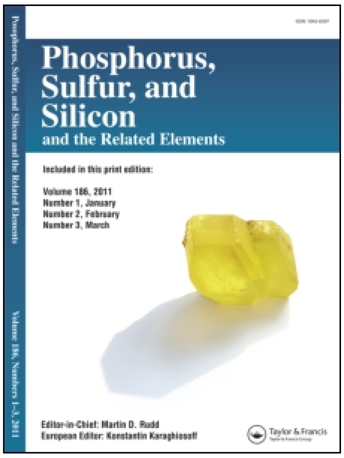

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STRUCTURES IN SOLUTION OF ADDUCTS OF HEXAMETHYLPHOSPHORUS TRIAMIDE AND SUBSTITUTED BENZILS

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STRUCTURES IN SOLUTION OF ADDUCTS OF HEXAMETHYLPHOSPHORUS TRIAMIDE AND SUBSTITUTED BENZILS

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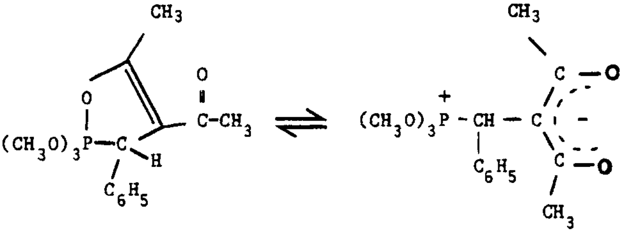
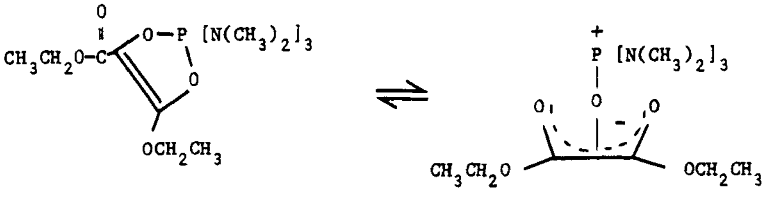
Hexamethylphosphorus triamide has been allowed to react with p,p'-dinitrobenzil, p-chlorobenzil, p,p'-difluorobenzil, p,p'-dimethylbenzil and p,p'-dimethoxybenzil. All of these materials in benzene-d_6 had negative δ ^{31}P chemical shifts except for the p,p'-dinitro adduct whose resonance was found at δ $+17.6$. In dichloromethane-d_2 the resonances ranged from δ $+38.2$ for the p,p'-dinitro adduct to δ -22.5 for the p,p'-dimethoxy adduct. The ^{13}C NMR spectra of these compounds all showed coupling J_{POCC} to the ipso carbons except for the p,p'-dinitro adduct. These data indicate that the p,p'-dinitro adduct is ionizing rapidly and that the others are phosphoranes. On cooling the coupling was lost for the p,p'-difluoro adduct and for the p-chloro adduct. These spectral changes are attributed to rapid ionization which occurs because of the change of the dielectric constant with change in temperature.

The addition of trivalent phosphorus compounds to various α,β-unsaturated materials has proven to be a valuable route to phosphoranes.[1,2] In some cases it has been shown that there is an equilibrium between the phosphorane and a zwitterion. Equilibration above 155°C has been noted for conversion of **1** ⇌ **2**.[2c,2d]



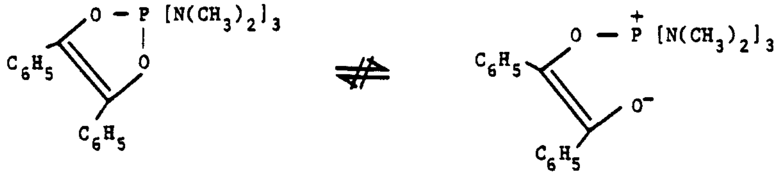
1 **2**

A similar ionization **3** ⇌ **4** has been investigated by ^1H and ^{13}C NMR and it occurs rapidly on the ^1H (80 MHz) NMR time scale at *ca.* room temperature.[3]



3 **4**

An equilibrium **5** ⇌ **6** was not found by NMR investigations. There was a considerable change in δ ^{31}P with solvent change and this was attributed to increased contribution by ionic contributors to the hybrid.[3] Variable temperature ^{13}C NMR spectra of **5** indicated that it undergoes rapid ligand reorganization at −75°C.

