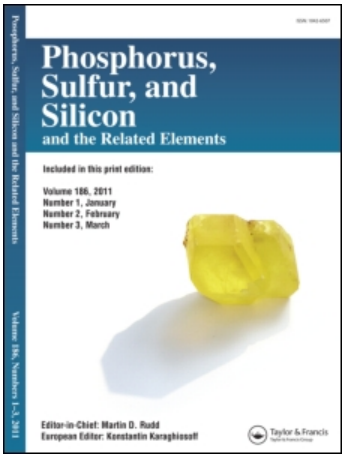

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STRUCTURES IN SOLUTION OF ADDUCTS OF 2,10-DIMETHYL-2,6,10-TRIAZA-1-PHOSPHABICYCLO[4.4.0]DECANE AND SUBSTITUTED BENZILS

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STRUCTURES IN SOLUTION OF ADDUCTS OF 2,10-DIMETHYL-2,6,10-TRIAZA-1-PHOSPHABICYCLO[4.4.0]DECANE AND SUBSTITUTED BENZILS

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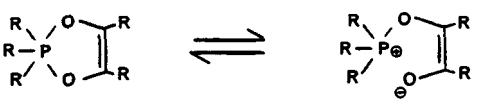
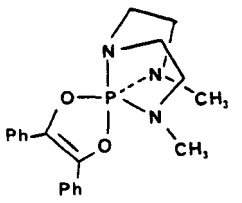
2,10-Dimethyl-2,6,10-triaza-1-phosphabicyclo[4.4.0]decane has been allowed to react with *p,p'*-dimethoxybenzil, *p,p'*-dimethylbenzil, *p*-methoxy-*p'*-fluorobenzil, *p*-fluorobenzil, *p,p'*-difluorobenzil, *p*-nitrobenzil and *p,p'*-dinitrobenzil. Although these materials could not be isolated in pure form because of rapid decomposition, the ^{31}P and ^{13}C NMR spectra indicated that they are all pentacoordinated. Variable temperature NMR studies showed that they all undergo intramolecular ligand reorganization reactions. These rearrangements could be slowed on cooling for all of the adducts except for the *p*-nitro and *p,p'*-dinitro compounds. The activation energies were very similar, 11–12 kcal/mole, for those adducts which showed variable temperature changes in their NMR spectra. The ligand reorganization process is discussed.

The condensation of trivalent phosphorus compounds with α-dicarbonyl compounds has been used as a major route to phosphoranes, **1** and in some instances it has been shown that zwitterionic substances, **2**, are in equilibrium with these materials.[1,2] Recently the adducts of hexamethylphosphorous triamide and various substituted benzils have been investigated.[2a] It was found that the equilibrium **1** ⇄ **2** is set up in some cases and that it is dependent on structure, solvent and temperature. It was also found that the various NMR measurements showed no temperature dependence which could be attributed to a slowing of intramolecular ligand reorganization, pseudorotation. Previously compounds **3** and **4** had been prepared.[2b] Compound **3** has the static structure depicted over the temperature range investigated. Compound **4** on the other hand showed temperature dependent ^{13}C NMR spectra which indicated that **4** is the preferred structure at −55°C. On warming intramolecular ligand rearrangement become rapid on the NMR time scale. It was concluded that the ligand reorganization involved interconversion of **4** and **5** and its enantiomer. The availability of the substituted benzils has prompted a study of the products of their condensation with 2,10-dimethyl-2,6,10-triaza-1-phosphabicyclo[4.4.0]decane. The main reason for conducting this study was to compare the structures of the products derived from these condensations with those from hexamethylphosphorous triamide.



