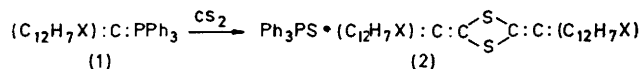


Reaction of Benzylidenetriphenylphosphorane with Carbon Disulphide

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Benzylidenetriphenylphosphorane (4) reacts with carbon disulphide to give 2,4-dibenzylidene-1,3-dithietan (10), 2-phenyl-2-triphenylphosphoniodithioacetate (5), 2-benzylidene-4-phenyl-1,3-dithiole (11), and 2-phenyl-1-(phenyldithioacetyl)-2-triphenylphosphonioethenethiolate (16). The isolation and yield of each compound depend strictly on the experimental conditions and, in particular, on the work-up procedure.

SCHÖNBERG *et al.*¹ report that some fluorenylidene-triphenylphosphoranes (1) react with carbon disulphide



in refluxing chloroform to give 2,4-difluorenylidene-1,3-dithietans (2). Since compounds (1) have no hydrogen

atoms attached to the ylide carbon atom, their overall reaction with carbon disulphide is necessarily restricted to dimerization of the intermediate thioketen system to give 1,3-dithietan derivatives.¹⁻⁵ However in the case of compounds such as (4) we considered that the initial adduct (5) might react in a different way, producing alkynethiolates [*e.g.* (7) and/or (8)] from which 1,3-

¹ A. Schönberg, L. Vargha, and H. Kaltschmit, *Ber.*, 1931, **64**, 2582.

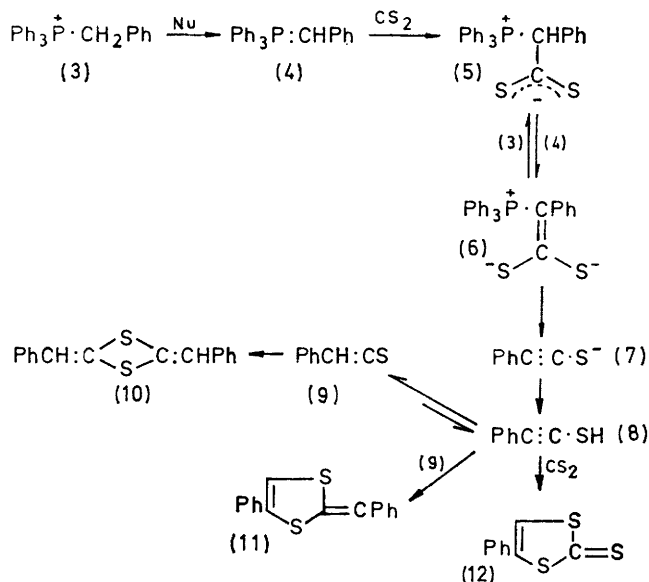
² A. Schönberg, E. Frese, and K. Brosowski, *Chem. Ber.*, 1962, **95**, 3077.

³ K. Dickoré and R. Wegler, *Angew. Chem. Internat. Edn.*, 1966, **5**, 970.

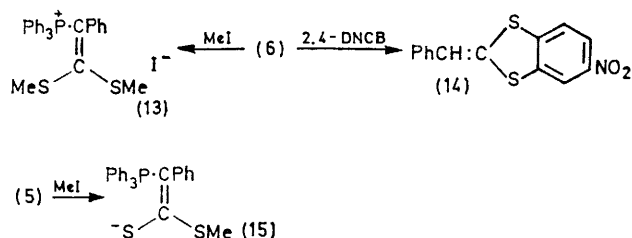
⁴ H. Ulrich, in 'Cycloaddition Reactions of Heterocumulenes,' ed. A. T. Blomquist, Academic Press, New York, 1967, p. 95.

⁵ H. Behringer and E. Meinetsberger, *Tetrahedron Letters*, 1973, 1915.

dithiols [*e.g.* (11)] could be obtained.⁶ (The latter can also be formed *via* species such as $\text{Ph}\dot{\text{C}}:\text{CH}\cdot\text{S}^- \leftrightarrow \text{Ph}\dot{\text{C}}:\text{CH}\cdot\text{S}^{\cdot}$,^{7,8})