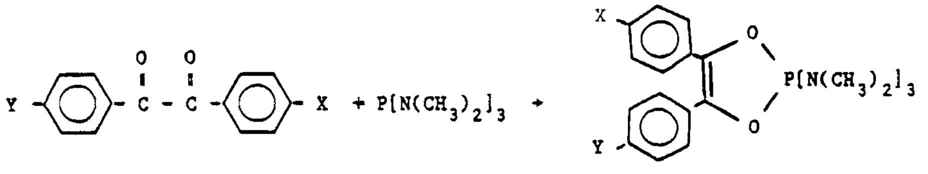


5 **6**

The large change in δ ^{31}P for **5** as a function of solvent, hexane δ −30.5 to methylene chloride δ −12.8, is certainly remarkable and worthy of further investigation. Introduction of substituents into para positions of benzil might also lead to changes in δ ^{31}P NMR values depending on whether the groups are electron donating or accepting. Highly accepting groups might lead to facile ionization.

RESULTS AND DISCUSSION

Compounds, **8a–8e**, were prepared from the benzils **7a–7e**. The ^{31}P NMR chemical shifts of these substances in benzene-d_6 are collected in Table I. All of the materials except for the *p,p′*-dinitro adduct have negative chemical shifts and they are found in the region expected for phosphoranes.[1a] The *p,p′*-dinitro adduct has its ^{31}P resonance at δ +17.6. A plot of δ ^{31}P for the various compounds against σ^4 is shown in Figure 1. It is clear that the substituent effect is normal except for the *p,p′*-dinitro adduct.



7a X = Y = NO_2
7b X = H; Y = Cl
7c X = Y = F
7d X = Y = CH_3
7e X = Y = OCH_3

8a X = Y = NO_2
8b X = H; Y = Cl
8c X = Y = F
8d X = Y = CH_3
8e X = Y = OCH_3

The same compounds in dichloromethane-d_2 had dramatic differences in their ^{31}P chemical shifts. They ranged from δ +38.2 for the *p,p′*-dinitro adduct to δ −22.5 for the *p,p′*-dimethoxy adduct. The change in solvent from benzene, dielectric

TABLE I

Chemical shifts of substituted benzil adducts of hexamethylphosphorus triamide

Compound	δ ^{31}P NMR (26°C)		
	σ	Benzene-d_6^{a}	Dichloromethane-d_2^{b}
8a	0.778	+17.6	+38.2
b	0.227	−28.9	+1.5
c	0.062	−29.4	−0.4
d	−0.170	−30.4	−20.0
e	−0.268	−30.8	−22.5

[a] Conc. = 0.83 mol/L.

[b] Conc. = 1.0 mol/L except for **8a**, which was 0.5 mol/L due to low solubility.

constant 2.28, to dichloromethane, 9.08, causes downfield shifts in all cases. These changes in δ values support the concept of increased delocalization on changing solvents and substituents.

The ^{13}C NMR spectrum of the p,p'-dinitro adduct in dichloromethane at both 0 and −50°C has a singlet at δ 143.4 which is assignable to either the olefinic carbons or the ipso carbons. The other expected resonance is probably coincident with an aromatic carbon resonance. In general coupling has been observed between phosphorus and the olefinic and ipso carbons. Loss of coupling would arise under the conditions of fast ionization[5] and this seems to be the most reasonable means of explaining this observation.

