes (Scheme 4). The reaction thus appears to have some limited use as a route to pyrroles.

The reactions of the dibenzoyl imidoylide (2c) with several other electrophiles were investigated. With hydrogen chloride the sulphonium group was lost, the product being the enamine (4), isolated in good yield.

² (a) E. Winterfeldt, *Chem. Ber.*, 1965, **98**, 1581; E. Winterfeldt and H. J. Dillinger, *ibid.*, 1966, **99**, 1558; (b) M. Takaku, Y. Hayashi, and H. Nozaki, *Tetrahedron Letters*, 1969, 2053; M. Higo and T. Mukaiyama, *ibid.*, 1970, 2565; Y. Hayashi, M. Kobayashi, and H. Nozaki, *Tetrahedron*, 1970, **26**, 4353; Y. Hayashi and H. Nozaki, *ibid.*, 1971, **27**, 3085.

³ Y. Hayashi, Y. Iwagami, A. Kadoi, T. Shono, and D. Swern, *Tetrahedron Letters*, 1974, 1071.

dimethylsulphonium 1,2-dibenzoyl-2-(3-chlorophenylimino)ethylide (2e) (65%), m.p. 228—230° (from dichloromethane-hexane), isolated after 2 h by filtration (Found: C, 68.55; H, 4.7; N, 3.45. $C_{24}H_{20}ClNO_2S$ requires C, 68.4; H, 4.75; N, 3.3%); ν_{max} 1 670 cm^{-1} (C=O); $\delta(CDCl_3)$ 3.20 (6 H), 6.5—7.0 (4 H, m), 7.2—7.4 (8 H, m), and 7.75 (2 H, m); m/e 423 and 421 (M^+); *dimethylsulphonium 1,2-dibenzoyl-2-(phthalimidoimino)ethylide* (2f) (30%), m.p. 168—170° (from chloroform), isolated after 12 h by layer chromatography (Found: C, 68.7; H, 4.2; N, 6.3. $C_{26}H_{20}N_2O_4S$ requires C, 68.4; H, 4.4; N, 6.1%); ν_{max} 1 785, 1 726, and 1 676 cm^{-1} (C=O); m/e 456 (M^+); *dimethylsulphonium 1,2-dibenzoyl-2-(2-pyridylimino)ethylide* (2g) (60%), m.p. 207—208° (from ethanol), isolated after 12 h by filtration (Found: C, 71.0; H, 5.3; N, 7.1. $C_{23}H_{20}N_2O_2S$ requires C, 71.1; H, 5.2; N, 7.2%); ν_{max} 1 675 cm^{-1} (C=O); $\delta(CDCl_3)$ 3.07 (6 H) and 6.48—7.90 (14 H, m); m/e 388 (M^+); *dimethylsulphonium 2-(4-chlorophenylimino)-1-formyl-2-phenylethylide* (2h) (75%), m.p. 165—167° (from dichloromethane-hexane), isolated after 2 h by layer chromatography (chloroform-acetone, 9:1) (Found: C, 64.0; H, 5.1; N, 4.2. $C_{17}H_{16}ClNOS$ requires C, 64.2; H, 5.05; N, 4.4%); ν_{max} 1 590 and 1 535br cm^{-1} ; $\delta(CDCl_3)$ 3.10 (6 H), 6.42 (2 H, d, J 9 Hz), 6.93 (2 H, d, J 9 Hz), 7.08—7.24 (5 H, m), and 8.70 (1 H); m/e 319 and 317 (M^+), and 254 (base); and *dimethylsulphonium 1-formyl-2-phenyl-2-(phthalimidoimino)ethylide* (2j) (55%), m.p. 189—191° (from chloroform), isolated after 24 h by layer chromatography (chloroform-acetone, 4:1) (Found: C, 65.0; H, 4.2; N, 8.1. $C_{19}H_{16}N_2O_3S$ requires C, 64.8; H, 4.6; N, 8.0%); ν_{max} 1 778, 1 760, 1 712, and 1 611 cm^{-1} ; $\delta(CDCl_3)$ 3.20 (6 H), 7.3—7.6 (9 H, m), and 8.57 (1 H); m/e 352 (M^+).

