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Formation of Novel 1:2 Adducts Between $Bu^n_3P.CS_2$ and Electron-deficient Alkynes†

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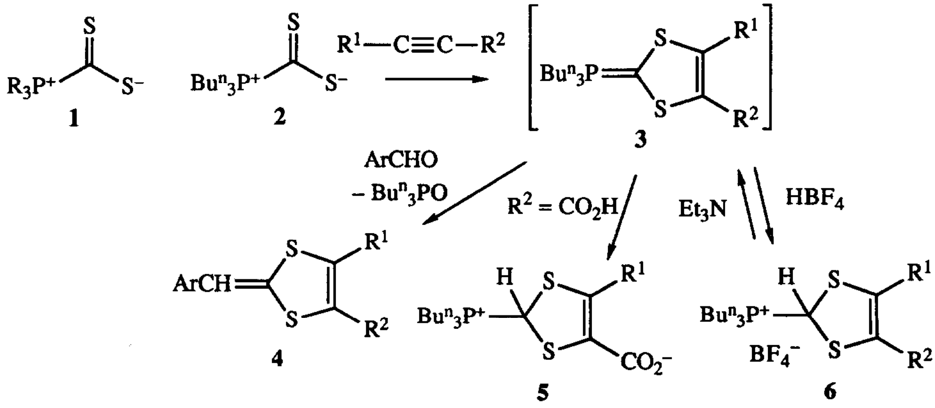
Abstract: The zwitterionic adduct between tri-n-butylphosphine and carbon disulphide reacts under neutral conditions with two equivalents of dimethyl- and diethyl acetylenedicarboxylate, dibenzoylacetylene and methyl benzoylpropiolate to give novel crystalline dithiole-containing phosphorus ylides. An X-ray structure, spectroscopic and chemical properties all show these to be significantly stabilised by delocalisation.

In 1861 A. W. Hofmann reported the occurrence of a violently exothermic reaction between the newly discovered trialkylphosphines and carbon disulphide to give red crystalline adducts.[1] Over the succeeding century the chemistry of these adducts was little studied and their formation was mainly used as a confirmatory colour test for the presence of phosphines.[2] The considerable controversy over their structure[3] was finally settled in 1961 when an X-ray diffraction study on $Et_3P.CS_2$ showed it to have the trialkylphosphoniodithioformate structure **1**.[4] Despite the apparent synthetic potential of this unusual 1,3-dipolar structure, studies on its cycloaddition have largely been confined to electron-deficient alkynes as dipolarophiles. Thus Hartzler[5] reported the formation of 2-alkylidene-1,3-dithioles **4** in good yield upon treating **2** with dimethyl acetylenedicarboxylate (DMAD) in the presence of aromatic aldehydes to trap the intermediate phosphoranylidenedithiole **3** by a Wittig reaction. Addition of **2** to propiolic or acetylenedicarboxylic acid was accompanied by intramolecular proton transfer in the



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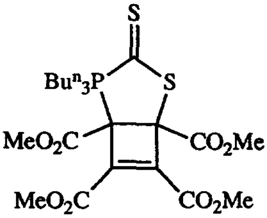
† Dedicated to Professor Charles Rees on the occasion of his retiral from the Hofmann Chair of Organic Chemistry at Imperial College

initial adducts **3** to give **5**.[6] A most useful development was the discovery by Cava[7] that intermolecular protonation of **3** was also possible by carrying out the addition to DMAD in the presence of anhydrous HBF_4. The resulting stable salt **6** acts as a convenient source of **3** by simple treatment with Et_3N and this has allowed the use of **3** in the construction of a variety of tetrathiafulvalene analogues of interest as electron donors for organic conductors.[8]

We have undertaken a detailed study of the cycloaddition reactions of **2** with a wide range of different dipolarophile types and describe here details of the reaction with electron-deficient alkynes such as DMAD under neutral conditions.[9]