In the event, the reaction between benzylidene-triphenylphosphorane (4) and carbon disulphide in ether at room temperature afforded the betaine anion (6) rather than the expected betaine (5) (Scheme 1). In fact when methyl iodide was added to the reaction mixture the di-S-methyl derivative (13) separated, and by adding 2,4-dinitrochlorobenzene (2,4-DNCB)⁹ the benzodithiole (14) was obtained. From the reaction of compound (4) with carbon disulphide it is possible to obtain different products by varying the work-up procedure. When the reaction mixture is poured into chloroform the betaine (5) can be isolated; this compound does not react with 2,4-DNCB but reacts with methyl iodide to give the mono-S-methyl derivative (15). When the reaction mixture is poured into water,



dilute aqueous potassium hydroxide or methanol, 2,4-dibenzylidene-1,3-dithietan (10) is obtained together with small amounts of 2-benzylidene-4-phenyl-1,3-dithiole (11). Use of an excess of carbon disulphide

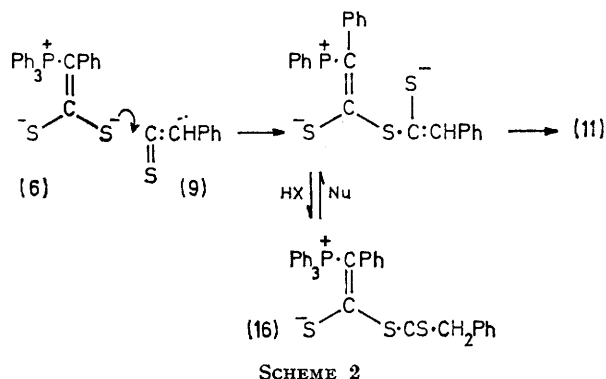
⁶ R. Reap, *Canad. J. Chem.*, 1968, **46**, 2251.

⁷ W. Kirmse and L. Horner, *Annalen*, 1958, 614, 4; W. Kirmse, in 'Carbene Chemistry,' ed. A. T. Blomquist, Academic Press, New York, 1964, p. 139.

sometimes affords small amounts of 4-phenyl-1,3-dithiole-2-thione (12) (Scheme 1). The ratio between compounds (10) and (11) indicates that in the protic medium the production of the thioketen (9) rather than the ynthiol (8) is strongly preferred. In agreement with this, the yield of (11) increases considerably when the reaction is carried out in refluxing dioxan.

The betaine (5) does not react under conditions which allow the formation of compounds (10)–(12), and thus cannot be considered as their precursor; these compounds are presumably derived from the anion (6), probably by the pathway outlined in Scheme 1.

When the reaction mixture is left at room temperature for several days before being worked up and then is poured into dilute hydrochloric acid, the main product is an orange compound, $\text{C}_{34}\text{H}_{27}\text{PS}_3$. The compound does not dissolve in dilute aqueous acid but does so in concentrated sulphuric acid, giving a colourless solution from which it can be recovered by dilution with water; it reacts with methyl iodide to give a mono-S-methyl derivative and with nucleophiles such as morpholine and potassium hydroxide to give the dithiole (11); on this basis and in the light of spectral and analytical data,



structure (16) is assigned. Several mesomeric and tautomeric structures can be written for this material; a possible pathway for its production is outlined in Scheme 2.

EXPERIMENTAL

Reaction of Benzylidene-triphenylphosphorane (4) with Carbon Disulphide.—(A) Benzyltriphenylphosphonium chloride (10 g) suspended in dry ether (100 ml) was stirred while a solution (17%; 13.8 ml) of phenyl-lithium in benzene-ether was added dropwise. After 30 min dry carbon disulphide (2.2 g) in dry ether was added to the stirred orange mixture. After 5 h the mixture, which had turned yellow, was worked up as described in procedures (a)–(e). T.l.c. showed the absence of compounds (4), (10), and (11).

(a) Methyl iodide was added in large excess to the stirred mixture, which was set aside for 1 h at room temperature, then poured into water. The solid was collected

⁸ K. P. Zeller, H. Meier, and Eu. Muller, *Tetrahedron Letters*, 1971, 537.