This suggestion is strongly supported by variable temperature ^{13}C NMR studies of the p,p'-difluoro and the monochloro adducts. In both cases, on cooling the δ ^{31}P

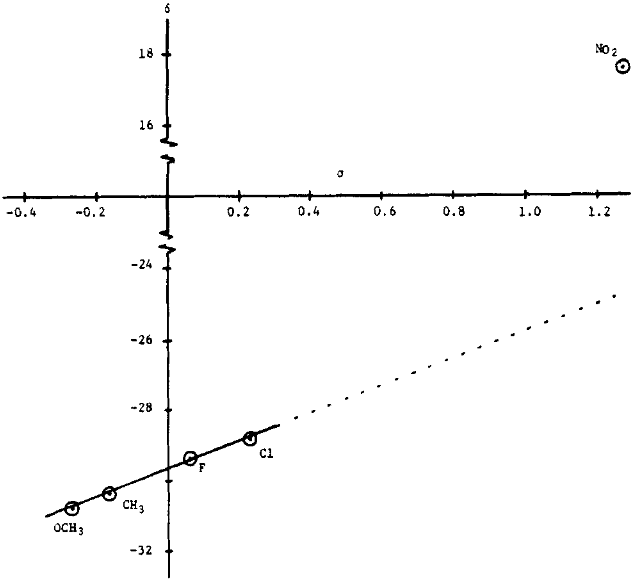


FIGURE 1 ^{31}P Chemical shift of **8a–e** as a function of σ in benzene-d_6.

TABLE II

Variation of ^{31}P chemical shift of **8b–c** with temperature

	δ ^{31}P NMR	
Temperature (°C)	**8b**	**8c**
26	1.4	−0.4
20	3.7	—
11	—	2.9
−19	14.3	—
−47	25.5	—
−50	—	21.1
−66	28.2	—
−70	31.1	24.8

values became more positive as illustrated by the changes collected in Table II. It is known that the dielectric constants of solvents change with temperature[6] and it is suggested that this change is responsible for the large changes in chemical shifts of **8b** and **8c**. These data are also plotted against dielectric constant change in Figure 2.[7] It is found that nearly straight lines arise. Once again these results support the increased delocalization mechanism.

The variable temperature ^{13}C NMR spectra of **8a–8e** show no evidence for the slowing down of intramolecular ligand exchange. The ^{13}C NMR spectra of **8d** and

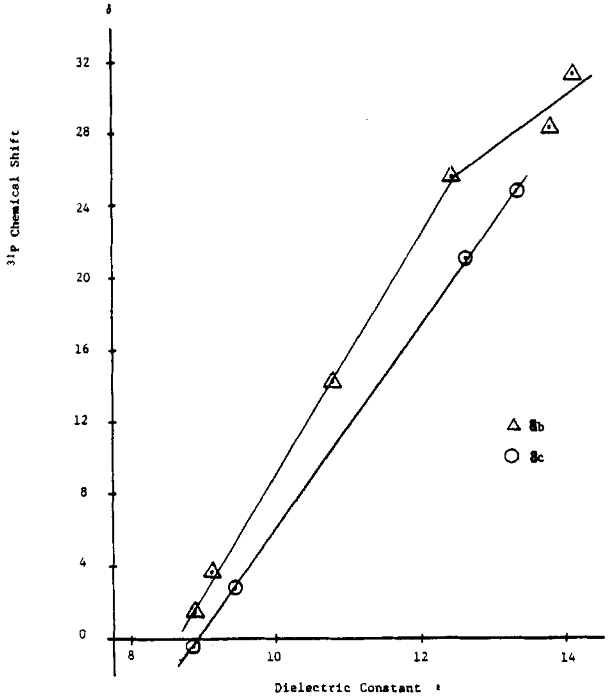


FIGURE 2 ^{31}P chemical shift of **8b–c** as a function of dielectric constant of the medium.

