First Evidence for a Curtius-Type Rearrangement Involving a Pentacoordinated Atom

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Abstract: The photolytic behavior of four λ^5 phosphorus azides derivatives was investigated to study the scope and limitation of the Curtius rearrangement involving an azide group bonded to a pentacoordinated atom. Three different types of reaction were observed depending on the nature of the phosphorus substituents: (i) expected Curtius-type rearrangements which lead either to an exo- or endocyclic λ^4 phosphorus nitrogen double bonded compounds **5** or **16**, (ii) a tautomeric equilibrium between the cyclic phosphorane azide **2** and the corresponding opened acyl azide **12**, and (iii) a hydrogen abstraction reaction involving a transient phosphorane nitrene, **20**, which gives rise to an aminophosphorane, **19**. These new findings considerably increase the scope of the Curtius rearrangement.

In organic chemistry, the Curtius rearrangement is a well-known method for obtaining imines and isocyanates from the corresponding azides.[1] More recently, the photolysis of tricoordinated or tetracoordinated azides proved also to be a powerful route to various new dicoordinated or tricoordinated species containing a metal–nitrogen double bond: boro imines,[2] sila imines,[3] germa imines,[4] oxoimino-[5] or bis(iminophosphoranes),[6] and iminophosphenium salts[7] (Scheme I). Thus it may be concluded that the Curtius rearrangement is a general method allowing the coordination number of the atom bonded to the azido group to be decreased by one unit, keeping the number of valence bonds unchanged.

However, all the known examples involve reactions at tri- or tetracoordinate atoms, and, in order to determine the scope and limitation of the reaction, we have studied the photochemical behavior of azides in which the azide group is bonded to a pentacoordinate atom. We now report our results observed on the photolysis of azides of pentavalent, pentacoordinate phosphorus. Emphasis will be placed upon the role of the phosphorus substituents in the course of the reaction, as well as on the possible synthetic interest in the reactions.

Results and Discussion

Until now, only one azidophosphorane, **1** has been reported.[8] Derivatives **2–4** were synthesized in a similar way, using an exchange reaction involving the corresponding chlorophosphorane and azidotrimethylsilane (Scheme II).

Evolution of nitrogen was observed when **1** was irradiated at 254 nm in acetonitrile solution. According to the ^{31}P NMR spectrum, two new species containing pentacoordinate phosphorus ($\delta(^{31}P)$ −27.13, −34.78) were formed in equal amounts. Their structure were assigned to two diastereoisomers, *cis*- and *trans*-**6**.[9] The presence of a methyl substituent at nitrogen and the formation of a diazadiphosphetidine ring system strongly suggest the head to tail dimerization of a transient phosphorus species **5** with tetracoordinate phosphorus.[11] Apparently, **5** arises from a Curtius-type rearrangement involving the migration of a methyl group from phosphorus to nitrogen accompanied by elimination of N_2. This is the first example of such a rearrangement occurring at a pentacoordinate atom (Scheme III).

Additional interest in the Curtius rearrangement of λ^5P azides (λ^n refers to the coordination number n of phosphorus) is due to the possibility of ring expansion reactions leading to a λ^4P derivative possessing an intracyclic phosphorus–nitrogen double bond, a type of compound which is quite rare.[12] Therefore, a study

Scheme I. Previously Reported Rearrangements of the Curtis Type
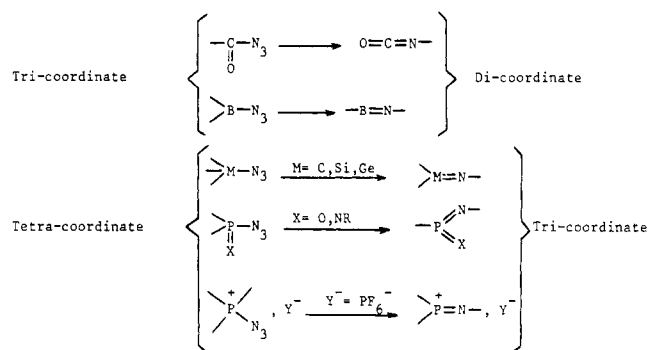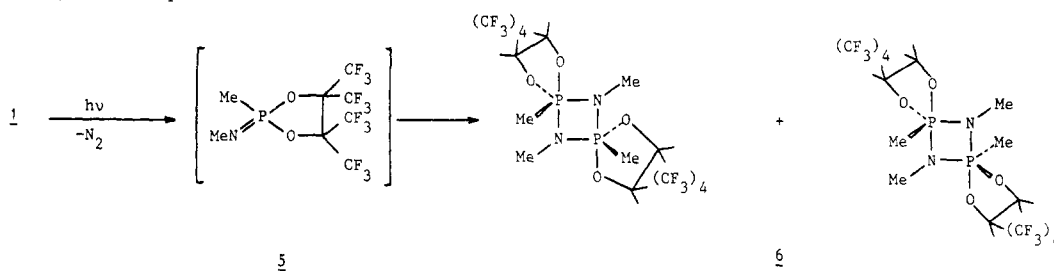

