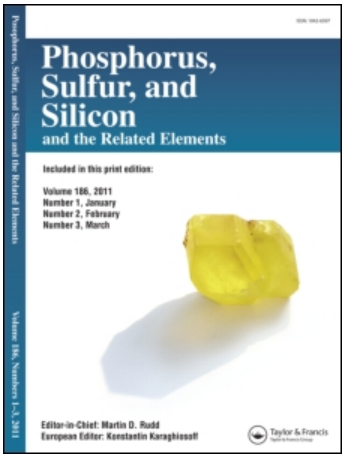

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REACTION OF 1-(DIPHENYLMETHYLENE)-2(1H)-AND 4-(DIPHENYLMETHYLENE)-1(4H)-NAPHTHALENONES WITH TRIS(DIALKYLAMINO)PHOSPHINES AND ETHYLDIPHENYLPHOSPHINITE

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REACTION OF 1-(DIPHENYLMETHYLENE)-2(1H)- AND 4-(DIPHENYLMETHYLENE)-1(4H)- NAPHTHALENONES WITH TRIS(DIALKYLAMINO)PHOSPHINES AND ETHYLDIPHENYLPHOSPHINITE

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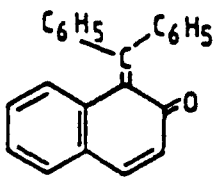
Naphthalenone **1** reacts with tris(dialkylamino)phosphines **3** in refluxing benzene to give the corresponding 1,2-dihydro-2-dialkylamino-1,1-diphenylnaphth[1,2-d-][1, 2]oxaphosphine-2-oxides (**7a, b**). Reaction of **1** with **3a** in boiling methanol affords the oxaphosphole **8** and adduct **9**. The oxaphosphine **11** is obtained upon reacting **1** with ethyldiphenylphosphinite (**10**). Naphthalenone **2** reacts with **3a** to give triaminodioxyphosphorane **13**. Pyrolysis of **13** yields **2** and aminophosphine **3a**. Upon reacting **2** with **10**, adduct **14** is obtained. Structural assignments are based on analytical, chemical and spectroscopic evidence.

Key words: Phosphines; phosphinites; NMR, IR.

INTRODUCTION

From our previous works,[1–4] it was shown that the products obtained from the reaction of 1-(diphenylmethylene)-2-(1H)-naphthalenone (**1**) and 4-(diphenylmethylene)-1(4H)-naphthalenone (**2**) with trivalent or pentavalent phosphorus reagents depends on the nature of the phosphorus reagents used as well as on the stability of the first step of addition of these reagents on naphthalenones **1** and **2**. These observations prompted us to study the reactions of **1** and **2** with other trivalent phosphorus reagents, namely, tris(dialkylamino)phosphines (**3**) and ethyldiphenylphosphinite (**10**).



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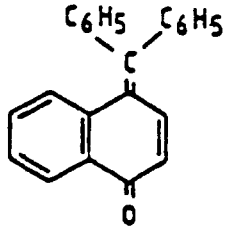

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RESULTS AND DISCUSSION

We have found that naphthalenone **1** failed to react with reagent **3** at room temperature in all organic solvents even on standing for about one week. The starting material I obtained was practically unchanged.

