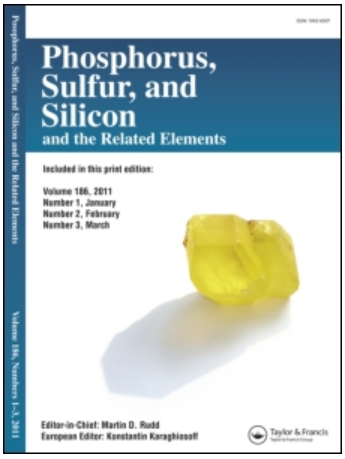

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STRUCTURES IN SOLUTION OF ADDUCTS OF 2,8-DIOXA-5-AZA-1-PHOSPHABICYCLO[3.3.0]-OCTANE AND SUBSTITUTED BENZILS

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STRUCTURES IN SOLUTION OF ADDUCTS OF 2,8-DIOXA-5-AZA-1-PHOSPHABICYCLO[3.3.0]-OCTANE AND SUBSTITUTED BENZILS

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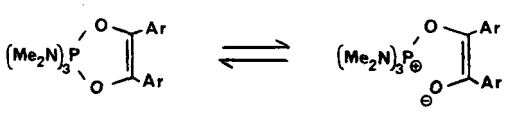
Adducts of 2,8-dioxa-5-aza-1-phosphabicyclo[3.3.0]octane and *p*,*p*′-dimethylbenzil, *p*-methoxy-*p*′-fluorobenzil, *p*-fluorobenzil, *p*,*p*′-difluorobenzil, *p*-nitrobenzil and *p*,*p*′-dinitrobenzil have been prepared. Although these materials could not be isolated in pure form because of rapid decomposition, the ^{31}P and other NMR spectral data indicate that all of these materials are pentacoordinate in solution. The NMR data also indicate that all of these adducts undergo rapid intramolecular ligand reorganization at room temperature. Variable temperature NMR measurements indicate that these rearrangements can be slowed and that they all have virtually the same activation energies, $\Delta G^{\ddagger}$ 11.4–11.9 kcal/mole. The barrier to ligand reorganization is associated with the 5-membered dioxa containing ring adopting a diequatorial disposition. These results are discussed and compared to other systems.

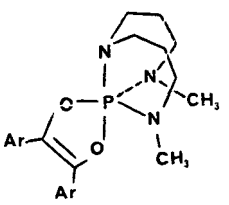
During the past few years research in this laboratory has been aimed at a delineation of those factors which govern stabilities and formation of pentacoordinated phosphorus compounds as well their intramolecular ligand reorganization reactions, pseudorotations. One approach has involved studies of materials prepared by condensation of various α-dicarbonyl compounds with tricoordinate phosphorus compounds.[1] These reactions are some of the most common routes to pentacoordinated phosphorus compounds.[2]

As part of this study a number of substituted benzils were allowed to react with hexamethylphosphorous triamide to give adducts, **1**.[1a] It was found that in some cases ionization of **1** could occur to give **2** in equilibrium with **1**. Some of the factors which govern the equilibration were determined. Variable temperature NMR measurements of compounds, **1**, indicated that intramolecular reorganization reactions remained rapid on the NMR time scale. Intramolecular ligand reorganization could be distinguished from ionization i.e **1** ⇄ **2** by the observation of the appropriate couplings to phosphorus in the intramolecular process.



1 **2**

More recently a series of compounds, **3**, was prepared.[2b] These substances did not undergo ionization to a zwitterion and in some cases inhibition of pseudorotation was observed on cooling.



