Formation and Structure of a Novel Zwitterionic Phosphoniocyclopentenonide From Bu_3P, DMAD and COS

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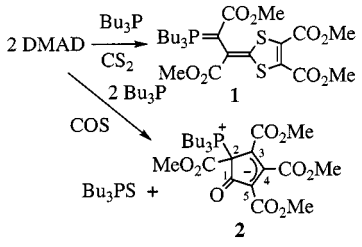
Tributylphosphane, DMAD and carbonyl sulfide react in a 2:2:1 ratio to give Bu_3PS and the crystalline adduct **2** which is stabilised by extensive delocalisation; the sulfur analogue **5** has also been obtained.

Introduction

Some time ago we reported that tributylphosphane, carbon disulfide and DMAD react in a ratio of 1:1:2 to give the stabilised ylide **1**.[1,2] More recently we have described the interaction of tributylphosphane and CS_2 with strained double bonds leading to a variety of synthetically useful cycloaddition processes.[3−6] In an attempt to extend the scope of this work we have investigated the reaction of tributylphosphane and carbonyl sulfide with DMAD and report here the formation and structure of a novel zwitterionic product (Scheme 1).



Scheme 1

Results and Discussion

We initially examined the addition of tributylphosphane to a solution of COS in CH_2Cl_2 at −78 °C but, in contrast to the case of CS_2, where the deep red 1:1 adduct is formed immediately, no colour developed and, upon evaporation, the phosphane was recovered unchanged. This is in agreement with an early report that COS does not form an adduct with trialkylphosphanes.[7] However, addition of DMAD to the cold solution of COS and tributylphosphane led to immediate development of a deep red colour which gradually faded to pale yellow upon warming to room temperature over several hours. Evaporation of the solution followed by chromatography of the residue led to isolation of tributylphosphane sulfide (15%; δ_P = +43.2) and a new crystalline organophosphorus compound (12%; δ_P = +36.2) to which we assign the zwitterionic structure **2**. Analytical and spectroscopic data showed the product to have the composition $Bu_3P{\cdot}CO{\cdot}2DMAD$ and to have four different CO_2Me groups. The ^{13}C NMR spectroscopic data were particularly informative, with the magnitude of the couplings to phosphorus being fully in agreement with the structure **2**. The high frequency of the signal for C-4, which brings it into the region of the ester carbonyls, and the low frequencies for C-3 and C-5 point to the delocalised nature of the allylic anion.

In order to confirm the structure and obtain a measure of the extent of delocalisation we carried out an X-ray structure determination; the resulting structure is shown in Figure 1. The existence of **2** as a stable compound is due to the extensive possible delocalisation of the negative charge and the bond lengths provide support for this. Thus, C(2)−C(3), C(3)−C(4) and C(4)−C(5) are all intermediate between the normal double and single bond lengths and the fact that C(3)−C(8) and C(5)−C(12) are significantly shorter than C(4)−C(10) indicates participation of the C(3) and C(5) ester groups in the delocalisation.

We rationalise the formation of **2** by the sequence of reactions shown in Scheme 2, where tributylphosphane first reacts with two molecules of DMAD in a well precedented process[8] to give the intermediate **3**, which may then attack COS. Electrocyclisation could give a six-membered ring intermediate which may then be desulfurised by a second equivalent of phosphane. Alternatively, the mechanism may involve a seven-membered ring intermediate as shown.

Consideration of the structure of **2** shows that it is nothing more than an adduct between tributylphosphane and tetramethyl cyclopentadienonetetracarboxylate, and this suggested a possible alternative synthesis. On grounds of polarisation, addition of nucleophiles to a cyclopentadienone would normally be expected to occur at the 3-position to give, in this case, the isomeric compound **4** (Scheme 3). However, it is clear that there is more opportunity for delocalisation of the negative charge in **2** and, although **4** might be kinetically favoured, **2** is likely to be a more thermodynamically stable product. In an attempt to confirm this we prepared tetramethyl cyclopentadienonete-

