# ORGANOPHOSPHORUS COMPOUNDS-XVIII

## THE REACTION OF ALKYL PHOSPHITES WITH 4-TRIPHENYLMETHYL-1,2-BENZOQUINONE

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Abstract – Dialkyl phosphites react with 4-triphenylmethyl-1,2-benzoquinone (6) to give dihydroxyphosphonates having structure (7). Trialkyl phosphites, on the other hand, attack the carbonyl oxygen of 6, yielding cyclic unsaturated pentaoxyphosphoranes (17). These are converted into the o-quinol phosphate esters (16) by hydrogen chloride.

Possible reaction mechanisms are considered and the structural assignments are based on chemical and spectroscopic evidence.

Formation of *o*-quinol-monophosphates (such as 1, 2 and 3) by the reaction of *o*-quinones with dialkyl phosphites seems to be general.<sup>1-3</sup> In one

diisopropyl phosphites, in dry benzene, colourless crystalline 1:1 adducts were formed in quantitative yields. These adducts are formulated as dialkyl



X = Cl or Br; R = Alkyl

case, however, the reaction of 1,2-benzophenazine-3,4-quinone with dialkyl phosphites, both the quinol-phosphate (4) and its lactam form (5) were obtained.<sup>2</sup>



We would like to report a novel type of compounds not previously observed in the reaction of o-quinones and dialkyl phosphites.

## **RESULTS AND DISCUSSION**

When 4-triphenylmethyl-1,2-benzoquinone (6) was allowed to react with dimethyl, diethyl, and

 $(5,6-dihydroxy-\alpha,\alpha,\alpha-triphenyl-m-tolyl)$ phosphonates (7) for reasons given below.



(1) The IR spectra of these adducts reveal the absence of a C=O function, while they show strong OH absorption near  $3400 \text{ cm}^{-1}$ .

(2) The H<sup>1</sup> NMR spectrum of 7a exhibits a doublet centered at  $\tau$  6.44 with  $J_{HP} = 11$  Hz, due to the two OMe groups attached to phosphorus. It also shows a doublet of doublets centered at  $\tau$  3.25, with  $J_{HP} = 15.2$  Hz and  $J_{HH} = 2.4$  Hz, ascribed to the C-2 proton. The C-4 proton appears as a doublet at  $\tau$  2.90 with  $J_{HH} = 2.4$  Hz. The coupling constant ( $J_{HH} = 2.4$  Hz) is in good agreement with the value expected for aromatic

protons in a *meta* position to each other.<sup>4</sup> The additional splitting (doublet of doublets with  $J_{HP} = 15 \cdot 2 \text{ Hz}$ ) is attributed to further coupling with phosphorus.<sup>5</sup> A singlet at  $\tau 2 \cdot 77$  is due to the aromatic protons of the trityl group, and the broad signal resonating around  $\tau 2 \cdot 02$ , exchangeable with D<sub>2</sub>O, accounts for two phenolic OH groups. The diethyl and diisopropyl phosphite-adducts (7b,c) give comparable H<sup>1</sup> NMR results. Structure 7 accommodates these data most adequately, whereas formula like 8a, in which the substituents are



arranged in pairs (1,2,4,5) and the two protons are *para* to each other, predicts a negligible interproton coupling (less than 1 Hz).<sup>6</sup> On the other hand, if the four substituents are arranged consecutively (*cf* **8b**), the two aromatic protons are *ortho* to each other and a pair of broad doublets  $(J_{\rm HH} = 6-10 \text{ Hz})$  would then result.<sup>4,6</sup> Structure **8** is also improbable due to steric factors as illustrated by Dreiding stereo and Framework molecular models.<sup>7</sup>

(3) Compounds 7a-c reacted with methyl iodide, in presence of acetone and anhydrous potassium carbonate, to give the corresponding dimethyl ethers 9a-c. The H<sup>1</sup> NMR spectrum of 9a is in