1 **2**



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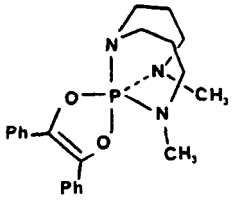

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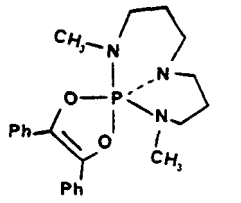

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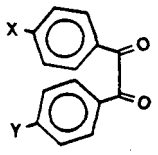
RESULTS AND DISCUSSION

The benzils, **6a–g** had para substituents, **a**, X = Y = OCH_3; **b**, X = Y = CH_3; **c**, X = OCH_3, Y = F; **d**, X = H, Y = F; **e**, X = Y = F; **f**, X = H; Y = NO_2; **g**, X = Y = NO_2 and these yielded the adducts, **7a–g** with 2,10-dimethyl-2,6,10-triaza-1-phosphabicyclo[4.4.0]decane. Table I contains the ^{31}P NMR spectral data for these substances as well as variable temperature NMR studies. Attempts to isolate these materials led to decomposition and mixtures of compounds.



6

a. X = Y = OCH_3
b. X = Y = CH_3
c. X = OCH_3; Y = F
d. X = H; Y = F
e. X = Y = F

The ^{31}P NMR show remarkably small changes with changes in the nature of the substituent on the starting benzils and furthermore the negative δ values indicate that the materials are phosphoranes. This conclusion is supported by the ^{13}C NMR spectra at 26°C which show three equivalent pairs of methylene carbon atoms in each substance. All other potentially equivalent carbon atoms are found to be so and also appropriate couplings of phosphorus to carbon are observed which eliminates ionization as the means of rendering them equivalent. It is concluded that all compounds are true phosphoranes at room temperature and that they undergo rapid ligand reorganization.

It is interesting to contrast these results with those obtained from the hexamethylphosphorous triamide adducts.[2a] Those materials had ^{31}P NMR chemical shift values ranging from δ +38.2 X = Y = NO_2 to −22.5 X = Y = OCH_3. The ^{13}C NMR data indicated that the compound, X = Y = NO_2, was ionizing rapidly on the NMR time scale at room temperature.

The differences between the two series of adducts indicates that the adducts **7a–g** have more pentacoordinate character than those from hexamethylphosphorous tri-

TABLE I

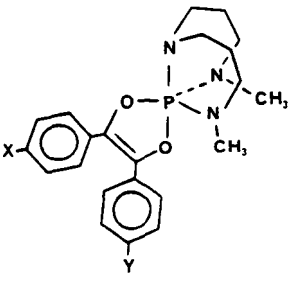
The ^{31}P NMR and variable temperature NMR spectral data of **7a–g**

Compound	^{31}P NMR (CD_2Cl_2)	Variable temperature NMR (CD_2Cl_2)			
		Observed Nucleus	Coalescence Temp. (°C)	$\Delta\delta$ (Hertz)	$\Delta G^{\neq}$ (kcal/mol)
7a	−37.7	^{13}C (para carbon)	−30.5	14.1	12.4
7b	−37.4	^{13}C (para carbon)	−41	22.3	11.6
7c	−37.1	^{19}F	−32	88.4	11.4
7d	−36.8	^{19}F	−33	90.5	11.4
7e	−36.7	^{19}F	−35.5	89.7	11.3
7f	−35.3	^{13}C	—	—	a
7g	−33.5	^{13}C	—	—	b

[a] Coalescence was not observed at −87°C.
[b] Coalescence was not observed at −85°C.

amide. Similar differences were noted for adducts with phenanthrenequinone.[2a] The reason for these differences was attributed to greater steric interactions in the hexamethylphosphorous triamide adducts which leads to destabilization of the pentacoordinated structure.

