

## Formation of Novel 1 : 2 Adducts Between $\text{Bu}^n_3\text{P}\cdot\text{CS}_2$ and Electron-deficient Alkynes

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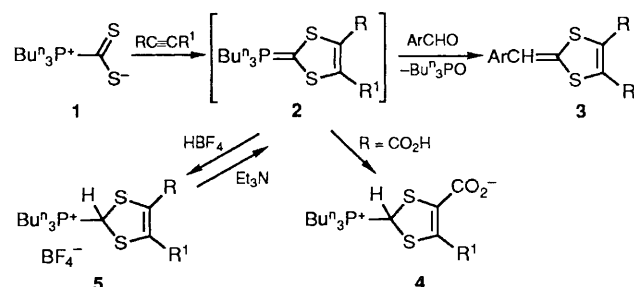
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The zwitterionic adduct between tri-*n*-butylphosphine and carbon disulphide reacts under neutral conditions with two equivalents of dimethyl and diethyl acetylenedicarboxylate, dibenzoylacetylene and methyl benzoylpropiolate to give novel crystalline dithiole-containing ylides whose structure is established by X-ray crystallography.

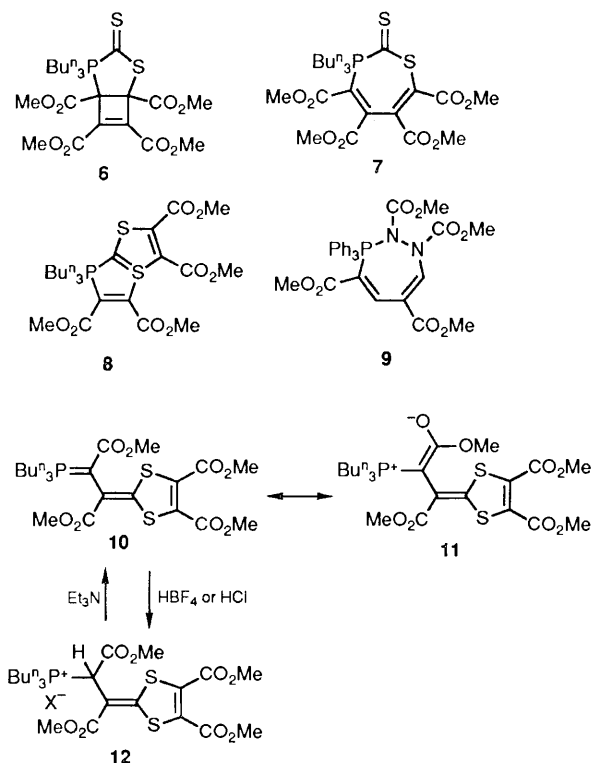
Although the red crystalline adducts formed between trialkylphosphines and  $\text{CS}_2$  were first reported as early as 1860<sup>1</sup> and their zwitterionic phosphoniodithioformate structure was established by X-ray crystallography in 1961,<sup>2</sup> the cycloaddition reactions of this unusual type of 1,3-dipole have been little investigated. Reaction of **1** with acetylenic dipolarophiles such as dimethyl acetylenedicarboxylate (DMAD) does give 2-alkylidene-1,3-dithioles **3** if the addition is carried out in the presence of aromatic aldehydes to trap the initial 1 : 1 adducts **2** by a Wittig reaction.<sup>3</sup> These intermediates can also be trapped by protonation, either intramolecularly<sup>4</sup> to give **4** or by carrying out the addition in the presence of  $\text{HBF}_4$  to give **5**.<sup>5</sup> Treatment of the stable salts **5** with  $\text{Et}_3\text{N}$  regenerates the phosphorane **2** thus allowing its use in the construction of a

variety of tetrathiafulvalene derivatives of interest as donors for organic conductors.<sup>6</sup> We now report that, in the absence of any trap, **1** reacts with a variety of electron-deficient alkynes in a 1 : 2 ratio to form stable crystalline adducts.

