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TRIAMINOOXYPHOSPHONIUM DIPOLAR IONS AND TRIAMINODIOXY PHOSPHORANES FROM THE REACTION OF TRIAMINOPHOSPHINES WITH α-DIKETONES

DEMONSTRATION OF THE CO-EXISTENCE OF 4-COORDINATED AND 5-COORDINATED PHOSPHORUS IN SOLUTION. P^{31} NMR SPECTRA[1]

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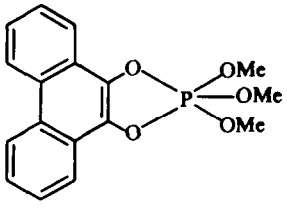
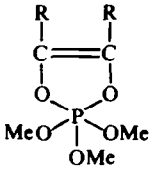
Abstract—The phosphorus of *tris*dimethylaminophosphine added to the oxygen of the α-diketone, benzil, and gave a 1:1 adduct. This adduct could be isolated in two crystalline forms: one of them was a triaminooxyphosphonium dipolar ion, and the other was a cyclic triaminodioxyphosphorane. Solutions of these crystalline adducts contained the same molecular species in equilibrium with each other. Certain solvents favoured the cyclic form with 5-coordinated phosphorus, while others favoured the dipolar ion with 4-coordinated phosphorus. The value of the P^{31} NMR shifts varied from +30·2 ppm vs H_3PO_4 in 0·8M hexane to +13·1 ppm in 1·2M methylene chloride solutions. In methylene chloride solutions, the value of the shift varied significantly with concentration. The 1:1 adducts made from the reactions of the 5-membered cyclic triaminophosphines, 2-N-pyrrolidino-, 2-dimethylamino-, and 2-methoxy-1,3,2-diazaphospholanes with benzil existed exclusively as cyclic triaminodioxyphosphoranes in the crystalline state and in solutions. The reaction of acenaphthenequinone with the cyclic aminophosphines produced the corresponding aminophosphine oxides *via* unstable adducts with P—O—C bonds, which were formed at −70°.

THE phosphorus of trialkyl phosphites add to the CO-*oxygen* of *p*-quinones (I).[3] This observation, in 1957 led us to the preparation of derivatives of the 2,2-dihydro-1,3,2-dioxaphospholene ring system, for example, II, III and IV, which were made by reaction of trialkyl phosphites with *o*-quinones, (V), and α-diketones, (VI), respectively.[4] Two other groups of investigators[5,6] also reported on the reactions of trialkyl phosphites with α-diketones at about the same time.



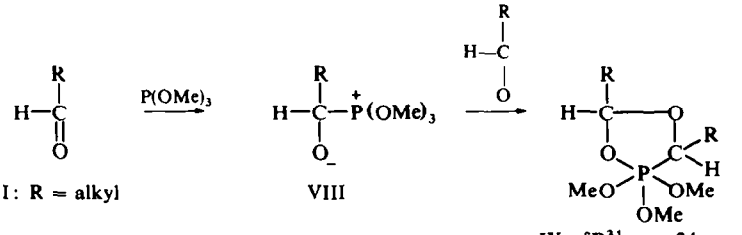
II: δP^{31} = +45·1 ppm



III: R = Ph; δP^{31} = +49·5 ppm
IV: R = Me; δP^{31} = +48·9 ppm

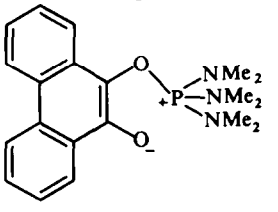
Further studies[7–17] have shown that phosphite esters will add to CO-oxygen whenever the CO function is activated by electron-withdrawing groups. On the other hand, the phosphites added to CO-carbon in the case of unsubstituted aliphatic

aldehydes (VII).[18] The isolated derivatives of the 2,2-dihydro-1,4,2-dioxaphospholane ring system (IX) were formed *via* 1:1-adducts with P—C—O bonds (VIII). It is possible that in all cases, the phosphite added first to CO-carbon but ended on CO-oxygen when electron-withdrawing groups were present in the molecule; i.e. adduct VIII would be transformed into adduct $(RO)_3\overset{+}{P}—O—\overset{-}{C}(HR)$ (X). This mechanism appears more probable with aromatic aldehydes like *p*-nitrobenzaldehyde (XI),[13] than with aromatic ketones, but the problem remains unsolved.

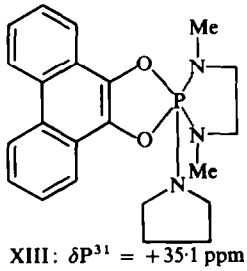


VII: R = alkyl VIII IX: δP^{31} = +34 ppm

Although the behaviour of many CO compounds toward trialkyl phosphites has now been established[3–18] little is known about related reactions of other types of trivalent phosphorus compounds.[19] Triaminooxyphosphonium dipolar ions (XII) have been obtained from the reactions of trisdimethylaminophosphine with *o*-quinones, vicinal triketones and oxomalonic esters.[20,21] On the other hand, spirotriaminodioxyphosphoranes (XIII) resulted from the reactions of 5-membered cyclic *tris*dialkylaminophosphines with the same CO compounds.[20] These differences have been attributed to steric effects which operate in the trigonal bipyramidal structure of these compounds.[10]