Results and Discussion

Reaction of **2** with one equivalent of DMAD in either Et_2O or CH_2Cl_2 resulted in a slow reaction to produce a new adduct, isolated after flash chromatography and recrystallisation as yellow prisms. Analytical and spectroscopic data clearly showed this to be a 1:2 adduct with, for example, four different CO_2Me signals in both ^1H and ^{13}C NMR spectra. This initially suggested that the cycloaddition might have taken place across the P and S atoms to give a structure such as **7**, **8** or **9**. Structure **8** in particular had a precedent in the intermediate adduct



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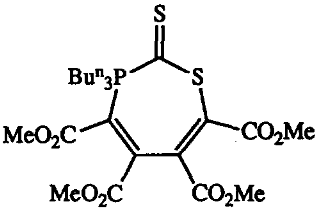

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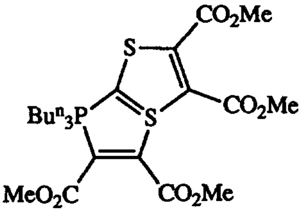

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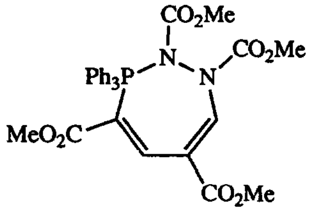

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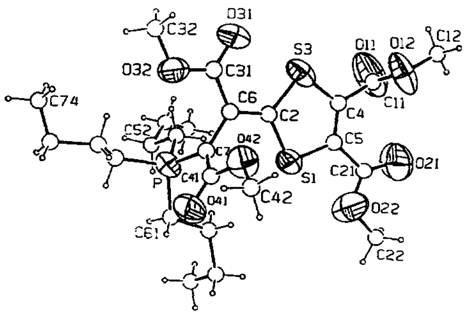
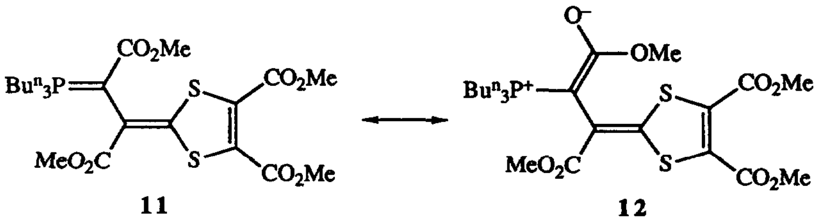
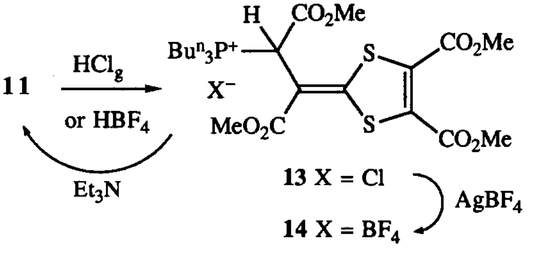


X-ray Structure of **11**

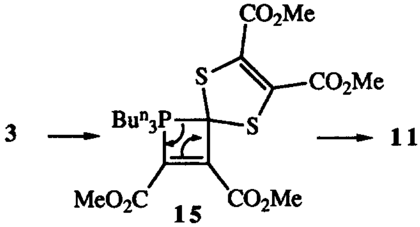


11 **12**

10 postulated by Huisgen in the reaction of triphenylphosphine and dimethyl azodicarboxylate with methyl propiolate.[10] However careful examination of the ^{13}C NMR data, and in particular the highly informative P-C coupling constants, made it clear that none of these was the correct structure. The true structure was only revealed by a single crystal X-ray diffraction study to be **11**. Details of the structure determination together with the main features of the structure have already been reported.[9] The significant contribution from the phosphonium enolate form **12** ,which is clear from the bond lengths[11], is reflected in the reactivity of this ylide. It is a typical stabilised ylide which is readily converted to the conjugate phosphonium salts **13** and **14** on treatment with mineral acids and can be reformed from them with a weak base such as Et_3N. This makes it quite unreactive in the Wittig reaction and it was recovered unchanged after heating with 2,4-dinitrobenzaldehyde for an extended period.