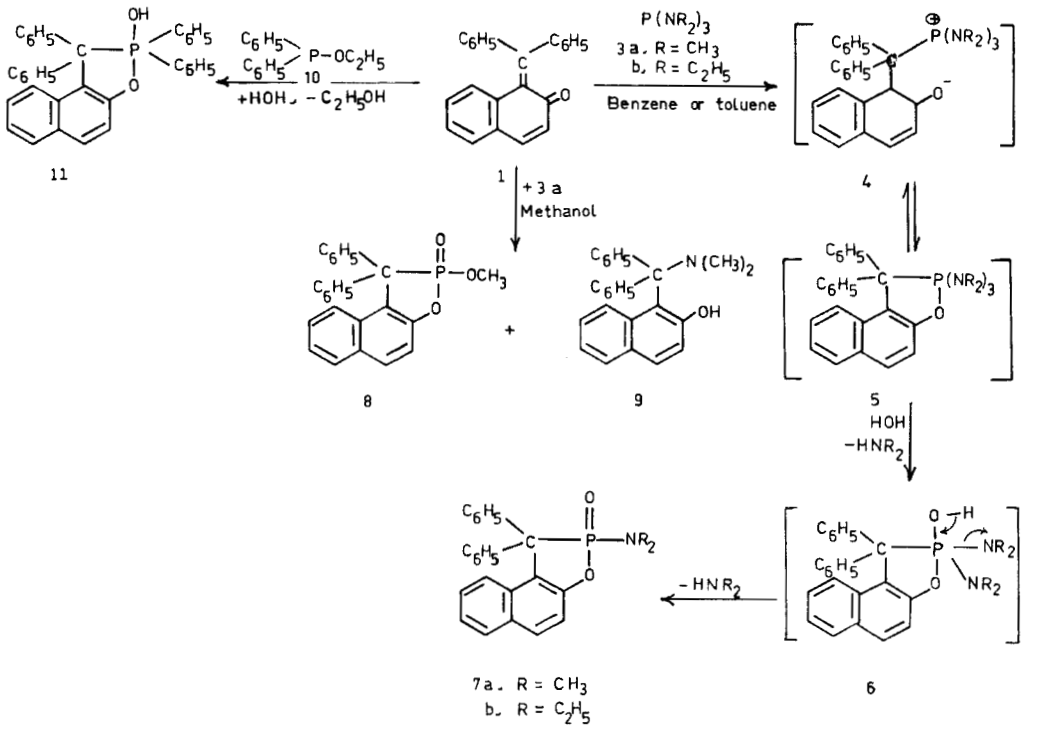
In refluxing benzene or toluene compound **1** reacted with tris(dimethylamino)phosphine (**3a**) to give the first reported 1,2-dihydro-2-dimethylamino-1,1-diphenylnaphth[1,2-d-][1,2]oxaphosphine-2-oxide (**7a**). These are yellow crystalline stable substances with sharp melting points.

Correct combustion values and molecular weights (MS) were obtained for structure **7a**. The oxaphosphine structure **7a** was assigned to this adduct: a) The IR spectrum of **7a** (in chloroform) revealed the absence of the carbonyl absorption and the characteristic absorption band attributable to the stretching frequency of the enolate carbonyl function[5] and the $\diagdown\!\diagup C{=}C\diagdown\!\diagup$ conjugated with aromatic ring.[6] It exhibited intense bands at 1240 cm^{-1} corresponding to $\diagdown P{=}O$ absorption[7] and two bands at 1320 cm^{-1} and 860 cm^{-1} due to the absorptions of $P{-}N(CH_3)_2$.[8] (b) The ^{1}H-NMR spectrum (in $CDCl_3$) of the adduct showed a doublet centered at δ = 2.20 ppm (J_{HP} = 11.09 Hz) due to the 6H of the dimethylamino group. The 16H of the aromatic protons appeared as multiplets at δ = 7.05–7.90. (c) The ^{31}P-NMR gave one signal at δ = +50.76 ppm. (d) The mass spectrum of **7a** gave prominent peak at m/e 399 (M^+, 100%), 355 ($M^+ - N(CH_3)_2$, 50%), 308 (355-P(O), 70%). The latter then fragments in a pattern similar to that observed in the case of the parent naphthalenone **1** as described previously.[1]

We propose the reaction course depicted in Scheme I. Thus, a nucleophilic attack of the phosphite-phosphorus on the exocyclic C atom of naphthalenone **1** leads to the dipolar adduct **4** which undergoes ring closure giving structure **5**. The latter, due to its structural features[9] could collapse to the most stable form **7** through the rapid hydrolysis of **5** (by the presence of unavoidable moisture) to give intermediate **6** which undergoes further decomposition yielding **7**.

When the reaction of naphthalenone **1** with reagent **3a** was performed in refluxing methanol, two products were obtained, the precipitated product proved to be 1,2-dihydro-2-methoxy-1,1-diphenylnaphth[1, 2-d-][1, 2]oxaphosphole-2-oxide (**8**) (from m.p., mixed m.p. and comparative IR and ^{1}H-NMR spectra with an authentic sample).[1] The filtrate, on evaporation, gave 1,2-dihydro-1-dimethylamino-1,1-diphenylmethylene-2-naphthol (**9**). Adduct **9** was equally produced via reaction of **1** with dimethylamine in refluxing methanol (m.p., mixed m.p. and comparative IR and ^{1}H-NMR spectra). Adducts **8** and **9** probably arise from the hydrolysis of reagent **3a** in refluxing methanol to give trimethyl phosphite and dimethylamine, the latter two compounds then reacted with naphthalenone **1** at the same time to yield **8** and **9**. The oxaphosphine **7a** was found to be stable when it was boiled in methanol for 12 hr, this observation indicates that adduct **9** does not arise from the hydrolysis of **7a** in the reaction medium.

