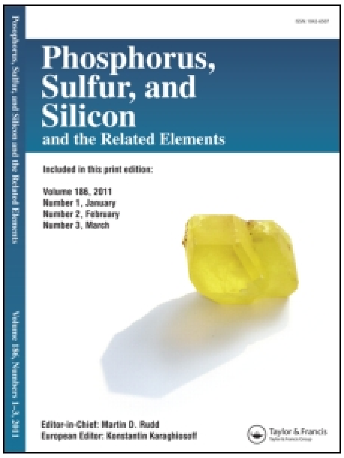

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STUDIES ON PHOSPHONIUM YLIDES-XIX.† REACTIONS OF CYANOMETHYLENETRIPHENYLPHOSPHORANE WITH CERTAIN DICARBONYL COMPOUNDS

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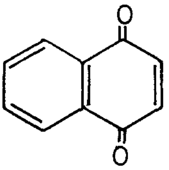
Cyanomethylenetriphenylphosphorane (**I**) reacted with 1,4-naphthoquinone **1** to give the new ylidphosphorane adduct **4** and the dimeric product **5**. Reaction of acenaphthenequinone (**2**) with phosphorus ylide I afforded compounds **6** and **7**. On the other hand, ylide I reacts with phenanthrenequinone (**3**) yielding adducts **8**, **9** and **10**, respectively. Structural reasoning for the new products was based on compatible analytical and spectral data (IR, ^{1}H, ^{31}P-NMR and MS). The mechanism that accounts for the formation of the new adducts is discussed.

Key words: Phosphonium ylides; NMR; Wittig reagents; cyanomethylenetriphenyl phosphorane.

INTRODUCTION

The action of Wittig reagents on dicarbonyl compounds has been extensively studied.[1–8] However, no information is in the literature regarding the behaviour of these compounds towards cyanomethylenetriphenylphosphorane. It was of interest to study the reactivity of 1,4-naphthoquinone (**1**), acenaphthenequinone (**2**), and phenanthrenequinone (**3**) towards cyanomethylenetriphenylphosphorane (**I**).



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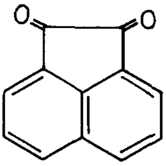

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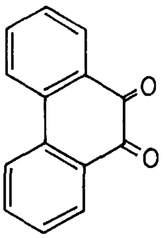

3

$(C_6H_5)_3\overset{+}{P}-\overset{-}{C}H-CN$

I

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†For Part XVIII see Leila Sadek Boulos and Nahed Khir Eldin, Tetrahedron, 49, No. 18, 3871 (1993).

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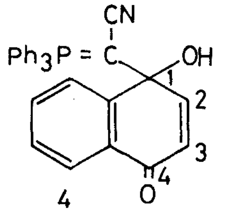
RESULTS AND DISCUSSION

When 1,4-naphthoquinone (**1**) was treated with one equivalent of cyanomethylenetriphenylphosphorane (**I**)[9] in dry benzene at room temperature for 5 hr, adducts **4**, **5**, and triphenylphosphine oxide were isolated. Carrying out the reaction using two moles of phosphonium ylides instead of one, led to the formation of adducts **4**, **5** and triphenylphosphine oxide in good yields. The structure of the new compound **4** is deduced from its analysis, IR, ^{1}H-NMR, ^{31}P-NMR and mass spectral data.



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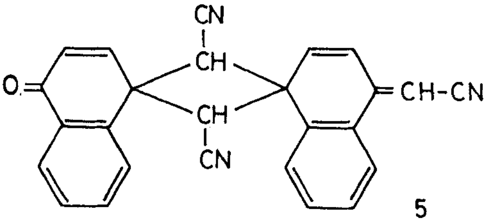