13 X = Cl
14 X = BF_4



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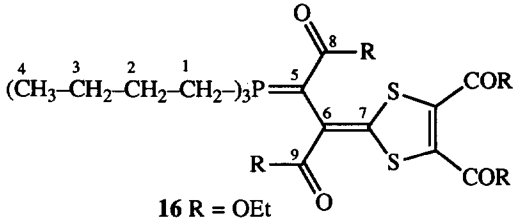
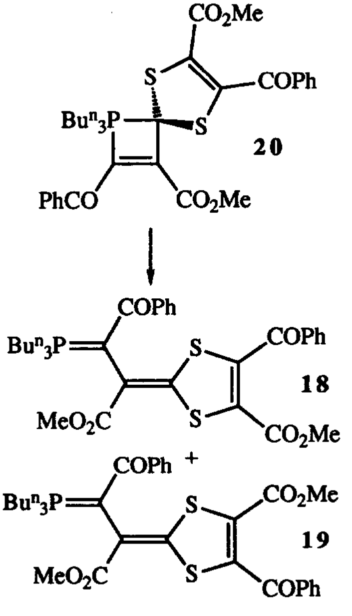
The mechanism of the reaction seems clear: addition of **2** initially occurs in the expected way to afford the phosphoranylidenedithiole of type **3**. In the absence of any other trap this undergoes a [2 + 2] cycloaddition with a second molecule of DMAD to give phosphacyclobutene **15** which then undergoes electrocyclic ring-opening to **11**. This type of reaction, which results in overall insertion of the DMAD fragment into the P=C bond has previously been reported between DMAD and both phosphinimines, $Ph_3P{=}NAr$,[12] and ylides such as $Ph_3P{=}CHPh$ and $Ph_3P{=}CPh_2$.[13] More recently activated nitriles were reported to undergo similar


16 R = OEt
17 R = Ph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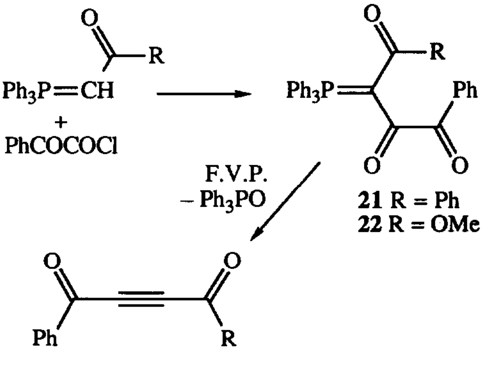


21 R = Ph
22 R = OMe

[2 + 2] cycloaddition followed by ring-opening with stabilised ylides and phosphinimines.[14] It is notable that only the 1:2 adduct **11** is formed, even in the presence of an excess of **2**, implying that the intermediate 1:1 adduct reacts with DMAD much more readily than does **2**.

Other electron-deficient alkynes give adducts of similar structure. Thus, diethyl acetylenedicarboxylate and dibenzoylacetylene give **16** and **17** respectively. In the case of the unsymmetrical methyl benzoylpropiolate only two of the four possible isomers were formed and the observation of a substantial P-C coupling on one Ph$\underline{C}$O signal of each ($^2J_{P\text{-}C}$ 8.5 Hz) made it clear that these were the *E* and *Z* isomers **18** and **19**. By analogy with **17** the alternative isomers would be expected to have $^3J_{P\text{-}C}{\approx}0$ for Ph$\underline{C}$O and $\delta_{C\text{-}5}$ nearer to 41.7 than to 71.8. This points to complete regioselectivity in the [2+2] cycloaddition to give only **20** which can then open with formation of the new C=C double bond in either sense as shown.