accordance with the assigned structure. It shows the presence of a doublet centered at  $\tau$  6.29 with  $J_{\rm HP} = 11$  Hz [P(OCH<sub>3</sub>)<sub>2</sub>]. The two C—OMe groups give sharp singlets at  $\tau$  6.38 and  $\tau$  6.02. Also, the two OMe groups in 9b appear as two singlets at  $\tau$  6.47 and  $\tau$  6.01, while in 9c they lie at  $\tau$  6.42 and  $\tau$  6.03. In each case, the signal appearing more downfield is associated with the OMe group in position 6. This conclusion is reached through a consideration of the H<sup>1</sup> NMR data of the authentic compounds (10a-c). Again, all the aromatic protons fall in the region  $\tau 2.60-\tau 3.42$  and integrate for 17 protons. The fact that compound 9a is not identical with either 11a or 12a-prepared by the action of dimethyl chlorophosphonate on 4-tritylguaiacol (10a) and 3-hydroxy-4-methoxytetraphenylmethane (10b) respectively-affords additional evidence for structure 9, (cf 7). Similarly,



the IR and  $H^1$  NMR spectra of compounds **9b** and **9c** are inconsistent with those of compounds **11b,c** and **12b,c**, prepared by an authentic route (Experimental).

The dihydroxy phosphonates 7a-c, thus formed, would appear to be the products of kinetically controlled pathways. We propose the reaction course depicted in Scheme 1 to account for this unexpected result. The reaction, which can be rationalized in terms of carbon-attack (carbophilic), presumably is initiated by nucleophilic addition of the phosphite phosphorus to the C atom in position 6 (cf 6). Subsequent rearrangement of the phosphonium species (13) to the phosphonate intermediate (14), is followed by proton transfer to give the final product 7.

The alternative pathway (cf Scheme 2) cannot be overlooked, since initial attack by dialkyl phosphite on the carbonyl C atom is frequently met within a variety of carbonyl compounds.<sup>8</sup> It is unlikely that the reaction of quinone **6** with dialkyl phosphites involves a free radical path,<sup>9</sup> since it proceeds to give compounds **7** in the dark as well as in the presence of free radical inhibitors such as hydroquinone.

It can be seen from the results of the present investigation that dialkyl phosphites react with quinone 6 to give dihydroxyaryl phosphonates (7) and not hydroxyaryl phosphates (vide infra) as observed with other o-quinones.<sup>1-3</sup> It appeared, therefore, of interest to investigate the possibility of the preparation of the two isomeric hydroxyaryl phosphates 15 and 16 via an independent route. This was achieved by allowing trialkyl phosphites to react with quinone 6, and the resulting compounds were treated with dry HCl. As example, the cyclic unsaturated pentaoxyphosphoranes 17 derived from the reaction of trimethyl, triethyl, and triisopropyl phosphites with quinone 6 are now reported. The structure of these addition







Mechanism for the action of dialkyl phosphites on quinone 6.







compounds (17) was verified by their correct analytical values and compatible IR and NMR spectra (Experimental).

Treatment of adduct 17a in ether with hydrogen chloride resulted in the quantitative formation of the o-quinol-phosphate (16, R = Me) which upon





methylation with methyl iodide yielded compound 12a, identical (IR and H<sup>1</sup> NMR) with that obtained by the action of dimethyl chlorophosphonate on 3-hydroxy-4-methoxytetraphenylmethane (vide supra). A similar treatment of adduct 17b with hydrogen chloride gave the o-quinol-monophos-

phate (16, R = Et) which was likewise identified. This reaction involves presumably a nucleophilic attack by the chloride ion on the activated alkyl group of a trialkoxyaryloxyphosphonium salt.<sup>10</sup>



The acid hydrolysis of the oxyphosphorane (17) thus provides a convenient route for preparing o-quinol-monophosphates of structure 16, not available by the normal reaction of dialkyl phosphites.

#### **EXPERIMENTAL**

All m.ps are uncorrected. The benzene (thiophene-free) and light petroleum (b.p. 40-60°) were dried over Na. The dialkyl phosphites and dialkyl chlorophosphonates were freshly prepared. The trialkyl phosphites were purified by treatment with Na ribbon followed by fractional distillation. All reactions were carried out under  $N_2$ .

The IR spectra were taken in KBr disks with a Carl Zeiss Infracord spectrophotometer Model "UR 10". The H<sup>1</sup> NMR spectra were recorded in  $CDCl_3$ , on a Varian A-60, T-60, or HA-100 spectrometers, using TMS as internal standard. The molecular weights were determined by the osmometric method in  $CHCl_3$ .