Reaction of **1** with DMAD in either ether or dichloromethane at room temperature for 18–24 h followed by



† For enquiries concerning the X-ray structure determination.



evaporation and column chromatography afforded an adduct as yellow prisms (32%, m.p. 114–115 °C,  $\delta_p$  +21.9). Analytical and spectroscopic data clearly showed this to be a 1 : 2 adduct and the presence of four different ester groups initially led us to suspect that addition had occurred through the P and S atoms of **1** to give a structure like **6**, **7** or **8**. We particularly favoured **7** since this had good precedent in the intermediate **9** postulated by Huisgen<sup>7</sup> in the reaction of  $\text{Ph}_3\text{P}$  and dimethyl azodicarboxylate with methyl propiolate. However none of these structures was in full accord with the <sup>13</sup>C NMR spectroscopic data<sup>‡</sup> and the real structure was revealed by an X-ray diffraction study<sup>§</sup> to be **10**.

In molecule **10** (Fig. 1), the atoms C(6) and C(7) are essentially coplanar with the dithiole ring plane [torsion angle S(1)–C(2)–C(6)–C(7) 1.1(6)°]. The relatively long P–C(7) [1.726(5) Å] and C(41)–O(41) [1.234(6) Å] distances together with the short value for C(7)–C(41) [1.402(7) Å] provide the first X-ray evidence for the contribution of the phosphonium enolate form **11** in an ester-stabilised phosphorane,<sup>¶</sup> a feature consistent both with the only previous X-ray structures of

<sup>‡</sup>  $\delta_c$  (75 MHz,  $\text{CDCl}_3$ ) 13.6, 22.1[55], 24.2[15], 24.6[4], 42.1[122], 50.0, 51.5, 53.0, 53.1, 109.3[9], 130.7, 136.2, 160.4, 160.45, 161.7[4], 167.8 and 169.2[20] (Figures in square brackets are  $J_{C-P}$  in Hz).

<sup>§</sup> Crystal data for **10**:  $\text{C}_{25}\text{H}_{39}\text{O}_8\text{PS}_2$ ,  $M = 562.69$ , crystal dimensions 0.28 × 0.36 × 0.51 mm, monoclinic space group  $P2_1/n$ ,  $a = 13.039(3)$ ,  $b = 17.909(4)$ ,  $c = 13.226(2)$  Å  $\beta = 100.23(2)^\circ$ ,  $V = 3039.4$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.23$  g cm<sup>-3</sup>,  $\mu$  (Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å) = 2.6 cm<sup>-1</sup>. Intensity data were measured at 21 °C using an Enraf-Nonius CAD4 diffractometer. Lorentz and polarisation corrections were applied to the data. The structure was solved by direct methods and refined by full-matrix least-squares calculations with hydrogens allowed for as riding atoms. At convergence  $R = 0.055$ ,  $R_w = 0.077$  for 2271 reflections with  $I > 3\sigma(I)$ . Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

<sup>¶</sup> Note added in proof: after submission of our paper the structure of  $\text{Ph}_3\text{P}=\text{C}(\text{CO}_2\text{Et})\text{CO}(\text{CH}_2)_3\text{CO}_2\text{H}$  was reported, but in that case the delocalisation is mainly into the keto carbonyl group; A. D. Abell, J. Trent and W. T. Robinson, *J. Chem. Soc., Chem. Commun.*, 1991, 362.

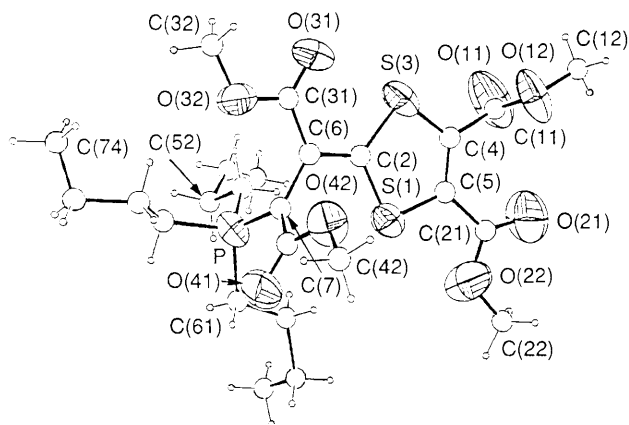
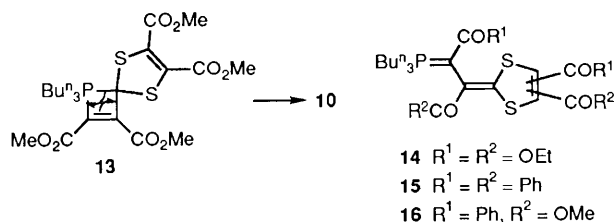