1,2-Dihydro-2-diethylamino-1,1-diphenylnaphth[1,2-d-] [1, 2]oxaphosphine-2-



SCHEME I

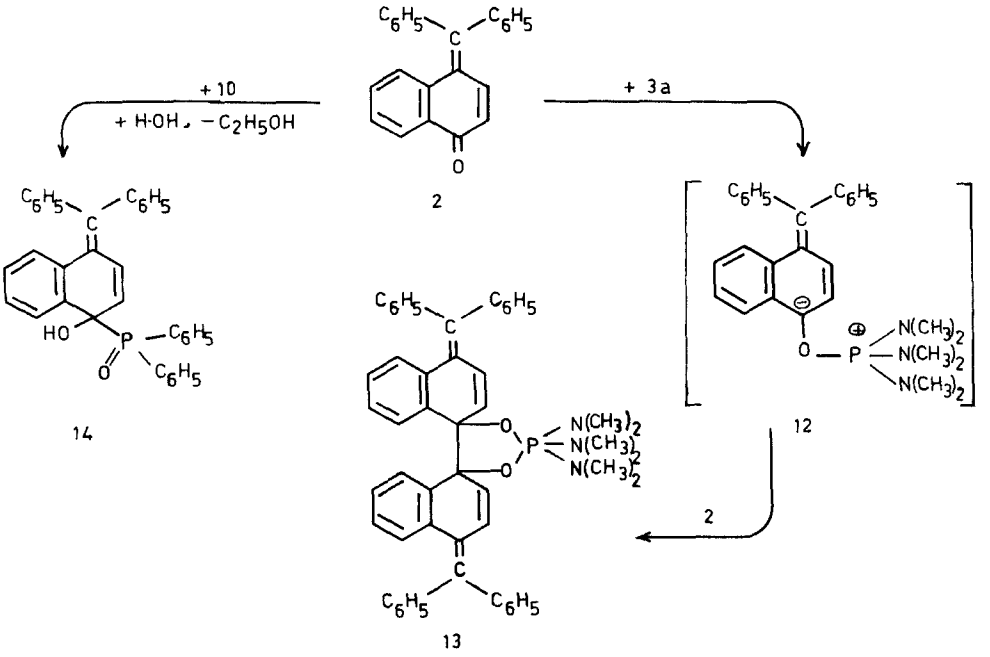
oxide (**7b**) was obtained from the reaction of **1** with tris(diethylamino)phosphine (**3b**). The analytical and spectral data support structure **7b**.

The reaction of **1** with ethyldiphenylphosphinite (**10**) occurred in refluxing benzene to afford 1,2-dihydro-2-diphenyl-1,1-diphenylnaphth[1, 2-d-][1, 2]oxaphosphine-2-hydroxy (**11**).

When naphthalenone **2** was allowed to react with reagent **3a** in refluxing benzene, a crystalline 2:1 adduct was isolated. The analytical and spectral data supported the triaminophosphorane structure 13. The ^{1}H-NMR of 13 (in $CDCl_3$) had 32 aromatic protons as multiplet at δ = 7.20–8.10 ppm and 18 aliphatic protons of the three equivalent dimethylamino groups as doublet at δ = 2.45 with J_{HP} = 10.1 Hz. The ^{31}P-NMR shift recorded for adduct **13** was δ = −46.35 ppm. This value supports the cyclic structure **13**.[10]

Pyrolysis of triaminophosphorane **13** at 210°C under reduced pressure gave the starting naphthalenone **2** and the reagent **3a** and not the dimeric product **2**. This observation suggested that product **13** underwent thermal dissociations to the dipolar intermediate **12** and **2**. Then the dipolar **12** gave **2** and **3a** (Scheme II) via further dissociation.