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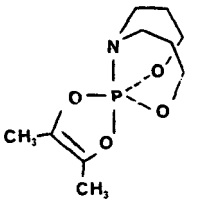

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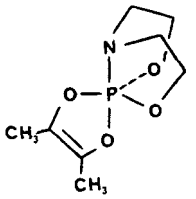

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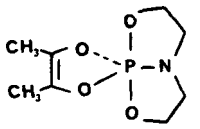

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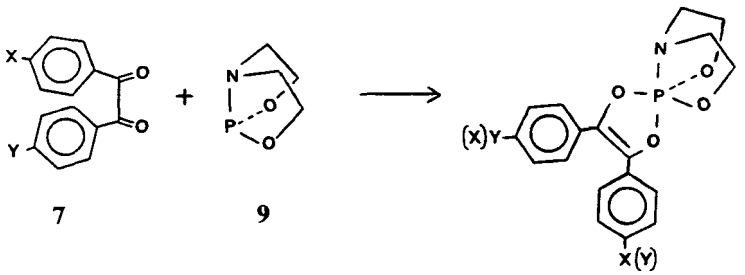
Compounds **4** and **5** have also been studied. Compound **5** exhibited variable temperature NMR spectra which demanded that structure **6** be passed through during the pseudorotation process. The availability of a series of benzils, **7**, suggested that adducts **8** derived from them and **9** would provide another probe of the electronic effect if any on pseudorotation rates.

RESULTS AND DISCUSSION

The condensation of the benzils, **7a–f**, with **9** gave the adducts, **8a–f**. The ^{31}P NMR chemical shifts of these adducts are presented in Table I. The δ values are virtually



7 9 8

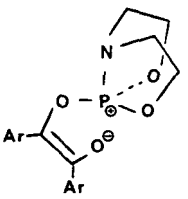
identical and coupled with other NMR data establish that all of the adducts are pentacoordinate and that ionization is not occurring rapidly on the NMR time scale. Attempts to isolate these substances led to mixtures of materials. When the solutions containing the adducts were monitored by ^{31}P NMR spectroscopy it became clear

that the adducts were decomposing to phosphoryl compounds with varying rates depending on structure. The nitro substituted compounds were for example extremely unstable.

	X	Y		X	Y
7a	CH_3	CH_3	**8a**	CH_3	CH_3
b	OCH_3	F	**b**	OCH_3	F
c	H	F	**c**	H	F
d	F	F	**d**	F	F
e	H	NO_2	**e**	H	NO_2
f	NO_2	NO_2	**f**	NO_2	NO_2

Variable temperature NMR measurements established that all of these substances undergo pseudorotation and that pseudorotation can be slowed on the NMR time scale. Interestingly the activation energies for these rearrangements of **8a–f** are virtually identical i.e. within the limits of the experimental measurement. These results coupled with the virtual identity of the ^{31}P NMR chemical shifts show that the presence of substituents on the para positions of the benzils has essentially no effect on their structure or their rates of intramolecular reorganization. The ^1H NMR spectra establish that in all cases the ligand reorganization process involves a transition state or intermediate entirely analogous to that of **6**.

The lack of phosphonium character in the adducts **8** i.e. **10** as compared to **2** in particular and to a considerably lesser degree **11** can be attributed to a diminished ability of oxygen to stabilize the positive charge on phosphorus as compared to nitrogen. There is also less steric congestion in the adducts **8** than in **1**. Of prime importance to the destabilization of **10** relative to **2** is the increase in bond angle of the 5-membered rings in a true intermediate **10** as compared to **8**. If **10** is a contributor to a hybrid some bond angle change would be expected as well. The small membered ring effect in phosphorane stabilization is well-known and has been discussed in detail.[2]



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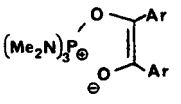

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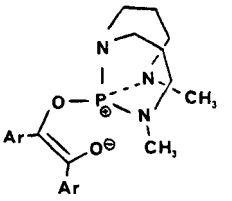

