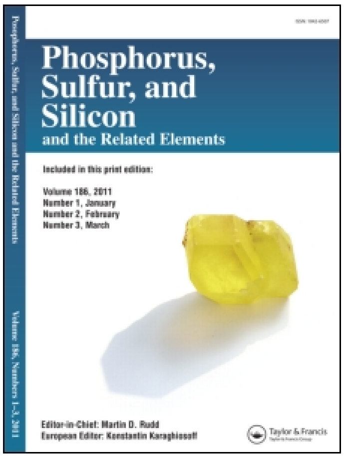

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THE BEHAVIOUR OF PHENANTHRENEQUINONE DERIVATIVES TOWARDS ACYCLIC AMINOPHOSPHINES

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Tris(dimethylamino)phosphine (**IIIa**) and/or Bis-dimethylaminophenyl-phosphine (**IIIb**) react with 9,10-dihydro(9-dicyanomethylene)phenanthrene-10-one (**Ib**) to produce 1:1 adducts which have the aminophosphonium dipolar ion structure (**V**) in the crystalline state and in solutions. The 1:1 adduct isolated from the reaction of **IIIb** with 9,10-phenanthrenequinonemonoimine (**Ic**) has a similar dipolar structure (**XII**) in the crystalline state. Solutions of the latter contained the same molecular species (**XII**) in equilibrium with a cyclic aminophospholene species (**XIII**). Only decomposition products could be observed from the reaction of **IIIa** with **Ic**. The products in this case were the phosphoroamidate (**X**), 9,10-phenanthrenequinone (**Ia**) and phenanthroxazine **XI**. A mechanism is proposed to explain the formation of these compounds.

Key words: Tris(dimethylamino)phosphine (**IIIa**); bis-(dimethylamino)-phenyl-phosphine (**IIIb**); 9,10-dihydro(9-dicyanomethylene)phenanthrene-10-one (**Ib**); 9,10-phenanthrenequinonemonoimine (**Ic**); phosphonium dipolar ions (**V,XII**); cyclic aminophospholene ring system (**XIII**); phenanthroxazine (**XI**); hexamethylphosphoroamidate (**X**).

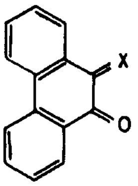
INTRODUCTION

The reaction of aminophosphines with 9,10-phenanthrenequinone (**Ia**) has been studied in considerable detail by Ramirez and his co-workers.[1–3] Whereas triaminooxyphosphonium dipolar ion (**II**) was obtained from the reaction of acyclic tris(dimethylamino)phosphine (**IIIa**) with quinone **Ia**, triaminodioxyphosphoranes (**IVa,b**) were isolated from the reaction of cyclic triaminophosphines with the same quinone.

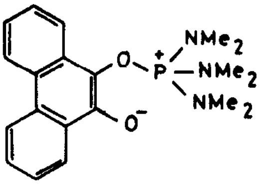
However, to the best of our knowledge, there appears to be no information in the literature regarding the behaviour of 9,10-phenanthrenequinone derivatives (**Ib,c**) towards these aminophosphines. It was therefore of interest to undertake a study to determine whether these derivatives would behave in a manner similar to the parent quinone (**Ia**). We wish to report here our findings on the reaction of acyclic aminophosphines **IIIa** and **IIIb** with quinones **Ib** and **Ic**.

RESULTS AND DISCUSSIONS

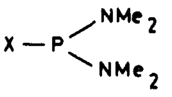
We have found that the reaction of tris(dimethylamino)phosphine (**IIIa**) with 9,10-dihydro-9-(dicyanomethylene)phenanthrene-10-one (**Ib**), in benzene, proceeded at room temperature to give chromatographically pure 1:1 adduct (**Va**). Changing the reaction medium (using methylene chloride) or letting the reactants stand in the solvent for 3 days did not change the properties of the stable adduct. The tria-