The variable temperature NMR spectra of **7a**, **7b** and **7c** show changes which demonstrate that ligand reorganization has been slowed on the NMR time scale. The data support the structures **7a**, **7b**, **7e** as being the thermodynamically most stable. Thus three pairs of methylene carbons were found as well as two sets of nonequivalent aromatic and olefinic carbons with appropriate couplings to phosphorus. The activation energies for the ligand reorganization processes are remarkably similar 11–12 kcal/mol and comparable to the 13 kcal/mole found for **4**. The adducts **7c** and **7d** also showed variable temperature ^{19}F NMR spectra which indicated that ligand reorganization was slowed on the ^{19}F NMR time scale. The ^{19}F NMR low temperature spectra indicated that two kinds of fluorines were present in each case in the ratio of ca. 1 : 1. This will be the case if **7c'** and **7d'** are present along with **7c** and **7d**. Other spectral measurements support this conclusion.



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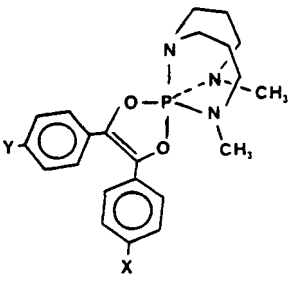


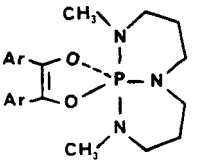
7'

a.. X = Y = OCH_3
b. X = Y = CH_3
c. X = OCH_3; Y = F
d. X = H; Y = F
e. X = Y = F

c'. X = OCH_3; Y = F
d'. X = H; Y = F

The variable temperature ^{13}C NMR spectra of **7f** and **7g** showed no change over the temperature range investigated. These results could be due to fortuitous identities of chemical shift values for nonequivalent carbons. It is more likely that intramolecular inhibition of pseudorotation was not slowed. This could arise if the adducts **7f** and **7g** are more delocalized, i.e. the P—O bonds are longer and more polar. It should be noted that such an effect would not have to be very large, 1–2 kcal/mole, to lower the coalescence temperature sufficiently to make it unobservable.

The ^1H NMR spectra of the adducts, **7a–7g**, indicate that the ligand reorganization process involves **4** to **5** type interconversions. A conformation, **8**, is specifically excluded. Such a conformation leads to quite simple ^1H spectra. The structure, **9**, is an important case. The various reasons for adopting or not adopting these structures have been discussed earlier.[2]



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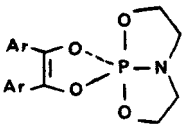

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The results of this work show that structural changes in the trivalent triamide leads to structural changes in the resulting pentacoordinated phosphorus adducts with benzils and that these are also manifested in rates of ligand reorganization in a very modest way.

EXPERIMENTAL

^1H, ^{19}F, ^{13}C, and ^{31}P NMR spectra were taken on a Varian model FT-80 spectrometer equipped with a broad band probe. All ^1H NMR chemical shifts are reported in ppm relative to tetramethylsilane. ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. ^{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. ^{13}C NMR were acquired using a 30° flip angle, a 2-s repetition rate with no pulse delay, and with full proton decoupling.

Commercially available starting materials were verified for identity and purity by TLC and NMR spectroscopy. All deuterated solvents were obtained commercially at $\geqslant$ 99.6% purity. All reaction solvents used were of spectroscopic or reagent grade and they were dried prior to use when necessary with appropriate drying agents.

All reactions were carried out in an oven-dried apparatus under a nitrogen atmosphere. All phosphoranes were prepared in a specially made one-piece apparatus consisting of a flask with a pressure-equalizer addition funnel and a septum inlet. After preparation, the phosphoranes were transfered via a syringe to septum stoppered NMR tubes under argon.

General Procedure for Preparation of Phosphoranes **7a–g**. To a stirred solution of 2.5 mmol of the appropriate 1,2-dione[2]a,[3] in 2 mL of dichloromethane-d_2 at −78°C was added dropwise over a few minute period in solution of 0.47 g (2.5 mmol) of **3** in 0.5 mL of dichloromethane-d_2. The reaction mixture was stirred for ten minutes at −78°C and then it was allowed to warm to room temperature. The NMR spectral data were obtained immediately without attempted purification (Table II). Attempts to isolate these substances led to mixtures as is described in the Results and Discussion section.

