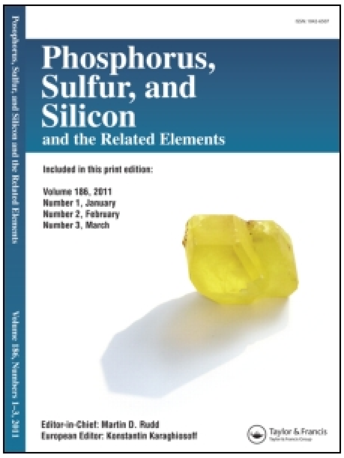

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ORGANOPHOSPHORUS COMPOUNDS, XXXII THE REACTION OF ALKYL PHOSPHITES WITH 1-(DIPHENYLMETHYLENE)-2(1*H*)- AND 4-(DIPHENYLMETHYLENE)-1(4*H*)-NAPHTHALENONES

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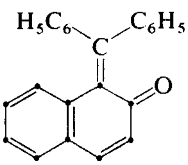
1-(Diphenylmethylene)-2(1*H*)-naphthalenone (**1**) reacts with trialkyl phosphites to give the corresponding 1,2-dihydro-2-alkoxy-1,1-diphenylnaphth[1,2-*d*-][1,2]-oxaphosphole-2-oxides (**3a–c**). The latter compounds are equally obtained by the reaction of dialkyl phosphites with **1**. A mechanism for this reaction is presented which accounts for the experimental results. On the other hand, 4-(diphenylmethylene)-1(4*H*)-naphthalenone (**2**) reacts only with dialkyl phosphites to give dialkyl[4-diphenylmethylene)-1,4-dihydro-1-hydroxy-1-naphthyl]-phosphonates (**9a–c**). Structural assignments are based on analytical, chemical and spectroscopic evidence.

INTRODUCTION

Although 1-(diphenylmethylene)-2-(1*H*)-naphthalenone (**1**) and 4-(diphenylmethylene)-1(4*H*)-naphthalenone (**2**) are known to undergo a number of reactions with nucleophiles,[1] their behaviour towards phosphorus nucleophiles has not hitherto been reported.



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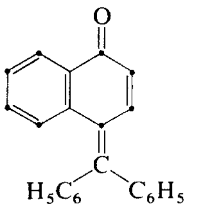

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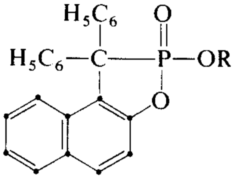
RESULTS AND DISCUSSION

Trialkyl phosphites, namely, trimethyl-, triethyl-, and triisopropyl phosphites react with **1** to give the first reported 1,2-dihydro-2-alkoxy-1,1-diphenylnaphth[1,2-*d*-][1,2]oxaphosphole-2-oxides (**3**). These are colourless crystalline stable substances with sharp m.ps. Correct combustion values and molecular weights (MS) were obtained for all the new compounds (**3a–c**).



3a, R = Me
3b, R = Et
3c, R = *i*-Pr

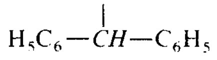
The assigned oxaphosphole structure **3** is based on the following evidence: (i) The IR spectra of these compounds reveal the absence of carbonyl absorption which is recorded with **1** at 1630 cm^{-1}. The spectra also lack the characteristic absorption band attributable to the stretching frequency of an enolate carbonyl function.[2] In addition, they exhibit intense bands corresponding to the