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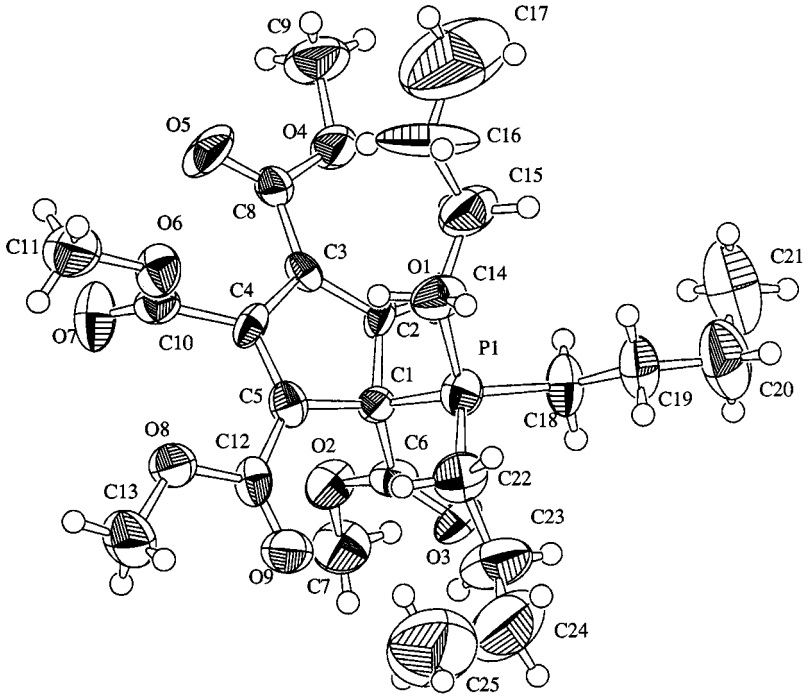
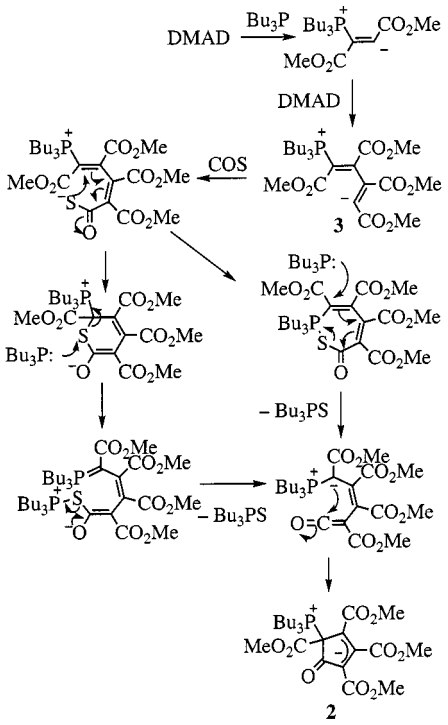
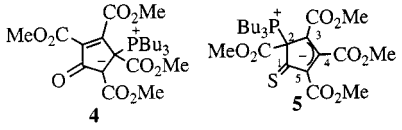


Figure 1. X-ray structure of the zwitterionic compound **2** showing crystallographic numbering scheme; selected bond lengths (Å) and angles (°): P(1)−C(1) 1.870(7), P(1)−C(18) 1.796(7), C(1)−C(2) 1.57(1), C(2)−O(1) 1.220(8), C(2)−C(3) 1.40(1), C(3)−C(4) 1.42(1), C(3)−C(8) 1.45(1), C(4)−C(5) 1.37(1), C(4)−C(10) 1.52(1), C(5)−C(1) 1.51(1), C(5)−C(12) 1.45(1); C(1)−C(2)−C(3) 107.1(8), C(2)−C(3)−C(4) 108.3(9), C(3)−C(4)−C(5) 113.6(8), C(4)−C(5)−C(1) 107.3(8), C(5)−C(1)−C(2) 103.3(7)



Scheme 2

tracarboxylate by the reported method[9] and treated it with an excess of tributylphosphane. Unfortunately, however, reaction with the phosphane was unable to compete with the extremely facile Diels Alder dimerisation of the cyclopentadienone and no new phosphorus-containing products were formed.



Scheme 3

It is clear that the different behaviour of COS and CS_2 in these reactions is due to the failure of the former to form an adduct with tributylphosphane, which is then free to interact with DMAD to give **3**. It occurred to us that the CS_2 reaction might be induced to follow a similar path by adding the reagents together in a different order and indeed this proved to be the case. Thus, when a solution of two equivalents each of Bu_3P and DMAD in CH_2Cl_2 was stirred at 0 °C for 1 h and then one equivalent of CS_2 was added and the mixture stirred at room temperature for 20 h, the corresponding phosphoniocyclopentenethionide **5** (3%) was formed together with Bu_3PS. It seems likely that this type of reaction may also occur with other types of heterocumulene and this is currently under investigation.

Experimental Section

Melting points were recorded on a Reichert hot-stage microscope and are uncorrected. Infra red spectra were recorded as Nujol mulls on a Perkin−Elmer 1420 instrument. NMR spectra were obtained for ^1H at 300 MHz and for ^{13}C at 75 MHz using a Bruker AM300 instrument, and for ^{31}P at 121 MHz using a Varian Gemini 2000 instrument. All spectra were run on solutions in $CDCl_3$ with internal Me_4Si as reference for ^1H and ^{13}C and external 85% H_3PO_4

as reference for ^{31}P. Chemical shifts are reported in ppm to high frequency of the reference and coupling constants *J* are in Hz. Mass spectra were obtained on an AEI/Kratos MS-50 spectrometer by electron impact at 70 eV.

