Tetrahedron Letters No.26, pp. 3053-3058, 1966. Pergamon Press Ltd.
Printed in Great Britain.

ISOLATION OF A TRIAMINODIOXYPHOSPHORANE AND OF THE CORRESPONDING TRIAMINOOXYPHOSPHONIUM DIPOLAR ION AND DEMONSTRATION OF THEIR EQUILIBRATION IN SOLUTION

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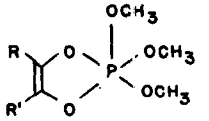
(Received 19 April 1966)

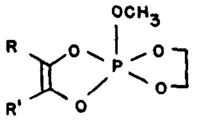
The nature of the atom, X, directly attached to the phosphorus in a trivalent phosphorus compound, $(C\text{-}X)_3P$, and the steric requirements of the carbon atom, C, once removed from the phosphorus, determine whether the 1:1 adduct which is formed in the reaction with a given polycarbonyl compound has pentavalent phosphorus. Thus, the adducts I[2] and IV[3] made from the reaction of trimethyl phosphite with phenanthrenequinone and with diphenylpropanetrione, respectively, were 2,2,2-trimethoxy-1,3,2-dioxaphospholenes; however, the corresponding adducts, VIII[4] and IX[4], made from trisdimethylaminophosphine were open dipolar ions, in the crystalline state and in solutions. When two of the nitrogens in the aminophosphines were held together by means of a five-membered ring, cyclic spiroaminooxyphosphoranes, X and XI, XII and XIII, or XIV, were produced in the reactions with polycarbonyl compounds[5]. Spiropenta oxyphosphoranes, V-VII, were obtained from methyl ethylenephosphite and from other 5- and 6-membered cyclic phosphites[6].

Structures I-XIV were based on ^{31}P nmr and infrared spectra.

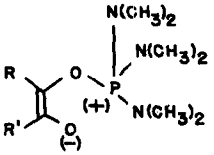
The X-ray analysis of a dioxaphospholene, I, disclosed a trigonal bipyramidal structure in the crystal, with the ring in an apical-equatorial plane[7]. Dioxaphospholenes were made also from phosphonite and phosphinite esters and from triphenylphosphine[8]. Structures II and III were proposed independently by two other groups of investigators[9,10]. Acyclic oxyphosphoranes are known[11].



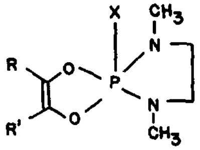
I, From Phenanthrenequinone, (PQ)
II, From Benzil, (BZ)
III, From Biacetyl, (BI)
IV, From Diphenylpropanetrione, (DP)



V, From PQ
VI, From BZ
VII, From BI



VIII, From PQ
IX, From DP



X, From PQ; X = N◁
XI, From DP; X = N◁
XII, From PQ; X = $N(CH_3)_2$
XIII, From DP; X = $N(CH_3)_2$
XIV, From PQ; X = OCH_3

This Communication shows that both forms, the dipolar ion XVA and the cyclic phosphorane XVB, of the same adduct can be isolated in crystalline form. The two forms exist as an equilibrium mixture in solution. Certain solvents favor the cyclic form XVB, while others favor the dipolar ion XVA. In solvents that favor the ion XVA, the value of the ^{31}P nmr shift varies greatly with concentration. Perhaps this is due to different geometry or to different state of aggregation of XVA as a function of solvent and concentration. The P-nmr data for this system, and for the related structures I-XIV, are given in Figure 1. Other values of the shift of the benzil-adduct XV were: +19.0, +15.1 and +13.1 ppm in 2M, 1.5M and 1.0M CH_2Cl_2 solutions, respectively; +29.9 ppm in 1M benzene; +30.2 ppm in 0.8M hexane, without much change with concentration.