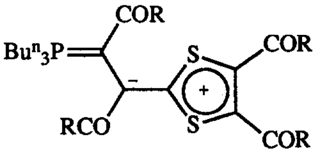
The dibenzoylacetylene and methyl benzoylpropiolate required for this study were conveniently obtained in good yield by flash vacuum pyrolysis of the novel β,γ,β'-trioxoylides **21** and **22** as shown. Further details of this route will be reported elsewhere.[15]

The ^{13}C NMR data for these compounds, summarised in **Table 1**, are particularly informative. The significant P-C coupling to C-8 in **11** and **16** which is greatly reduced on protonation to **13** or **14** provides additional evidence for the contribution of the enolate form **12**. The smaller P-C-8 coupling in the ketone stabilised compound **17** suggests more delocalisation than in the ester stabilised cases.[16] The chemical shift values

Table 1: ^{13}C NMR data – δ_C in ppm ($J_{C\text{-}P}$ in Hz) – Numbering as in **16** (*= assignments may be interchanged)

Compound No.	**11**	**16**	**17**	**13**	**14**	**18/19**
C-1	21.8 (55)	21.1 (55)	22.5 (53)	20.0 (44)	19.6 (44)	21.5/21.8 (53)
C-2	24.2 (3)	24.4 (3)	25.0 (4)	24.4 (5)	24.1	24.6/24.8 (4)
C-3	23.9(15)	24.0 (15)	24.2 (15)	24.1 (16)	24.0 (14)	24.1/24.2 (13)
C-4	13.4	13.4	13.5	13.4	13.3	13.6/13.7
C-5	41.7 (122)	41.8 (122)	71.8 (100)	45.7 (53)	45.1 (53)	66.1/65.7 (103)
C-6	109.1 (9)	109.4 (9)	117.3 (9)	100.6 (4)	100.5 (5)	110.4/110.6
C-7	166.4 (15)	166.2 (15)	167.2 (6)	166.3*	166.0*	162.4/162.5
C-8	168.8 (20)	168.7 (20)	182.0 (8)	163.4	163.0 (6)	186.2/186.7 (8.5)
C-9	161.2 (6)	161.1 (6)	189.6*	159.3*	159.3*	167.5/167.7*
Other Signals	**11** 130.3, 135.9 (ring carbons 4+5), 160.0, 167.4 (C=O on ring), 49.6, 51.2 and 52.9 (2C) 4 x Me). **16** 130.3, 136.1 (ring carbons 4+5), 159.8, 167.4 (C=O on ring), 13.7 (2C), 14.4, 15.1, 57.5, 60.3 and 62.2 (2C) (4 x Et). **17** 136.6, 136.7, 138.1, 139.4, 140.4 and 144.8 (ring carbons 4+5 and C-1 of Ph), 187.0, 187.1 (C=O on ring)*, 127.1, 127.9, 128.0, 128.2, 128.5, 128.6, 128.7, 128.8, 128.9, 129.4, 130.9 and 133.7 (CH of 4 x Ph). **13** 129.8, 137.0 (ring carbons 4+5), 158.6, 164.3 (C=O on ring)*, 52.8, 53.9, 54.0 and 54.1 (4 x Me). **14** 129.2, 137.6 (ring carbons 4+5), 158.4, 164.2 (C=O on ring)*, 52.9, 53.9, 54.0 and 54.2 (4 x Me). **18/19** 159.4/159.2 ($\underline{C}O_2Me$ on ring)*, 188.3/187.4 ($\underline{C}$OPh on ring), 51.71/51.66 and 52.64/52.73 (Me), 133.2, 134.4, 134.5, 135.3, 135.4, 142.6, 142.7 and 148.2 (ring carbons 4+5 and C-1 of Ph), 126.4, 126.6, 127.1, 127.3, 128.4, 128.6, 128.9, 129.2, 131.9, 132.1, 134.4 and 134.5 (CH of Ph).					

for C-6 (100-120) and C-7 (160-170) in all the compounds indicate a significant polarisation of this double bond in the sense indicated by the extreme structure **23**. The chemical shift values for **24** shown provide a useful comparison.[8b] The negative charge at C-6 can be stabilised by enolate formation while the dithiolium cation is stabilised as it is a 6π-system. Protonation of ylide **11** to form **13** or **14** does result in increased shielding at C-6 indicating a greater contribution from structure **25**. The 8π-system involved in resonance structure **26** is highly disfavoured and there is no evidence for any contribution from this. A further feature of interest occurs in the ^1H NMR spectra of the phosphonium salts. The signal due to the single CH occurs at δ 5.9 in the chloride **13** but at δ 4.7 in tetrafluoroborate **14**. We attribute this sizeable difference to a conformational change between **13**, where Cl^- coordinates to P^+, and **14** where the non-coordinating nature of BF_4^- means that one of the ester oxygens has to fulfill this role.