### Dimethyl (5,6-dihydroxy- $\alpha, \alpha, \alpha$ -triphenyl-m-tolyl)phosphonate (7a)

(a) In boiling benzene. A mixture of 611 (1 g, 3.0 mmole), dimethyl phosphite<sup>12a</sup> (0.35 g, 3.2 mmole), and dry benzene (50 ml) was boiled under reflux for 2 hr, whereby the colour of the soln faded considerably. The benzene soln was concentrated to about fifth its original volume and light petroleum then added. The mixture was kept in the ice-chest overnight and the solid material, so obtained, was filtered off, washed with light petroleum and then crystallized from benzene-light petroleum to give 7a as colourless crystals, m.p. 204-205° (yield 90%); 1R 3450  $cm^{-1}$  (OH), 1600  $cm^{-1}$  (C=C), 1235  $cm^{-1}$  (P=O),<sup>13</sup> 1040 cm<sup>-1</sup> (P—O—Me);<sup>13</sup> NMR (T-60)  $\tau$  6·44 (d,  $J_{\rm HP}$  = 11 Hz, 6 H), 3.25 (d of d,  $J_{HH} = 2.4$  Hz,  $J_{HP} = 15.2$  Hz, 1 H), 2.90 (d,  $J_{HH} = 2.4$  Hz, 1 H), 2.77 (s, 15 H, C-trityl), 2.02 (broad s, 2 H, exchanges with D<sub>2</sub>O); Mol. Wt. 454. (Found: C, 70.35; H, 5.52; P, 6.65. Calc. for  $C_{27}H_{25}O_5P$ (460·47): C, 70·43; H, 5·47; P, 6·72%).

(b) At room temperature. A mixture of dimethyl phosphite (0.2 g, 1.8 mmole) and 6 (0.5 g, 1.5 mmole) in dry benzene (10 ml) was stirred at room temp for 48 hr. After removal of the volatile materials under reduced pressure, the residue was washed several times with light petroleum. The solid product was then crystallized from benzene-light petroleum to give colourless crystals, m.p. 204-205° which was not depressed with a sample obtained from the reaction in boiling benzene.

A similar result was obtained when the same reaction was carried out in the dark using hydroquinone (0.02 g). Similarly, the following compounds 7b and 7c were produced as colourless crystals by the action of diethyl-(6 hr reflux) and diisopropyl phosphites<sup>12</sup> (time of reflux was 12 hr).

Diethyl (5,6-dihydroxy-α,α,α-triphenyl-m-tolyl)phosphonate (7b) (92% yield), m.p. 187–188° from benzenelight petroleum; IR 3465 cm<sup>-1</sup> (OH), 1600 cm<sup>-1</sup> (C=C), 1240 cm<sup>-1</sup> (P=O), 1030 cm<sup>-1</sup> (P-O-Et); NMR (A-60)  $\tau$  8·70 (t, 6 H, Me), 6·03 (quintet, 4 H, P-OCH<sub>2</sub>), 3·20 (d of d, J<sub>HH</sub> = 2·4 Hz, J<sub>HP</sub> = 15·2 Hz, 1 H), 2·87 (d, J<sub>HH</sub> = 2·4 Hz, 1 H), 2·77 (s, 15 H, C-trityl); Mol. Wt. 480. (Found: C, 71·23; H, 5·88; P, 6·40. Calc. for C<sub>29</sub>H<sub>29</sub>O<sub>5</sub>P (488·53): C, 71·30; H, 5·98; P, 6·34%).

Diisopropyl (5,6-dihydroxy -  $\alpha, \alpha, \alpha$ -triphenyl-m-tolyl)phosphonate (7c) (85% yield), m.p. 165–166° from benzene-light petroleum; IR 3185 cm<sup>-1</sup> (OH), 1595 cm<sup>-1</sup> (C==C), 1250 cm<sup>-1</sup> (P==O), 1010 cm<sup>-1</sup> (P==O=C\_3H\_7-i); NMR (T-60)  $\tau$  8-91 (m, 12 H, Me), 5-63 (m, 2 H, P==OCH), 3-60–2-93 (m, 2 H, ArH), 2-79 (s, 15 H, Ctrityl); Mol. Wt. 507. (Found: C, 72-02; H, 6-58; P, 6-05. Calc. for C<sub>31</sub>H<sub>33</sub>O<sub>5</sub>P (516-58): C, 72-08; H, 6-44; P, 5-99%).

All the above mentioned compounds 7a-c respond positively to the ferric chloride colour reaction, giving a violet colour.

