A New Crystalline Zwitterionic Product from the Reaction of Bu_3P and DMAD

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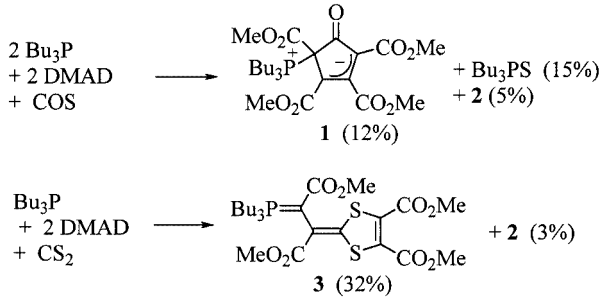
Tributylphosphane reacts with DMAD to give the crystalline adduct **2** which is stabilised by extensive delocalisation and whose formation involves an unusual rearrangement. The isomeric structure **7** for the previously reported adduct with triphenylphosphane is supported by ^{13}C NMR spectroscopy.

Introduction

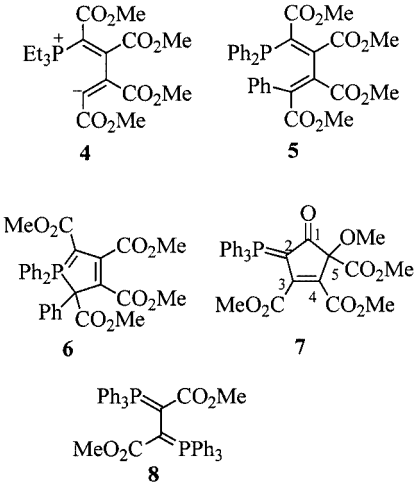
We recently reported that tributylphosphane, DMAD and carbonyl sulfide react in a ratio of 2:2:1 to give Bu_3PS and the novel zwitterionic product **1**, whose structure was proved beyond doubt by X-ray diffraction.[1] At the same time it was mentioned that, by adding CS_2 to a solution of Bu_3P and DMAD, the major 1:1:2 adduct **3**[2] was accompanied by a minor product **2** which we suspected to be the thione analogue of **1** based on the available spectroscopic data (Scheme 1). Further work has now revealed that this same product can also be isolated in low yield from the reaction of Bu_3P and DMAD with COS (5%) or PhNCS (8%) and, more significantly, also with PhNCO (5%) and even PhNCNPh (7%), thus clearly ruling out the thione structure. We now report the isolation of this new product in pure form, its unambiguous characterisation and structure determination, and a plausible mechanism for its formation.



Scheme 1

Results and Discussion

Compound **2** was obtained in low yield by stirring a solution of Bu_3P and DMAD in CH_2Cl_2 at room temp. for 24 h followed by evaporation of the solvents and chromatographic purification. It exhibits very similar spectroscopic data to **1**, with an essentially identical ^{31}P NMR shift (**2**: $\delta_P = +36.1$ ppm; **1**: $\delta_P = +36.2$ ppm) and the only significant differences from the ^1H and ^{13}C NMR spectroscopic data of **1** being the shift of one of the four OMe signals from the range $\delta_H = 3.7-4.0$ ppm down to $\delta_H = 3.25$ ppm, and the apparent absence of one ester carbonyl signal. The interaction of phosphanes with DMAD in various ways has been known for a long time. Almost 50 years ago Horner and Hoffmann suggested structure **4** for the 2:1 adduct formed with triethylphosphane,[3] while, depending upon the reacting ratios, triphenylphosphane can form either the 2:1 adduct initially thought to be **5**[4] but later corrected to **6**,[5] together with the isomeric ylide **7**,[6] or the 1:2 adduct **8**.[7]



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Although analytical and mass spectrometric data confirmed our adduct **2** to have the formula $Bu_3P{\cdot}2DMAD$, the highly informative ^{31}P coupled ^{13}C NMR spectroscopic data were not in agreement with structures corresponding to **4**−**8** but were indicative of a close analogue of **1**. The problem was finally solved when crystals of **2** suitable for X-ray diffraction were obtained. The resulting structure is shown in Figure 1 and is simply the analogue of **1** with the CO_2Me group on C(2) replaced by OMe.