Scheme II. Synthesis of Phosphorane Azides 1-4

1- 4

1

2

3

4
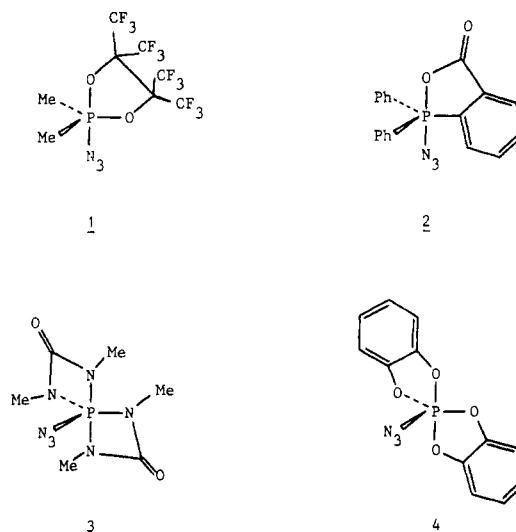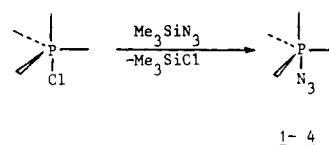
of the rearrangement of compound **2** was undertaken. Although the phosphorane azide **2** is stable enough to be characterized by
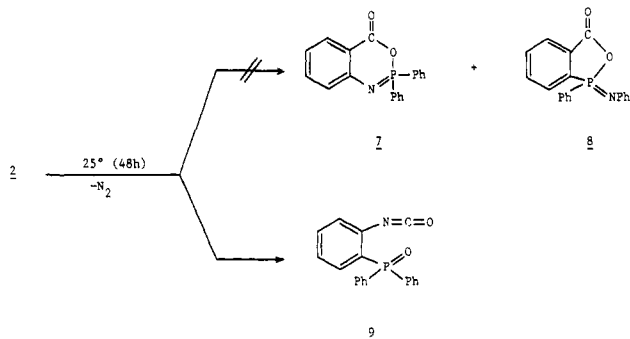

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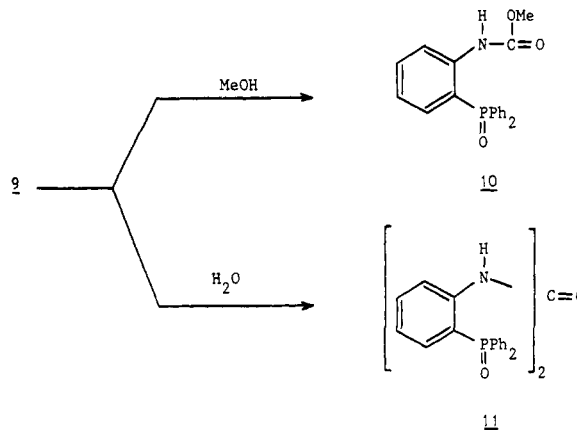
Scheme III. Photolysis of Phosphorane Azide 1

Scheme IV. Rearrangement of Phosphorane Azide 2

Scheme V. Methanolysis and Hydrolysis of Compound 9

IR and NMR spectroscopy, it decomposes completely within 48 h at room temperature. We did not obtain either the expected product **7** resulting from ring expansion or derivative **8**, which could be formed due to migration of a phenyl group from phosphorus to nitrogen. Instead, the isocyanate **9** was formed in 87% yield. Likewise, low-temperature (−50 °C) photolysis of **2** led to **9** (Scheme IV), which was characterized spectroscopically as well as chemically. Thus addition of methanol or water on the isocyanate **9** gave rise respectively to the carbamate **10** or the urea derivative **11**[13] (Scheme V).