Dimethyl (5,6-dimethoxy- $\alpha$ , $\alpha$ , $\alpha$ -triphenyl-m-tolyl)phosphonate (9a). A mixture of 7a (0.5 g, 1.1 mmole) and anhyd powdered K<sub>2</sub>CO<sub>3</sub> (2 g) in dry acetone (50 ml) was stirred at room temp for 30 min. Freshly distilled MeI (0.35 g, 2.5 mmole) was added dropwise and the mixture was gently heated under reflux for 12 hr. After removal of the inorganic residue and volatile materials, the solid product, thus obtained (yield 88%), was crystallized from cyclohexane-light petroleum, as colourless crystals, m.p. 135-137°; IR 1585 cm<sup>-1</sup> (C=C), 1270 cm<sup>-1</sup> (P=O), 1040 cm<sup>-1</sup> (P=O-CH<sub>3</sub>); NMR (T-60)  $\tau$  6.38 (s, 3 H, C-OMe), 6.29 (d, J<sub>HP</sub> = 11 Hz, 6 H), 6.02 (s, 3 H, C-OMe), 3.12-2.67 (m, 17 H, ArH). (Found: C, 71.42; H, 5.91; P, 6.38. Calc. for C<sub>29</sub>H<sub>29</sub>O<sub>5</sub>P: C, 71.30; H, 5.98; P, 6.34%).

Similarly, compounds 7b and 7c reacted with MeI to give 9b and 9c, respectively.

Diethyl (5,6-dimethoxy- $\alpha,\alpha,\alpha$ -triphenyl-m-tolyl)phosphonate (9b), (yield 90%) was crystallized from cyclohexane-light petroleum, m.p. 126-127°; IR 1585 cm<sup>-1</sup> (C=C), 1260 cm<sup>-1</sup> (P=O), 1035 cm<sup>-1</sup> (P-O-Et); NMR (A-60)  $\tau$  8-81 (t, 6 H, Me), 6-47 (s, 3 H, C-OMe), 6-01 (s, 3 H, C-OMe), 5-87 (quintet, 4 H, P-OCH<sub>2</sub>), 3-25-2-48 (m, 17 H, ArH). (Found: C, 72-02; H, 6-48; P, 5-94. Calc. for C<sub>31</sub>H<sub>33</sub>O<sub>8</sub>P: C, 72-08; H, 6-44; P, 5-99%).

Diisopropyl (5,6-dimethoxy- $\alpha,\alpha,\alpha$ -triphenyl-m-tolyl)phosphonate (9c), (yield 85%) was crystallized from cyclohexane-light petroleum, m.p. 131-132°; IR 1585 cm<sup>-1</sup> (C=C), 1260 cm<sup>-1</sup> (P=O), 1025 cm<sup>-1</sup> (P-O--i-Pr); NMR (T-60)  $\tau$  8.79 (q, 12 H, Me), 6.42 (s, 3 H, C-OMe), 6.03 (s, 3 H, C--OMe), 5.32 (m, 2 H, P--OCH), 3.15 (d, J<sub>HH</sub> = 2.4 Hz, 1 H), 2.80 (s, 15 H, C-trityl), 2.83 (d of d, J<sub>HH</sub> = 2.4 Hz, J<sub>HP</sub> = 15.2 Hz, 1 H). (Found: C, 72.76; H, 6.89; P, 5.66. Calc. for C<sub>33</sub>H<sub>37</sub>O<sub>5</sub>P: C, 72.77; H, 6.84; P, 5.68%).

3,4-Dimethoxytetraphenylmethane (10c). A mixture of  $10a^{14}$  (0.5 g, 1.35 mmole), MeI (0.2 g, 1.5 mmole), and dry powdered K<sub>2</sub>CO<sub>3</sub> (1 g) in dry acetone (50 ml) was heated under reflux for 10 hr. After removal of the inorganic residue the soln was evaporated to leave a solid product which was crystallized from benzenelight petroleum to give 10c (yield 95%) as colourless crystals, m.p. 170-171° (lit.<sup>15</sup> 170.5°); IR no band for OH,  $1595 \text{ cm}^{-1}$  (C==C); NMR (A-60)  $\tau$  6·38 (s, 3 H, C-OMe), 6·17 (s, 3 H, C-OMe), 3·22 (broad S, 3 H, ArH), 2·75 (s, 15 H, C-trityl).