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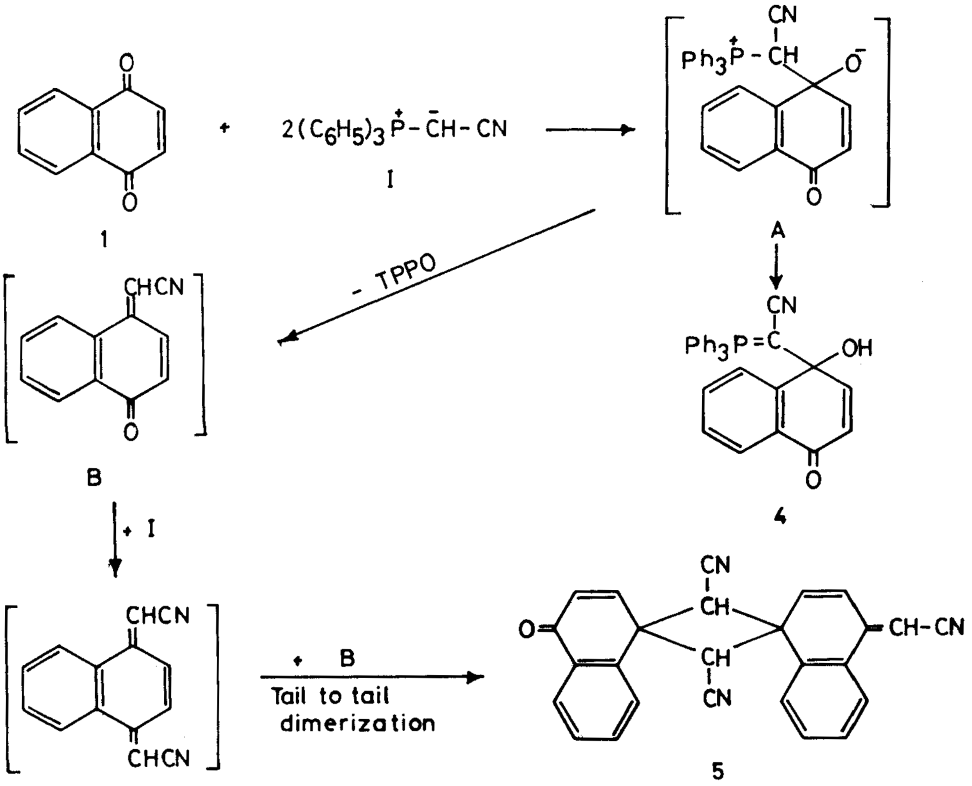
Elemental and mass spectral analyses of adduct **4** corresponded to an empirical formula of $C_{30}H_{22}NO_2P$. The IR spectrum of adduct **4** revealed the presence of strong-OH and C═O absorption bands at 3100 cm^{-1} and 1648 cm^{-1}. The IR spectrum of **4** exhibited strong bands at 1670 and 1518 cm^{-1} characteristic for the C═P group absorption,[10] at 1410 cm^{-1} for the $>$P—C—(phenyl) absorption[11] and at 2208 (C≡N). Adduct **4** possessed an ylid-phosphorane structure since it exhibited a positive shift in its ^{31}P-NMR spectrum (δ = +19.41, vs. 85% H_3PO_4) and absorbed in the region characteristic for this class of compounds.[10,12–14] ^{1}H-NMR spectrum (200 MHz) of **4** showed two proton doublets at 6.83 and 6.85 ppm with a coupling constant value of $J_{2,3} = J_{3,2}$ = 10 Hz (H-2, H-3). The exchangeable D_2O (OH) appeared at δ = 8.1. The aromatic protons appeared as a multiplet at 7.3–8.0 ppm (Ar, 19 H). The mass spectrum of adduct **4** showed a prominent ion peak M^+ at 459 which supported structure **4**. The structure of the other isolated compound **5** was assigned from its analysis, ^{1}H-NMR and mass spectral data (cf. Experimental). The ^{1}H-NMR (400 MHz) of compound **5** showed two singlets at 1.3 and 1.37 ppm (s, 1H, CH-CN), due to the two CH-CN protons of the cyclobutane ring. The methylene proton appeared as two singlets at 6.8 and 6.85 ppm suggesting the presence of two isomeric forms for compound **5**. The aromatic protons appeared as a multiplet at 6.95–8 ppm (12 H).

