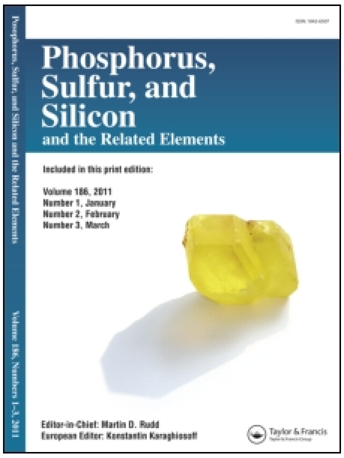

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REACTION OF WITTIG REAGENTS AND PHOSPHACUMULENES WITH 1-(DIPHENYLMETHYLENE)-2(1*H*)- AND 4-(DIPHENYLMETHYLENE)-1(4*H*)-NAPHTHALENONES

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REACTION OF WITTIG REAGENTS AND PHOSPHACUMULENES WITH 1-(DIPHENYLMETHYLENE)-2(1*H*)- AND 4-(DIPHENYLMETHYLENE)-1(4*H*)-NAPHTHALENONES

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Depending upon the type of Wittig reagents, naphthalenone **1** reacts with reagents **3a** and **3b** to give adducts **4** and **5** respectively. Reaction of **1** with phosphacumulene **6** gives the phosphorane **7**. On the other hand, naphthalenone **2** reacts with **3a** and **3b** to give adducts **8** and **9**. The identity of the new compounds is established from analytical and spectroscopic evidences.

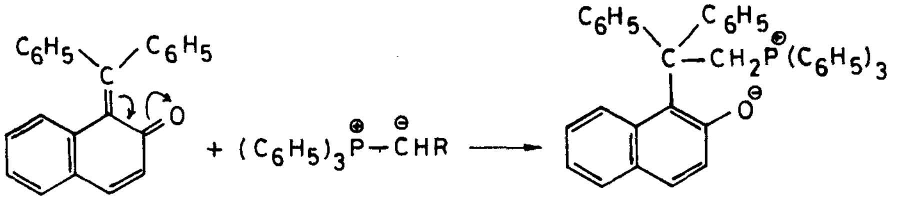
Key words: o-, p-Naphthalenone; methylenetriphenylphosphorane; cyanomethylenetriphenylphosphorane; phosphacumulene; phosphonium ylides and pyran phosphorane.

INTRODUCTION

During the course of our studies on the behaviour of 1-(diphenylmethylene)-2(1H)-naphthalenone **1** and 4-(diphenylmethylene)-1(4H)-naphthalenone **2** towards organophosphorus compounds,[1,2] we concluded that the reaction of naphthalenone **1** with alkyl phosphites is in complete variance with that already reported with other quinone methides.[3,4] This gives us the interest to examine the reactivity of **1** and **2** towards Wittig reagents and phosphacumulenes, and also to prepare new phosphorus derivatives of naphthol which are of interest as possible pharmacological agents.

RESULTS AND DISCUSSION

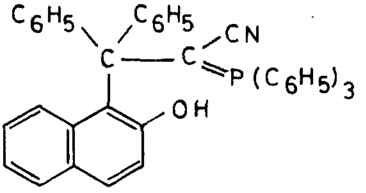
It was found that the yellow naphthalenone **1** reacts with methylenetriphenylphosphorane **3a** in refluxing benzene under nitrogen to give colourless 1:1 adducts formulated as structure **4**. Reasons for structure **4** were: (a) correct elemental analysis and molecular weight determination by (MS), (b) the IR spectrum of **4** (in $CDCl_3$, expressed in cm^{-1}) revealed the absence of the carbonyl absorption which is recorded at 1630 in the starting material **1** and also lacked the strong band around 1625 for the (C=C, conjugated with aromatic ring),[5] it showed a band at 1460 [P—C—(aryl)]. (c) The ^{1}H-NMR spectrum of **4** (in $CDCl_3$, expressed in δ scale) showed a doublet centred at 3.42 (2H, CH_2 group) and a multiplet centred at 7.60–7.20 (31H, aromatics). (d) The ^{31}P-NMR measurement supports structure **4**, it exhibits a sharp signal at $\delta = +15.80$ (vs. H_3PO_4).[6]



1 3 a, R = H
b, R = CN 4

The reaction of naphthalenone **1** with cyanomethylenetriphenylphosphorane (**3b**, R=CN) gave adduct **5**. The elemental microanalysis, IR, ^{1}H-, ^{31}P-NMR and MS data agree with structure **5** (c.f. experimental).

The phosphacumulenes ylid **6** reacted with **1** in ethyl acetate at 20°C for 5 hr. under nitrogen to give the corresponding pyran-substituted phosphorane **7**.