⁹ M. Yokayama, *J. Org. Chem.*, 1970, **35**, 283.

and dissolved in chloroform; the solution was filtered and evaporated. The residue was crystallized from ethanol to give 2,2-bismethylthio-1-phenylvinyl(triphenyl)phosphonium iodide (13) (2.25 g, 15.1%), m.p. 220—222°; λ_{\max} (EtOH) 222, 272, and 327sh nm (log ϵ 4.61, 4.37, and 3.80); δ (CDCl₃) 7.65 (15 H, m), 7.18 (5 H, m), 2.48 (3 H, s), 1.96 (3 H, s); *m/e* 457 (*M*⁺ - 1, 1%), 442 (457 - Me, 44), 437 (31), 395 (442 - SMe, 99), 363 (44), 294 (Ph₃PS⁺, 32), 262 (Ph₃P⁺, 59), 183 (100), and 142 (MeI⁺, 86) (Found: C, 57.2; H, 4.65; I, 21.5; P, 5.35; S, 11.15. C₂₈H₂₆IPS₂ requires C, 57.55; H, 4.5; I, 21.7; P, 5.3; S, 10.95%).

(b) 2,4-DNCB (2.6 g) in benzene (20 ml) was added to the reaction mixture, which was poured into water after 1 h. Extraction with benzene and evaporation of the extracts under reduced pressure left a residue which afforded 2-benzylidene-5-nitro-1,3-benzodithiole (14) as red needles (0.5 g, 6.9%), m.p. 170—171°; λ_{\max} (CHCl₃) 295, 316, and 343 nm (log ϵ 4.34, 4.30, and 3.61); ν_{\max} (KBr) 1 515 (asym. NO₂) and 1 332 cm⁻¹ (sym. NO₂); δ 7—7.9; *m/e* 287 (*M*⁺, 11%), 286 (*M*⁺ - 1, 100), 256 (286 - NO, 1), 241 (*M*⁺ - NO₂, 78), 228 (256 - CO, 12), and 134 (PhCH₂CS⁺, 26) (Found: C, 58.35; H, 3.35; N, 5.05; S, 22.1. C₁₄H₉NO₂S₂ requires C, 58.5; H, 3.15; N, 4.85; S, 22.3%). Column chromatography also afforded triphenylphosphine oxide and bis-2,4-dinitrophenyl sulphide, m.p. 190° (lit.¹⁰ 193°).

(c) The reaction mixture was poured into chloroform; filtration and evaporation of the solution gave a solid which was extracted thoroughly with benzene. The residue insoluble in benzene was benzyltriphenylphosphonium salt (3.5 g). 2-Phenyl-2-triphenylphosphoniiodithioacetate (5) (1.5 g, 13.3%) separated from the concentrated solution and was recrystallized from acetone; m.p. 281—282°; λ_{\max} (CHCl₃) 287 and 363 nm (log ϵ 4.23 and 3.93); δ (CDCl₃) 7.5 (15 H, m), 7.1 (5 H, m), and 5.12 (H s); *m/e* 428 (*M*⁺, 0.5%), 427 (*M*⁺ - 1, 1), 395 [(*M* - SH)⁺, 28], 294 (Ph₃PS⁺, 96), 262 (Ph₃P⁺, 84), 217 (Ph₂PS⁺, 36), and 183 (100) (Found: C, 72.65; H, 5.1; P, 7.45; S, 14.8. C₂₆H₂₁PS₂ requires C, 72.85; H, 4.95; P, 7.25; S, 14.95%).

(d) The reaction mixture was poured into methanol; 2,4-dibenzylidene-1,3-dithietan (10) separated after some hours (2.6 g, 75.3%); m.p. 223—224°; λ_{\max} (CHCl₃) 305sh, 315, and 365 nm (log ϵ 3.84, 3.83, and 3.73); δ (CDCl₃) 7.5 (10 H, m) and 6.92 (2 H, m); *m/e* 268 (*M*⁺, 100%), 191 (*M*⁺ - 77, 74), 134 (PhCH₂CS⁺, 46), and 77 (Ph⁺, 45) (Found: C, 71.4; H, 4.7; S, 23.7. C₁₆H₁₂S₂ requires C, 71.6; H, 4.5; S, 23.9%). Compound (10) was also obtained when the reaction mixture was poured into water or into dilute aqueous potassium hydroxide; after 6 h the solid was collected and dissolved in ethanol and the solution was refluxed for 3 h and cooled (yield 2.5 g).