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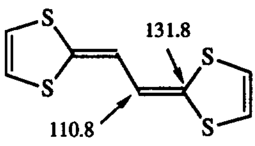

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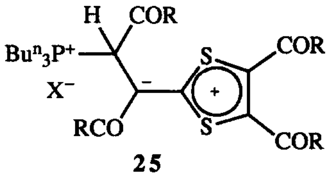

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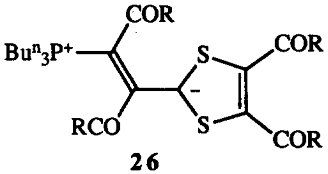

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We have thus confirmed the previous finding that the tributylphosphine - carbon disulphide adduct **2** reacts with electron-deficient alkynes to initially give **3**. In the absence of a suitable trapping reagent, however, this rapidly reacts with a further molecule of alkyne in a [2+2] fashion to give 1:2 adducts such as **11** *via* the phosphacyclobutene **15**. Reaction of **2** with other types of dipolarophile to give a wide variety of adducts of novel structure will be reported shortly.

Experimental

General

All NMR spectra were recorded on solutions in deuteriochloroform. ^1H spectra were recorded at 300 MHz and ^{13}C spectra at 75 MHz on a Bruker AM300 instrument with tetramethylsilane as internal reference. ^{31}P spectra were recorded at 32 MHz on a Varian CFT20 instrument and are referenced to external H_3PO_4. Low and high resolution mass spectra were obtained on a Finnegan Incos 50 mass spectrometer. Elemental analyses for C and H were performed on a Carlo-Erba 1106 analyser and analyses for P and S were carried out by the Department of Chemistry, University of Durham. Melting points were determined on a Reichert hot-stage microscope and are uncorrected. Column chromatography was performed using BDH silica gel for flash chromatography (particle size 40-63 μm).

1. Preparation of tri-n-butylphosphoniodithioformate 2

Tri-*n*-butylphosphine (20 g, 0.10 mol) in dry petroleum ether (b.p. 40-60°C, 50 ml) was added dropwise to a mixture of carbon disulphide (7.5 g, 0.10 mol) and dry petroleum ether (100 ml) at 0-5°C. After complete addition the mixture was stirred at R.T. for a further 4-5 h. The product was filtered off and washed with petroleum ether to give **2** as dark red needles (19.7 g, 74%), m.p. 65-66°C (lit.[2a], m.p. 65.5°C).

2. *Reaction of 2 with alkynes*

a. *With dimethyl acetylenedicarboxylate*

Dimethyl acetylenedicarboxylate (2.04 g, 14.4 mmol) was added to a well stirred solution of tri-*n*-butylphosphoniodithioformate **2** (2.0 g, 7.2 mmol) in dry ether or dichloromethane (50 ml) and the mixture stirred for 18 h at R.T. Evaporation of the solvent gave a thick red oil. Flash column chromatography of this (silica gel, ethyl acetate:ether 1:1) followed by recrystallisation from hexane gave the 1:2 adduct **11** (1.3 g, 32%) as bright yellow prisms, m.p. 114-115°C. (Found: C, 53.7; H, 6.95; S, 11.2; P, 5.6. $C_{25}H_{39}O_8PS_2$ requires C, 53.4; H, 7.0; S, 11.4; P, 5.5%); δ_P +21.9; δ_H 0.90 (9H, t), 1.4-1.6 (12H, m), 1.8-2.25 (6H, m), 3.55 (3H, s), 3.75 (3H, s), 3.90, (3 H, s) and 3.92 (3 H, s); δ_C See Table 1; m/z 562 (M^+, 7%), 491 (14.5), 361 (48), 344 (11), 301 (23), 285 (16), 259 (10), 243 (33), 201 (72), 176 (17), 159 (20), 145 (21), 117 (16) and 59 (100).