Preparation of 2: A solution of carbonyl sulfide (ca. 0.50 g, 8 mmol) was prepared by bubbling carbonyl sulfide into dichloromethane (25 mL) at −78 °C and to this was added DMAD (2.27 g, 16 mmol) at −78 °C. Tributylphosphane (3.23 g, 16 mmol) was added to give a red colour. The solution was evaporated and flash column chromatography of the red oil (SiO_2, ethyl acetate) gave two fractions.

2,3,4,5-Tetra(methoxycarbonyl)-5-(tributylphosphonio)cyclopent-2-en-1-on-4-ide (**2**) was obtained as yellow crystals (0.48 g, 12%), m.p. 184−192 °C. − IR (CH_2Cl_2): ν = 3055 cm^{-1}, 2987, 2411, 2306, 1713, 1422, 1363, 1268, 1224, 897. − ^1H NMR: δ = 0.95 (t, *J* = 7 Hz, 9 H), 1.4−1.6 (m, 12 H), 2.3−2.45 (m, 6 H), 3.68 (s, 3 H), 3.72 (s, 3 H), 3.76 (s, 3 H), 3.95 (s, 3 H). − ^{13}C NMR: δ = 13.4 (Bu C-4), 17.9 (d, *J* = 45 Hz, Bu C-1), 24.3 (d, *J* = 16 Hz, Bu C-3), 24.9 (d, *J* = 5 Hz, Bu C-2), 50.9 (OMe), 51.4 (OMe), 52.4 (OMe), 53.5 (OMe), 63.6 (d, *J* = 52 Hz, C-2), 96.7 (d, *J* < 2 Hz, C-3), 102.2 (C-5), 162.7, 163.2 (d, *J* = 8 Hz), 163.8, 167.0, 167.1 (C-4), 183.7 (C-1). − ^{31}P NMR: δ = +36.2. − MS (70 eV): *m/z* (%) = 514 (92) [M^+], 483 (75), 455 (65), 411 (30), 312 (75), 281 (70), 76 (100). − $C_{25}H_{39}O_9P$ (514.6): calcd. C 58.35, H 7.64; found C 58.54, H 7.70.

Tributylphosphane sulfide (0.28 g, 15%): ^1H NMR: δ = 0.96 (t, *J* = 3 Hz, 9 H), 1.38−1.64 (m, 12 H), 1.77−1.90 (m, 6 H). − ^{31}P NMR: δ = +43.2.

Preparation of 5: A Solution of tributylphosphane (1.42 g, 7 mmol) and DMAD (1.00 g, 7 mmol) in dichloromethane (50 mL) was stirred at 0 °C for 1 h. Carbon disulfide (0.53 g, 7 mmol) was added dropwise whereupon the solution immediately turned red. The solution was allowed to stir for 20 h at room temp. and then evaporated. Flash column chromatography (SiO_2, petroleum/diethyl ether/ethyl acetate, 1:1:1) gave mainly the known adduct **1** but a minor fraction was found to be 2,3,4,5-tetra(methoxycarbonyl)-5-(tributylphosphonio)cyclopent-2-en-1-thion-4-ide (**5**) as a brown oil (50 mg, 3%). − ^1H NMR: δ = 0.94 (t, *J* = 7 Hz, 9 H), 1.4−1.8 (m, 12 H), 2.15−2.30 (m, 6 H), 3.25 (s, 3 H), 3.70 (s, 3 H), 3.77 (s, 3 H), 3.95 (s, 3 H). − ^{13}C NMR: δ = 13.2 (Bu C-4), 16.5 (d, *J* = 43 Hz, Bu C-1), 24.0 (d, *J* = 16 Hz, Bu C-3), 24.2 (d, *J* = 6 Hz, Bu C-2), 50.7 (OMe), 50.8 (OMe), 52.1 (OMe), 53.7 (d, *J* = 12 Hz, OMe), 85.5 (d, *J* = 64 Hz, C-2), 93.5 (C-3), 101.1 (C-5), 162.2, 163.6, 165.2 (d, *J* = 10 Hz), 167.5 (2 C), 188.6 (d, *J* = 2 Hz, C-1). − ^{31}P NMR: δ = +36.1. − MS (CI): *m/z* (%) = 486 (7) [MH^+ − Bu], 456 (18), 424 (100), 395 (54).

Crystal data for 2: $C_{25}H_{39}O_9P$, *M* = 514.55, yellow plate, crystal dimensions 0.35 × 0.15 × 0.03 mm, monoclinic, space group $P2_1/c$ (#14), *a* = 8.369(5), *b* = 37.561(8), *c* = 9.21(1) A, β = 101.50(7)°, *V* = 2837(3) A^3, *Z* = 4, D_c = 1.205 Mg m^{-3}, *T* = 293 K, *R* = 0.103, R_W = 0.095 for 1848 reflections with $I > 3\sigma(I)$ and 317 variables. Data were collected on a Rigaku AFC7S diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71069 A). The structure was solved by direct methods (SIR92) and refined by full-matrix least-squares methods.

Crystallographic data (excluding structure factors) for the structure included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139580. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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