A possible explanation for the course of the reaction of cyanomethylenetriphenylphosphorane (**I**) with 1,4-naphthoquinone (**1**) is shown in (Scheme I).

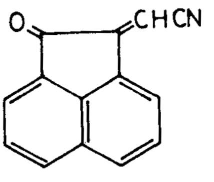
1,4-Naphthoquinone (**1**) reacted with ylide **I** via 1:2 addition to give the stable phosphorane **4**. Adduct **5** can be obtained via carbonyl olefination with one molecule of ylide **I** to give intermediate (**B**) which reacted with another molecule of ylide **I** to give intermediate (**C**) followed by dimerization with (**B**) under the experimental conditions (tail to tail dimerization) to give the final product **5**. The reaction of acenaphthenequinone (**2**) with ylide **1** (1:2 molar ratio) was performed in refluxing benzene to give two chromatographically pure adducts formulated as **6** and **7**. Triphenylphosphine oxide was also isolated from the reaction mixture.



Scheme I

Structure 6 was deduced from correct elemental microanalysis, IR, ^{1}H, ^{13}C-NMR and mass spectroscopic data (cf. Experimental).

The structure of the other isolated compound 7 was assigned from elemental analysis, IR, ^{1}H-NMR, and mass spectral data. Elemental and mass spectral analyses for compound 7 corresponded to an empirical formula of $C_{28}H_{14}N_2O_2$. The ^{1}H-NMR (400 MHz) of compound 7 revealed the presence of a singlet at 6.45 ppm corresponding to the two methylene =CH— protons. The aromatic protons appeared as a multiplet at 7.6–8.5 ppm (12 H, Ar, m). The IR spectrum of compound 7 showed the absence of the C=O absorption band recorded at 1700 cm^{-1} in the starting quinone 2. The mass spectrum of 7 by the Field Ionization Method yielded



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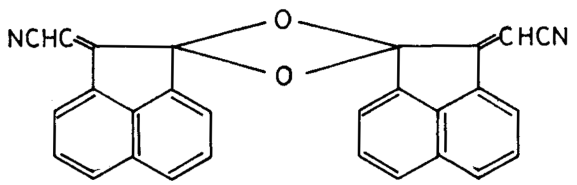

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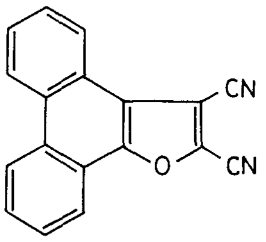
a prominent ion peak at 410 which supports structure **7**. ^{13}C-NMR (400 MHz) furnished strong evidence in support of structure **7**. The ^{13}C-NMR in $CDCl_3$ showed the ketal carbon as one signal at 95.8 ppm. The methylene protons appeared as one signal at 125 ppm.

Treatment of compound **7** with 10% HCl resulted in the formation of adduct **6** in quantitative yield.

When phenanthrene-9,10-quinone (**3**) was treated with one equivalent of cyanomethylenetriphenylphosphorane (**I**) in benzene at reflux temperature for 6 hr, adducts **8**, **9** and **10** were isolated. Carrying out the reaction using two moles of the phosphonium ylides instead of one, led to the formation of adducts **8**, **9** and **10** in good yields.



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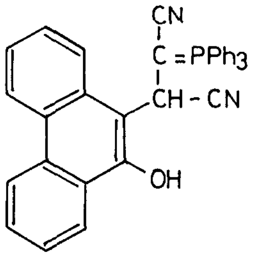

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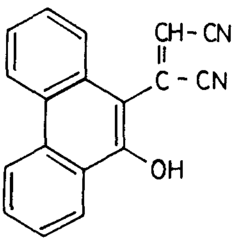

