Formation of Novel 1 : 2 Adducts Between $Bu^n{}_3P{\cdot}CS_2$ and Electron-deficient Alkynes

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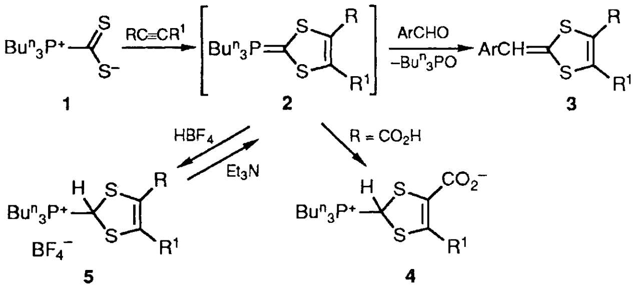
The zwitterionic adduct between tri-n-butylphosphine and carbon disulphide reacts under neutral conditions with two equivalents of dimethyl and diethyl acetylenedicarboxylate, dibenzoylacetylene and methyl benzoylpropiolate to give novel crystalline dithiole-containing ylides whose structure is established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

Although the red crystalline adducts formed between trialkylphosphines and CS_2 were first reported as early as 1860[1] and their zwitterionic phosphoniodithioformate structure was established by X-ray crystallography in 1961,[2] 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.[3] These intermediates can also be trapped by protonation, either intramolecularly[4] to give **4** or by carrying out the addition in the presence of HBF_4 to give **5**.[5] Treatment of the stable salts **5** with Et_3N regenerates the phosphorane **2** thus allowing its use in the construction of a variety of tetrathiafulvalene derivatives of interest as donors for organic conductors.[6] 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



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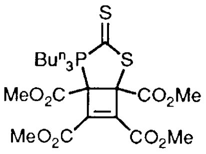
† For enquiries concerning the X-ray structure determination.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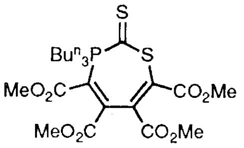
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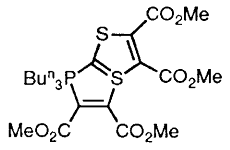
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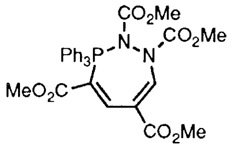
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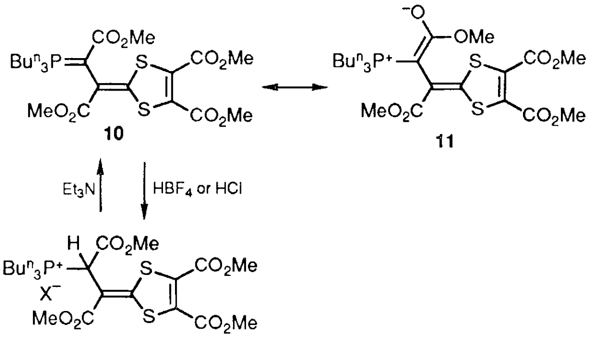

10 **11** **12**

evaporation and column chromatography afforded an adduct as yellow prisms (32%, m.p. 114–115 °C, δ_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[7] in the reaction of Ph_3P and dimethyl azodicarboxylate with methyl propiolate. However none of these structures was in full accord with the ^{13}C NMR spectroscopic data‡ and the real structure was revealed by an X-ray diffraction study§ 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,¶ a feature consistent both with the only previous X-ray structures of

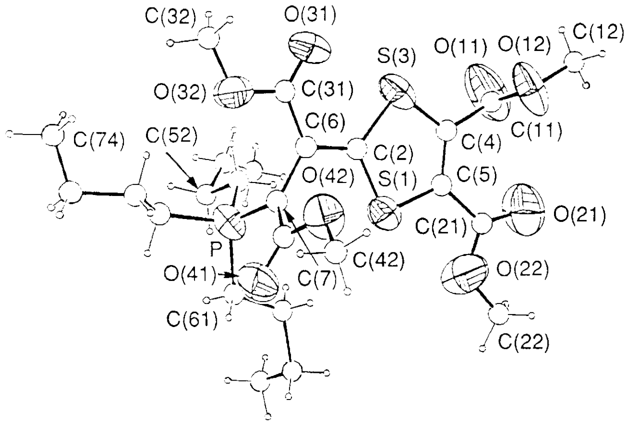
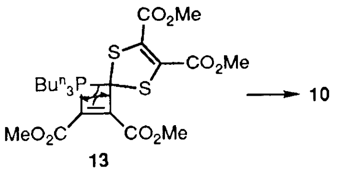


Fig. 1 An ORTEP projection of **10**. [C(41), the atom bonded to C(7), O(41) and O(42), is not labelled for space considerations]. Selected bond lengths (Å) and angles (°): P–C(7) 1.726(5); C(7)–C(41) 1.402(7); C(41)–O(41) 1.234(6); C(41)–O(42) 1.350(6); C(7)–C(6) 1.492(6); C(6)–C(31) 1.450(7); C(31)–O(31) 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).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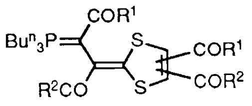
14 R^1 = R^2 = OEt
15 R^1 = R^2 = Ph
16 R^1 = Ph, R^2 = OMe

β-oxophosphoranes[8] and with reactivity, dipole moment, UV[9] and IR studies.[10] The compound showed typical reactivity for a stabilised yield: 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, $Ph_3P{=}NAr$,[11] and with ylides such as $Ph_3P{=}CHPh$ and $Ph_3P{=}CPh_2$[12] while both stabilised ylides and phosphinimines are reported to undergo similar [2 + 2] cycloaddition followed by ring-opening with activated nitriles.[13] 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, δ_P +21.4) and dibenzoylacetylene gave **15** (12%, m.p. 161–162 °C, δ_P +19.5). In the case of the unsymmetrical alkyne $PhCOC{\equiv}CCO_2Me$ only two of the four possible isomers were formed in a 3 : 2 ratio (23%, m.p. 95–96 °C, δ_P +20.5, 20.4). The presence of a two-bond phosphorus coupling (≈8.5 Hz) on one PhCO signal of each isomer showed these to be the *E*- and *Z*-isomers **16** pointing to complete regiospecificity 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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‡ δ_C (75 MHz, $CDCl_3$) 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 $J_{C\text{-}P}$ in Hz).

§ *Crystal data* for **10**: $C_{25}H_{39}O_8PS_2$, 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 β = 100.23(2)°, V = 3039.4 Å^3, Z = 4, D_c = 1.23 g cm^{-3}, μ (Mo-Kα radiation, λ = 0.71073 Å) = 2.6 cm^{-1}. 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.

¶ *Note added in proof*: after submission of our paper the structure of $Ph_3P{=}C(CO_2Et)CO(CH_2)_3CO_2H$ 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.

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