$$\geqslant P{=}O \quad \text{and} \quad P{-}O{-}C\,(\text{alkyl})$$

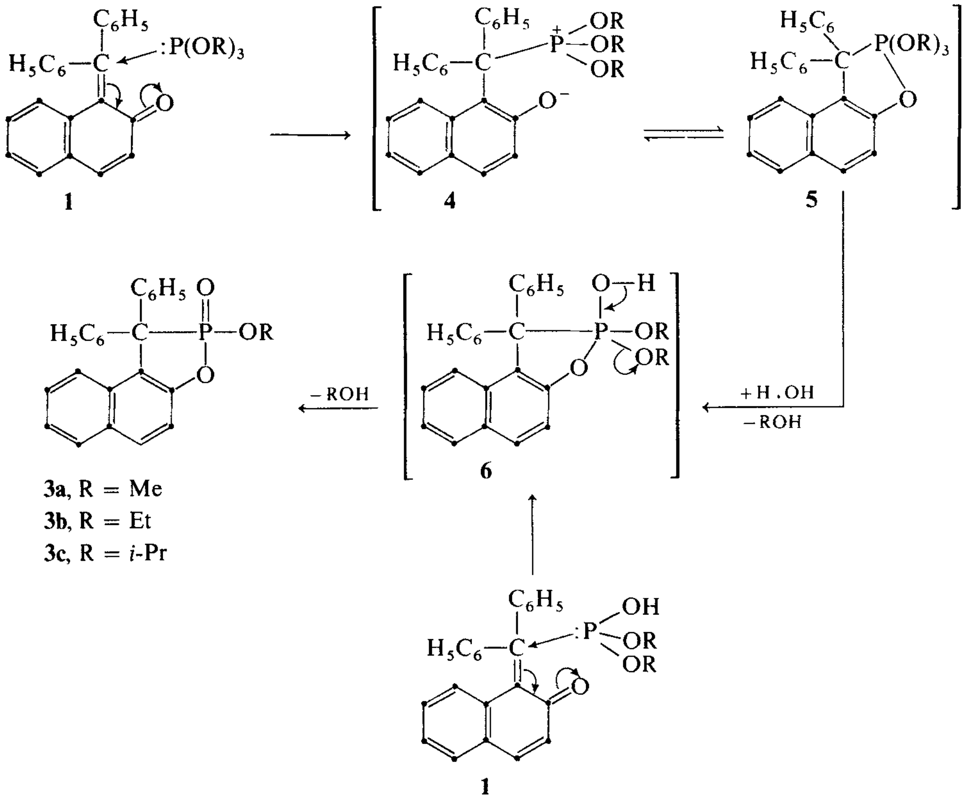
stretching vibrations.[3] (ii) The ^{1}H NMR spectrum of **3a** gives signals at $\delta = 3.30$ (3H, doublet, ^{J}HP = 11.5 Hz, for protons of the methoxyl group attached to phosphorus), and at $\delta = 7.15$–8.00 (16H, multiplet, due to the aromatic protons), (iii) The ^{31}P NMR measurement of **3c** supports the oxaphosphole structure; it exhibits a sharp signal at $\delta = 41.7$ ppm (*vs* H$_3$PO$_4$).[4] (iv) The mass spectrum of **3a** gives a prominent peak at m/e 386 (M$^+$, 87%). Loss of P(O)(OCH$_3$) molecule from the latter ion affords the positive radical at m/e 308 (100%). The latter then fragments in a pattern similar to that observed in the case of the parent naphthalenone **1** (m/e 308, M^+). Thus, ejection of a CO molecule from the ion at m/e 308 gives rise to the positive radical at m/e 280 (10%), which suffers further loss of a C_6H_5 radical to give the cation at 203 (20%). This latter can also originate through expulsion of a C_6H_5 radical from the ion at m/e 308 followed by expulsion of a CO molecule from the resulting cation at m/e 231 (60%).

We propose the reaction course depicted in Scheme 1 to account for this interesting result. The reaction, which is presumably initiated by nucleophilic attack of the phosphite-phosphorus on the exocyclic *C* atom of the naphthalenone **1**, leads to the dipolar adduct **4** which undergoes ring-closure giving structure **5**. The latter, due to its structural features,[5] would collapse to the most stable form **3**. This involves the rapid hydrolysis of **5** (by unavoidable moisture) to give intermediate **6** which undergoes further decomposition affording **3**. The same oxaphospholes **3a–c** were obtained by allowing **1** to react with dimethyl-, diethyl-, and diisopropyl phosphite, respectively. It is worthy to note that the decomposition of cyclic adducts such as **6** to give oxaphospholes (cf. **3**) *via* expulsion of alcohol, is observed in other cases, namely, in the reaction of ethylidene-, and benzylidene acetoacetic ester as well as ethylidene acetyl acetone with alkyl phosphites.[6,7]

Next, the reaction of naphthalenone **2** with alkyl phosphites was undertaken. No reaction, however, was observed with the trialkyl phosphites of the present study and the reactants were recovered practically unchanged. With dialkyl phosphites, on the other hand, the reaction proceeded with formation of colourless crystalline 1:1 adducts as inferred from their elemental analyses and molecular weight determination (MS). The presence of strong OH absorption bands around 3200 cm^{-1} in the IR spectra of the latter adducts and the absence of