2-Methoxy- $\alpha$ , $\alpha$ , $\alpha$ -triphenyl-p-tolyl dimethyl phosphate (11a). A mixture of 10a (1 g, 2·7 mmole), dry acetone (100 ml), and dry powdered K<sub>2</sub>CO<sub>3</sub> (2 g) was stirred for 1 hr. Dimethyl chlorophosphonate<sup>18a</sup> (0·4 g, 2·8 mmole) was added and the mixture was refluxed for 12 hr. After separating the inorganic material, the excess of acetone and dimethyl chlorophosphonate was removed under reduced pressure. The solid product, thus obtained, was crystallized from benzene-light petroleum to give 11a as colourless crystals (yield 92%), m.p. 152–153°; IR 1595 cm<sup>-1</sup> (C=C), 1285 cm<sup>-1</sup> (P=O), 1040 cm<sup>-1</sup> (P-O-CH<sub>3</sub>); NMR (T-60)  $\tau$  6·38 (s, 3 H, C--OMe), 6·12 (d,  $J_{HP} = 11.5$  Hz, 6 H), 3·34–2·85 (m, 3 H, ArH), 2·77 (s, 15 H, C-trityl). (Found: C, 70·79; H, 6·70; P, 6·46. Calc. for C<sub>28</sub>H<sub>27</sub>O<sub>5</sub>P: C, 70·88; H, 5·74; P, 6·52%).

In a similar manner, **10a** reacted with diethyl-, and diisopropyl chlorophosphonates<sup>12b, 16b</sup> with the formation of the corresponding **11b** and **11c**. Also, compounds **12a**, **12b** and **12c** were obtained from the reaction of  $10b^{17}$  with dimethyl-, and diethyl- and/or diisopropyl chlorophosphonates.

Diethyl 2-methoxy-α,α,α-triphenyl-p-tolyl phosphate (11b), (yield 96%) was crystallized from benzene-light petroleum as colourless crystals, m.p. 144–145°; IR 1595 cm<sup>-1</sup> (C==C), 1280 cm<sup>-1</sup> (P==O), 1030 cm<sup>-1</sup> (P=-O=Et); NMR (A-60)  $\tau$  8·67 (d of t,  $J_{HH} = 7$  Hz,  $J_{HP} = 1.2$  Hz, 6 H, Me), 6·38 (s, 3 H, C=-OMe), 5·72 (quintet, 4 H, P=-OCH<sub>2</sub>), 3·22–2·73 (m, 3 H, ArH), 2·75 (s, 15 H, C-trityl). (Found: C, 71-66; H, 6·15; P, 6·11. Calc. for C<sub>30</sub>H<sub>31</sub>O<sub>5</sub>P: C, 71·70; H, 6·22; P, 6·16%).

Diisopropyl 2-methoxy- $\alpha,\alpha,\alpha$ -triphenyl-p-tolyl phosphate (11c), (yield 95%) was crystallized from benzenelight petroleum to give colourless crystals, m.p. 164-165°; IR 1595 cm<sup>-1</sup> (C=C), 1285 cm<sup>-1</sup> (P=O), 1015 cm<sup>-1</sup> (P-O-i-Pr); NMR (T-60)  $\tau$  8-68 (q, 12 H, Me), 6-42 (s, 3 H, C-OMe), 5-22 (m, 2 H, P-OCH), 3-37-2\*87 (m, 3 H, ArH), 2-77 (s, 15 H, C-trityl). (Found: C, 72-37; H, 6-62; P, 5-89. Calc. for C<sub>32</sub>H<sub>35</sub>O<sub>5</sub>P: C, 72-44; H, 6-64; P, 5-83%).

6-Methoxy-α,α,α-triphenyl-m-tolyl dimethyl phosphate (12a), (yield 94%) was crystallized from benzene-light petroleum. The colourless crystals, thus obtained, had m.p. 162-163°; IR 1600 cm<sup>-1</sup> (C=C), 1285 cm<sup>-1</sup> (P=C), 1040 cm<sup>-1</sup> (P=O-Me); NMR (T-60)  $\tau$  6·29 (d,  $J_{HP}$  = 11·5 Hz, 6 H), 6·15 (s, 3 H, C-OMe), 3·37-2·90 (m, 3 H, ArH), 2·77 (s, 15 H, C-trityl). (Found: C, 70·85; H, 6·69; P, 6·58. Calc. for C<sub>28</sub>H<sub>27</sub>O<sub>5</sub>P: C, 70·88; H, 5·74; P, 6·52%).