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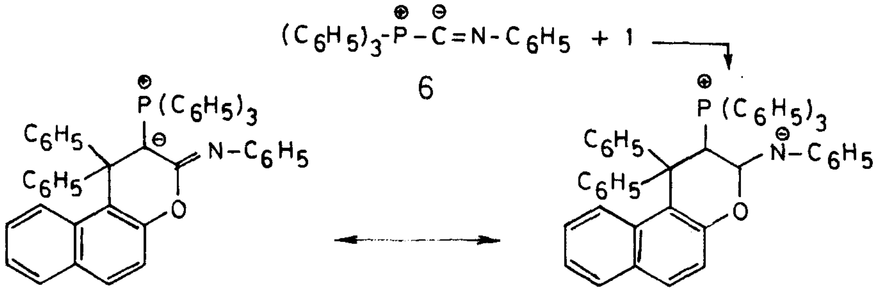
Structure **7** was deduced from correct elemental microanalysis, IR, ^{1}H, ^{31}P-NMR and MS data. The ^{31}P-NMR spectrum of **7** gives a signal at $\delta = +21.6$ which supports structure **7**.[7]



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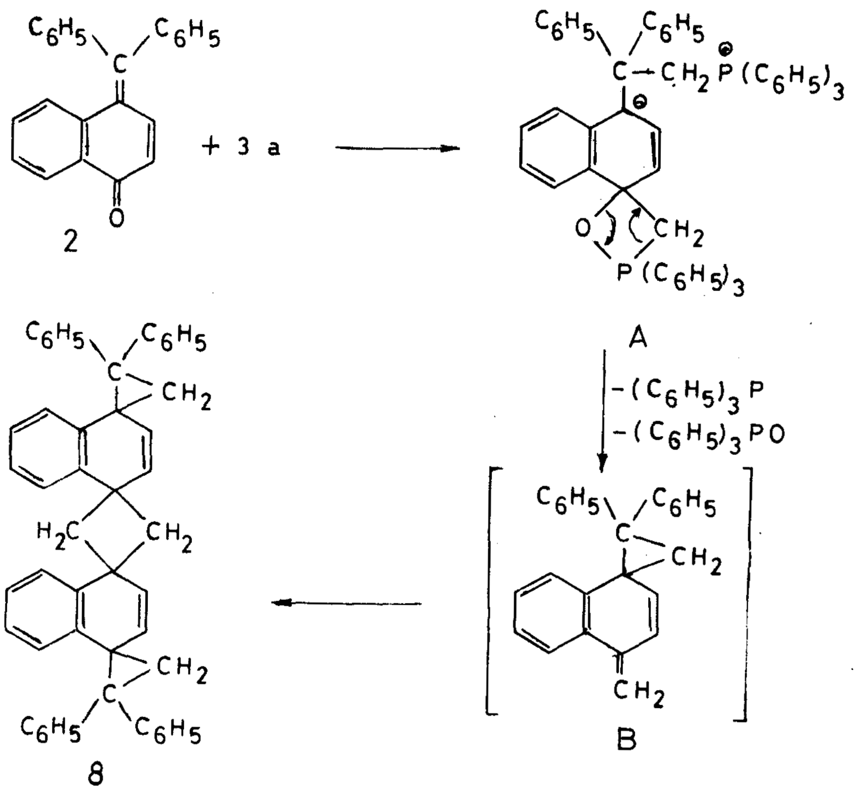
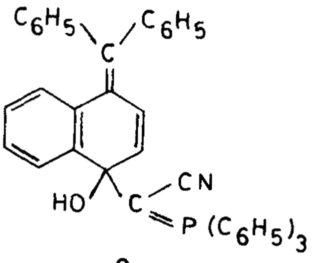
Next, the reaction of naphthalenone **2** with ylid **3a** was preformed in refluxing toluene in 1:2 molar ratio to give the dimeric form **8**. Triphenylphosphine and triphenylphosphine oxide were also isolated from the reaction mixture. The elemental analysis, IR and ^{1}H-NMR spectra and molecular weight determination (MS) were in agreement with structure **8**.



Formation of adduct **8** can be explained in terms of addition of 2 moles of Wittig reagent **3a** to the starting naphthalenone **2** to give the intermediate **A** which gives **B** through ejection of triphenylphosphine and triphenylphosphine oxide, followed by dimerization[8] of B under the experimental condition to give the final product **8**. When this reaction was carried out in a molar ratio of **2** and **3a**, adduct **8** and the starting material **2** were isolated with triphenylphosphine and triphenylphosphine oxide (Scheme I).

Naphthalenone **2** reacted with ylid **3b** in dry toluene to give adduct **9** (c.f. experimental).



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No reaction was observed when naphthalenone **1** and **2** were allowed to react with ylides of types **10** and **11** in all solvents or when **2** was allowed to react with ylid **6**.

$(C_6H_5)_3P{=}CHCOOR$ $\quad$ $(C_6H_5)_3P{=}C{=}C{=}X$

10 $R{=}CH_3$ or C_2H_5 $\quad$ **11** $X{=}O$ or S

From the above results, it can be seen that the reactions of the naphthalenones **1** and **2** with ylids lead to different products depending on the nature of the ylid used as well as on the structure of naphthalenones and also on the stability of the addition product.

EXPERIMENTAL

All melting points are uncorrected. All solvents used were pure and dried. Methylenetriphenylphosphorane,[9] cyanomethylenetriphenylphosphorane[10] and phosphacumulene ylids[11] were prepared according to established procedures. The IR spectra were recorded on 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 Varian CFT 20, 32 MHz Spectrometer. The mass spectrua were run at 70 eV on Kratos MS 50 equipment.