In order to account for these unexpected findings we propose

an equilibrium between the phosphorane azide **2** and the corresponding acyclic tautomeric acyl azide **12**, followed by a "normal" Curtius rearrangement.[1] Some precedents of this type of tautomeric equilibrium have been reported for closely related systems.[14] Depending on the nature of the functional groups at phosphorus, either λ^5P or λ^4P is favored in the equilibrium. For example, only the tautomeric forms **13** and **14**[14a] are detected spectroscopically (Scheme VI). Although the ^{31}P chemical shift (−60 ppm) of **2** is in good agreement with a P^V structure and absorbances consistent with acyl azide **12** were *not observed* by IR monitoring of the reaction, it seems quite likely that the rearrangement **2** → **9** involves the tautomeric compound **12**.

In order to prevent such an equilibrium we studied the phosphorane azide **3** which is one of the first thermally stable derivatives in which λ^5P is bonded to five nitrogen atoms. Photolysis of **3** quantitatively furnished new spirocyclic phosphoranes **15**[9] in a 95/5 ratio ($\delta(^{31}P)$ −59.8 and −62.6) which were characterized by spectroscopy and by some of their chemical reactions (Scheme VII).

The formation of *N,N'*-dimethylurea (**17**) and of the semicarbazide **18** upon addition of methanol to **15** proved the presence of the four-and five-membered rings. The mass spectrum is in good agreement with the dimeric structure for **15** (e.g., *m/e* 434 (M⁺) and *m/e* 217 (M/2)).

Although we have not, as yet, been able to spectroscopically detect the phosphazene **16**, we can conclude that the desired ring-expansion reaction occurred. Interestingly, a similar Curtius rearrangement took place when **3** was heated overnight at 130 °C in toluene solution.

It was also of mechanistic interest to study compound **4**, which possesses four nonmigrating moieties. Indeed, the photolysis reaction led only to aminophosphorane **19**,[15] most probably resulting from a hydrogen abstraction reaction with the solvent (benzene) by a transient nitrene.[20] (Scheme VIII).

In conclusion, we have demonstrated that a Curtius-type rearrangement occurs with an azido group bonded to a penta-

(1) (a) Curtius, Th. *Ber.* **1890**, *23*, 3023. (b) Pataï, S. "The Chemistry of the Azido Group"; Wiley-Interscience: New York, 1971. (c) Lwowski, W. "Nitrenes"; Wiley-Interscience: New York, 1970.

(2) (a) Paetzold, P. I.; Grundke, H. *Synthesis* **1973**, 635. (b) Pieper, W; Schmitz, D.; Paetzold, P. *Chem. Ber.* **1981**, *114*, 3801.

(3) (a) Parker, D. R.; Sommer, L. H. *J. Am. Chem. Soc.* **1976**, *98*, 618. (b) Parker, D. R.; Sommer, L. H. *J. Organomet. Chem.* **1976**, *110*, C1. (c) Elsheikh, M.; Pearson, N. R.; Sommer, L. H. *J. Am. Chem. Soc.* **1979**, *101*, 2491. (d) Elsheikh, M.; Sommer, L. H. *J. Organomet. Chem.* **1980**, *186*, 301. (e) Baceiredo, A.; Bertrand, G.; Majoral, J. P.; Mazerolles, P. *Nouv. J. Chim.* **1983**, *7*, 645.

(4) (a) Reichle, W. T. *Inorg. Chem.* **1964**, *3*, 402. (b) Baceiredo, A.; Bertrand, G.; Mazerolles, P. *Tetrahedron Lett.* **1981**, *22*, 2553.

(5) (a) Bertrand, G.; Majoral, J. P.; Baceiredo, A. *Tetrahedron Lett.* **1980**, *21*, 5015. (b) Wiseman, J.; Westheimer, F. H. *J. Am. Chem. Soc.* **1974**, *96*, 4262. (c) Breslow, R.; Feiring, A.; Herman, F. *Ibid.* **1974**, *96*, 5937. (d) Harger, M. J. P.; Stephen, M. A. *J. Chem. Soc. Perkin Trans. 1* **1981**, 736. (e) Harger, M. J. P.; Westlake, S. *Tetrahedron* **1982**, *38*, 1511. (f) Harger, M. J. P.; Westlake, S. *Tetrahedron Lett.* **1982**, *23*, 3621.