TABLE III

Variation of $^2J_{CNP}$ of **8a–e** and **5** with temperature

Compound	$^2J_{CNP}$ (26°C)	$^2J_{CNP}$ (°C)
8a	4.3 Hz	4.2 Hz (−50)
b	2.5 Hz	3.3 Hz (−47)
c	2.4 Hz	3.5 Hz (−50)
d	br s	1.0 Hz (−51)
e	1.1 Hz	br s (−47)
5	2.0 Hz	2.1 Hz (−50)

8e at 26°C clearly show the expected coupling to the ipso carbon by phosphorus, J_{POCC}. No loss of coupling was observed on cooling **8d** to −51°C and **8e** to −47°C.

The ambient temperature ^{13}C NMR spectra of **8b** and **8c** in dichloromethane clearly show coupling of their aromatic ipso carbons to phosphorus, which is in accord with phosphorane structures. On cooling **8b** to −47°C and **8c** to −50°C the coupling to the ipso carbons is lost. The change in ^{31}P δ and the loss of coupling is clearly indicative of rapid ionization and it supports the conclusion concerning the *p,p'*-dinitro adduct.

The explanation is further supported by the observation that long range coupling between fluorine and phosphorus of **8c** is lost on cooling. A doublet of triplets of triplets was observed in the ambient temperature ^{19}F NMR spectrum, no ^{1}H decoupling of **8c**. On cooling to −36°C the coupling $^7J_{FP} = 0.9$ Hz disappeared which once again supports ionization.

Another interesting observation is the variation of $^2J_{CNP}$ as a function of temperature. These data are collected in Table III. In particular the coupling constants for the *p,p'*-difluoro and *p*-chloro adducts increase which is indicative of a change in hybridization at phosphorus. The trend toward $^2J_{CNP}$ noted with the *p,p'*-dinitro adduct is supportive of the ionization hypothesis.

These results all support the concept of increased delocalization with ultimate ionization as the dielectric constant of the medium is increased and/or the substituents on the benzil become more electron accepting.

In earlier work it was recognized that the dimethylamino groups are also responsible for enhancing delocalization. Their effect is primarily steric in origin as is evidenced by the normal behavior of other adducts with three nitrogens bonded to phosphorus.[3]

The adducts **9a**, **9b**, and **9c** of trimethyl phosphite with **7a**, **7c** and **7d** respectively have been prepared[8] and their ^{31}P NMR absorptions are found at δ −49.1, δ −49.3 and δ −49.3. In these cases there is no evidence for extensive delocalization.

EXPERIMENTAL

^{1}H NMR spectra were recorded with Varian Models T-60 and FT-80 spectrometers. Chemical shift values are reported in parts per million relative to internal tetramethylsilane. ^{13}C and ^{31}P spectra were recorded with a Varian Model FT-80 spectrometer equipped with a variable-temperature broad band probe. In all cases nuclei which are deshielded relative to their respective standard are assigned a positive chemical shift. ^{13}C NMR spectra were obtained by using full proton decoupling, a 45° flip angle and a 2-s

TABLE IV

NMR Spectral Parameters[a]