XII: SP^{31} = −38·6 ppm



XIII: δP^{31} = +35·1 ppm

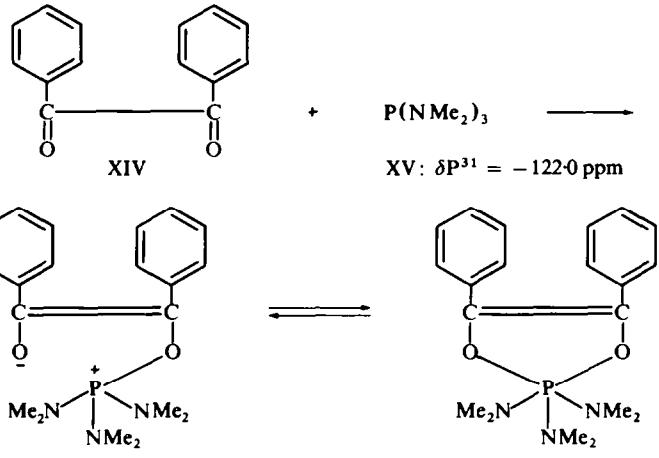
The reactions of several types of trivalent phosphorus compounds with α,β-unsaturated ketones have been studied.[22] In all cases, the phosphorus performed a 1,4-addition to the carbon of the unsaturated system.

This paper describes the reactions of acyclic and of 5-membered cyclic *tris*dialkylaminophosphines with the α-diketones benzil and acenaphthenequinone[1].

RESULTS

Reaction of benzil with trisdimethylaminophosphine. The acyclic aminophosphine reacted rapidly with benzil (XIV) in hexane at 5°. The insoluble deep yellow 1:1-adduct formed in this reaction was formulated as the triaminooxyphosphonium dipolar ion (XVI). This ion dissolved in hexane over a period of several hours, giving a nearly colourless solution which contained mostly 2,2,2-*tris*dimethylamino-4,5-diphenyl-1,3,2-dioxaphospholene (XVII) in equilibrium with a small, but un-

determined, amount of the dipolar ion (XVI). When this solution was concentrated and cooled, it deposited the phospholene (XVII) as large colourless prisms, m.p. 83–85°. Once formed, the crystalline phospholene, XVII, dissolved in hexane within seconds.



The P^{31} NMR spectrum of the hexane solutions of the phospholene, XVII, had a signal with a large positive chemical shift relative to 85% H_3PO_4; see Table 1.

TABLE 1. P^{31} NMR SHIFTS OF THE BENZIL-*tris*DIMETHYLAMINOPHOSPHINE 1:1 ADDUCT, XVI ⇆ XVII, IN VARIOUS SOLVENTS. In ppm *vs* H_3PO_4

Solvent	Conc. M	δP^{31}
hexane	1·0[a]	+30·2
benzene	1·0[a]	+29·9
ether	dil.	+29·7
CH_2Cl_2	1·0	+13·1
CH_2Cl_2	1·5	+15·1
CH_2Cl_2	2·0	+19·0
DMF[b]	dil.	+21·6

[a] Not affected by concentration.
[b] Dimethylformamide.

The sign and the magnitude of this shift demonstrated the pentacovalency of the phosphorus in the species present in the solution. If the only species present in this solution were the open dipolar ion, the P^{31} NMR shift should be in the neighbourhood of −38 ppm as had been observed in the case of the phenanthrenequinone-*tris*-dimethylaminophosphine adduct (XII).[20] Further evidence on this point will be given below.

The IR spectrum of the hexane solution had a band at 6·05 μ which is characteristic of the C=C of related 2,2,2-trimethoxy-4,5-diphenyl-1,3,2-dioxaphospholenes (IV).

A relatively weak and broad band at 6·7–6·9 μ may be attributed to the relatively small amounts of the open dipolar structure, XVI, present in the solution. The H^1 NMR of the hexane solution contained only one doublet at τ 7·36, J_{HP} = 10·8 c/s. Apparently, the three dimethylamino groups in the phospholene, XVII, were magnetically equivalent or indistinguishable as had been observed in the case of the corresponding trimethoxy phospholene, IV.

When the reaction of *tris*dimethylaminophosphine with benzil was carried out in benzene solution at 5°, a clear solution containing predominately the phospholene (XVII) was obtained. The P^{31} and H^1 NMR and IR spectra were identical to those of the hexane solution.

The reaction of the aminophosphine (XV) with benzil in methylene chloride at 0° gave a solution whose spectral properties differed significantly from those of the hexane and benzene solutions. In particular, the P^{31} NMR signal appeared at significantly lower magnetic field as shown in Table 1. Moreover, the shift varied significantly with the concentration of the methylene chloride solution, as seen in Table 1. The P^{31} NMR shift was not affected by concentration in benzene and in hexane solutions. These observations strongly suggested that in methylene chloride solutions, the equilibrium between the open-dipolar structure (XVI) and the phospholene (XVII) was shifted in favour of the former. If the equilibrium was established rapidly relative to the time scale of the NMR phenomenon, only one signal should be observed. This signal should be an average of the negative value of the open-dipolar structure and of the positive value of the phospholene structure. The exact values of the shifts of these two forms were not known, but they could be approximated from the figures for the corresponding structure of the adducts XII and XIII previously made from the reactions of phenanthrenequinone with *tris*dimethylaminophosphine and with a 5-membered cyclic aminophosphine.