11

The adducts, **8b**, **8c** and **8e**, can exist as two isomers below their coalescence temperatures. Both **8b** and **8c** were found as 1 : 1 mixtures of the two potential isomers. The ^{13}C NMR spectrum of **8e** at $-73°C$ shows two nonequivalent ipso carbon atoms of the aromatic rings of unequal intensity, 2 : 1 ratio of peak heights, at δ 137.6, major, and δ 137.4, minor, with $^3J_{CCOP} = 13.2$ Hz and 13.0 Hz, respectively. Such a spectrum can arise if two isomers are present in unequal quantities. If the reasonable assumption is made that the T_1 values of the two ipso carbons are the same then the major isomer will be that one in which the *p*-nitrophenyl group is in the equatorial belt. This conclusion is based on the slightly larger coupling constant which has been noted to be larger in many cases for equatorial ligands versus apical ligands. Delocalization of charge from an apical

TABLE I

The ^{31}P NMR and variable temperature NMR spectral data of **8a–f**

Compound	^{31}P NMR (CD_2Cl_2)	Variable Temperature NMR (CD_2Cl_2)			
		Observed Nucleus	Coalescence Temp (°C)	$\Delta\delta$ (Hertz)	$\Delta G^{\ddagger}$ (kcal/mol)
8a	δ −7.4	^{13}C (para carbon)	−48	15.6	11.4
8b	δ −7.2	^{19}F	−27	62.6	11.9
8c	δ −6.9	^{19}F	−28	67.0	11.8
8d	δ −6.9	^{19}F	−26	61.0	11.9
8e	δ −6.3	^{13}C (para carbon)	−41	19.8	11.7
8f	δ −5.7	^{13}C (para carbon)	−41	22.5	11.6

oxygen into the π-system of the adduct can account for this small isomer preference ca. 0.5 kcal/mole difference in energy between the two. This result further substantiates the other findings that delocalization is not particularly important in the adducts **8**.

EXPERIMENTAL

All melting points were determined in open capillary tubes on a Thomas–Hoover melting point apparatus and are uncorrected. ^1H NMR spectra were taken on a Varian model T-60 or FT-80 spectrometer. ^{13}C, ^{19}F, 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. ^{19}F chemical shifts are reported in ppm relative to trichlorofluoromethane, where a positive shift 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 obtained 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 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 oven-dried apparatus under a nitrogen atmosphere. All phosphoranes were prepared in a specially constructed one-piece apparatus consisting of a flask with a pressure-equalizer addition funnel and a septum inlet. After preparation, the phosphoranes were transferred via a syringe into septum stoppered NMR tubes under argon and their NMR spectra were immediately taken.

2-(4-Nitrophenyl) acetophenone. The acetophenone was prepared following the procedure reported by Corey *et al.*[3] from 60 g (0.33 mol) of 4-nitrophenylacetic acid, 50 g (0.36 mol) of phosphorus trichloride, 55 g (0.41 mol) of anhydrous aluminum chloride, and 400 ml of benzene. The reaction residue was recrystallized from a methyl alcohol: benzene mixture to give 13.5 g (19%) of a tan solid mp 141–142°C (lit.[3] 143.5–144°C); ^1H NMR (deuteriochloroform): δ 4.41 (s, $-CH_2-$, 2 H), 7.26–8.24 (c, ArH, 9 H); ^{13}C NMR (deuteriochloroform): δ 44.8 (s, $-CH_2-$), 123.6, 128.3, 128.8, and 130.5 (four s, *o* and *m*), 133.6 (s, *p*), 136.1 and 142.0 (two s, *ipso*), 146.9 (s, O_2N-C_{ar}), 195.9 (s, C=O).