Heating **2** with excess ester **10** without solvent at 100°C leads to the formation of diphenyl[4-(diphenylmethylene)-1,4-dihydro-1-hydroxynaphthyl]phosphine-oxide (**14**). Product **14** was confirmed from correct microanalysis and spectral data (cf. experimental).



SCHEME II

CONCLUSIONS

From the results of the present investigation and our previous studies, it seems that the reaction of naphthalenone **1** with reagent **3** and trialkyl phosphites gave unstable dipolar adducts which collapse to give finally the cyclic structures **7** and **8**, respectively, through the expulsion of **2** moles of dimethylamine in the case of reagents **3** and **2** moles of alcohol in the case of trialkyl phosphites,[1] in contrast the reaction of **1** with methylenetriphenylphosphorane $[(C_6H_5)_3P{=}CH_2]$[2] led to the formation of stable dipolar adduct. In the reaction of compound 1 with the ethyldiphenylphosphinite (**10**) one mole of ethanol was ejected and produced adduct **11**. On the other hand the reaction of naphthalenone **2** with compound **3a** afforded a 2:1 adduct through a phosphorus oxygen bond. This is in contrast to the formation of the 1:1 adduct of a phosphorus-carbon bond in the reaction of the same compound **2** with the analogous phosphite ester[1] and ethyldiphenylphosphinite.

EXPERIMENTAL

Materials and Methods

All melting points are uncorrected. Solvents were dried and distilled using common methods. The starting naphthalenones **1** and **2** were prepared according to established procedures.[11] The infrared spectra were taken in chloroform with a Perkin-Elmer Infracord Spectrometer Model 1576. The ^{1}H-NMR spectra were taken on a varian A-60, T.60. The ^{31}P-NMR spectra were measured (vs. H_3PO_4 as external standard) on a Varian CFT20, 32 MHz spectrometer. The mass spectra were run at 70 eV on Kratos MS 50 equipment.

Reaction of naphthalenone **1** *with tris(dimethylamino)phosphine* (**3a**). A mixture of naphthalenone **1** (0.6 g, 0.002 mol) and reagent **3a**[12] (0.64 g, 0.004 mol) in dry benzene or toluene (30 ml) was heated under reflux for 8 hr. After evaporation of the volatile materials under reduced pressure, the residue was placed on a column of silica-gel and eluted with a mixture of acetone-petroleum ether (2:8) to give **7a**, which was crystallized from benzene as yellow crystals m.p. 250°C (60%).

Anal. Calcd. for $C_{25}H_{22}NO_2P$: C, 75.18; H, 5.55 N, 3.50; P, 7.76.
Found: C, 74.89; H, 5.46; N, 3.44; P, 7.92.

Reaction of **1** *with* **3a** *in methanol.* A mixture of 1(0.6 g, 0.002 mol) and **3a** (0.004 mol) in methanol (30 ml) was refluxed for 2 hr. The precipitate formed after cooling was collected and crystallized from chloroform to give the oxaphosphole (**8**) (40%) (proved from m.p., mixed m.p. and comparative IR and ^{1}H-NMR spectra with authentic sample).[1] The filtrate was concentrated and cooled, the precipitate formed was crystallized from methanol to afford **9** as colorless crystals m.p. 275°C (30%). IR:3220 (OH, exchangeable with D_2O), ^{1}H-NMR (in $CDCl_3$) singlet at δ = 2.10 [6H, $(CH_3)_2$], broad singlet at δ = 9.25 (1H, OH), multiplet at δ = 7.85 (16H, aromatic protons).

Anal Calcd. for $C_{25}H_{23}NO$: C, 84.98; H, 6.15; N, 3.96.
Found: C, 84.78; H, 6.00; N, 3.88.

Compound 9 was equally produced (80%) (m.p., mixed m.p. and comparative IR spectra) upon refluxing 1 with dimethylamine (1:1.50 mol) in methanol and for 1.5 hr., and working up as described before.