(e) The reaction mixture was left at room temperature for 5 days and then poured into 10% hydrochloric acid. The solid was filtered off and dissolved in ethanol; the solution was filtered and evaporated and the residue was crystallized from acetone. The orange product was recrystallized from ethanol to give 2-phenyl-1-(phenyldithioacetyl)-2-triphenylphosphoniethenethiolate (1.5 g, 20.8%), m.p. 298°; λ_{\max} (CHCl₃) 257, 275, 325, 370, and 473 nm (log ϵ 4.16, 4.10, 4.13, 3.93, and 3.81); δ (CDCl₃) 8.0 (2 H, m), 7.65 (15 H, m), 7.15 (10 H, m); *m/e* 562 (*M*⁺, 1.4%), 395

[(*M* - PhCH₂CSS)⁺, 1.6], 294 (Ph₃PS⁺, 100), 262 (Ph₃P⁺, 42), 185 (Ph₂P⁺, 67), 183 (80), 152 (15), 139 (26), and 108 (28) (Found: C, 72.75; H, 5.1; P, 5.2; S, 17.25. C₃₄H₂₇PS₃ requires C, 72.55; H, 4.85; P, 5.5; S, 17.1%).

Isolation of 2-benzylidene-4-phenyl-1,3-dithiole (11). The mother liquor from (d) or (e), when evaporated, gave a residue which was chromatographed on a column of silica gel; elution with light petroleum and light petroleum-benzene (10 : 2) afforded small amounts of compound (11), m.p. 205° (lit.⁷ 205—207°); u.v., i.r., and n.m.r. spectra as expected.

Isolation of 4-phenyl-1,3-dithiole-2-thione (12). When an excess of carbon disulphide was used, column chromatography (see above) also gave small amounts of compound (12), as red crystals, m.p. 116° (lit.¹¹ 116°); u.v., i.r., and n.m.r. spectra as expected.

(B) Nearly identical results were obtained when the reaction was carried out under dry nitrogen.

(C) The reaction was repeated with dry dioxan as solvent, under dry nitrogen; carbon disulphide was added to the refluxing mixture and the reflux was continued for 5 h. The mixture was then poured into methanol and the solid was collected and chromatographed on a column of silica gel to give compound (11) (0.3 g, 8.7%), m.p. 204—205°. Neither compound (5) nor (10) could be obtained from this reaction mixture.

Methylation of Compound (5).—An excess of methyl iodide (0.5 g) was added to a stirred suspension of compound (5) (0.5 g) in aqueous methanolic potassium hydroxide (0.2 g); compound (5) dissolved and after some hours a solid was obtained which was collected, washed with water, and dissolved in ethanol. Ether was added to the solution and 1-methylthio-2-phenyl-2-triphenylphosphoniethenethiolate (15) (0.42 g, 82%) separated; m.p. 179—180°; λ_{\max} (EtOH) 272 and 325 nm (log ϵ 4.42 and 3.89); δ (CDCl₃) 7.60 (15 H, m), 7.2 (5 H, m), and 1.78 (3 H, s); *m/e* 442 (*M*⁺, 1.7%), 395 [(*M* - SMe)⁺, 20], 294 (Ph₃PS⁺, 92), 262 (Ph₃P⁺, 38), and 183 (100) (Found: C, 73.4; H, 5.35; P, 6.8; S, 14.55. C₂₇H₂₃PS₂ requires C, 73.25; H, 5.25; P, 7.0; S, 14.5%).

Methylation of Compound (16).—To a stirred solution of (16) (0.34 g) in pyridine, methyl iodide (0.35 g) was added; stirring was continued for ca. 4 h and then the solution was diluted with ether. The yellow solid was collected, washed with water, and crystallized from aqueous ethanol to give the mono-S-methyl derivative (0.24 g, 69.1%), m.p. 220—221°; λ_{\max} (EtOH) 264 and 330 nm (log ϵ 4.30 and 3.62); δ (CDCl₃) 7.68 (15 H, m), 7.24 (11 H, m), and 2.13 (3 H, s) (Found: C, 72.6; H, 5.2; P, 5.6; S, 16.45. Calc. for C₃₅H₂₆PS₃: C, 72.9; H, 5.05; P, 5.35; S, 16.7%).

Reaction of Compound (16) with Morpholine.—Compound (16) (0.25 g) was dissolved in morpholine (2 ml); the solution was heated at 100 °C for 6 h and then poured into water. After 1 h the yellow solid was collected and crystallized from toluene to give compound (11) (0.05 g), m.p. 204° (lit.⁷ 205—207°).

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¹⁰ F. Beilstein and A. Kurbatow, *Annalen*, 1879, **197**, 75.

¹¹ F. Runge, Z. El-Hewehi, H. Renner, and E. Taeger, *J. prakt. Chem.*, 1960, **11**, 284.