TABLE II

The NMR spectral data of phosphoranes **7a–g** in dichloromethane-d_2

Compound	^{1}H NMR	^{13}C NMR
7a	δ 1.53–3.33 (c, CH_2, 12 H), 2.80 (d, NCH_3, $^3J_{HCNP}$ = 10 Hz, 6 H), 3.73 (s, OCH_3, 6 H), 6.67–7.53 (c, ArH, 8 H)	δ 25.8 (s, CH_2), 40.4 (unresolved d, NCH_3), 48.8 (d, NCH_2, $^2J_{CNP}$ = 4.7 Hz), 50.9 (s, NCH_2), 55.5 (s, OCH_3), 114.0 and 127.8 (two s, *o* and *m*), 125.8 (d, *ipso*, $^3J_{CCOP}$ = 11.0 Hz), 132.9 (br s, olefinic), 159.0 (s, *p*)
7b	δ 1.56–3.86 (c, CH_2, 12 H), 2.27 (s, $ArCH_3$, 6 H), 2.80 (d, NCH_3, $^3J_{HCNP}$ = 10.4 Hz, 6 H), 7.00–7.53 (c, ArH, 8 H)	δ 21.5 (s, $ArCH_3$), 25.9 (s, CH_2), 40.4 (d, NCH_3, $^2J_{CNP}$ = 2.8 Hz), 48.9 (d, NCH_2, $^2J_{CNP}$ = 4.8 Hz), 51.0 (s, NCH_2), 126.6 and 129.3 (two s, *o*, and *m*), 130.5 (d, *ipso*, $^3J_{CCOP}$ = 10.9 Hz), 133.8 (br s, olefinic), 137.1 (s, *p*)
7c	δ 1.81–3.91 (c, CH_2, 12 H), 2.98 (d, NCH_3, $^3J_{HCNP}$ = 10.3 Hz, 6H), 3.95 (s, OCH_3, 3 H), 6.87–8.16 (c, ArH, 8 H)	δ 25.7 (s, CH_2), 40.1 (d, NCH_3, $^2J_{CNP}$ = 2.4 Hz), 48.6 (d, NCH_2, $^2J_{CNP}$ = 4.9 Hz), 50.8 (s, NCH_2), 55.5 (s, OCH_3), 114.0 (s), 115.2 (d, *m*, $^2J_{CCF}$ = 21.1 Hz), 125.4 (d, *ipso*, $^3J_{CCOP}$ = 11.2 Hz), 127.7 (d, *o*, $^3J_{CCCF}$ = 7.9 Hz), 128.1 (s), 129.3 (d of d, *ipso*, $^3J_{CCOP}$ = 11.1 Hz), 159.2 (s, *p*), 161.8 (d, *p*, $^1J_{CF}$ = 245.3 Hz)[a]