(6) (a) Baceiredo, A.; Majoral, J. P.; Bertrand, G. *Nouv. J. Chim.* **1983**, *7*, 255. (b) Majoral, J. P.; Bertrand, G.; Baceiredo, A.; Mazerolles, P. *ACS Symp. Ser.* **1981**, *No. 171*, 123.

(7) Mulliez, M.; Majoral, J. P.; Bertrand, G. *J. Chem. Soc., Chem. Commun.* **1984**, 284.

(8) Volkholz, M.; Stelzer, O.; Schmutzler, R. *Chem. Ber.* **1978**, *111*, 890.

(9) Since strained four- and five-membered rings are found to assume a conformation spanning axial equatorial sites,[10] only the two diastereoisomers cis and trans can be formed.[11] However, we have not as yet been able to isolate one isomer from the other and consequently to attribute the NMR signals to each one.

(10) See, for example: (a) Sheldrick, W. S. *Top. Curr. Chem.* **1978**, *73*, 1. (b) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

(11) (a) Grapov, A. F.; Razvodovskaya, L. V.; Mel'nikov, N. N. *Usp. Khim.* **1981**, *50*, 606; *Russ. Chem. Rev. (Engl. Transl.)* **1981**, *50*, 324. (b) Day, R. O.; Holmes, R. R.; Tautz, H.; Weinmaier, J. H.; Schmidpeter, A. *Inorg. Chem.* **1981**, *20*, 1222.

(12) See, for example: Sheldrick, W. S.; Schomburg, D.; Schmidpeter, A.; von Criegern, T. *Chem. Ber.* **1980**, *113*, 55. Tautz, H.; Schmidpeter, A. *Ibid.* **1981**, *114*, 825. Marre, M. R.; Boisdon, M. T.; Sanchez, M. *Tetrahedron Lett.* **1982**, 853.

(13) Ozaki, S. *Chem. Rev.* **1972**, *72*, 457.

(14) (a) Granoth, I.; Alkabets, R.; Segall, Y. *J. Chem. Soc., Chem. Commun.* **1981**, 622. (b) Granoth, I.; Alkabets, R.; Shirin, E. *Ibid.* **1981**, 981. (c) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 4618. (d) Ramirez, F.; Nowakowski, M.; Marecek, J. F. *Ibid.* **1977**, *99*, 4515. (e) Livant, P.; Martin, J. C. *Ibid.* **1977**, *99*, 5761.

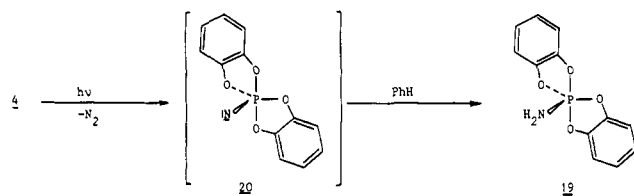(15) Gross, H.; Rieche, A.; Höft, E. *Chem. Ber.* **1961**, *94*, 544.