The IR spectrum of the methylene chloride solution had a very strong and broad band at 6·7–6·9 μ and a very weak band at 6·1 μ. This is consistent with the presence of relatively large amounts of the open dipolar structure, XVI, whose enolate CO should give rise to the strong band at the longer wave length. Analogous IR bands had been observed in related open-dipolar structures like XII.

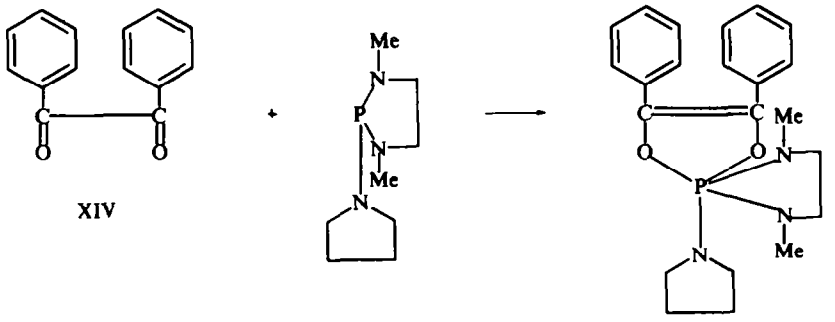
The H^1 NMR spectrum of the methylene chloride solution had one doublet at τ 7·33, J_{HP} = 10·7 c/s.

The P^{31} NMR shift suggested that the phospholene (XVII) greatly predominated over the dipolar structure in ether solution (Table 1).

The crystalline open dipolar structure was less stable and more susceptible to moisture than the phospholene. The dipolar form (XVI) dissolved instantaneously in methylene chloride, and the spectral data of these solutions were identical to the data for solutions prepared by the addition of the aminophosphine to benzil in methylene chloride.

Reaction of benzil with 5-membered cyclic triaminophosphines and phosphoramidites. 2-N-Pyrrolidino-1,3-dimethyl-1,3,2-diazaphospholane (XVIII) reacted rapidly with benzil in methylene chloride, even at −70°. This extraordinary reactivity of the aminophosphine with benzil was easily recognized by the instantaneous disappearance of the yellow colour of the α-diketone. The product of this reaction was the crystalline, relatively stable, spirotriaminodioxyphosphorane, XIX.

The P^{31} NMR shift of this material in a variety of solvents and at various con-

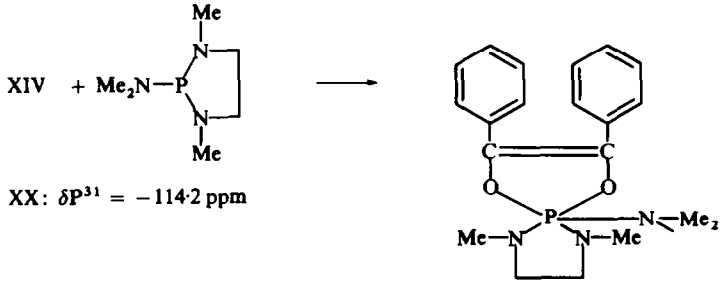


XIV

XVIII: $\delta P^{31} = -104{\cdot}9$ ppm XIX: $\delta P^{31} = +41{\cdot}8$ ppm

centrations was strongly positive and was consistent with the view that in these solutions, the 1:1-adduct existed predominately or exclusively in the phospholene form (XIX). The H^1 NMR spectrum had a doublet at τ 7·27, $J_{HP} = 9{\cdot}6$ c/s, due to the two equivalent or indistinguishable methyl groups attached to nitrogen. The IR spectrum of the phospholene had a band at 6·12 μ attributed to the C=C of the phospholene.

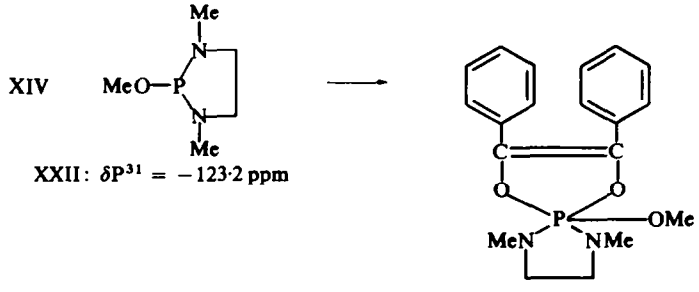
The reaction of 2-dimethylamino-1,3-dimethyl-1,3,2-diazaphospholane (XX) with benzil (XIV) in methylene chloride at $-70°$ gave a spirotriaminooxyphosphorane in nearly quantitative yield. The spectral properties were very similar to those of the analogous spirooxyphosphorane (XIX).



XX: $\delta P^{31} = -114{\cdot}2$ ppm

XXI: $\delta P^{31} = +36{\cdot}9$ ppm

2-Methoxy-1,3-dimethyl-1,3,2-diazaphospholane (XXII) was somewhat less reactive toward benzil than the corresponding aminophosphines. The spirodiaminooxyphosphorane, XXIII, was obtained in quantitative yield.