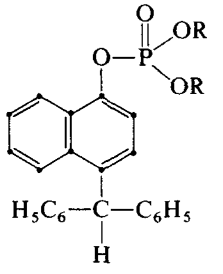


$H_5C_6-\overset{|}{C}H-C_6H_5$



SCHEME 1

singlet in the region $\delta = 5$–6 ppm[8] in their ^{1}H NMR spectra, exclude structure like **7** from further consideration. That the 1:1 adducts are quite stable towards methylating agents (CH_2N_2



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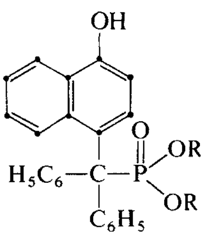

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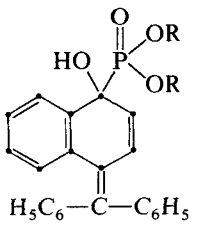

9a, R=Me
9b, R=Et
9c, R = *i*-Pr

and CH_3I) and do not respond positively to the ferric chloride colour reaction, support the conclusion that these products are α-hydroxyphosphonates of type **9** and not the dialkyl [(4-hydroxy-1-naphthyl)diphenylmethyl]phosphonates (**8**). In favour of structure **9** is the presence of a strong absorption band around 1625 cm^{-1} (C=C, conjugated with aromatic ring)[9] in the IR spectra of the adducts. Moreover, dimethyl [4-(diphenylmethylene)-1,4-dihydro-1-hydroxynaphthyl]phosphonate (**9a**) regenerates the starting naphthalenone **2** upon treatment with lead tetraacetate in chloroform or upon thermolysis above its melting point. The carbon-phosphorus bond in *O,O*-dialkyl-α-hydroxy phosphonates is known to cleave easily by the action of heat to regenerate the starting materials.[10] Further support for structure **9** was also gained from the behaviour of adducts **9** under electron impact. The MS of **9a**, for example, showed the molecular ion peak at m/e 418. This ion suffers loss of a $(CH_3O)_2POH$ molecule to give the ion at m/e 308. The latter ion then fragments in a pattern similar to that observed in the mass spectrum of **2** (m/e 308, M^+). Thus, ejection of a CO molecule from the ion at m/e 308 affords the positive radical at m/e 280 (15%) which suffers further loss of a C_6H_5 radical to give the cation at 203 (12%). The latter ion can also arise through removal of a C_6H_5 radical from the ion at m/e 308 followed by expulsion of a CO molecule from the cation at m/e 231 (25%) thus formed.

It is of interest to conclude that the behaviour of naphthalenone **2** towards alkyl phosphites is in complete variance with that already noted with other quinone methides.[11,12]

EXPERIMENTAL

All melting points are uncorrected. The benzene (thiophene-free) and light petroleum (b.r. 40–60°) used, were dried (Na). Trialkyl phosphites[13,14] were purified by treatment with sodium followed by fractional distillation and dialkyl phosphites[15,16] were freshly distilled.

The Ir spectra were taken in KBr with a Carl Zeiss Infracord Model "UR 10." The ^{1}H NMR spectra were performed on a Varian A 60 Spectrometer, using TMS as an internal reference. The ^{31}P NMR spectra were performed (*vs.* H_3PO_4) on Perkin-Elmer R 32 equipment. The mass spectra were run at 70 eV on Varian MAT 112 Spectrometer.

Reaction of Trialkyl Phosphites with 1

A mixture of naphthalenone **1** (1.54 g; 0.005 mol)[17] and trimethyl phosphite (2.5 g; 0.02 mol) in benzene (30 ml) was heated under reflux for 10 hr. After evaporation of the volatile materials, *in vacuo*, the residual substance was recrystallized from benzene-petroleum ether to give **3a** as colourless crystals (ca. 1.2 g; 65%), m.p. 224–226°C (dec.). Anal. Calcd. for $C_{24}H_{19}O_3P$: C, 74.61; H, 4.92; P, 8.30. Found: C, 74.89; H, 4.63; P, 8.54%. Mol Wt. (MS): Calcd: 386; Found: 386. IR: Bands at 1600, 1510, 1500 cm^{-1} (C=C, aromatic), 1260 cm^{-1} (P=O)[3] and 1000 cm^{-1} (P—O—CH_3)[3]. ^{1}H NMR: Signals at $\delta = 3.30$ (3H, doublet, ^{J}HP = 11.5 Hz, for the OCH_3 protons attached to phosphorus) and $\delta = 7.15$–8.00 (16H, multiplet, for the aromatic protons). ^{31}P NMR: $\delta = +41.70$ ppm. MS: Ion peaks at m/e 386 (M^+, 87%), 308 [M—$\underset{\cdot}{P}(O)(OCH_3)$, 100%], 280 (m/e 308–CO, 10%), 203 (m/e 280–$\dot{C}_6H_5$, 20%) and m/e 231 (m/e 308–$\dot{C}_6H_5$, 60%).