7d	δ 1.71–3.30 (c, CH_2, 12 H), 2.85 (d, NCH_3, $^3J_{HCNP}$ = 10.3 Hz), 6.88–7.60 (c, ArH, 9 H)	δ 25.7 (s, CH_2), 40.3 (d, NCH_3, $^2J_{CNP}$ = 2.6 Hz), 48.7 (d, NCH_2, $^2J_{CNP}$ = 4.9 Hz), 50.9 (s, NCH_2), 115.4 (d, *m*, $^2J_{CCF}$ = 22.6 Hz), 126.4 (s), 127.3 (s, *p*), 128.4 (d, *o*, $^3J_{CCCF}$ = 7.5 Hz), 128.5 (s), 129.1 (d of d, *ipso*, $^3J_{CCOP}$ = 7.8 Hz, $^4J_{CCCCF}$ = 2.8 Hz), 162.1 (d, *p*, $^1J_{CF}$ = 245.9 Hz)[c]
7e[d]	δ 1.61–3.69 (c, CH_2, 12 H), 2.82 (d, CH_3, $^3J_{HCNP}$ = 10.3 Hz, 6 H), 6.86–8.11 (c, ArH, 8 H)	δ 25.7 (s, CH_2), 40.2 (d, NCH_3, $^2J_{CNP}$ = 2.7 Hz), 48.7 (d, NCH_2, $^2J_{CNP}$ = 5.0 Hz)), 50.9 (d, NCH_2, $^2J_{CNP}$ = 1.5 Hz), 115.4 (d, *m*, $^2J_{CCF}$ = 21.6 Hz), 128.2 (d, *o*, $^3J_{CCCF}$ = 7.9 Hz), 129.3 (d of d, *ipso*, $^3J_{CCOP}$ = 10.9 Hz, $^4J_{CCCCF}$ = 3.3 Hz), 132.9 (br s, olefinic), 162.1 (d, *p*, $^1J_{CF}$ = 246.2 Hz)
7f	δ 1.70–3.29 (c, CH_2, 12 H), 2.82 (d, CH_3, $^3J_{HCNP}$ = 10.4 Hz), 7.29–8.09 (c, ArH, 9 H)	δ 25.6 (s, CH_2), 40.2 (d, NCH_3, $^2J_{CNP}$ = 2.7 Hz), 48.6 (d, NCH_2, $^2J_{CNP}$ = 5.0 Hz), 51.0 (d, NCH_2, $^2J_{CNP}$ = 1.7 Hz), 123.8, 125.1, 127.8, and 128.9 (four s, *o*, *m*, and *p*), 131.3 (d, olefinic, $^2J_{COP}$ = 0.8 Hz), 132.6 (d, *ipso*, $^3J_{CCOP}$ = 10.1 Hz), 139.4 (d, *ipso*, $^3J_{CCOP}$ = 11.1 Hz), 140.2 (s, olefinic), 145.5 (s, *p*)
7g	δ 1.60–3.51 (c, CH_2, 12 H), 2.78 (d, NCH_3, $^3J_{HCNP}$ = 10.6 Hz, 6 H), 7.59–8.18 (c, ArH, 8 H)	e