Reaction of **1** *with* **3b**. Naphthalenone **1** reacted with **3b** as described in case of **3a**, refluxing time 40 hr, elution solvent was a mixture of ethylacetate-petroleum ether (2:7). Product **7b** was obtained as colorless crystals from benzene (65%) m.p. 247°C. IR:1245 (—P=O), 1250, 940[P—N$(C_2H_5)_2$]. The ^{1}H-NMR (in $CDCl_3$) of **7b** (in δ scale), triplet at 1.00 (6H, $(CH_3)_2$), multiplet at 2.25 [4H, $(CH_2)_2$], multiplet at 7.10–7.95 (16 aromatic protons). ^{31}P-NMR δ = 45.57 ppm. The mass spectrum gave a prominent peak at m/e 427(M^+, 98%), 355[M^+ − N$(C_2H_5)_2$, 90%], 308[355-P(O), 75%].

Anal. Calcd. for $C_{27}H_{26}NO_2P$: C, 75.87; H, 6.08, N, 3.27; P, 7.25.
Found: C, 75.78; H, 6.19; N, 3.31; P, 7.34.

Reaction of **1** *with ethyldiphenylphosphinite* (**10**). A mixture of **1** (0.002 mol) and reagent **10**[13] (0.003 mol) in dry benzene (30 ml) was refluxed for 10 hr. After evaporation of the volatile materials in vacuo, the residue was eluted with a mixture of acetone-petroleum ether (2:7) to give **11** as colorless crystals from chloroform m.p. 210°C (80%). IR:1445 [P—C—(aryl)], 3280 (OH), it lacks the —P=O absorption band and C=C conjugated with aromatic ring. ^{1}H-NMR of 11 (in δ scale), broad singlet at 9.00 (1H, OH), multiplet at 6.50–7.80 (26 H, aromatic protons).

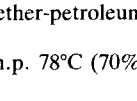
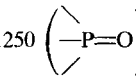
Anal. Calcd. for $C_{35}H_{27}O_2P$: C, 82.33; H, 5.24; P, 6.01
Found: C, 82.20; H, 5.12; P, 6.13. Mol. Wt. (MS) Calcd 510.581; found 510, 433 (M^+-C_6H_5), 356 (433-C_6H_5), 292(356-P(O)OH), 308[M^+-$(C_6H_5)_2$POH)]

Reaction of **2** *with reagent* **3a**. A mixture of **2** (0.002 mol) and **3a** (0.003 mol) in benzene (30 ml) was refluxed for 10 hr. After evaporation of the volatile materials in vacuo, the residue was triturated several times with petroleum ether (40–60) and eluted with a mixture of acetone-petroleum ether (2:8) to give triaminodioxyphosphorane **13** as orange brown crystals from benzene m.p. 205°C (60%). IR: 1310 and 950[P—N$(CH_3)_2$], C=C conjugated with aromatic ring at 1625, it lacks the enolate carbonyl absorption band.[14]

Anal. Calcd. for $C_{52}H_{50}N_3O_2P$: C, 80.07; H, 6.46; N, 5.38; P, 3.97.
Found: C, 79.86; H, 6.39; N, 5.30; p, 4.09.

Pyrolysis of adduct **13**. Adduct **13** (0.3 g) was heated in a cold-finger sublimator at 210°C for 30 minutes under reduced pressure (0.9 mm/Hg). The dark residue was boiled with a mixture of benzene-petroleum ether (2:3) and filtered, upon evaporation of the volatile materials on a water bath, the

remaining oil proved to be reagent **3a** (T.L.C and comparative IR spectra with an authentic sample). The remaining solid in the sublimator was crystallized from acetic acid to give the naphthalenone **2** (as proved from m.p., mixed m.p. and comparative IR spectra with an authentic sample).[11]

Reaction of **2** *with* **10**. A mixture of 2 (0.002 mol) and reagent 10 (0.01 mol) was heated under reflux in an oil bath at 100°C for 30 hr, the mixture was kept under cooling 24 hr, the precipitate was filtered, washed with cold ether-petroleum ether several times and then crystallized from ether to give **14** as colorless crystals m.p. 78°C (70%). IR: 1250  , 1625  , conjugated with aromatic ring), 1440 [P—C—(aryl)], 3250 (OH), ^{1}H-NMR (in δ scale), broad singlet at 11.1 (1H, OH), multiplet at 6.50–8.10 (26 H, aromatic protons).

Anal. Calcd. For $C_{35}H_{27}O_2P$: C, 82.33; H, 5.33; P, 6.06.
Found: C, 82.21; H, 5.20; P, 6.14. Mol. Wt. (MS). Calcd: 510.581. Found: 510.

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