Reaction of naphthalenone **1** *with methylenetriphenylphosphorane* **3a**. A mixture of **1**[12] (0.6 gm, 0.002 mole) and ylid **3a** (0.54, 0.002 mole) in benzene, was refluxed under nitrogen for 10 hrs., the reaction solvent was removed under reduced pressure, the residue was placed on a column of silica-gel and eluted with a mixture of chloroform-petroleum ether (2:8) to give adduct **4**, which was crystallized from chloroform-petroleum ether as colourless crystals m.p. 214°C (60%). Anal. Calcd. for $C_{42}H_{33}OP$ (584.706). C, 86.27; H, 5.68; P, 5.29%. Found: C, 86.25; H, 5.69; P, 5.28% Mol. wt. (MS) = 584.

Reaction of naphthalenone **1** *with cyanomethylenetriphenylphosphorane* **3b**. A mixture of **1** (0.6 gm, 0.002 mole) and ylid **3b** (1.2 gm, 0.004 mole) was refluxed in dry toluene for 25 hrs. After cooling, a yellow precipitate was formed which was filtered and crystallized from benzene to give adduct **5** as a yellow crystalline materials m.p. 225°C in 75% yield. Anal. Calcd. for $C_{43}H_{32}NOP$ (609.717). C, 84.70; H, 5.29; N, 2.29; P, 5.08%. Found: C, 84.68; H, 5.30; N, 2.28; P, 5.09% Mol. wt. (MS) = 609.

IR, bands at 3200 (OH), 2205 (CN), 1420 (P—C—aryl) 1575 $\left(>C{=}P\right)$, 1558, 1550 (C=C, aromatics) and it revealed the absence of $\left(>C{=}C\right)$, conjugated with aromatic ring). ^{1}H-NMR (in $CDCl_3$ expressed in δ scale, 10.11 (1H, broad singlet OH), 7.04–8.23 (32H, multiplet, aromatics). ^{31}P-NMR (in $CDCl_3$) $\delta = +21.92$ ppm.

Reaction of **1** *with phosphacumulenes ylid* **6**. A mixture of **1** (0.6 gm, 0.002 mole) and phosphacumulenes **6** (0.74, 0.002 mole) in absolute ethyl acetate was stirred for 5 hrs. at room temperature (20°C) and eluted with a mixture of ethylacetate-petroleum ether (2:8) as described before, to give adduct **7** as yellowish green crystals with m.p. 260°C in 70% yield. Anal. Calcd. for $C_{49}H_{37}NOP$ (686.823), C, 85.69; H, 5.43; N, 2.03; P, 4.51. Found: C, 85.68; H, 5.42; N, 2.04; P, 4.52% Mol. wt. (MS) = 686.

IR, bands at 1580 (C=P), 1425 [P—C(aryl)], and 1570 (C=N).

Reaction of **2** *with ylid* **3a**. A mixture of **2**[12] (0.3 gm, 0.001 mole) and ylid **3a** (0.54, 0.002 mole) in toluene was refluxed for 5 hrs. under nitrogen, then chromatographed on silica gel and eluted with a mixture of acetone-petroleum ether (1:9). Triphenylphosphine, triphenylphosphine oxide and adduct **8** were isolated. Adduct **8** was crystallized from acetone-petroleum ether as pale orange crystals with, m.p. 265°C in 60% yield. Anal. Calcd. for $C_{50}H_{40}$ (640.81), C, 93.71; H, 6.29. Found: C, 93.70; H, 6.28% Mol. wt. (MS) = 640.

IR, lacks the C=O absorption and the C=C conjugated with aromatic ring. ^{1}H-NMR spectrum of **8** (in $CDCl_3$, in δ scale) showed two singlet at 1.75 and 1.85 for the $2CH_2$ groups of the cyclopropane ring and two singlet at 2.25 and 2.42 for the $2CH_2$ groups of the cyclobutane ring. The aromatic protons appeared as multiplet at 6.50–8.00 (32H).

Reaction of **2** *with ylid* **3b**. A mixture of **2** and ylid **3b** (1:2 mole) was refluxed in dry toluene for 40 hrs., after cooling a dark residue was precipitated which was scrached with petroleum ether till solidified, filtered and crystallized from benzene to give adduct **9** with m.p. 330°C in 65% yield. Anal. Calcd. for $C_{43}H_{32}NOP$ (609.717). C, 84.70; H, 5.29; N, 2.29; P, 5.08%. Found: C, 84.68; H, 5.28; N, 2.30; P, 5.09% Mol. wt. (MS) = 609.

IR gave bands at 3205 (OH), 2208 (CN), 1585 $\left(>C{=}P\right)$, 1625 (C=C conjugated with aromatic). ^{1}H-NMR (in $CDCl_3$, in δ scale), 10.05 (1H, broad singlet, OH exchangeable), 6.47–8.09 (32H, aromatics). ^{31}P-NMR (in $CDCl_3$) $\delta = +19.54$.

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