Compd	^{1}H	^{13}C
8a[b]	δ 2.83 (d, NCH$_3$, $^3J_{HCNP}$ = 10.8 Hz, 18 H), 6.83–8.40 (c, aromatic, 8 H)	δ 147.9(s), 143.4(s), 125.2(s), 124.3(s), 37.9 (d, $^2J_{CNP}$ = 4.3 Hz)
8b	δ 2.71 (d, NCH$_3$, $^3J_{HCNP}$ = 10.6 Hz, 18 H), 7.14–7.29 (c, aromatic, 9 H)	δ 135.5(s), 131.53(s), 130.5(s), 130.0 (d, ipso, $^3J_{CCOP}$ = 7.1 Hz), 129.3 (d, ipso, $^3J_{CCOP}$ = 6.1 Hz), 128.3(s), 128.2(s), 127.6(s), 126.9(s), 126.2(s), 3.95 (d, $^2J_{CNP}$ = 2.5 Hz)
8c[c]	δ 2.73 (d, NCH$_3$, $^3J_{HCNP}$ = 10.8 Hz, 18 H), 6.70–7.53 (c, aromatic, 8 H)	δ 160.8 (d, $^1J_{CF}$ = 243.1 Hz), 177.1(s), 132.9 (dd, ipso, $^4J_{CF}$ = 2.0 Hz, J_{CCOP} = 17 Hz), 128.1 (d, $^3J_{CF}$ = 7.5 Hz), 114.7 (d, $^2J_{CF}$) = 21.0 Hz), 39.0 (d, $^2J_{CNP}$ = 2.5 Hz)
8d	δ 2.28 (s, CH$_3$, 6 H), 2.67 (d, NCH$_3$, $^3J_{HCNP}$ = 11 Hz, 18 H), 6.80–7.93 (c, aromatic, 8 H)	δ 136.6(s), 134.6 (d, olefinic, $^2J_{COP}$ = 1.3 Hz), 131.2 (d, ipso, $^3J_{CCOP}$ = 10.4 Hz), 129.1(s), 126.5(s), 40.7 (br s), 21.4(s)
8e	δ 2.66 (d, NCH$_3$, $^3J_{HCNP}$ = 10.8 Hz, 18 H), 3.75 (s, OCH$_3$, 6 H) 6.73–7.86 (c, aromatic, 8 H)	δ 158.8(s), 132.2(s), 127.8(s), 126.5 (d, ipso, $^3J_{CCOP}$ = 10.7 Hz), 113.6(s), 55.6(s), 40.5 (d, $^2J_{CNP}$ = 1.1 Hz)
9a	δ 3.70 (d, OCH$_3$, $^3J_{HCOP}$ = 13.3 Hz, 9 H), 7.58–8.20 (c, aromatic, 8 H)	δ 147.4(s), 136.9 (d, ipso, $^3J_{CCOP}$ = 13.0 Hz), 135.0 (d, olefinic, $^2J_{COP}$ = 2.9 Hz), 127.3(s), 124.2(s), 55.9 (d, $^2J_{COP}$ = 10.7 Hz)
9b	δ 3.70 (d, OCH$_3$, $^3J_{HCOP}$ = 13.2 Hz) 7.00–7.49 (c, aromatic 8 H)	δ 162.5 (d, $^1J_{CF}$ = 247.2 Hz), 129.7 (s) 127.4 (dd, ipso, $^4J_{CF}$ = 3.4 Hz, $^3J_{CCOP}$ = 13 Hz), 128.6 (d, $^3J_{CF}$ = 8.1 Hz), 115.7 (d, $^2J_{CF}$ = 21.4 Hz), 55.6 (d, $^2J_{COP}$ = 10.6 Hz)
9c	δ 2.36 (s, —CH$_3$, 6 H), 3.73 (d, OCH$_3$, $^3J_{HCOP}$ = 13.2 Hz, 9 H), 7.07–7.49 (c, aromatic, 8 H)	δ 137.19(s), 133.6 (d, olefinic, $^2J_{COP}$ = 2.2 Hz), 129.3(s), 128.6 (d, ipso, $^3J_{CCOP}$ = 10.3 Hz), 55.6 (d, $^2J_{COP}$ = 10.3 Hz), 21.3(s))

Compd	^{19}F	Mp	%P	
			Calcd.	Found
8c	δ − 117.42 (dtt, $^3J_{FH}$ = 8.7 Hz, $^4J_{FH}$ = 5.5 Hz, $^7J_{FP}$ = 0.9 Hz)	—	—	—
9b	δ − 113.78 (ddt, $^3J_{FH}$ = 8.7 Hz, $^4J_{FH}$ = 5.5 Hz, $^7J_{FP}$ = 0.4 Hz)	—	—	—
9a[d]	—	100–103°C	7.3	7.6

[a] Solvent is dichloromethane-d$_2$ and temperature is 26°C.

[b] ^{13}C NMR taken at 0°C.

[c] ^{13}C NMR taken at 11°C.