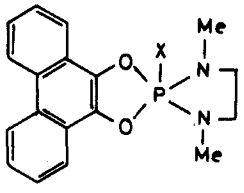
I a, X = O
b, X = C (CN)$_2$
c, X = NH



II, $^{31}P = 38.5$



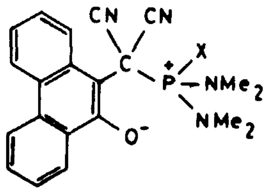
III a, X = NMe$_2$; $^{31}P = 122$
b, X = C$_6$H$_5$; $^{31}P = 100.3$



IV a, X = NMe$_2$; $^{31}P = -29.8$
b, X = N  ; $^{31}P = -35.1$

minophosphonium dipolar ion structure (Va) is assigned to this adduct for the following reasons:

(a) Elemental analysis and molecular weight determination (MS) of this adduct corresponds to $C_{23}H_{26}N_5OP$.



V a, X = NMe$_2$; $^{31}P = 33.47$
b, X = C$_6$H$_5$; $^{31}P = 36.86$

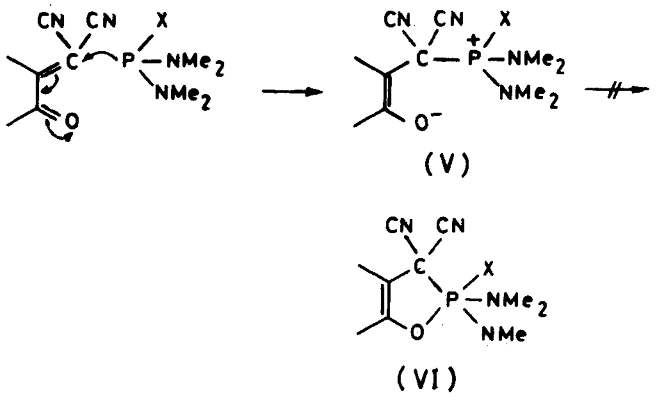
(b) The ^{31}P-NMR spectrum of this adduct has one signal at $\delta = +33.47$ ppm which indicates an open dipolar ion with quadruply-connected phosphorus.[4]

(c) The IR spectrum, in KBr, reveals the presence of a strong band at ν 1478 cm^{-1} ascribed to the "enolate" carbonyl absorption.[5] The two bands at 2160 cm^{-1} and at 2100 cm^{-1} are due to the cyano groups. The bands at 1310 cm^{-1} and at 865 cm^{-1} are attributed to the absorption of the P-N(CH$_3$)$_2$ group. The band at 1595 cm^{-1} (C=C) is consistant with the dipolar structure.[5]

(d) the ^{1}H-NMR spectrum of the adduct showed a doublet centered at $\delta = 2.37$ ppm ($J_{HP} = 10.05$ Hz) due to 18 H of the three magnetically equivalent dimethylamino groups. The aromatic protons appeared as two multiplets centered at $\delta = 7.65$ ppm and $\delta = 8.75$ ppm.

Similarly, the reaction of the acyclic Bis-dimethylamino-phenyl-phosphine (**IIIb**) with quinone **Ib** proceeded in dry benzene at room temperature to give mainly a 1:1 adduct having the aminophosphonium dipolar ion structure (**Vb**). This is based on analytical and spectroscopic data (cf. Experimental).

The formation of the dipolar ion (V) might arise[6,7] by the nucleophilic attack of the phosphorus of **III** on the methylene carbon in quinone **Ib**. Our results rule out the possibility of the formation of compounds having the cyclic structure (VI) since the latter would predict a band in the IR spectrum at ν 1630–1690 cm^{-1} for the C=C, and would also predict a negative value for the signal of the ^{31}P-NMR corresponding to the phospholene structure (VI).[3,7] Ramirez related the difficulty of **V** → **VI** transformation of similar adducts to the considerable intramolecular overcrowding which is present in the trigonal bipyramidal configuration of pentacovalent phosphorus compounds.[3,8]