Diethyl 6-methoxy- $\alpha$ , $\alpha$ , $\alpha$ -triphenyl-m-tolyl phosphate (12b), (yield 98%) was obtained as colourless crystals from benzene-light petroleum, m.p. 185-186°; IR 1600 cm<sup>-1</sup> (C=C), 1285 cm<sup>-1</sup> (P=O), 1035 cm<sup>-1</sup> (P-O-C<sub>2</sub>H<sub>8</sub>); NMR (A-60)  $\tau$  8-79 (d of t, J<sub>HH</sub> = 7 Hz, J<sub>HP</sub> = 1·2 Hz, 6 H, Me), 6·17 (s, 3 H, C-OMe), 5·88 (quintet, 4 H, P-OCH<sub>2</sub>), 3·29-2·79 (m, 3 H, ArH), 2·75 (s, 15 H, C-trityl). (Found: C, 71·62; H, 6·17; P, 6·12. Calc. for C<sub>30</sub>H<sub>31</sub>O<sub>5</sub>P: C, 71·70; H, 6·22; P, 6·16%).

Diisopropyl 6-methoxy- $\alpha,\alpha,\alpha$ -triphenyl-m-tolyl phosphate (12c), (yield 93%) was obtained as colourless crystals from benzene-light petroleum, m.p. 126-127°; IR 1600 cm<sup>-1</sup> (C=C), 1285 cm<sup>-1</sup> (P=O), 990 cm<sup>-1</sup> (P-O-i-Pr); NMR (T-60)  $\tau$  8·79 (q, 12 H, Me), 6·18 (s, 3 H, C-OMe), 5·38 (m, 2 H, P-OCH), 3·40-2·89 (m, 3 H, ArH), 2·80 (s, 15 H, C-trityl). (Found: C, 72.41; H, 6.67; P, 5.86. Calc. for  $C_{32}H_{35}O_5P$ : C, 72.44; H, 6.64; P, 5.83%).

2,2-Dihydro-2,2,2-trimethoxy-5-trityl-1,3,2-benzodioxaphosphole (17a). A mixture of 6 (1g, 3.0 mmole), dry benzene (50 ml), and trimethyl phosphite<sup>18a</sup> (0.4 g, 3.2 mmole) was kept with continuous stirring at ambient temp for 6 hr. After removal of the volatile materials under reduced pressure, the residue was triturated with light petroleum. The solid product was crystallized from benzene-light petroleum to give 17a as colourless crystals, m.p. 165-166°, yield 92%; IR 1630 cm<sup>-1</sup> (C==C, in phospholenes).<sup>19</sup> 1595 cm<sup>-1</sup> (aromatic band), 1070 cm<sup>-1</sup> (P=O-Me). (Found: C, 70.84; H, 5.77; P, 6.45. Calc. for C<sub>28</sub>H<sub>27</sub>O<sub>5</sub>P: C, 70.88; H, 5.74; P, 6.52%).

Carrying out the same reaction in benzene at reflux temp for 2 hr results in the isolation of 17a (yield 90%) (m.p. and mixed m.p.).

Compounds 17b and 17c were prepared in the same manner as described for 17a by the action of triethyland triisopropyl phosphites<sup>16b</sup> on quinone 6.

2,2,2-Triethoxy-2,2-dihydro-5-trityl-1,3,2-benzodioxaphosphole (17b), (yield 85%) was crystallized from benzene-light petroleum as colourless crystals, m.p. 152-153°; IR 1630 cm<sup>-1</sup> (C==C, in phospholene), 1600 cm<sup>-1</sup> (aromatic band), 1070 cm<sup>-1</sup> (P--O--Et); NMR (HA-100)  $\tau$  8.77 (d of t,  $J_{\rm HH} = 7$  Hz,  $J_{\rm HP} = 2$  Hz, 6 H, Me), 5.99 (quintet, 4 H, P--OCH<sub>2</sub>), 3.46-3.08 (m, 3 H, ArH), 2.78 (s, 15 H, C-trityl). (Found: C, 72.07; H, 6.51; P, 6.01. Calc. for C<sub>31</sub>H<sub>33</sub>O<sub>5</sub>P: C, 72.08; H, 6.44; P, 5.99%).