2-(4-Fluorophenyl) acetophenone. The acetophenone was prepared following the procedure for the 2-(4-nitrophenylacetophenone) from 23.12 g (0.15 mol) of 4-fluorophenylacetic acid, 10.99 g (0.08 mol) of phosphorus trichloride, 23.99 g (0.18 mol) of aluminum chloride, and 200 ml of benzene. The reaction residue was recrystallized from methyl alcohol to give 21.18 g (66%) of a white solid, mp 111–112°C (lit.[4] 110–110.5°C); ^1H NMR: (deuteriochloroform): δ 4.23 (s, $-CH_2-$, 2 H), 6.72–8.05 (c, ArH, 9 H); ^{19}F NMR (deuteriochloroform): δ −116.29 (t of t, $^3J_{FCCH}$ = 8.5 Hz, $^4J_{FCCCH}$ = 5.6 Hz); ^{13}C NMR (deuteriochloroform): δ 44.3 (s, $-CH_2-$), 115.4 (d, *m*, $^2J_{CCF}$ = 20.9 Hz), 128.4 and 128.6 (two s, *o* and *m*), 130.2 (d, *ipso*, $^4J_{CCCCF}$ = 2.5 Hz), 131.1 (d, *o*, $^3J_{CCCF}$ = 7.7 Hz), 133.2 (s, *p*), 136.4 (s, *ipso*), 161.8 (d, *p*, $^1J_{CF}$ = 245.3 Hz), 197.3 (s, C=O); Anal. Calcd. for $C_{14}H_{11}FO$: C, 78.5; H, 5.2. Found: C, 78.7; H, 5.5.