Similarly, compounds **3b** and **3c** were obtained upon reacting naphthalenone **1** with triethyl phosphite and triisopropyl phosphite, respectively.

Compound **3b** was obtained (65%) from benzene-petroleum ether as colourless crystals, m.p. 195–197°C (dec.). Anal. Calcd. for $C_{25}H_{21}O_3P$: C, 75.00; H, 5.25; P, 7.75. Found: C, 75.25; H, 5.50; P, 7.54%. Mol. Wt. (MS): Calcd. 400; Found: 400. IR: Bands at 1250 cm^{-1} (P=O) and 1025 cm^{-1}.

(P—O—C_2H_5)[3].

MS: Ion peaks at m/e 400 (M^+, 97%), 371 (M—$\dot{C}_2H_5$, 28%), 355 (M—$\dot{O}C_2H_5$, 8%), 323 (M—$\dot{C}_6H_5$, 10%).

308 [M—P(O)(OC_2H_5), 100%],

280 (m/e 308–CO, 8%), 231 (m/e 308–C_6H_5, 50%) and 203 (m/e 231–CO, 17%).

The colourless crystals of compounds **3c** were obtained (75%) from benzene-petroleum ether, m.p. 200–202°C (dec.). Anal. Calcd. for $C_{26}H_{23}O_3P$: C, 75.36; H, 5.55; P, 7.49. Found:

C, 75.93; H, 5.09; P, 7.85%. Mol. Wt. (MS): Calcd. 414; Found: 414. IR: Bands at 1250 cm^{-1} (P=O) and 1005 cm^{-1}

(P—O—C_3H_7-*i*)[3].

MS: Ion peaks at m/e 414 (M^+, 6%), 371 (M—$\dot{C}_3H_7$, 11%), 308 [M—P(O)(OC_3H_7-*i*), 100%], 280 (m/e 308-CO, 14%), 231 (m/e 308-$\dot{C}_6H_5$, 26%) and m/e 203 (m/e 380-$\dot{C}_6H_5$-CO, 11%).

Reaction of Dialkyl Phosphites with 1

A mixture of naphthalenone **1** (1.54 g; 0.005 mol) and dimethyl phosphite (2.2 g; 0.02 mol) was heated at 120–130°C (bath temperature) for 6 hr. Excess of the phosphite was distilled off under reduced pressure and the residual substance then recrystallized from benzene-petroleum ether to give colourless crystals (80%) proved to be **3a** (mixture m.p. and comparative IR spectra).

Similarly, compounds **3b** and **3c** were isolated (in ca. 85% yield) and identified (mixture m.p. and comparative IR spectra) upon reacting naphthalenone with diethyl phosphite and diisopropyl phosphite, respectively.

Attempted Reaction of Trialkyl Phosphites with 2

A mixture of naphthalenone **2**[17] (1.54 g; 0.005 mol) and trimethyl phosphite (2.5 g; 0.02 mol) was heated in absence of solvent at 150°C for 8 hr or refluxed in benzene (30 ml) for 24 hr. After evaporation of the volatile material(s), *in vacuo*, the residual substance was collected (1.5 g; ca. 97%) and recrystallized from dilute acetic acid to give orange yellow needles proved to be unchanged naphthalenone **2** (m.p., mixture m.p. 179°C[17] and comparative IR spectra).

Similarly, naphthalenone **2** was recovered in an almost quantitative yield and identified (mixture m.p. and comparative IR spectra) upon reaction with triethyl phosphite and triisopropyl phosphite, respectively.