Method B. To a solution of *N*-chlorosuccinimide (1.34 g, 10 mmol) in dry dichloromethane (25 ml) was added a solution of dimethyl sulphide (0.7 g, 11 mmol) in dichloromethane (5 ml) during 5 min at 0 °C. A colourless precipitate appeared. The aniline (10 mmol) in dichloromethane (5 ml) was added to the stirred mixture during 5 min; the mixture was then stirred at 0 °C for 10 min and at room temperature for 20 min. A clear solution resulted. The acetylene (7 mmol) in dichloromethane (5 ml) was added, followed by a solution of triethylamine (7 mmol) in dichloromethane (5 ml). The mixture was stirred for 12 h, and washed with aqueous sodium hydroxide. The solvent was removed from the organic phase to yield the crude betaine (80—100%), which was crystallised from dichloromethane-hexane. The betaines (2a) (85%), (2c) (95%), and (2h) (75%) were prepared by this method.

Tetramethyl 1-(4-Chlorophenyl)pyrrole-2,3,4,5-tetracarboxylate (3a).—The betaine (2a) (36 mg, 0.011 mmol) and dimethyl acetylenedicarboxylate (50 mg, 0.35 mmol) were heated in dry benzene (20 cm^3) under reflux for 22 h. Layer chromatography gave the title pyrrole (31 mg, 67%), m.p. 100—101° (from aqueous methanol) (Found: C, 52.5; H, 4.0; N, 3.4. $C_{18}H_{16}ClNO_8$ requires C, 52.7; H, 3.9; N, 3.4%); ν_{max} (KBr) 1 730 cm^{-1} ; $\delta(CDCl_3)$ 3.66 (6 H), 3.86 (6 H), 7.18 (2 H, d, J 9 Hz), and 7.40 (2 H, d, J 9 Hz); m/e 411 and 409 (M^+), 380, and 379.

Dimethyl 4,5-Dibenzoyl-1-(4-chlorophenyl)pyrrole-2,3-dicarboxylate (3b).—The betaine (2a) (165 mg, 0.5 mmol) and dibenzoylacetylene (210 mg, 0.9 mmol) were dissolved in toluene (75 cm^3) and the solution was heated under reflux for 18 h. Layer chromatography (chloroform) gave the

title pyrrole (126 mg, 50%), m.p. 281—283° (from dichloromethane-hexane) (Found: C, 66.8; H, 3.85; N, 2.6. $C_{28}H_{20}ClNO_6$ requires C, 67.0; H, 4.0; N, 2.8%); ν_{max} 1 730sh, 1 718, and 1 665 cm^{-1} (C=O); $\delta(CDCl_3)$ 3.60 (3 H), 3.70 (3 H), and 7.0—7.5 (14 H, m); m/e 503 and 501 (M^+).

2,3,4,5-Tetrabenzoyl-1-(4-chlorophenyl)pyrrole (3c).—The betaine (2c) (210 mg, 0.5 mmol) and dibenzoylacetylene (210 mg, 0.9 mmol) were dissolved in benzene (75 cm^3) and the solution was heated under reflux for 18 h. Layer chromatography (chloroform-acetone, 12:1) gave the title pyrrole (175 mg, 60%), m.p. 257—259° (from dichloromethane-hexane) (Found: C, 76.5; H, 4.1; N, 2.2. $C_{36}H_{24}ClNO_4$ requires C, 76.8; H, 4.1; N, 2.4%); ν_{max} 1 650 cm^{-1} (C=O); m/e 595 and 593 (M^+).

2,3,4,5-Tetrabenzoyl-1-(3-chlorophenyl)pyrrole (3d).—The betaine (2e) (100 mg, 0.24 mmol) and dibenzoylacetylene (56 mg, 0.24 mmol) were dissolved in acetonitrile (5 ml) and the solution was heated under reflux for 14 h. Layer chromatography (chloroform) gave the title pyrrole (71 mg, 50%), m.p. 198—200° (from dichloromethane-hexane) (Found: C, 76.5; H, 4.2; N, 2.2%); ν_{max} 1 665 cm^{-1} (C=O); m/e 595 and 593 (M^+).