TABLE II

The NMR spectral data of phosphoranes **8a–f** in dichloromethane-d_2

Compound	^{1}H NMR	^{13}C NMR
8a	δ 2.30 (s, CH_3, 6 H), 3.10 (d of t, CH_2N, $^3J_{HCNP}$ = 15.2 Hz, $^3J_{HCCH}$ = 5.8 Hz, 4 H), 4.03 (d of t, CH_2O, $^3J_{HCOP}$ = 14.2 Hz, $^3J_{HCCH}$ = 5.8 Hz, 4 H), 6.90–7.47 (c, ArH, 8 H).	(−24°C): δ 21.5 (s, CH_3), 45.7 (d, NCH_2, $^2J_{CNP}$ = 11.7 Hz), 62.5 (d, OCH_2, $^2J_{COP}$ = 5.6 Hz), 126.7 (s), 128.2 (d, *ipso*, $^3J_{CCOP}$ = 13.5 Hz), 130.2 (s), 138.1 (s, *p*)[a]
8b	δ 3.08 (d of t, NCH_2, $^3J_{HCNP}$ = 15.3 Hz, $^3J_{HCCH}$ = 6.2 Hz, 4 H), 3.75 (s, OCH_3, 3 H), 4.01 (d of t, OCH_2, $^3J_{HCOP}$ = 13.9 Hz, $^3J_{HCCH}$ = 6.2 Hz, 4 H), 6.70–8.00 (c, ArH, 8 H)	δ 45.8 (d, NCH_2, $^2J_{CNP}$ = 11.7 Hz), 55.5 (s, OCH_3), 62.4 (d, OCH_2, $^2J_{COP}$ = 6.0 Hz), 115.6 (d, *m*, $^2J_{CCF}$ = 21.9 Hz), 123.4 (d, *ipso*, $^3J_{CCOP}$ = 13.0 Hz), 127.3 (partially obscured d of d, *ipso*, $^4J_{CCCCF}$ = 3.4 Hz), 128.5 (d, *o*, $^3J_{CCCF}$ = 8.0 Hz), 128.5 (s), 130.1 (d, olefinic, $^2J_{COP}$ = 2.2 Hz), 159.9 (s, *p*), 162.3 (d, *p*, $^1J_{CF}$ = 246.5 Hz)[b]
8c	δ 3.09 (d of t, NCH_2, $^3J_{HCNP}$ = 15.0 Hz, $^3J_{HCCH}$ = 6.3 Hz, 4 H), 4.01 (d of t, OCH_2, $^3J_{HCOP}$ = 14 Hz, $^3J_{HCCH}$ = 6.3 Hz, 4 H), 6.86–7.53 (c, ArH, 9 H)	δ 45.9 (d, NCH_2, $^2J_{CNP}$ = 11.3 Hz), 62.6 (d, OCH_2, $^2J_{COP}$ = 6.1 Hz), 116.1 (d, *m*, $^2J_{CCF}$ = 21.6 Hz), 126.9 (s), 127.6 (partially obscured d of d, *ipso*, $^4J_{CCCCF}$ = 3.6 Hz), 128.6 (d, *o*, $^3J_{CCCF}$ = 10.0 Hz), 128.8 (s), 129.3 (s, *p*), 131.2 (d, *ipso*, $^3J_{CCOP}$ = 12.4 Hz), 162.7 (d, *p*, $^1J_{CF}$ = 247.8 Hz)[b]
8d	δ 3.10 (d of t, NCH_2, $^3J_{HCNP}$ = 15 Hz, $^3J_{HCCH}$ = 6.1 Hz, 4 H,) 4.03 (d of t, OCH_2, $^3J_{HCCH}$ = 6.1 Hz, $^3J_{HCOP}$ = 14.1 Hz, 4 H), 6.84–8.08 (c, ArH, 8 H)	δ 45.7 (d, NCH_2, $^2J_{CNP}$ = 11.9 Hz), 62.4 (d, OCH_2, $^2J_{COP}$ = 6.0 Hz), 115.6 (d, *m*, $^2J_{CCF}$ = 21.6 Hz), 127.3 (d of d, *ipso*, $^3J_{CCOP}$ = 9.8 Hz, $^4J_{CCCCF}$ = 3.0 Hz), 128.8 (d, *o*, $^3J_{CCCF}$ = 8.0 Hz), 129.8 (d, olefinic, $^2J_{COP}$ = 2.7 Hz), 162.5 (d, *p*, $^1J_{CF}$ = 247.5 Hz)
8e	δ 3.13 (d of t, CH_2N, $^3J_{HCNP}$ = 14.8 Hz, $^3J_{HCCH}$ = 6.0 Hz, 4 H), 4.06 (d of t, CH_2O, $^3J_{HCOP}$ = 14 Hz, $^3J_{HCCH}$ = 6.0 Hz, 4 H), 7.20–8.43 (c, ArH, 9 H)	δ 45.8 (d, NCH_2, $^2J_{CNP}$ = 12.0 Hz), 62.7 (d, OCH_2, $^2J_{COP}$ = 6.2 Hz), 123.9, 126.1, 127.1, and 129.0 (four s, *o* and *m*), 129.5 (s, *p*), 130.6 (d, *ipso*, $^3J_{CCOP}$ = 13.6 Hz), 137.6 (d, *ipso*, $^3J_{CCOP}$ = 13.1 Hz), 146.5 (s, *p*)[a]
8f	δ 3.14 (d of t, NCH_2, $^3J_{HCNP}$ = 14.9 Hz, $^3J_{HCCH}$ = 6.3 Hz, 4 H), 4.06 (d of t, OCH_2, $^3J_{HCOP}$ = 14.1 Hz, $^3J_{HCCH}$ = 6.3 Hz, 4 H), 7.48–8.18 (m, ArH, 8 H)	δ 45.9 (d, NCH_2, $^2J_{CNP}$ = 12 Hz), 63.1 (d, OCH_2, $^2J_{COP}$ = 6.0 Hz), 124.3 and 127.7 (two s, *o* and *m*), 135.3 (d, olefinic, $^2J_{COP}$ = 3.0 Hz), 137.0 (d, *ipso*, $^3J_{CCOP}$ = 13.2 Hz), 147.6 (s, *p*)

Compound	Low Temperature ^{13}C NMR	^{19}F NMR
8a	(−79°C): δ 21.7 (s, CH_3), 45.6 (d, NCH_2, $^2J_{CNP}$ = 10.5 Hz), 62.7 (d, OCH_2, $^2J_{COP}$ = 4.4 Hz), 126.5, 126.7, and 130.3 (three s, *o* and *m*), 128.0 (d, *ipso*, $^3J_{CCOP}$ = 12.9 Hz), 128.0 (d, *ipso*, $^3J_{CCOP}$ = 12.7 Hz), 136.3 and 136.6 (two s, olefinic), 137.9 and 138.7 (two s, *p*)	

TABLE II (*Continued*)