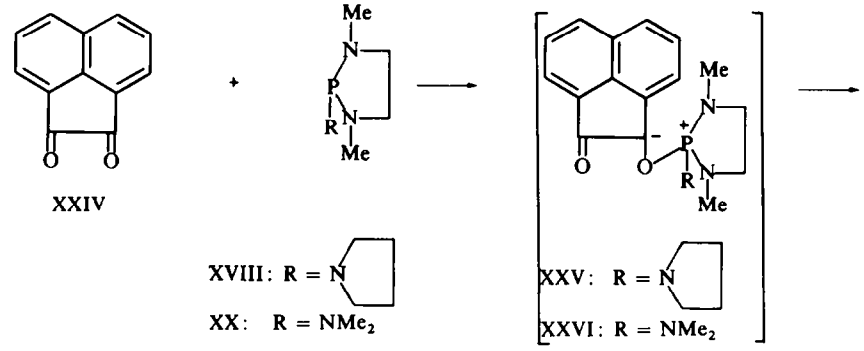
XXII: $\delta P^{31} = -123{\cdot}2$ ppm

XXIII: $\delta P^{31} = +38{\cdot}6$ ppm

The protons of the OMe group gave a doublet at τ 6·43, J_{HP} = 14·8 c/s, while the protons of the Me groups attached to the N gave a doublet at τ 7·26, J_{HP} = 9·5 c/s.

Reaction of acenaphthenequinone with 5-membered cyclic triaminophosphines. The reaction of 2-N-pyrrolidino-1,3-dimethyl-1,3,2-diazaphospholane (XVIII) with acenaphthenequinone (XXIV) was quite vigorous in methylene chloride solution even at −70°. When the solution was allowed to reach 20°, a deep brown mixture was produced from which the only isolable product was 2-N-pyrrolidino-2-oxo-1,3-dimethyl-1,3,2-diazaphospholane (XXVIII). The P_{31} NMR shift was similar to that of the corresponding compound, hexamethylphosphoroamidate (XXX). The band due to the P—O stretching was at 7·8 μ in the IR spectrum.

A similar behaviour was noted when acenaphthenequinone was treated with 2-dimethylamino-1,3-dimethyl-1,3,2-diazaphospholane (XX). The only isolable product was 2-dimethylamino-2-oxo-1,3-dimethyl-1,3,2-diazaphospholane (XXIX). No intermediate could be detected in these reactions, but it was assumed by analogy with previous reactions that the phosphorus of the cyclic aminophosphines attacked the oxygen of acenaphthenequinone to give a 1:1-dipolar adduct (XXV or XXVI). This dipolar adduct apparently was too unstable to form the cyclic phospholene analogous to XIX and XXI. Instead, the 1:1-dipolar adduct lost phosphoroamidate to yield a carbenoid fragment which underwent further transformations now being investigated further.



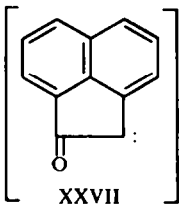
XXIV

XVIII: R = N

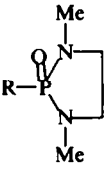
XX: R = NMe_2

XXV: R = N

XXVI: R = NMe_2

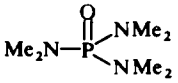


XXVII



XXVIII- R = N ; δP^{31} = −23·1 ppm

XXIX: R = NMe_2; δP^{31} = −26·4 ppm



XXX: δP^{31} = −24·6 ppm

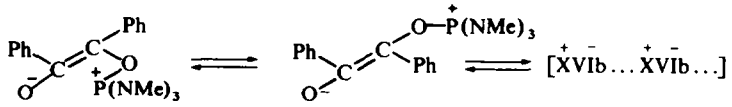
It should be emphasized that the reaction of acenaphthenequinone with trimethyl phosphite gave as the only isolable product a 2:1-adduct with the structure of a 2,2,2-trimethoxy-1,3,2-dioxaphospholane. The intermediate 1:1-adduct did not cyclize to the corresponding 2,2,2-trimethoxy-1,3,2-dioxaphospholene as in the benzil case (cf. formula IV). Apparently, the acenaphthenequinone-trialkyl phosphite 1:1-adduct had less tendency to decompose by the loss of trimethyl phosphate than the corresponding acenaphthenequinone-triaminophosphine adduct, XXV and XXVI; the latter lost phosphoroamidate very readily.

DISSCUSSION

This work demonstrated for the first time the co-existence in solutions of a structure containing quadruply-connected phosphorus (XVI) and the corresponding valence tautomer containing quintuply-connected phosphorus (XVII). The form with 4-co-ordinated phosphorus had a negative P^{31} NMR shift relative to H_3PO_4, while the form with 5-coordinated phosphorus had a positive shift relative to the same standard. The equilibration between the two forms was rapid relative to the NMR phenomenon, and consequently, the observed value of the shift lay between the two extreme values of the two forms. These extreme values of the two forms (XVI and XVII) were not known with certainty, but they could be approximated by comparisons with closely related compounds such as XII and XIX. In those cases, only one type of structure existed in solutions exclusively, or nearly so.

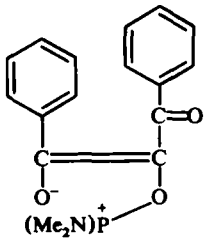
Certain solvents such as hexane, benzene, and ether, favour a structure, XVII, with pentavalent phosphorus, while other solvents like methylene chloride favour the structure with tetravalent phosphorus, XVI. It is not clear at present what specific property of the solvent is to be correlated with the shift in position of the equilibrium between the two valence states of the phosphorus; in general, however, low polarity seems to favour the pentacovalent phosphorus.