Reactions of the Betaine (2c) with Other Electrophiles.—(a) *With hydrogen chloride.* Dry hydrogen chloride was passed through a solution of the betaine (2c) (210 mg, 0.5 mmol) in dichloromethane (20 cm^3) at room temperature for 10 min. The solution was purged with nitrogen and evaporated to leave a yellow solid. Crystallisation of the solid gave (Z)-2-(4-chlorophenylamino)-1,4-diphenylbut-2-ene-1,4-dione (4) (160 mg, 90%), m.p. 150—151° (from ethanol) (Found: C, 72.8; H, 4.5; N, 3.8. $C_{22}H_{16}ClNO_2$ requires C, 73.0; H, 4.4; N, 3.9%); ν_{max} (KBr) 1 665, 1 597, 1 583, 1 571, and 1 550 cm^{-1} ; $\delta(CDCl_3)$ 6.09 (1 H), 6.85 (2 H, d, J 9 Hz), 7.07 (2 H, d, J 7 Hz), 7.3—7.6 (6 H, m), and 7.8—8.0 (4 H, m). An authentic specimen was obtained (90%) by dropwise addition of 4-chloroaniline (128 mg, 1 mmol) in ether (10 ml) to dibenzoylacetylene (246 mg, 1 mmol) in ether (25 ml) at room temperature.

(b) *With cyanogen bromide.* A solution of the betaine (2c) (160 mg, 0.38 mmol) and cyanogen bromide (320 mg, 3.0 mmol) in dichloromethane (20 cm^3) was heated under reflux for 16 h. Layer chromatography (chloroform-acetone, 9:1) gave (Z)-2-(*N*-cyano-4-chlorophenylamino)-3-methylthio-1,4-diphenylbut-2-ene-1,4-dione (5b) (99 mg, 60%), m.p. 120—122° (from dichloromethane-hexane) (Found: C, 66.5; H, 4.1; N, 6.3. $C_{24}H_{17}ClN_2O_2S$ requires C, 66.6; H, 3.9; N, 6.5%); ν_{max} (KBr) 2 220, 1 675, and 1 643 cm^{-1} ; $\delta(CDCl_3)$ 2.19 (3 H), 6.75 (2 H, d, J 9 Hz), 7.08 (2 H, d, J 9 Hz), 7.2—7.7 (8 H, m), and 8.00 (2 H, m).

(c) *With succinic anhydride.* A solution of the betaine (2c) (210 mg, 0.5 mmol) and succinic anhydride (50 mg, 0.5 mmol) in acetonitrile (25 cm^3) was heated under reflux for 16 h. Layer chromatography (chloroform) gave (Z)-2-(4-chlorophenylamino)-3-methylthio-1,4-diphenylbut-2-ene-1,4-dione (5c) (40 mg, 20%), m.p. 132—133° (from ethanol) (Found: C, 67.7; H, 4.4; N, 3.4. $C_{23}H_{18}ClNO_2$ requires C, 67.7; H, 4.4; N, 3.4%); ν_{max} (KBr) 1 660, 1 580, and 1 535br cm^{-1} ; $\delta(CDCl_3)$ 1.76 (3 H), 6.97 (2 H, d, J 9 Hz), 7.14 (2 H, d, J 9 Hz), 7.3—7.6 (6 H, m), 7.75 (2 H, m), and 7.95 (2 H, m).

(d) *With benzoyl chloride.* To a solution of the betaine (2c) (210 mg, 0.5 mmol) in dichloromethane (10 cm^3) was added a solution of benzoyl chloride (70 mg, 0.5 mmol) in

dichloromethane (5 cm³) during 5 min. The solution was evaporated and the residue was triturated with hexane-ether (10:1) to give a yellow solid (215 mg). Layer chromatography of the solid (chloroform) gave (i) (Z)-2-(N-4-chlorophenylbenzamido)-3-methylthio-1,4-diphenylbut-2-ene-1,4-dione (5a) (190 mg, 75%), m.p. 187—188° (from ethanol) (Found: C, 70.1; H, 4.3; N, 2.7. C₃₀H₂₂ClNO₃S requires C, 70.4; H, 4.3; N, 2.7%); ν_{\max} (KBr) 3 060, 1 650, 1 590, and 1 575 cm⁻¹; δ (CDCl₃) 1.93 (3 H), 6.70

(2 H, d, *J* 9 Hz), 6.89 (2 H, d, *J* 9 Hz), 7.0—7.7 (11 H, m), and 7.9—8.2 (4 H, m); *m/e* 513 and 511 (*M*⁺), and 464 and 462 (*M*⁺ - SMe); (ii) the enamine (4) (9 mg, 5%), m.p. 150—151°; and (iii) the enamine (5c) (20 mg, 10%), m.p. 132—133°.

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