Compound	Low Temperature ^{13}C NMR	^{19}F NMR
8b		δ −114.45 (t of t, $^3J_{FCCH}$ = 8.7 Hz, $^4J_{FCCCH}$ = 5.6 Hz)
8c		δ −113.70 (t of t, $^3J_{FCCH}$ = 8.7 Hz, $^4J_{FCCCH}$ = 5.4 Hz)
8d	(−68°C): δ 45.6 (d, NCH_2, $^2J_{NCP}$ = 11.6 Hz), 62.8 (d, OCH_2, $^2J_{COP}$ = 5.2 Hz), 115.8 (overlapping d, 2 *m*, $^2J_{CCF}$ = 21.2 Hz), 128.7 (overlapping d, two *o*, $^3J_{CCCF}$ = 11.2 Hz), 135.9 (overlapping d of d, two *ipso*), 162.1 (d, *p*, $^1J_{CF}$ = 246.9 Hz), 162.6 (d, *p*, $^1J_{CF}$ = 247.6 Hz)	δ −115.01 (d of t of t, $^3J_{FCCH}$ = 8.8 Hz, $^4J_{FCCCH}$ = 5.6 Hz, $^7J_{FP}$ = 0.6 Hz)
8e	(−83°C): δ 45.7 (br s, CH_2N), 63.1 (br s, OCH_2), 124.1, 124.6, 125.7, 126.9, 127.1, 127.8, 129.1, and 129.2 (eight s, *o* and *m*), 129.6 and 130.2 (two s, *p*), 131.8 (d, *ipso*, $^3J_{CCOP}$ = 10.0 Hz), 137.4 (d, *ipso*, $^3J_{CCOP}$ = 13.0 Hz, minor isomer), 137.6 (d, *ipso*, major isomer, $^3J_{CCOP}$ = 13.2 Hz), 133.9 (d, olefinic $^2J_{COP}$ = 1.4 Hz) 135.0 (d, olefinic, $^2J_{COP}$ = 5.9 Hz), 136.2 (d, olefinic, $^2J_{COP}$ = 1.2 Hz), 141.4 (d, olefinic, $^2J_{COP}$ = 4.7 Hz), 145.5 and 146.5 (two s, *p*)	
8f	(−86°C): δ 45.6 (d, NCH_2, $^2J_{CNP}$ = 12.2 Hz), 63.4 (d, OCH_2, ^2J = 2.9 Hz), 124.4, 127.0, and 128.1 (three s, *o* and *m*) 131.4 (d, olefinic, $^2J_{COP}$ = 3.3 Hz), 136.6 (d, *ipso*, $^3J_{CCOP}$ = 13.0 Hz), 136.9 (d, *ipso*, $^3J_{CCOP}$ = 12.8 Hz), 138.7 (d, olefinic, $^2J_{COP}$ = 5.6 Hz), 146.5 (s, *p*), 147.4 (s, *p*)	

[a] The olefinic carbon atoms were not observed.
[b] One olefinic carbon atom was not observed.