b. *With diethyl acetylenedicarboxylate*

A solution of diethyl acetylenedicarboxylate (2.5 g, 14.4 mmol) in dichloromethane (10 ml) was added to a well stirred solution of tri-*n*-butylphosphoniodithioformate **2** (2.0 g, 7.2 mmol) in dichloromethane (10 ml) and the mixture stirred at R.T. for 48 h. Evaporation of the solvent gave a dark orange oil which upon column chromatography (silica gel; ether:petroleum ether 2:1) gave the 1:2 adduct **16** (1.80 g, 43%) as yellow prisms, m.p. 90-91°C. (Found: C, 55.8; H, 7.0; m/z 618.2443. $C_{29}H_{47}O_8PS_2$ requires C, 56.3; H, 7.6% ; m/z 618.2450); δ_P +21.4; δ_H 0.9-1.5 (33H, m), 2.0 (6H, m) and 4.0-4.4 (8H, m); δ_C See Table 1; m/z 618 (M^+, 33%), 573 (7), 545 (9), 533 (84), 417 (100), 387 (70), 372 (10), 359 (9), 345 (41), 309 (10), 299 (13), 271 (16), 259 (23), 201 (80), 190 (16), 171 (20), 159 (14), 145 (16) and 103 (21).

c. *With dibenzoylacetylene*

A solution of tri-*n*-butylphosphoniodithioformate **2** (1.1 g, 4 mmol) in dry dichloromethane (10 ml) was added to a well stirred solution of the dibenzoylacetylene (0.9 g, 4 mmol) in dichloromethane (10 ml) and the reaction mixture was stirred for 18 h at R.T. Evaporation of the solvent gave an orange oil which upon column chromatography (silica gel, ether:ethyl acetate, 1:1) followed by crystallisation from hexane gave a sticky orange solid. Trituration with petroleum ether gave the 1:2 adduct **17**, (0.13 g, 12%) as an orange-red solid, m.p. 161-162°C. (Found: C, 71.7; H, 6.5 ; m/z 746.2643. $C_{45}H_{47}O_4PS_2$ requires C, 72.4; H, 6.3% ; m/z 746.2653); δ_P +19.54; δ_H 0.75-2.0 (27H, m) and 7.2-8.0 (20H, m); δ_C See Table 1; m/z 746 (M^+, 5%), 641 (3), 528 (7), 500 (5), 480 (5), 239 (12), 189 (25), 149 (25) and 105(100).

d. *With methyl benzoylpropiolate*

A solution of tri-*n*-butylphosphoniodithioformate **2** (0.28 g, 1 mmol) in dichloromethane (10 ml) was added to a well stirred solution of methyl benzoylpropiolate (0.19 g, 1 mmol) in dichloromethane (10 ml) and the mixture was stirred at R.T. for 48 h. Evaporation of solvent gave a brown oil which upon flash column chromatography (silica gel, ethyl acetate) gave the 1:2 adduct **18**/**19** as a 3:2 mixture of isomers (0.15 g, 23%) as an orange solid, m.p. 95-96°C. (Found: C, 64.8; H, 6.6. $C_{35}H_{43}O_6PS_2$ requires C, 64.2; H, 6.6%). δ_P +20.50 and +20.42; δ_H (major isomer) 0.75-2.5 (27H, m), 3.55 (3H, s), 3.9 (3H, s) and 7.2-8.0 (10H, m) (minor isomer) 0.75-2.5 (27H, m), 3.6 (3H, s), 3.8 (3H, s) and 7.2-8.0 (10H, m); δ_C see Table 1; m/z 654 (M^+, 36%), 596 (22), 549 (29), 526 (14), 436 (22), 419 (14), 405 (10), 387 (9), 378 (16), 363 (9), 349 (6.5), 334 (7), 219 (6), 201 (10), 189 (12), 161 (14) and 105 (100).