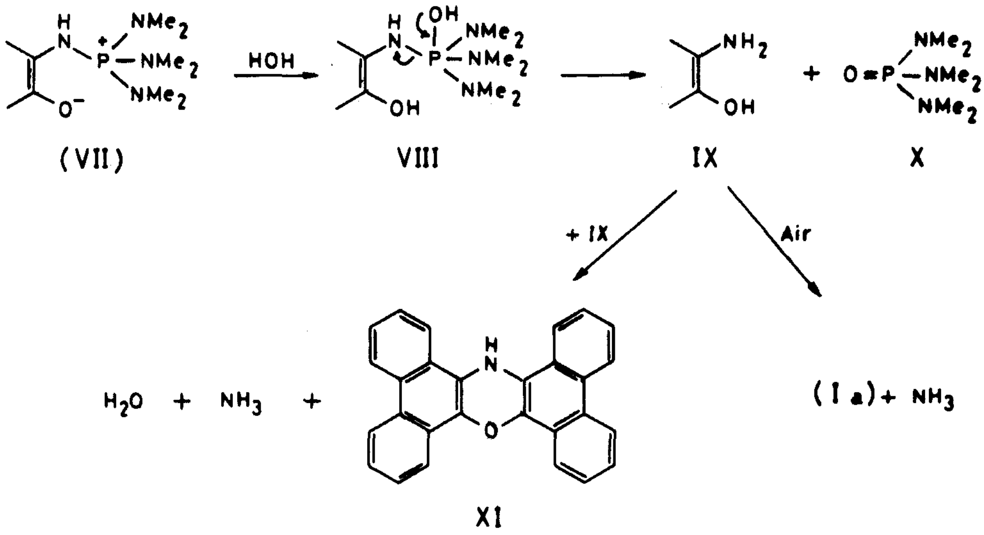


(V)

(VI)

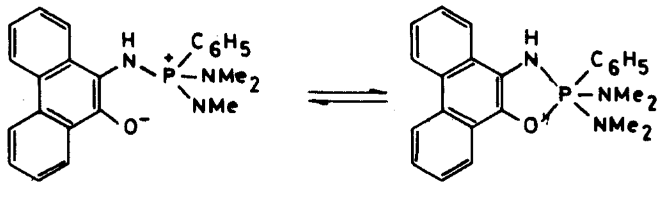
Next, we have investigated the behaviour of 9,10-phenanthrenequinonemonoimine (**Ic**) towards **IIIa**. The exothermic reaction proceeded in benzene or in methylene chloride at 5°C. The yellow colour of the solution turns brown immediately. The colour faded gradually after 10 minutes. TLC examination indicated the disappearance of both reactants (**Ic** and **IIIa**). Phenanthrenequinone (**Ia**), phenanthroxazine (**XI**) and hexamethylphosphoroamidate (**X**) were isolated and identified (cf. experimental). A mechanism which accounts for the formation of these compounds is depicted in "Scheme I." It is probable that this reaction gives first the expected phosphonium dipolar ion (**VII**). This can add the elements of water, which is unavoidably present in the medium yielding a transient intermediate (**VIII**).[9] Charge delocalization would cause phosphorus in this intermediate to act as a good leaving group,[10] thereby producing 9-amino-10-phenanthrol (**IX**) and hexamethylphosphoroamidate (**X**). The formation of **Ia** and **XI** from the oxidative decomposition of **IX** was previously described.[11] These transformations would be probably accelerated by the relatively high temperature at which the phosphonium ion (**VII**) was generated.[12] Unstable phosphonium ions were previously noted.[5,12] Acenaphthenequinone[5] and flurenone[12] form with aminophosphines unstable dipolar ions which lost phosphoramidates and underwent several transformations.

On the other hand, when bis-dimethylamino-phenyl-phosphine (**IIIb**) was al-



SCHEME I

lowed to react with quinone **Ic** at the same experimental conditions, a 1:1 adduct was produced and assigned the dipolar structure (**XII**). The spectral properties of this adduct differed from compound **V**. In KBr, the IR spectrum of this adduct showed bands at ν 1475 cm^{-1} (enolate carbonyl) and at 1590 cm^{-1} (C=C). However, in chloroform, a weak band appeared for the C=C at ν 1675 cm^{-1} attributed to a relatively small amounts of the phospholene **XIII**.