4-Fluoro-4'-Methoxybenzil (**7b**). To a solution of 2.48 g (0.04 mol) of potassium cyanide in 64 ml of ethyl alcohol and 32 ml of water was added 12.41 g (0.1 mol) of 4-fluorobenzaldehyde and 13.62 g (0.1 mol) of 4-methoxybenzaldehyde. The reaction mixture was heated on a steam bath for thirty minutes and then the volatiles were removed *in vacuo*. The residue was extracted with a benzene: dichloromethane mixture and the organic phase was dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and to the residue was added 80 ml of concentrated nitric acid and 160 ml of glacial acetic acid. The reaction mixture was heated on a steam bath for five hours and then it was poured onto crushed ice. The solid was collected by filtration, and it was dried and then recrystallized from methyl alcohol. The product was separated from 4,4'-difluorobenzil and 4,4'-dimethoxybenzil by flash chromatography[5] (MERCK Silica-gel 60, 230–400 mesh) to give 3.61 g (14%) of light-yellow crystals, mp 88–90°C; ^1H NMR (deuteriochloroform): δ 3.87 (s, OCH_3, 3 H), 6.87–8.17 (c, ArH, 8 H); ^{19}F NMR (deuteriochloroform): δ −101.93 (t of t, $^3J_{FCCH}$ = 8.6 Hz, $^4J_{FCCCH}$ = 5.6 Hz); ^{13}C NMR (deuteriochloroform): δ 56.1 (s, OCH_3), 114.9 (s), 116.7 (d, *m*, $^2J_{CCF}$ = 22.1 Hz), 126.3 (s, *ipso*), 130.2 (d, *ipso*, $^4J_{CCCCF}$ = 2.6 Hz), 132.8 (s), 133.1 (d, *o*, $^3J_{CCCF}$ = 10.6 Hz), 165.5 (s, *p*), 167.1 (d, *p*, $^1J_{CF}$ = 257.7 Hz), 193.1 and 193.5 (two s, C=O); Anal. Calcd. for $C_{15}H_{11}FO_3$: C, 69.8; H, 4.3. Found: C, 69.9; H, 4.0.

4-Nitrobenzil (**7e**). The benzil was prepared following the procedure of Corey *et al.*[3] from 5.19 g (21.5 mmol) of 2-(4-nitrophenyl) acetophenone, 2.62 g (23.7 mmol) of selenium dioxide, and 30 ml of glacial acetic acid. The reaction product was recrystallized from methyl alcohol to give 3.73 g (68%) of a dark-orange solid, mp 143–144°C (lit.[3] 142); ^1H NMR (deuteriochloroform): δ 7.51–8.29 (c, ArH); ^{13}C NMR (deuteriochloroform): δ 124.0, 129.1, 129.9, and 130.8 (four s, *o* and *m*), 132.2 (s, *ipso*), 135.3 (s, *p*), 137.2 (s, *ipso*), 151.0 (s, *p*), 191.1 and 192.7 (two s, C=O). Anal. Calcd. for $C_{14}H_9NO_4$: C, 65.9; H, 3.6; N, 5.5. Found: C, 65.8; H, 3.6; N, 5.5.

4-Fluorobenzil **7c**. Following the method used to prepare **7e**, compound **7c** was prepared from 4.60 g (21.5 mmol) of 2-(4-fluorophenyl)acetophenone, 2.62 g (23.7 mmol) of selenium dioxide, and 25 ml of glacial acetic acid. The reaction residue was recrystallized from methyl alcohol to give 3.20 g (65%) of a yellow solid, mp 64–65°C (lit.[4] 63.5–64.5°C); ^{1}H NMR (deuteriochloroform): δ 7.06–8.10 (c, ArH, 9 H); ^{19}F NMR (deuteriochloroform): δ −101.56 (t of t, $^3J_{FCCH}$ = 8.6 Hz, $^4J_{FCCCH}$ = 5.7 Hz); ^{13}C NMR (deuteriochloroform): δ 116.2 (d, *m*, $^2J_{CCF}$ = 22.1 Hz), 128.9 and 129.8 (two s, *o* and *m*), 130.8 (unresolved d, *ipso*), 132.6 (d, *o*, $^3J_{CCCF}$ = 9.2 Hz), 134.9 (s, *p*), 136.6 (s, *ipso*), 166.6 (d, *p*, $^1J_{CF}$ = 258.2 Hz), 192.6 and 193.9 (two *s*, C=O). Anal. Calcd. for $C_{14}H_9FO_2$: C, 73.7; H, 4.0. Found: C, 73.4; H, 4.1.

General Procedure for Preparation of Phosphoranes. To a stirred solution of 2.5 mmol of the appropriate benzil in 2 ml of dichloromethane-d_2 at −78°C was added dropwise a solution of 0.33 g (2.5 mmol) of **9** in 0.5 ml of dichloromethane-d_2 over a five minute period. 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.

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