An increase in the dilution of methylene chloride solution of the adducts, XVI $\rightleftarrows$ XVII, resulted in a decrease in the positive value of the P^{31} NMR shift. This interesting phenomenon suggested the existence of geometrical isomers, XVIa and XVIb of the open-dipolar structures. These forms should have slightly different negative values of the P^{31} NMR shift. Moreover, intramolecular associations of the dipolar ions (XVIa and XVIb) could affect the value of the P^{31} NMR shift. The degree of intramolecular association of these ions could depend on the concentrations in a given solvent.

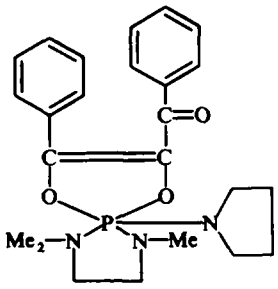


XVIa XVIb

This investigation and a previous one[20b] provided information on the relative stabilities of forms with 4- and 5-coordinated phosphorus in a series of 1:1-adducts made from vicinal polycarbonyl compounds and *tris*dialkylaminophosphines. The cyclic phosphorane structure is increasingly favoured over the corresponding open-dipolar structure in the series triketone < *o*-quinones < α-diketone. For example, *tris*dimethylaminophosphine tended to form a dipolar ion, XXXI, with diphenylpropanetrione and a phosphorane, XVII, with benzil.



XXXI: $\delta P^{31} = -35{\cdot}9$ ppm



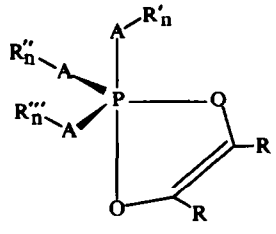
XXXII: $P^{31} = +37{\cdot}5$ ppm

Certain changes in the structure of the polycarbonyl compound led to more drastic differences in the stability of the 1:1-triaminophosphine-adduct. For example, the α-diketone, acenaphthenequinone, did not yield isolable 1:1-adducts of any type in the reactions with the *tris*dialkylaminophosphines.

It is now evident that the course of the reactions of trivalent phosphorus compounds, PX_3, with vicinal polycarbonyl compounds will depend on a combination of structural factors, as follows:

(1) With a given polycarbonyl compound, a trialkyl phosphite, $(RO)_3P$, will have a greater tendency than *tris*dialkylaminophosphines, $(R_2N)_3P$, to form a compound with pentavalent phosphorus. This may be related to the higher[23] electronegativity of the oxygen (3·5) than of the nitrogen (3·0).

(2) A 5-membered cyclic *tris*dialkylaminophosphine, for example, XVIII and XX, shows a greater tendency to form pentavalent phosphorus than an acyclic aminophosphine. This can be explained from the X-ray data obtained on a 2,2,2-trisubstituted-1,3,2-dioxaphospholene.[10]

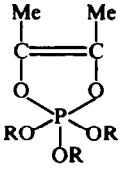


XXXIII: A = oxygen, $n = 1$
XXXIV: A = nitrogen, $n = 2$

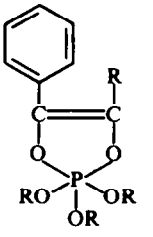
The phosphorus was at the centre of a trigonal bipyramid. The phospholene ring was situated in an apical-equatorial plane. The apical P—O bonds were significantly longer than the corresponding equatorial P—O bonds. The apical P—O bond involving the phospholene ring was longer than the apical P—O bond not involved in the ring. Likewise, the equatorial P—O bond associated with the ring was longer than the two equatorial P—O bonds not involved in the ring. One of the consequences of this geometry is that the molecule had four rather short (< 2·9 Å) intramolecular non-bonded distances involving the atoms directly attached to the phosphorus, i.e. O and A in formula XXXIII, and the atoms once removed from the phosphorus, i.e. R′, R″, and R‴ in XXXIII. This must represent a severe internal over-crowding

of the molecule. In the phosphorane structure, XXXIV, derived from *tris*dialkylaminophosphines, the atoms A attached to the phosphorus would carry two substituents. The intramolecular over-crowding discussed above may become quite significant, and would be minimized if some of the substituents, R′, R″, and R‴, are held relatively rigidly in the form of five-membered rings, as for example in structures XIII, XIX, XXI, and XXIII.

(3) The degree of delocalization of a negative charge on carbon would tend to favour an open-dipolar structure, for example in the cases of the triketone, XXXI, and of the *o*-quinone, XII. Conversely, the conjugation of a C=C bond with aromatic rings would tend to favour the phospholene structure. Thus, benzil adducts with phosphite and amino phosphines (IV, VIII, XVII, XIX, XXI, and XXIII) tend to show greater stability than the corresponding phospholenes[7,12] derived from aliphatic α-diketones such as XXXV, XXXVI, and XXXVII.