The P-nmr data suggest that a particular value of the shift of the benzil-adduct XV reflects the position of the equilibrium between the phosphorane XVB (positive shift) and the ion XVA (negative shift; cf. VIII and IX). The equilibrium must be rapid in the time scale of the nmr, since only one signal was observed at 20°. The ^1H nmr spectrum of XV in $CDCl_3$ had one doublet at τ 7.33, $J_{HP} = 10.7$ cps.

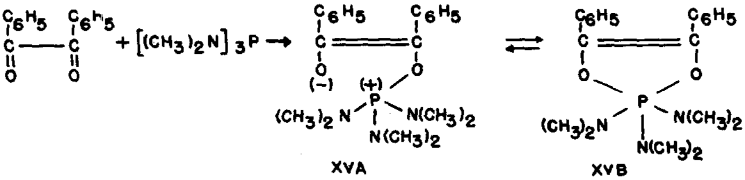
The IR-spectrum of hexane solutions prepared from the ion XVA or from the phosphorane XVB showed the expected[2] band at 6.05μ due to C=C. Methylene chloride solutions made from XVA or from XVB showed the bands due to both types of structures. Dipolar ions give a strong band at 6.60μ due to the enolate[4].

Crystalline, rather stable phosphoranes, XVI-XVIII, were made from benzil and the cyclic aminophosphines XX, XXI and XXII. The positive P-nmr shifts of these systems are shown in Figure 1. The shifts were not very sensitive to solvent and to concentration.

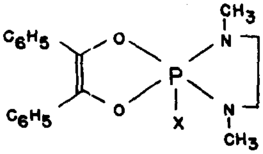
A formula like XVB has been mentioned by Burgada[12].

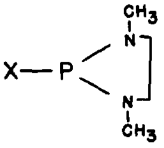
Experimental.- Trisdimethylaminophosphine was added to benzil in hexane at 5°, in amounts corresponding to an 0.8M solution. The yellow, crystalline ion XVA separated within minutes and was filtered after 30 minutes at 20°; it was handled under dry N_2. Several hours were required for dissolution of ion XVA in hexane, to make a clear 0.8M solution at 20°; the solution now contained the phosphorane XVB, as shown by the spectral data. When the 0.8M hexane solution was concentrated somewhat and cooled, it deposited fairly stable, colorless prisms 6-8 mm in length, mp 85-87°. This phosphorane XVB dissolved rapidly in hexane. The elemental analysis agreed with formula XV. When benzil and the aminophosphine were mixed in a 2M CH_2Cl_2 solution at 5°, a P-nmr shift of +18.4 ppm was observed. Further dilution gave the value +14.2 ppm. Evaporation of the CH_2Cl_2 gave yellow crystals of the ion XVA.

The crystalline adducts XVI-XVIII were made from XX-XXII in CH_2Cl_2 at -70°. All new compounds gave correct elemental analyses. The cyclic aminophosphines XX-XXII were prepared from the new chlorophosphine XIX (δ ^{31}P = -167.3 ppm)[13].