[d] Recrystallized from dichloromethane at −78°C.

repetition rate with no pulse delay. All ^{13}C chemical shifts are reported in parts per million relative to internal tetramethylsilane. ^{31}P NMR spectra were acquired using a 45° flip angle, a 1-s repetition rate with no pulse delay and with full proton decoupling. Chemical shifts are reported relative to external phosphoric acid (85%).

All manipulations were carried out under an atmosphere of nitrogen.

2-Methyl-4,5-Diphenyloxazole. The method of D. Davidson *et al.*[9] was followed using 63.4 g (0.25 mol) of benzoin acetate,[10] 100 g (1.30 mol) of ammonium acetate, and 250 mL of glacial acetic acid. The residue was distilled at reduced pressure to give 47.1 g (80%) of a light yellow liquid, bp 143–147°C @ 0.05 mm (lit. 210–213 @ 18 mm); ^{1}H NMR (deuteriochloroform): δ 2.38 (s, CH_3, 3 H), 6.95–7.75 (c, aromatic, 10 H); ^{13}C NMR (deuteriochloroform): δ 14.3 (CH_3), 126.9, 128.9, 129.1 (aromatic), 129.6, 129.0 (olefinic), 135.7, 145.7 (ipso aromatic), 160.5 (C=N).

Methyl-4,5-Bis(p-Nitrophenyl)oxazole. The method of van Es and Backeberg[11] was followed using 9.42 g (40 mmol) of 2-methyl-4,5-diphenyloxazole and 50 mL fuming nitric acid (sp. gr. 1.59–1.60). The product was recrystallized from toluene to give 7.83 g (60%) of yellow needles, mp 240–242°C (lit. 241–242°C); ^{1}H NMR (deuteriochloroform): δ 2.62 (s, CH_3, 3 H), 7.50–8.40 (c, aromatic, 8 H).

4,4'-Dinitrobenzil **7a**. The method of van Es and Backeberg[12] was followed using 6.51 g (20 mmol) of 2-methyl-4,5-bis(*p*-nitrophenyl)oxazole, 25 mL of water, and 250 mL of a 1 M solution of bromine in glacial acetic acid. The product was recrystallized from toluene to give 4.69 g (77%) of yellow crystals, mp 215–216°C (lit. 213–214°C); ^{1}H NMR (deuteriochloroform): δ 8.30 (c, aromatic, 8 H).

4,4'-Difluorobenzil **7c**. The method of Beak *et al.*[13] was followed using 15.78 grams (0.127 mol) of *p*-fluorobenzaldehyde and 1.5 g of potassium cyanide. The product was recrystallized from methyl alcohol to give 8.50 g (54%) of light yellow needles, mp 120–121°C (lit. 120–121°C); ^{13}C NMR (deuteriochloroform): δ 190.5 (s), 165.2 (d, $^{1}J_{FC}$ = 258 Hz), 127.7 (d, $^{4}J_{CCCCF}$ = 2.7 Hz), 131.1 (d, $^{3}H_{CCCF}$ = 9.8 Hz), δ 114.8 (d, $^{2}J_{CCF}$ = 22.0 Hz).

Preparation of Compounds **8a–8c** *and* **9a–9c**

In Benzene. Under a nitrogen atmosphere, a stirred solution of 2.5 mmole of the benzil in 2 mL benzene-d_6 was cooled with an ice-water bath and it was treated slowly with a solution of 2.5 mmole of tris(dimethylamino)phosphine in 1 mL benzene-d_6. The reaction mixture was allowed to warm to rt and the NMR spectra were taken without attempted purification.

In Dichloromethane. Under a nitrogen atmosphere, a stirred solution of 2.5 mmole of the benzil in 2.0 mL of dichloromethane-d_2 was cooled with an acetone: dry-ice bath and it was treated slowly with a solution of 2.5 mmole of tris(dimethylamine)phosphine in 0.5 mL of dichloromethane-d_2. The reaction mixture was allowed to warm to rt and the NMR spectra were obtained without attempted purification.

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