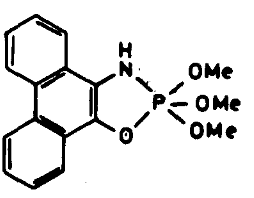


XII (^{31}P = 12.47 ppm) XIII

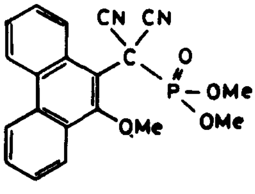
The ^{31}P-NMR signal of this adduct, in $CHCl_3$, appeared at = 12.47 ppm. These observations strongly suggest an equilibrium between the open dipolar structure (**XII**) and the cyclic phospholene structure (**XIII**). The ^{31}P-NMR signal should be an average value of both structures. The observed value suggests that the dipolar form greatly predominates over the phospholene structure. The presence of one signal indicates that the equilibrium between the two forms is established rapidly relative to the time scale of the NMR phenomenon. A similar finding was reported for the co-existance in solutions of a structure containing quadruply-connected phosphorus and the corresponding valence tautomer containing quintuply-connected phosphorus assigned to the 1:1 adduct formed when aminophosphine **IIIa** was reacted with benzil.[5]

The stability of the adducts formed in the forementioned reactions could be explained in terms of the concept of "hard and soft bases" discussed by Pearson[13] and by Hudson.[14,15] The methylene carbon of **Ib** seems to be a softer acid than the imino nitrogen of **Ic**. Therefore, aminophosphine (**IIIa,b**) which are soft bases, attack **Ib** forming highly stable phosphonium dipolar ions (**Va,b**). On the other hand, **Ic** forms relatively unstable dipolar ions (**VII** and **XII**) when attacked by the same soft bases. Whereas adduct **XII** was stabilized to some extent by the contributing pentacovalent phospholene structure (**XIII**), adduct **VII** decomposed to **IX** and **X**.

This disparity in behaviour of quinone **Ib** on one hand and quinone **Ic** on the other hand is not surprising as phenanthrenequinone derivatives are known to behave differently when reacted with trialkyl phosphites.[16–18] Trimethyl phosphite, for example, reacted with **Ic** forming the cyclophospholene ring system (**XIV**)[16] and with **Ib** forming the phosphonate adduct (**XV**).[17]



XIV



XV

EXPERIMENTAL

All melting points were uncorrected. The appropriate precautions in handling moisture-sensitive compounds were undertaken. Benzene and pet. Ether (40–60) were dried over Na. Phenanthrenequinone derivatives **Ib**[19] and **Ic**[20] were recrystallized and dried before use. Tris(dimethylamino)phosphine (**IIIa**)[21] and Bis(dimethylamino)-phenyl-phosphine (**IIIb**)[22] were freshly distilled before use. All manipulations were carried out under N_2. The IR spectra were recorded with Perkin-Elmer Spectrophotometer 157 G. The ^{1}H-NMR spectra were run in $CDCl_3$ on Varian Spectrometer at 90 MHz using TMS as an internal reference. The ^{31}P-NMR spectra were taken in $CDCl_3$ (vs. H_3PO_4 as external standard) on Varian CET 20,32 MHz Spectrometer. The MS spectra were performed at 70 eV on MS-50 Kratos (A.E.I) Spectrometer. Elemental analysis were carried out by "Microanalytical Centre, Cairo University, Gizza, Egypt."

Reaction of aminophosphines (**IIIa,b**) *with 9,10-dihydro-9-(dicyanomethylene)phenanthrene-10-one* (**Ib**). A solution of **IIIa** (1.65 g; 0.01 mole) in 25 ml of benzene was added to a solution of **Ib** (2.56 g; 0.01 mole) in 25 ml of benzene at room temperature with stirring. The colour of the solution changed immediately from orange to brown then faded gradually to yellow in 30 minutes. Benzene was removed under reduced pressure. The residue was crystallized with chloroform-pet. ether to give Va as yellow crystals, m.p. 198–200°C, yield 90%. Anal. Calcd for $C_{23}H_{26}N_5OP$ (419.437): C, 65.86; H, 6.24; N, 16.69; P, 7.38. Found: C, 65.80; H, 6.20; N, 16.65; P, 7.30%. MS: m/e 419 (M^+, <3%) and m/e 375 [M^+-$N(CH_3)_2$, 35%].