XVA XVB





XVI, X = N◁
XVII, X = $N(CH_3)_2$
XVIII, X = OCH_3

XIX, X = Cl
XX, X = N◁
XXI, X = $N(CH_3)_2$
XXII, X = OCH_3

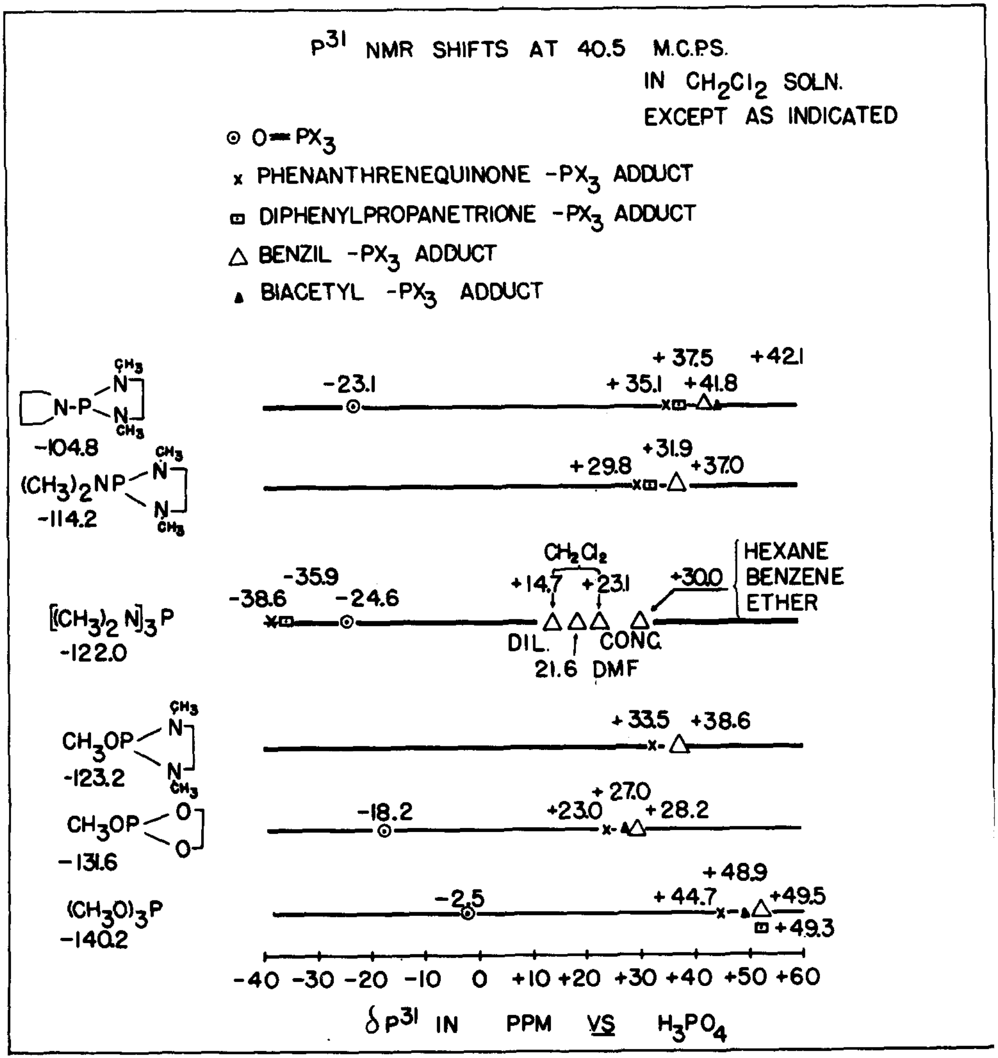

P31 NMR SHIFTS AT 40.5 M.C.P.S.
IN CH2Cl2 SOLN.
EXCEPT AS INDICATED
⊙ O=PX3
x PHENANTHRENEQUINONE -PX3 ADDUCT
⊡ DIPHENYLPROPANETRIONE -PX3 ADDUCT
△ BENZIL -PX3 ADDUCT
▲ BIACETYL -PX3 ADDUCT
-104.8
-23.1
+35.1
+37.5
+41.8
+42.1
(CH3)2NP
-114.2
+29.8
+31.9
+37.0
[(CH3)2N]3P
-122.0
-38.6
-35.9
-24.6
CH2Cl2
+14.7
+23.1
+30.0
HEXANE
BENZENE
ETHER
DIL.
CONC.
21.6 DMF
CH3OP
-123.2
+33.5
+38.6
CH3OP
-131.6
-18.2
+23.0
+27.0
+28.2
(CH3O)3P
-140.2
-2.5
+44.7
+48.9
+49.5
+49.3
-40 -30 -20 -10 0 +10 +20 +30 +40 +50 +60
δP31 IN PPM VS H3PO4

FIG. I

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