Fig. 1 An ORTEP projection of **10**. [C(41), the atom bonded to C(7), O(41) and O(42), is not labelled for space considerations]. Selected bond lengths (Å) and angles (°): P–C(7) 1.726(5); C(7)–C(41) 1.402(7); C(41)–O(41) 1.234(6); C(41)–O(42) 1.350(6); C(7)–C(6) 1.492(6); C(6)–C(31) 1.450(7); C(31)–O(31) 1.218(6); C(6)–C(2) 1.360(7); C(2)–S(1) 1.733(5); S(1)–C(5) 1.742(5); C(4)–C(5) 1.331(7); P–C(7)–C(41) 116.8(3); C(7)–C(41)–O(41) 126.2(5); P–C(7)–C(6) 120.4(4); C(7)–C(6)–C(31) 123.9(4); C(7)–C(6)–C(2) 118.8(4); S(1)–C(2)–S(3) 114.5(3); C(2)–S(1)–C(5) 95.2(3); S(1)–C(5)–C(4) 117.4(4); torsion angle P–C(7)–C(41)–O(41) 0.0(0.7).



β-oxophosphoranes<sup>8</sup> and with reactivity, dipole moment, UV<sup>9</sup> and IR studies.<sup>10</sup> The compound showed typical reactivity for a stabilised ylide: it could be readily converted by anhydrous acids to phosphonium salts **12** which reformed **10** upon treatment with triethylamine. It was resistant to Wittig reaction with 2,4-dinitrobenzaldehyde under forcing conditions.

The formation of this product is readily explained by initial reaction to give the 1 : 1 adduct of type **2** which then undergoes [2 + 2] cycloaddition with a second DMAD molecule to give phosphacyclobutene **13** followed by electrocyclic ring-opening to give **10**. DMAD is already known to react in this way with phosphinimines,  $\text{Ph}_3\text{P}=\text{NAr}$ ,<sup>11</sup> and with ylides such as  $\text{Ph}_3\text{P}=\text{CHPh}$  and  $\text{Ph}_3\text{P}=\text{CPh}_2$ <sup>12</sup> while both stabilised ylides and phosphinimines are reported to undergo similar [2 + 2] cycloaddition followed by ring-opening with activated nitriles.<sup>13</sup> It is notable that only the 1 : 2 adduct **10** was formed even in the presence of excess of **1** implying that the initial 1 : 1 adduct **2** reacts much more readily with DMAD than does **1**.

Reaction of **1** with other electron-deficient alkynes gave adducts of similar structure: diethyl acetylenedicarboxylate gave **14** (43%, m.p. 90–91 °C,  $\delta_p$  +21.4) and dibenzoylacetylene gave **15** (12%, m.p. 161–162 °C,  $\delta_p$  +19.5). In the case of the unsymmetrical alkyne  $\text{PhCOC}\equiv\text{CCO}_2\text{Me}$  only two of the four possible isomers were formed in a 3 : 2 ratio (23%, m.p. 95–96 °C,  $\delta_p$  +20.5, 20.4). The presence of a two-bond phosphorus coupling ( $\approx 8.5$  Hz) on one  $\text{PhCO}$  signal of each isomer showed these to be the *E*- and *Z*-isomers **16** pointing to complete regioselectivity in the [2 + 2] cycloaddition step. Further results on the cycloaddition of **1** with other types of dipolarophile will be reported shortly.

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