2,2-Dihydro-2,2,2-triisopropoxy-5-trityl-1,3,2-benzodioxaphosphole (17c), (yield 80%) was crystallized from benzene-light petroleum as colourless crystals, m.p. 168-169°; IR 1630 cm<sup>-1</sup> (C=C, in phospholene), 1600 cm<sup>-1</sup> (aromatic band), 1040 cm<sup>-1</sup> (P--O--i-Pr). (Found: C, 73-12; H, 7-01; P, 5-49. Calc. for  $C_{34}H_{39}O_5P$ : C, 73-09; H, 7-04; P, 5-54%).

Compounds 17a-c are insoluble in 5% NaOH aq and give no colour reaction with alcoholic  $FeCl_3$  soln.

6-Hydroxy-α,α,α-triphenyl-m-tolyl dimethyl phosphate (16, R = Me). A stream of dry HCl gas was passed in dry ether (50 ml) for 15 min, 2 g of 17a was then added and the mixture was shaken for 10 min. The colourless crystals were filtered off, and washed with light petroleum (yield 90%), crystallized from benzene-light petroleum, m.p. 175-176°; IR 3100 cm<sup>-1</sup> (OH), 1595 cm<sup>-1</sup> (C=C), 1250 cm<sup>-1</sup> (P=O), 1040 cm<sup>-1</sup> (P-O-Me); NMR (A-60) τ 6·26, 6·13 (2 d, J<sub>HP</sub> = 11·5 Hz, 6 H, P-OMe), 4·40 (broad s, 1 H, OH), 3·40-2·95 (m, 3 H, ArH), 2·75 (s, 15 H, C-trityl). (Found: C, 70·47; H, 5·52; P, 6·68. Calc. for C<sub>27</sub>H<sub>25</sub>O<sub>5</sub>P: C, 70·43; H, 5·47; P, 6·72%).

Diethyl 6-hydroxy- $\alpha$ , $\alpha$ , $\alpha$ -triphenyl-m-tolyl phosphate (16, R = Et). The reaction was carried out in a manner similar to that described above by the action of dry HCl gas on 17b. The colourless crystals (yield 88%), m.p. 179-180° from benzene-light petroleum; IR 3200 cm<sup>-1</sup> (OH), 1595 cm<sup>-1</sup> (C=C), 1285 cm<sup>-1</sup> (P=O), 1035 cm<sup>-1</sup> (P=O-Et); NMR (A-60)  $\tau$  8.84, 8.61 (2 d, 6 H, Me), 5.80 (q, 4 H, P=OCH<sub>2</sub>), 3.62 (broad s, 1 H, OH), 3.30-2.90 (m, 3 H, ArH), 2.78 (s, 15 H, C-trityl). (Found: C, 71-25; H, 5-91; P, 6.38. Calc. for C<sub>29</sub>H<sub>29</sub>O<sub>3</sub>P: C, 71:30; H, 5-98; P, 6.34%).

Reaction of methyl iodide with 6-hydroxy- $\alpha,\alpha,\alpha$ -triphenyl-m-tolyl dimethyl phosphate (16, R = Mc). A mixture of 16 (R = Mc) (0.5 g, 1.1 mmole) and anhyd powdered K<sub>2</sub>CO<sub>3</sub> (1 g) in dry acetone (50 ml) was stirred at room temp for 30 min. A freshly distilled MeI (0.18 g, 1.3 mmole) was added and the mixture was refluxed on steam bath for 10 hr. The mixture was then filtered, and the filtrate was evaporated to dryness. The resulting solid material (yield 92%) was crystallized from benzenelight petroleum to give colourless crystals identified as 12a by m.p., mixed m.p., and comparative IR spectra.

In a similar manner, Mel was reacted with 16 (R = Et) to give colourless crystals (yield 90%), from benzenelight petroleum. The product had m.p. and IR spectrum identical with 12b.