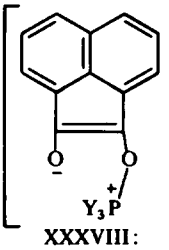


XXXV



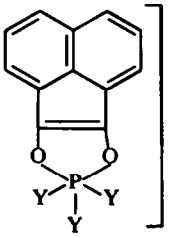
XXXVI: R = Me
XXXVII: R = H

For reasons which are not clearly understood, the 1:1-adducts derived from acenaphthenequinone are relatively unstable in both the dipolar (XXXVIII) and the phosphorane (XXXIX) structures.



XXXVIII:

Y = OR
Y = NR_2
not observed



XXXIX

It is possible that certain stereo-electronic features discourage the formation of the phospholene (XXXIX) while the dipolar structure (XXXVIII) may be unobservable due to the known reactivity of acenaphthenequinone itself toward nucleophiles (cf. formation of VI).

The oxidation of *tris*dialkylaminophosphines to the corresponding phosphine oxides or phosphoroamides (XXVIII and XXIX) by means of acenaphthenequinone should be noted. Some phosphoroamides display interesting physiological properties;[24] those of XXVIII and XXIX will be reported elsewhere.

A number of correlations involving the P^{31} NMR shifts of phosphoranes and dipolar ions are summarized in Fig. 1.

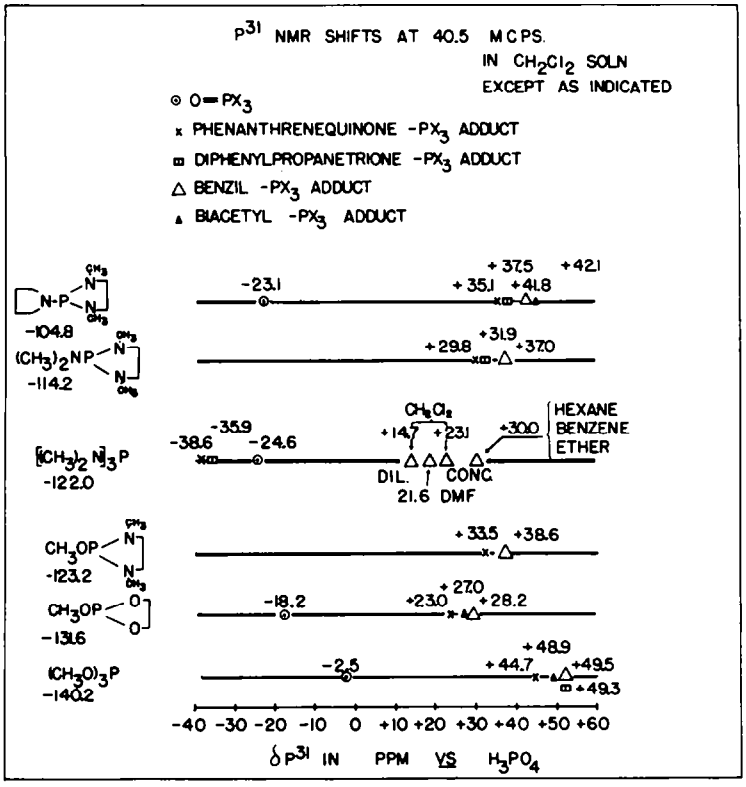


FIG. 1a.

EXPERIMENTAL

The analyses were performed by Schwarzkopf Analytical Laboratories, Woodside, New York. All P^{31} NMR are given in ppm from 85% H_3PO_4 as zero; they were determined at 40·5 Mc/s. All H^1 NMR are given in ppm vs TMS as 10 (τ values); they were determined at 60 Mc/s.

Reaction of benzil with trisdimethylaminophosphine

A soln of XV, (0·903 g, 5·5 mmoles) in 2·5 ml of the solvents indicated below was added to a soln or a suspension of XIV, (1·164 g, 5·5 mmoles) in 2·5 ml of the same solvent at 5° under N_2 with stirring. In all cases, the addition was carried out over a 5 min period, and the mixture was kept 15 min at 5°. The mixture was then allowed to reach 20° and analyzed by H^1 and P^{31} NMR spectrometry. The following observations were made:

(a) *In hexane.* The yellow, crystalline dipolar ion, XVI separated within min. This solid was decanted with protection against moisture and was then placed in CH_2Cl_2 soln. The P^{31} NMR shifts observed in fresh solns of various concentrations are indicated in Table 1. The H^1 NMR and the IR spectra of the fresh CH_2Cl_2 solns were identical to those observed when the aminophosphine was added to benzil in CH_2Cl_2 soln (*vide infra*).

In another experiment, the insoluble dipolar adduct, XVI which precipitated from hexane, was kept 19 hr at 20° in contact with the hexane mother liquid. The solid slowly went into soln. This hexane soln contained mainly XVII and had the following spectral characteristics: $\delta P^{31} = +30{\cdot}2$ ppm; a doublet at τ 7·36, $J_{HP} = 10{\cdot}8$ c/s; IR bands at(μ) 6·05 (m) [C=C], 6·25 (m), broad band at 6·7–6·9 (m), 7·52 (m), 7·75 (s), 7·90 (s), 8·35 (s), 8·68 (ms), 8·90 (m), 9·30 (s), 9·40 (s), 10·1 (vs), 10·5 (s), and 12·70 (vs).