Reaction of Dialkyl Phosphites with 2

A mixture of naphthalenone **2** (1.54 g; 0.005 mol) and dimethyl phosphite (2.2 g; 0.02 mol) was heated at 120–130°C (bath temperature) for 5 hr. Excess of the phosphite was distilled off under reduced pressure and the residual substance triturated with petroleum ether than cooled in the refrigerator. The precipitated material was collected (0.6 g; 70%) and recrystallized from benzene-cyclohexane to give phosphonate **9a** as colourless crystals, m.p. 270–272°C (dec.). Anal. Calcd. for $C_{25}H_{23}O_4P$: C, 71.77; H, 5.50; P, 7.41. Found: C, 72.03; H, 5.32; P, 7.52. Mol. Wt. (MS): Calcd. 418. Found: 418. IR: Bands at 3220 cm^{-1} (OH), 1625 cm^{-1} (C=C, conjugated with aromatic ring), 1608, 1600, 1500 cm^{-1} (C=C, aromatic), 1250 cm^{-1} (P=O) and 1040 cm^{-1} (P—O—CH_3). ^1H NMR ($CDCl_3$): Signals at $\delta = 3.40$ (6H, doublet, $^3HP = 11.5$ Hz, for the OCH_3 protons attached to phosphorus), $\delta = 6.82$–8.38 (16H, multiplet, for the aromatic) and at $\delta = 10.76$ (1H, broad exchangeable singlet, OH). MS: Ion peaks at m/e 418 (M^+, 10%), 308 (100%), 280 (15%), 231 (25%) and 203 (12%).

In a similar manner, phosphonates **9b** and **9c** were obtained upon reacting naphthalenone **2** with diethyl phosphite and diisopropyl phosphite, respectively.

Compound **9b** was obtained in a 65% yield as colourless crystals from benzene-petroleum ether, m.p. 295–297°C (dec). Anal. Calcd. for $C_{27}H_{27}O_4P$: C, 72.64; H, 6.05; P, 6.94. Found: C, 72.20; H, 6.34; P, 7.01%. IR: Bands at 3240 cm^{-1} (OH), 1625 cm^{-1} (C=C, conjugated with aromatic). 1601, 1530, 1510 cm^{-1} (C=C, aromatic), 1250 cm^{-1} (P=O) and 1030 cm^{-1} (P—O—C_2H_5).

The colourless crystals of phosphonate **9c** were obtained (69%) from benzene-cyclohexane, m.p. 265–267°C (dec.). Anal. Calcd. for $C_{29}H_{31}O_4P$: C, 73.41; H, 6.54; P, 6.54. Found: C, 73.69; H, 6.05; P, 6.73%. IR: Bands at 3230 cm^{-1} (OH), 1625 cm^{-1} (C=C, conjugated with aromatic), 1610, 1525, 1510 cm^{-1} (C=C, aromatic), 1245 cm^{-1} (P=O) and at 1010 cm^{-1} (P—O—C_3H_7-*i*).

Attempted Methylation of Phosphonate 9a

To a suspension of phosphonate **9a** (0.5 g) in dry ether (30 ml) was added an ethereal solution of diazomethane (from 4 g *N* nitrosomethylurea) and the mixture left at 10°C for 24 hr. After evaporation of the solvent till dryness, the residual substance was recrystallized from benzene-cyclohexane to give colourless needles (>95%) proved to be phosphonate **9a** (m.p., mixture m.p. and comparative IR spectra).

Similarly, compound **9a** (0.5 g) was recovered practically unchanged and identified (m.p., mixture m.p. and comparative IR spectra) upon reaction with CH_3I (5 ml) and anhydrous K_2CO_3 (3 g) in boiling dry acetone (100 ml) for 8 hr, followed by working-up of the hot acetone solution in the usual manner.

Degradation Experiment with Phosphonate 9a

a) Action of lead-tetraacetate A suspension of phosphonate **9a** (0.5 g) in dry chloroform (100 ml) was treated with freshly crystallized lead tetraacetate (0.5 g) and the mixture heated for 15 minutes at 50°C. After cooling, the insoluble residue was filtered off and the filtrate evaporated till dryness. The substance that left behind, was recrystallized from glacial acetic acid to give orange crystals proved to be naphthaleone **2** (m.p., and mixture m.p. 179°C)[17]; (yield 65%).

b) Action of heat Compound **9a** (0.5 g) was heated under reduced pressure (1.0 mm/Hg) in an apparatus equipped for fractional distillation. The drops that collected at 50°C gave the violet colour reaction described for dimethyl phosphite.[18]

The substance that left behind was collected (69%), recrystallized from glacial acetic acid to give yellow-orange needles proved to be naphthalenone **2** (m.p. and mixture m.p. 179°C).[17] MS: Ion peaks at m/e 308 (M^+, 100%), 280 (M—CO, 20%), 231 (M—$\dot{C}_6H_5$, 66%) and m/e 203 (M—$\dot{C}_6H_5$—CO, 30%).

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