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### REFERENCES

- <sup>1a</sup>E. Diefenbach, Ger. Pat., 937.956 (1956); Chem. Abstr. 52, 20106 (1958); <sup>b</sup>F. Ramirez, S. B. Bhata, A. V. Patwardhan, E. H. Chen and C. P. Smith, J. Org. Chem. 33, 20 (1968)
- <sup>2</sup>A. Mustafa, M. M. Sidky and F. M. Soliman, *Tetra*hedron 23, 107 (1967)
- <sup>3</sup>M. M. Sidky and F. H. Osman, U.A.R. J. Chem. 14, 225 (1971)
- <sup>4a</sup>D. H. Williams and I. Flemming, Spectroscopic Methods in Organic Chemistry. p. 128. McGraw-Hill, London (1966); <sup>b</sup>R. M. Silverstein and G. C. Bassler, Spectroscopic Identification of Organic Compounds, (2nd Edition). p. 145. Wiley, New York (1967)
- <sup>5a</sup>P. C. Lauterbur, Determination of Organic Structures by Physical Methods, (Edited by F. C. Nachod and W. D. Phillips). Vol. 2, Chap. 7, cf pp. 515-523.
  Academic Press, New York (1962); <sup>b</sup>J. A. Pople, W. G. Schneider and H. J. Bernstein, High-Resolution Nuclear Magnetic Resonance, Chap. 12, cf p. 346.
  McGraw-Hill, New York (1959)
- <sup>6</sup>M. Zanger, Organic Magnetic Resonance 4, 1 (1972)

- <sup>7</sup>Rinco Instrument Company, Inc., Greenville, Illinois, U.S.A.
- <sup>8</sup>A. J. Kirby and S. G. Warren, *The Organic Chemistry* of *Phosphorus*, Chap. 3, p. 58. Elsevier, Amsterdam (1967)
- <sup>9</sup>F. Ramirez and S. Dershowitz, J. Org. Chem. 22, 1282 (1957)
- <sup>10a</sup>J. S. Cohen, J. Am. Chem. Soc. 89, 2543 (1967);
  <sup>b</sup>K. D. Berlin, D. M. Hellwege, M. Nagabhushanam and E. T. Gaudy, Tetrahedron 22, 2191 (1966); <sup>c</sup>D. B. Denney and J. Giacin, Tetrahedron Letters 1747 (1964); <sup>e</sup>A. Schmidpeter, B. Wolf and K. Dull, Angew. Chem. Intern. Ed. Eng. 4, 712 (1965); <sup>e</sup>H. Teichmann, M. Jatkowski and G. Hilgetag, Ibid. 6, 372 (1967)
- <sup>11</sup>Th. Zincke and E. Wugk, *Liebigs Ann.* 363, 284 (1908)
- <sup>12a</sup>P. W. Gann and R. L. Heider, U.S. Pat., 2,692,890 (1954); *Chem. Abstr.* 49, 12529 (1955); <sup>b</sup>H. McCombie, B. C. Saunders and G. J. Stacey, *J. Chem. Soc.* 380 (1945)
- <sup>13</sup>L. J. Bellamy, The Infrared Spectra of Complex Molecules, (2nd Edition). Wiley, New York (1964)
- <sup>14a</sup>G. Chuchani, J. Chem. Soc. 1753 (1959); <sup>b</sup>Ibid. 325 (1960)
- <sup>18</sup>M. Gomberg and G. C. Forrester, J. Am. Chem. Soc. 47, 2373 (1925)
- <sup>16a</sup>E. E. Hardy and G. M. Kosolapoff, U.S. Pat., 2,409,039 (1946); *Chem. Abstr.* 41, 1233 (1947); <sup>b</sup>F. R. Atherton, H. T. Howard and A. R. Todd, *J. Chem. Soc.* 1106 (1948)
- <sup>17</sup>N. Barroeta, G. Chuchani and J. Zabicky, *J. Org. Chem.* **31**, 2330 (1966)
- <sup>18a</sup>T. Milobendzki and A. Sachnowski, Chem. Polski 15, 34 (1917); Chem. Abstr. 13, 2865 (1919); <sup>b</sup>A. H. Ford-Moore and B. J. Perry, Organic Syntheses, 31, 111 (1951)
- <sup>190</sup>W. C. Hamilton, S. J. LaPlaca and F. Ramirez, J. Am. Chem. Soc. 87, 127 (1965); <sup>b</sup>W. C. Hamilton, S. J. LaPlaca, F. Ramirez and C. P. Smith, *Ibid.* 89, 2268 (1967); <sup>c</sup>R. D. Spratley, W. C. Hamilton and J. Ladell, *Ibid.* 89, 2272 (1967)