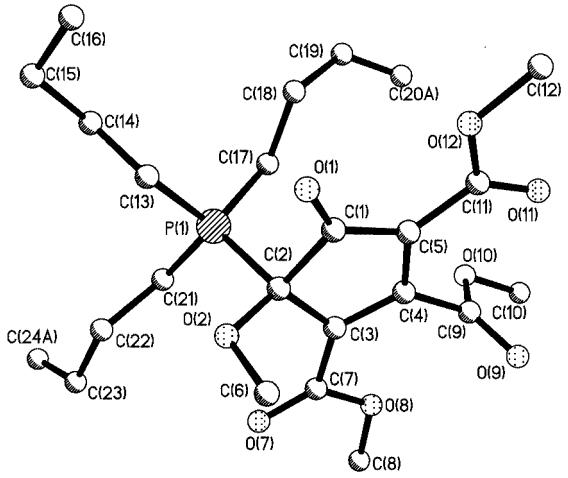
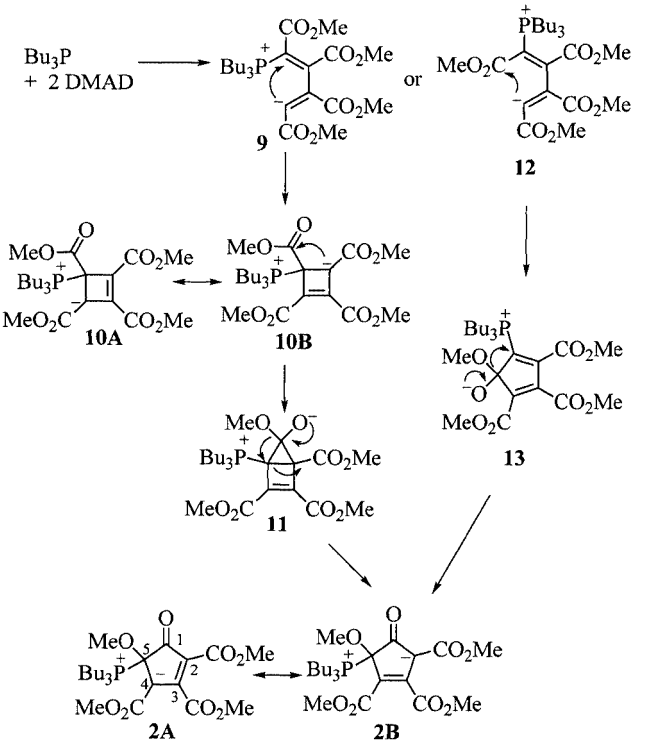


Figure 1. X-ray structure of the zwitterionic compound **2** showing crystallographic numbering scheme; selected bond lengths (Å) and angles (°): P(1)−C(2) 1.853(4), P(1)−C(21) 1.796(5), C(1)−C(2) 1.569(5), C(1)−O(1) 1.227(4), C(2)−C(3) 1.522(5), C(3)−C(4) 1.376(5), C(3)−C(7) 1.442(5), C(4)−C(5) 1.418(5), C(4)−C(5) 1.418(5), C(4)−C(9) 1.495(9), C(5)−C(1) 1.426(5), C(5)−C(11) 1.433(6); C(1)−C(2)−C(3) 103.0(3), C(2)−C(3)−C(4) 107.2(3), C(3)−C(4)−C(5) 114.0(3), C(4)−C(5)−C(1) 107.9(3), C(5)−C(1)−C(2) 107.0(3)

As in the case of **1**, this is stabilised by extensive delocalisation. Thus, C(3)−C(4), C(4)−C(5) and C(5)−C(1) are all intermediate between the normal double and single bond lengths and the fact that C(3)−C(7) and C(5)−C(11) are significantly shorter than C(4)−C(9) indicates participation of the C(3) and C(5) ester groups in the delocalisation. The delocalised nature of the allyl anion as shown in structures **2A/2B** is also reflected in the ^{13}C NMR chemical shifts of δ_C = 93.5 and 101 ppm for C-2 and C-4, while C-3 gives a signal in the carbonyl region at just over δ = 160 ppm.

We rationalise the formation of **2** by the sequence of reactions shown in Scheme 2 where, as in the formation of **1**,[1] tributylphosphane first reacts with two molecules of DMAD to give the intermediate **9** corresponding to Horner's adduct **4**. Rather than interact with the added heterocumulene, this may undergo cyclisation to give the resonance-stabilised cyclobutenide structure **10**. A further cyclisation gives the strained bicyclo[2.1.0]pentene intermediate **11** which then undergoes a 1,2-shift of the methoxy group to afford **2** directly. Alternatively the process may involve the isomeric adduct **12** which can cyclise directly to the five-membered ring intermediate **13** which then undergoes a 1,2-methoxy shift to afford **2**.



Scheme 2

In view of the structure found for **2** we thought it worthwhile checking that the compound obtained by Tebby and co-workers did indeed have the structure **7** and was not instead the triphenyl analogue of **2**. The compound was readily prepared by reacting Ph_3P with DMAD in boiling diethyl ether followed by chromatographic separation of **6** and **7**. The ^{13}C NMR spectrum confirmed that structure **7** is correct for the minor product, the key difference being the large phosphorus coupling ($J_{P,C}$ = 119 Hz) observed for the doubly bonded ylide carbon as compared to the smaller value ($J_{P,C}$ = 64 Hz) for the singly bonded carbon of **2**. The spectrum also revealed a high extent of polarisation of the ring double bond (δ = 87.0, 160.0 ppm) as expected for a β,γ-unsaturated ylide structure. It seems likely that the ylide **7** also results from a 1,2-methoxy shift in the intermediate corresponding to **13** but, perhaps because of the greater steric bulk of the Ph_3P group, it occurs in the opposite sense to give the product with OMe on the other side of the carbonyl group to phosphorus.