3. *Formation and Reactions of Phosphonium salts 13 and 14*

a. *Reaction of 11 with HCl*

A solution of the adduct **11** (0.5 g, 1 mmol) in dry ether (15 ml) was stirred at 0-5°C (ice bath) while HCl gas was passed through for 15 min. A sticky yellow solid precipitated out which crystallised on standing giving the corresponding phosphonium chloride **13** (0.15 g, 25%) as a pale yellow solid, m.p. 60-61°C. δ_P +39.2; δ_H 0.95 (9H, t), 1.4-1.7 (12H, m), 2.4-2.8 (6H, m), 3.75 (3H, s), 3.85 (3H, s), 3.90 (3H,s), 3.95 (3H, s) and 5.9 (1H, d, J 20 Hz); δ_C See Table 1; m/z 562 (M^+–HCl, 5%), 504 (20), 491 (8), 473 (6), 445 (9), 433 (40), 405 (10), 391 (9), 373 (9), 361 (19), 345 (9), 303 (100), 287 (23), 271 (9), 252 (12), 243 (21), 201 (49), 185 (21), 173 (25), 159 (18), 148 (18), 131 (13) and 117 (14). The hygroscopic nature of this salt prevented satisfactory analytical data from being obtained but its identity is established by conversion to the more stable tetrafluoroborate **14**.

*b. Reaction of **11** with HBF_4*

Tetrafluoroboric acid etherate (0.175 g) was added to a solution of **11** (0.56 g, 1 mmol) in dry ether (25 ml) at 0°C. The deep yellow solution immediately turned pale yellow and a yellow oil separated out. The reaction mixture was stirred at R.T. for a further 15 min and the corresponding phosphonium tetrafluoroborate **14** (0.55g, 91%) was filtered off as a pale yellow solid, m.p. 140-141°C; (Found: C 46.3; H, 6.2. $C_{25}H_{40}BF_4O_8PS_2$ requires C, 46.2; H, 6.15%); δ_P +39.75; δ_H 0.75-2.7 (27H, m), 3.8 (3H, s), 3.95 (3H, s), 4.0 (3H, s), 4.025 (3H, s) and 4.7 (1H, d, J 16 Hz); δ_C See Table 1; m/z 563 (M^+-BF_4, 13%), 491 (23), 361 (100), 345 (24), 303 (21), 285 (10), 243 (24), 201 (68), 183 (49), 176 (13), 159 (10), 145 (11), 134 (8) and 117 (10).

*c. Conversion of **13** to **14***

The chloride **13** was prepared as in 3a. using (0.56 g, 1 mmol) of the adduct **11** in dry ether (25 ml) at 0°C. The product was filtered off and taken up in dry THF (5 ml) and silver tetrafluoroborate (0.195 g, 1 mmol) was added. The reaction mixture was stirred at R.T. for 15 min. and the precipitated silver chloride filtered off. Evaporation of the filtrate gave the tetrafluoroborate **14** (0.15 g, 25%) as a yellow solid, δ_P +39.9, identical in all respects to that prepared in 3b.

*d. Reaction of **13** with triethylamine*

The phosphonium chloride **13** (0.1 g), was stirred with triethylamine (0.5 ml) in dry THF (50 ml) at R.T for 2 h. Evaporation of the solvent followed by recrystallisation gave yellow crystals of **11**, m.p. 112-113°C, identical in all respects to that prepared in 2a.

*e. Reaction of **14** with triethylamine*

The phosphonium tetrafluoroborate **14** (0.1 g), was stirred with triethylamine (0.5 ml) in dry ether (50 ml) at R.T for 2 h. Evaporation of the solvent gave an orange oil which was recrystallised from hexane to give orange yellow crystals of **11**, identical in all respects to that prepared in 2a.

4. *Attempted Wittig reaction of **11***

A solution of **11** (0.56 g, 1.0 mmol) and 2,4-dinitrobenzaldehyde (0.185 g, 1.0 mmol) in dry toluene (25 ml) was boiled under reflux for 18 h. Evaporation gave a brown solid which proved to be a mixture of the unchanged starting materials.

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