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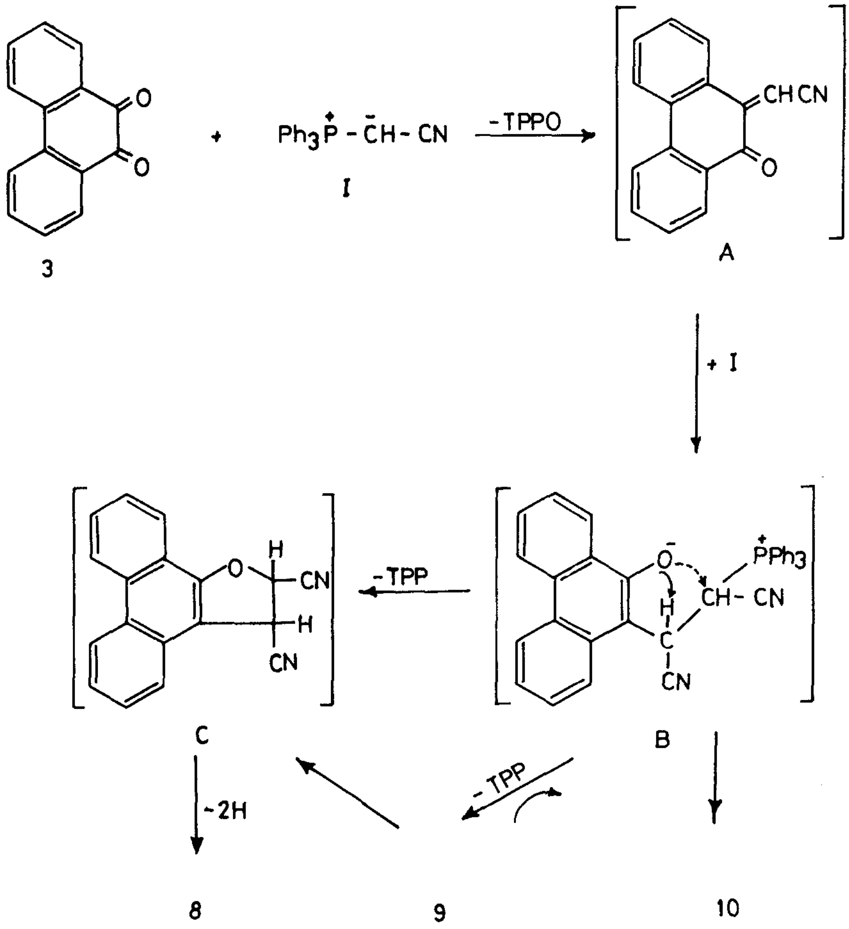
The structure of 2,3-dicyanophenanthro[9,10-b]furan (**8**) was deduced from analysis, IR and mass spectral data (cf. Experimental). The IR spectrum of compound **9** revealed the presence of a strong —OH band at 3420 cm^{-1}, C=C at 1616 cm^{-1}, and at 2208 (C≡N). The ^{1}H-NMR (400 MHz) of 2-(9-hydroxyphenanthrene-10-yl)-1,2-dicyanoethylene (**9**) exhibited signals at 5.4 ppm (s, $C{=}\underline{CH}{-}CN$), and at 9.25 ppm (s, 1H, OH).

The structure of the other isolated compound **10** was deduced from analysis, IR, ^{1}H-NMR, ^{31}P-NMR and mass spectral data. Elemental and mass spectral analyses of adduct **10** corresponded to an empirical formula of $C_{36}H_{25}N_2OP$. IR spectrum of adduct (**10**) (in KBr) revealed the presence of —OH absorption band at 3392 cm^{-1}. The strong absorption band at 1680 cm^{-1} recorded for the C=O in quinone **3** was absent in the IR spectrum of adduct **10**. The IR spectrum of **10** exhibited strong bands at 1665 and 1500 cm^{-1} characteristic for the $>$C=P group absorption and at 1410 cm^{-1} for the $>$P—C—(phenyl) absorption. Adduct **10** possessed an ylide-phosphorane structure since it exhibited a positive shift in its ^{31}P-NMR spectrum ($\delta = +19.56$, vs. 85% H_3PO_4) and absorbed in the region characteristic for this class of compounds. ^{1}H-NMR spectrum of **10** showed a doublet at 2.2 ppm with J_{HP} = 10 Hz. The exchangeable (D_2O) proton (OH) appeared at δ = 9.25. The mass spectrum of **10** yielded a prominent ion peak M^+ at 532 which supported structure **10**.