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 using chemical ionisation with isobutane as ionising gas.

Preparation of Adduct 2: A Solution of tributylphosphane (2.02 g, 10 mmol) and DMAD (2.84 g, 20 mmol) in dichloromethane (50 mL) was stirred at room temp. for 20 h and then the solvents were evaporated. Flash-column chromatography of the residue (SiO_2, hexane/ethyl acetate, 1:1) gave mainly hydrolysis products such as Bu_3PO, dimethyl fumarate and unchanged DMAD but a minor fraction was found to be 5-methoxy-5-tributylphosphonio-2,3,4-tri(methoxycarbonyl)cyclopent-2-en-1-on-4-ide (**2**; 0.42 g, 9%) as yellow prisms, m.p. 143−144 °C. IR (Nujol): $\tilde{\nu}$ = 1735 cm^{-1}, 1658, 1513, 1347, 1100, 1017, 918, 785, 759, 725, 630. ^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, 5-OMe), 3.70 (s, 3 H), 3.77 (s, 3 H), 3.95 (s, 3 H) ppm. ^{13}C NMR: δ = 13.2 (d, *J* = 1 Hz, Bu C-4), 16.5 (d, *J* = 43 Hz, Bu C-1), 24.05 (d, *J* = 15 Hz, Bu C-3), 24.14 (d, *J* = 5 Hz, Bu C-2), 50.6 (OMe), 50.8 (OMe), 52.1 (OMe), 53.6 (d, *J* = 13 Hz, 5-OMe), 85.4 (d, *J* = 64 Hz, C-5), 93.5 (d, *J* = 2 Hz, C-4), 101.1 (C-2), 162.1 and 163.5 (each d, *J* = 1 Hz, 2-CO and C-3), 165.1 (d, *J* = 10 Hz, 4-CO), 167.5 (3-CO), 188.5 (d, *J* = 3 Hz, C-1) ppm. ^{31}P NMR: δ = +36.1 ppm. MS (CI): *m*/*z* (%) = 487 (5) [MH^+], 455 (7), 285 (88), 253 (50), 219 (19), 203 (100). $C_{25}H_{39}O_8P$ (486.58): calcd. C 59.24, H 8.08; found C 59.43, H 8.35.

The same product was also obtained by stirring a solution of Bu_3P (10 mmol) and DMAD (20 mmol) in dichloromethane (50 mL) in the presence of a heterocumulene (10 mmol) at room temp. for 24 h followed by evaporation of the solvents and chromatography as above. The yields obtained were: CS_2 0.14 g (3%); COS 0.24 g (5%); PhNCO 0.24 g (5%), PhNCS 0.39 g (8%), PhN=C=NPh 0.34 g (7%).

Crystal Data for 2: $C_{24}H_{39}O_8P$, *M* = 486.52, yellow prism, crystal dimensions 0.19 × 0.1 × 0.1 mm, monoclinic, space group $P2_1/c$, *a* = 8.4495(1), *b* = 35.479(1), *c* = 9.1735(3) Å, β = 99.527(1)°, *V* = 2712.1(1) $Å^3$, *Z* = 4, D_c = 1.192 $Mg·m^{-3}$, *T* = 293 K, R = 0.0603, R_W = 0.1314 for 1993 reflections with $I > 2\sigma(I)$ and 317 variables. Data were recorded on a Bruker SMART diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined using full-matrix least-squares methods.

CCDC-187176 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Preparation of Adduct 7: Reaction of Ph_3P with 2 equiv. of DMAD in boiling diethyl ether following the method of Tebby and co-workers[6] gave, after chromatographic separation, compound **6** (38%; ^{31}P NMR: δ = +49.5 ppm) and compound **7** (13%) as yellow crystals, m.p. 224−226 °C (ref.,[6] 222−224 °C). ^1H NMR: δ = 3.10 (s, 3 H, 5-OMe), 3.42 (s, 3 H), 3.67 (s, 3 H), 3.78 (s, 3 H), 7.45−7.70 (m, 15 H) ppm. ^{13}C NMR: δ = 51.0 (OMe), 51.7 (OMe), 52.3 (2 × OMe), 70.6 (d, *J* = 119 Hz, P=C), 87.0 (d, *J* = 13 Hz, C-4), 107.4 (d, *J* = 10 Hz, C-5), 121.9 (d, *J* = 93 Hz, Ph C-1), 128.9 (d, *J* = 13 Hz, Ph C-3), 133.2 (Ph C-4), 134.0 (d, *J* = 10 Hz, Ph C-2), 160.0 (d, *J* = 14, C-3), 162.2, 166.1 and 168.0 (3 × CO_2Me), 194.9 (d, *J* = 8 Hz, CO) ppm. ^{31}P NMR: δ = +11.7 ppm.

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