Similarly, **IIIb** (1.72 g; 0.01 mole) reacted with **Ib** (2.56 g; 0.01 mole) in benzene (50 ml) to produce **Vb**, as yellow crystals (from chloroform-pet. ether), m.p. 170–171°C, yield 90%. Anal. Calcd for $C_{27}H_{25}N_4OP$ (452.468): C, 71.67; H, 5.56; N, 12.38; P, 6.84. Found: C, 71.60; H, 5.50; N, 12.30; P, 6.80%. MS: m/e 452 (M^+). IR: bands at 2180 cm^{-1} and 2110 cm^{-1} ($C\equiv N$), 1590 cm^{-1} ($C=C$), 1490 cm^{-1} (enolate carbonyl), 1310 cm^{-1} and 870 cm^{-1} [P-$N(CH_3)_2$]. ^{31}P-NMR: δ = 36.86 ppm. ^{1}H-NMR: signals at δ = 2.85 ppm (12H, d) (J_{HP} = 10.5 Hz), 7.52 ppm and 8.71 ppm (13H, 2 multiplets).

Repeating these experiments using methylene chloride instead of benzene gave the same results.

Reaction of aminophosphine **IIIa** *with 9,10-phenanthrenequinonemonoimine* (**Ic**). A cold solution of **IIIa** (1.65 g; 0.01 mole) in 25 ml of benzene was added dropwise to a cold solution of **Ic** (2.07 g; 0.01 mole) in 25 ml of benzene with stirring. The temperature was not allowed to rise above 5°C by continuous cooling. The colour of the solution changed from yellow to brown then faded to yellowish brown in 10 minutes. The solution was warmed to room temperature and the solvent was removed. TLC examination of the residual oil indicated the disappearance of **Ic** and **IIIa** and the presence of many products. This oil was extracted several times with pet. ether. The extracts were collected, solvent was removed, then was subjected to vacuum distillation at 0.1 mm, 100°C, whereby hexamethylphosphoroamidate (X)[6,23] was obtained (1.4 g) (^{31}P-NMR: δ = 24.15 ppm; ^{1}H-NMR: δ = 2.60, d, J_{HP} = 9.5 Hz). The solid residue was first extracted with hot ethanol to separate yellow crystals (1.2 g), m.p. 203°C which proved to be phenanthrenequinone (**Ia**)[24] (TLC, mixed m.p. and comparative IR). Thereafter the undissolved brown solid was crystallized from dimethylformamide to give deep brown crystals (0.4 g), m.p. >350°C. It was proved to be phenanthroxazine (**XI**). It was identified by comparison of its TLC and IR spectrum with an authentic sample,[11] and by elemental analysis. Anal. Calcd for $C_{28}H_{17}NO$: C, 87.72; H, 4.41; N, 3.65. Found: C, 87.68; H, 4.35; N, 3.60%. No other products could be isolated, although TLC examination showed more spots than the above identified compounds.

Reaction of aminophosphine **IIIb** *with 9,10-phenanthrenequinonemonoimine* (**Ic**). A solution of **IIIb** (1.72 g; 0.01 mole) in 25 ml of benzene was added to a solution of **Ic** (2.07 g; 0.01 mole) in 25 ml of benzene with stirring. The colour of the solution faded in 10 minutes. Solvent was removed under reduced pressure. The residue was crystallized from toluene to give **XII** as yellow crystals, m.p. 258°C, yield 80%. The same compound was obtained when this reaction was carried out in methylene chloride. Anal. Calcd for $C_{24}H_{26}N_3OP$ (403.436): C, 71.45; H, 6.49; N, 10.41; P, 7.67. Found: C, 71.40; H, 6.42; N, 10.40; P, 7.60%. MS: m/e 403 (M^+). ^{1}H-NMR: signals at δ = 2.30 ppm (12H, d) (J_{HP} = 10.2 Hz) and a complex pattern of aromatic protons in the region δ = 7.28–8.7 ppm (13H).

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