The hexane soln of XVII, was concentrated and cooled, yielding nearly colourless prisms 6–8 mm in length, m.p. 85–87° (in sealed capillary). The phosphorane, XVII, dissolved instantaneously in hexane from

which it was recovered unchanged with the same m.p. (Found: C, 65·8; H, 8·1; N, 10·5; P, 7·8. $C_{20}H_{28}N_3O_2P$ requires: C, 64·3; H, 7·5; N, 11·3; P, 8·3%.)

For δP^{31} NMR shifts under various conditions, see Table 1.

The H^1 NMR spectrum in $CDCl_3$ had a doublet at τ 7·33, J_{HP} = 10·7 c/s. The IR spectrum in hexane was identical with that described above.

(b) *In benzene.* A clear orange soln was obtained immediately and faded to pale yellow within 10 min at 5°. After 30 min at 20°, the soln had the following spectral characteristics: δP^{31} = +29·9 ppm (1M soln, no significant change with concentration); a doublet at τ 7·36, J_{HP} = 10·3 c/s. The IR spectrum was identical with that described above for the hexane soln.

In another experiment, XV (8·15 g) in 20 ml of benzene was added to XIV (10·5 g) in 30 ml benzene at 5° under N_2, over a 30 min period. A dark red soln was obtained within 8 min and was pale yellow after 30 min. The solvent was removed at 20°, 20 mm, and than at 1 mm. The tan solid was triturated with 20 ml cold hexane, filtered and dried at 20° and 1 mm. The pale yellow needles (13·5 g, 72%) had the spectral characteristics expected of XVII in various solvents.

(c) *In methylene chloride.* The soln became orange and remained so for several hr. This soln had the following spectral characteristics: δP^{31} = +13·1 ppm (1·0M); a doublet at τ 7·33, J_{HP} = 10·7 c/s; IR bands at (μ) 5·9 (w), 6·1 (w), 6·2 (w), and a strong doublet at 6·75 and 6·95. The spectra of this soln showed little change within 8 hr when protected against moisture.

The reaction was carried out at various concentrations, and the corresponding P^{31} NMR shifts are given in Table 1. The crystals obtained after evaporation of the CH_2Cl_2 soln appeared to consist mostly of the dipolar ion, XVI.

(d) *In ether.* The mixture became pale yellow within 10 min at 0°. After 1 hr at 20°, more ether was added to obtain a pale clear yellow soln with δP^{31} = +29·7 ppm, and τ 7·32, J_{HP} = 10·7 c/s; after 20 hr at 20°, δP^{31} = +29·8 ppm.

(e) *Dimethylformamide.* The orange soln had δP^{31} = +21·6 ppm. There was evidence of further reactions of the adduct in this solvent.

Reaction of 2-N-*pyrrolidino*-1,3-*dimethyl*-1,3,2-*diazaphospholane* (XVIII) *with benzil*

A soln of 2·24 g (10·7 mmoles) benzil in 50 ml CH_2Cl_2 was reacted with 2·0 g (10·7 mmoles) of XVIII in 20 ml CH_2Cl_2 at −70°. After warming the reaction mixture to room temp, the solvent was evaporated at 20° (20 mm). The residue, at first a thick gum, crystallized on standing at room temp. Recrystallization from hexane–CH_2Cl_2 afforded 3·8 g, (90%) of XIX with a m.p. 88–90°. (Found: C, 66·5; H, 7·3; P, 7·7. $C_{22}H_{26}N_3O_2P$ requires: C, 66·4; H, 7·1; P, 7·8%.)

The H^1 NMR in $CDCl_3$ had the following signals: a multiplet at τ 2·62 (10 H^1, aromatic) a multiplet at τ 6·93 (8 H^1, two kinds of N—CH_2—), a doublet at τ 7·27 with J_{HP} = 9·6 c/s (6 H^1, —NCH_3—), and a broad signal at τ 7·18 (4 H^1, C—CH_2—CH_2—C); δP^{31} = +41·8 ppm (CH_2Cl_2).

The IR spectrum in CH_2Cl_2 had bands at (μ): 6·12 (w), 6·28 (w), 6·71 (w), 7·75 (m), 8·6 (ms), and 9·36 (ms).

Reaction of 2-*dimethylamino*-1,3-*dimethyl*-1,3,2-*diazaphospholane* (XX) *with benzil*

A soln of 8·5 g, (40 moles) benzil in 30 ml CH_2Cl_2, cooled to −70°, was treated at once with 6·5 g (40 mmoles) of XX in 14 ml CH_2Cl_2. The reaction mixture was allowed to warm to room temp and kept at this temp for 3 hr. About 50% of the solvent was then evaporated at 20° (20 mm). Dry pentane (50 ml) was added to the remaining soln and evaporation of both solvents was continued at 20° (20 mm). After evaporation of about 70% of the solvent mixture, 13·5 g, of the new adduct, XXI, had crystallized and was obtained in 90% yield, m.p. 98–99°. (Found: C, 65·3; H, 6·8; N, 11·2; P, 8·3. $C_{16}H_{26}N_3O_2P$: requires: C, 65·0; N, 7·0; N, 11·3; P, 8·3%.)

The H^1 NMR in $CDCl_3$ had the following signals: a multiplet at τ 2·63 (10 H^1, aromatic) a broad doublet at τ 7·06 with J_{HP} = 21·0 c/s (4 H^1, N—CH_2—CH_2—N), a doublet at τ 7·29 with J_{HP} = 10·5 c/s (6 H^1, NMe_2), and a doublet at τ 7·33 with J_{HP} = 9·5 c/s, (6 H^1, —NMe—); δP^{31} = +36·9 ppm (CH_2Cl_2).