The mechanism proposed in "Scheme II" can account for the formation of products **8**, **9** and **10**. Wittig mono-olefination of **3** by **I** gave the intermediate (**A**), which reacted further with a second ylide **I** to afford the intermediate (**B**). Intramolecular hydrogen abstraction of the B-hydrogen, or nucleophilic attack at the α-carbon of the phosphonium group by the phenoxy anion in (**B**), accompanied by triphenylphosphine elimination, resulted in the formation of **9** and (**C**).[8] Further dehydrogenation of the intermediate (**C**), [possibly also formed from (**9**)] gave product **8**. Intermediate (**B**) can form the stable phosphorane adduct **10**.

In view of the above results, it can be seen that the reaction of cyanomethylenetriphenylphosphorane with quinones (**1–3**) led to diverse products depending on the nature of the quinone used and also on the stability of the addition products.



Scheme II

It is safe to conclude that p-naphthoquinone (**1**), acenophthenequinone (**2**) and 9,10-phenanthrenequinone behave in a manner different from that already known with other Wittig reagents[1,3,7,8] towards cyanomethylenetriphenylphosphorane (**I**). The significance of these findings is not only the discovery of a new pattern of Wittig reaction but also the establishment of a novel method for the synthesis of the dimeric products **5** and **7**.

EXPERIMENTAL

All melting points are uncorrected. The benzene used was dried over Na. Cyanomethylenetriphenylphosphorane[9] was prepared according to established procedures. The IR spectra were measured in KBr, on a Perkin-Elmer Infracord Spectrophotometer Model 157 (Grating). The ^{1}H-NMR spectra were run in $CDCl_3$ at 90 MHz on a varian Spectrometer using TMS as an internal reference. The ^{31}P-NMR spectra were recorded in $CDCl_3$ (vs. H_3PO_4 as external standard) on JNM-PS-200 Fa Jeol Spectrometer. The mass spectra were run at 70 eV on kratos MS equipment and/or Varian MAT 311 Spectrometer.

Reaction of 1,4-naphthoquinone (**1**) *with cyanomethylenetriphenylphosphorane* **I**. A mixture of **1** (0.16 g, 0.001 mole) and ylide **I** (0.6 g, 0.002 mole), in benzene (25 ml) was stirred for 24 hrs at room temperature.

The reaction solvent was removed under reduced pressure, the residue was placed on a column of silica gel and eluted with a mixture of acetone-petroleum ether (4:6) to give adduct **4** as violet crystals (from acetone-petroleum ether), m.p. 205–7°C (65%). Anal. Calcd. for $C_{30}H_{22}NO_2P$ (459.4). C, 78.42; H, 4.82; N, 3.10; P, 6.71%. Found: C, 78.46; H, 4.89; N, 3.14; P, 6.75%. Mol. wt (MS) = 459.

The second isolated compound was eluted with a mixture of acetone-petroleum ether (8:2) and crystallized from chloroform to give adduct **5** as violet-green crystals, m.p. 260–2°C (30%). Anal. Calcd. for $C_{26}H_{15}N_2O$ (385.43). C, 81.02; H, 3.92; N, 10.90%. Found: C, 81.07; H, 3.95; N, 10.82%. Mol. wt (MS) = 385. IR: C=O at 1648 and C=C at 1611 cm^{-1}. Triphenylphosphine oxide was also isolated from the reaction mixture, m.p. and mixed m.p. 151°C.