TABLE II (*Continued*)

Compound	Low Temperature ^{13}C NMR	^{19}F NMR
7a	(−71°C): δ 25.7 (s, CH_2), 40.1 (d, NCH_3, $^2J_{CNP}$ = 2.3 Hz), 48.6 (s, NCH_2), 50.8 (s, NCH_2), 55.7 (s, OCH_3), 113.8, 127.3 and 128.0 (three s, *o* and *m*), 125.3 (d, *ipso*, $^3J_{CCOP}$ = 10.8 Hz), 130.3 (d, olefinic, $^2J_{COP}$ = 3.0 Hz), 134.7 (s, olefinic, 158.2 and 158.9 (two s, *p*)	—
7b	(−65°C): δ 21.9 (s, $ArCH_3$), 25.5 (s, CH_2), 40.1 (d, NCH_3, $^2J_{CNP}$ = 2.4 Hz), 48.6 (d, NCH_2, $^2J_{CNP}$ = 3.5 Hz), 50.7 (s, NCH_2), 125.9, 126.8, and 129.3 (three s, *o* and *m*), 129.9 (d, *ipso*, $^3J_{CCOP}$ = 12.5 Hz), 130.1 (d, *ipso*, $^3J_{CCOP}$ = 9.4 Hz), 131.1 (d, olefinic, $^2J_{COP}$ = 3.1 Hz), 135.9 (s, olefinic), 136.7 (s, *p*), 137.8 (s, *p*)	—
7c	(−60°C): δ 25.1 (s, CH_2), 25.2 (s, CH_2), 39.7 (d, NCH_3), 48.1 (d, NCH_2) $^2J_{CNP}$ = 2 Hz), 48.4 (d, NCH_2, $^2J_{CNP}$ = 5 Hz), 50.2 (s, NCH_2), 50.3 (s, NCH_2)[b]	δ −115.88 (t of t, $^3J_{FCCH}$ = 8.5 Hz, $^4J_{FCCC}$ = 5.4 Hz)
7d	(−75°C): δ 25.5 (s, CH_2), 40.0 (d, NCH_3, $^2J_{CNP}$ = 2.5 Hz), 48.3 (d, NCH_2, $^2J_{CNP}$ = 1.5 Hz), 50.6 (s, CH_2N), 115.6 (d, *m*, $^2J_{CCF}$ = 21.3 Hz), 125.8, 126.7, 127.0, 127.6, 128.0, 128.7, 129.2 (seven s, *o* and *m*), 130.9 (d of d, *ipso*, $^3J_{CCOP}$ = 8.3 Hz, $^4J_{CCCCF}$ = 1.8 Hz), 132.5 (d, *ipso*, $^3J_{CCOP}$ = 10.8 Hz), 135.8 (d, *ipso*, $^3J_{CCOP}$ = 8.2 Hz), 132.8 (s, olefinic), 161.4 (d, *p*, $^1J_{CF}$ = 244.7 Hz), 162.2 (d, *p*, $^1J_{CF}$ = 246.2 Hz)	δ −115.14 (t of t, $^3J_{FCCH}$ = 8.6 Hz, $^4J_{FCCCH}$ = 5.6 Hz)
7e	(−78°C): 25.5 (s, CH_2), 40.0 (d, NCH_3, $^2J_{CNP}$ = 2.8 Hz), 48.4 (br s, NCH_2), 50.7 (br s, NCH_2), 115.7 (d, *m*, $^2J_{CCF}$ = 21.4 Hz), 128.5 (c), 130.4 (d, olefinic, $^2J_{COP}$ = 1.5 Hz), 133.2 (br s olefinic), 161.9 (d, *p*, $^1J_{CF}$ = 256.4 Hz), 162.2 (d, *p*, $^1J_{CF}$ = 246.8 Hz)[e]	−115.04 (t of t, $^3J_{FCCH}$ = 8.0 Hz, $^4J_{FCCCH}$ = 5.6 Hz)
7f	(−87°C): δ 25.4 (s, CH_2), 40.1 (d, NCH_3, $^2J_{CNP}$ = 2.8 Hz), 48.4 (br s, NCH_2), 50.5 (d, NCH_2, $^2J_{CNP}$ = 1.8 Hz), 124.1, 125.0, 127.7, and 129.1 (four s, *o*, *m*, and *p*), 130.9 (s, olefinic), 132.2 (d, *ipso*, $^3J_{CCOP}$ = 10.0 Hz), 139.2 (d, *ipso*, $^3J_{CCOP}$ = 11.2 Hz), 140.7 (s, olefinic), 144.8 (s, *p*).	—
7g	(−85°C): δ 25.2 (s, CH_2), 40.0 (d, NCH_3, $^2J_{CNP}$ = 2.4 Hz), 48.1 (d, NCH_2, $^2J_{CNP}$ = 1.9 Hz), 50.6 (d, NCH_2, $^2J_{CNP}$ = 1.5 Hz), 124.3 and 126.9 (two s, *o* and *m*), 138.7 (d, *ipso*, $^3J_{CCOP}$ = 10.4 Hz), 135.9 (s, olefinic), 146.2 (s, *p*)	—

[a] Olefinic carbon was not observed.
[b] Aromatic resonances complex and were not assigned.
[c] One olefinic and one ipso carbon were not observed.
[d] Recrystallized slowly from dichloromethane at −78°C to give 0.71 g (66%) of a yellow solid, mp 107–110°C; Anal. Calcd. for $C_{22}H_{26}F_2N_3O_2P$: P, 7.2. Found: P, 7.4.
[e] Decomposed rapidly at rt.

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