The IR spectrum in CH_2Cl_2 had bands at (μ): 6·10 (w), 6·25 (w), 6·70 (m), 7·75 (m), 8·55 (s), 9·30 (s), 9·40 (shoulder), 9·52 (s), 10·10 (s), and 10·45 (vs).

Reaction of 2-*methoxy*-1,3-*dimethyl*-1,3,2-*diazaphospholane* (XXII) *with benzil*

A soln of 7·9 g (37 mmoles) benzil, dissolved in 30 ml CH_2Cl_2 at −70°, was treated with 5·5 g, (37 mmoles) of XXII in 10 ml CH_2Cl_2. The reaction mixture was allowed to warm to room temp, and the solvent was evaporated at 20° (20 mm) after 3 hr. The residue, (XXIII), a thick gum, could not be crystallized or distilled.

(Found: C, 63·6; H, 6·8; N, 7·7; P, 8·7. $C_{19}H_{23}N_2O_3P$ requires: C, 63·7; H, 6·5; N, 7·8; P, 8·7%.)

The H1 NMR had the following signals: a multiplet at τ 2·63 (10 H^1, aromatic), a doublet at τ 6·43 with J_{HP} = 14·8 c/s, (3 H^1, MeO—P), a broad absorption at τ 7·15 (4 H^1, N—CH_2—CH_2—N), and a doublet at τ 7·26 with J_{HP} = 9·5 c/s (6 H^1, —NMe—). δP^{31} = +38·6 ppm (CH_2Cl_2).

The IR spectrum in CH_2Cl_2 had bands at (μ): 6·10 (w), 6·25 (w), 6·70 (m), 7·75 (m), 8·15 (m), 8·20 (m), 8·55 (s), 9·30 (s), 9·42 (shoulder), 9·50 (vs), 9·75 (m), and 10·40 (vs).

Reaction of acenaphthenequinone with 2-N-*pyrrolidino*-1,3-*dimethyl*-1,3,2-*diazaphospholane* (XVIII)

A soln of XVIII (10 g, 55 mmoles) in 50 ml CH_2Cl_2 was added over a 5 min period to a suspension of acenaphthenequinone (10 g, 55 mmoles) in 100 ml CH_2Cl_2 at −70°. The soln became purple at −70°, and the colour turned to blue then to red-brown while it was allowed to warm to 20° (2 hr). Approximately ⅔ of the solvent was removed at 20° and 20 mm, and the mixture was diluted with ether. The dark gum which separated was decanted. The ether–CH_2Cl_2 layer was evaporated, and the purple-red oil was submitted to short path distillation at 0·1 mm. The dark, thick, oil (4 g) which distilled at 170° (0·1 mm) was redistilled to give a still coloured oil (3 g). Molecular distillation at a bath temp of 170° and 0·1 mm gave the sample of XXVIII; δP^{31} = −23·1 ppm (CH_2Cl_2).

The H^1 NMR spectrum in $CDCl_3$ had a multiplet al τ 7·0, a doublet at τ 7·50 with J_{HP} = 9·5 c/s, and a multiplet at τ 8·2. (Found: C, 47·2; H, 9·1; N, 20·5; P, 15·5. $C_8H_{18}ON_3P$ requires: C, 47·3; H, 8·8; N, 20·7; P, 15·2%.)

The IR spectrum in CH_2Cl_2 had characteristic bands at (μ): 3·50 (m), 6·8–6·9 (m), 7·8–7·9 (m), 8·26 (ms), 8·60 (s), 9·65 (m), and 10·61 (m).

Reaction of acenaphthenequinone with 2-*dimethylamino*-1,3-*dimethyl*-1,3,2-*diazaphospholane* (XX)

Compound XX (21 g, 130 mmoles) in 50 ml CH_2Cl_2 was added over a 10 min period to a suspension of acenaphthenequinone (23·5, 130 mmoles) in 250 ml CH_2Cl_2 at −70°. The soln turned purple at −70°, and the colour changed to red and red-brown while the mixture was allowed to reach 20° (1 hr). Approximately ⅓ of the solvent was removed at 20° and 20 mm, and the mixture was diluted with ether. The purple gum that separated was decanted and the ether–CH_2Cl_2 layer was evaporated at 20° and 20 mm. Short path distillation at 0·1 mm gave XXIX (11 g) as a thick oil, b.p. 110°; δP^{31} = −26·4 ppm (CH_2Cl_2).

The H^1 NMR spectrum in $CDCl_3$ had a multiplet at τ 6·9, two doublets, one at τ 7·30 and the other at τ 7·50, both with J_{HP} = 9·0 c/s. (Found: C, 40·4; H, 9·2; N, 23·4; P, 17·1. $C_6H_{16}N_3O$ P requires: C, 40·7; H, 9·0; N, 23·7; P, 17·5%.)

The IR spectrum had characteristics bands at (μ): (in CH_2Cl_2) 3·50 (m), 6·85 (m), 6·95 (m), 7·75–7·85 (m), 8·30 (s), 8·60 (ms), 9·65 (m), 10·05 (ms), and 10·55 (m).

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