Reaction of Acenaphthenequinone (**2**) *with ylide* (**I**). A mixture of 2 (0.18 g, 0.001 mole) and ylide **I** (0.6 g, 0.002 mole) in benzene (25 ml) was refluxed for 10 hrs. After evaporation of the volatile materials under reduced pressure, the residue was subjected to silica gel column chromatography using the eluent stated below. The melting points and yields are also given.

Cyanomethyleneacenaphthenone (**6**). Eluent acetone-petroleum ether (4:6), yield (65%), m.p. 163–5°C. Anal. Calcd. for: $C_{14}H_7NO$ (205.22) C, 81.94; H, 3.44; N, 6.82%. Found: C, 81.9; H, 4.50; N, 6.83%. Mol. wt (MS) = 205. IR C=O at 1700, C=C at 1620 cm^{-1}. ^{1}H-NMR: =CH at δ = 6.4 (1H, s); 7.5–8.5 ppm (6H, m, Ar). ^{13}C-NMR (expressed in ppm), (189, C=O, 124.9, =CH—CN, 116.8, $\underline{C}N$.

Adduct 7. Eluent: acetone-petroleum ether (5:5), yield (25%), yellow crystals from chloroform, m.p. 256–8°C. Anal. Calcd. for: $C_{28}H_{14}N_2O_2$ (410.346) C, 81.94; H, 3.44; N, 6.82. Found: C, 81.95; H, 3.5; N, 6.87%. Mol. wt (MS) = 410. IR: C=C at 1620 cm^{-1}. ^{1}H-NMR: singlet at 6.45 (s, 2H, =$\underline{C}$H—CN). ^{13}C-NMR 95.8 (ketal carbon), 125 (=$\underline{C}$H—CN), 116.7 ($\underline{C}$N).

Triphenylphosphine oxide was also isolated, m.p., mixed m.p. 150°C.

Acid hydrolysis of Adduct **7**. 0.2 g of adduct **7** in 30 ml dil hydrochloric acid (10%) was refluxed for 5 hr. After cooling, the precipitated material was filtered off, washed with water, crystallised from acetone-petroleum ether to give compound **6** in quantitative yield (m.p., and mixed m.p., comparative IR spectra).

Reaction of phenanthrenequinone (**3**) *with ylide* (**I**). To a suspension of phenanthrenequinone **3** (0.21 g, 0.001 mole) in dry benzene (25 ml), ylide **I** (0.6 g, 0.002 mole) was added and the reaction mixture was refluxed for 12 hrs. After evaporation of the volatile materials under reduced pressure, the residue was subjected to silica-gel column chromatography using the eluent stated below. The melting points and yield are also given.

2,3-Dicyanophenanthro[9,10-b]furan (**8**). Eluent: acetone-petroleum ether (1:9). Anal. Calcd. for $C_{18}H_8N_2O$ (268.278) C, 80.59; H, 3.00; N, 10.44%. Found: C, 80.61; H, 3.12; N, 10.5%. Mol. wt. (MS) = 268. Yield (35%) as pale yellow crystals, m.p. 87–9°C.

2-(9-Hydrophenanthrene-10-yl)-1,2-dicyanoethylene (**9**). Eluent: acetone-petroleum ether (5:5), orange crystals, m.p. 240–2°C (30% yield). Anal. Calcd. for: $C_{18}H_{10}N_2O$ (270.291) C, 79.98; H, 3.72; N, 10.36%. Found: C, 79.99; H, 3.75; N, 10.4%. Mol. wt. (MS) = 270.

2-(9-Hydrophenanthrene-10-yl)-1-cyanomethylene-2-cyanomethylenetriphenylphosphoranylidene (**10**). Eluent: acetone-petroleum ether (6:4), pale yellow crystals, m.p. 210–2°C (yield 25%). Anal. Calcd for $C_{36}H_{25}N_2OP$ (532.232) C, 81.17; H, 4.73; N, 5.26; P, 5.82. Found: C, 81.2; H, 4.70; N, 5.3; P, 5.87%. Mol. wt. (MS) = 532.

Triphenylphosphine and triphenylphosphine oxide were also isolated and identified.

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