Scheme VI. Proposed Mechanism for the Rearrangement of **2**: Examples of Tautomeric Equilibria
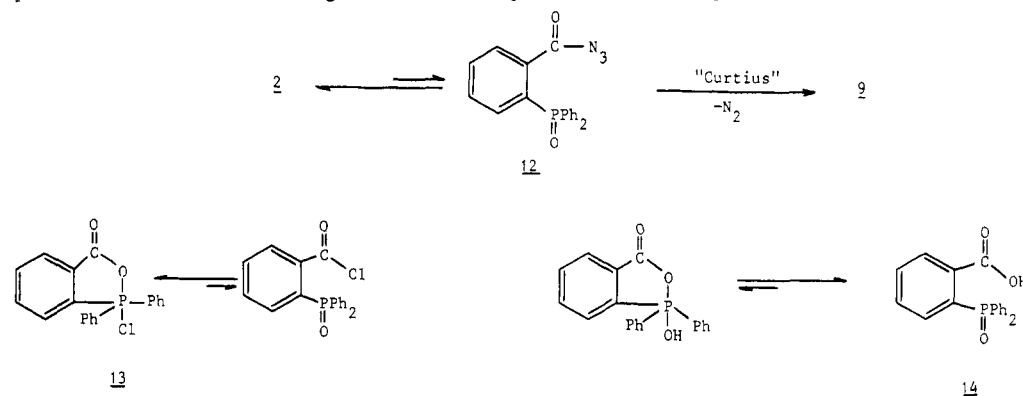
Scheme VII. Photolysis of Phosphorane Azide **3** and Chemical Characterization of
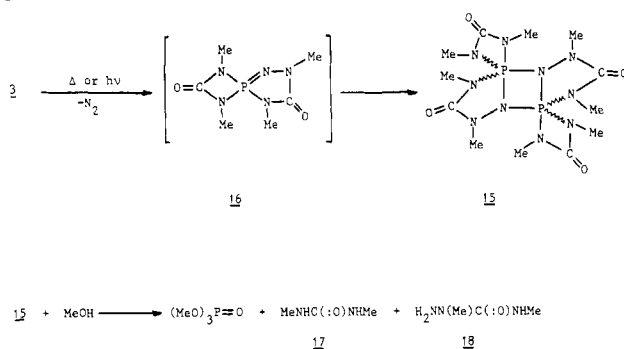
Scheme VIII. Photolysis of Phosphorane Azide **4**

coordinated atom and quite likely processes via preliminary formation of a transient phosphorane–nitrene. Extensions of this work to other metal atoms are under way.

Experimental Section

All experiments were performed in an atmosphere of dry argon or nitrogen. Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Varian T-60 or Brucker WM 250 spectrometer. ^{1}H chemical shifts are reported in ppm relative to Me$_4$Si as internal standard. ^{31}P NMR spectra were obtained on Perkin-Elmer R32 spectrometer at 36.4 MHz or Brucker WM 250 at 101.21 MHz. Downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H$_3$PO$_4$. ^{13}C NMR spectra were recorded on a Brucker WM 250 at 62.86 MHz. Infrared spectra were recorded on a Beckman IR 10 spectrometer, using polystyrene film for calibration. Mass spectra were obtained on a Ribermag R10-10E instrument.

Photochemical reactions were performed in quartz tubes, using a Rayonnet photochemical reactor.

Photolysis of Phosphorane Azide 1. Irradiation at 254 nm of a solution of **1**[8] (600 mg, 1.38 mmol) in 5 mL of acetonitrile for 18 h at room temperature produced white crystals which precipitated from the reaction mixture. After filtration and several rinses with dry acetonitrile, 505 mg (90%) of **6** (mp 75–85 °C) was obtained: ^{31}P NMR (CDCl$_3$), two singlets of equal intensity at −27.1 and −34.8 ppm; ^{1}H NMR (250 MHz, CDCl$_3$) 1.93 (d, *J*(HP) = 17 Hz, CH$_3$P), 1.97 (d, *J*(PH) = 17.6 Hz, CH$_3$P), 2.76 (t, *J*(HP) = 14.67 Hz, CH$_3$N), 2.78 (t, *J*(HP) = 14.09 Hz, CH$_3$N); IR(KBr) 1250 and 1215 (CF$_3$), 1120 (P–O–C), 960 (P–N) cm^{-1}; mass spectrum, *m/e* 814 (M$^+$), 407 (M/2, 100%). Attempted separation of the two diastereoisomers was unsuccessful.

Synthesis of the Phosphorane Azide 2. Trimethylsilyl azide (1 g, 9 mmol) was added to a solution of acyloxychlorophosphorane **13**[14a] (2.04 g, 6 mmol) in 30 mL of benzene. The solution was stirred for 1 h at room temperature. The solvent, trimethylchlorosilane, and excess silyl azide

were then removed at reduced pressure (15 mm). The crude phosphorane azide **2** was obtained as white crystals (2 g): mp 40 °C dec; ^{31}P NMR (C$_6$H$_6$) −60 ppm (s); ^{1}H NMR (C$_6$D$_6$, 60 MHz) 7.7–9.1 ppm [m, H-(aromatic)]; IR (C$_6$H$_6$) 2150 (P–N$_3$), 1710 (C=O), 1450 (P–Ph), 1130 (C–O–P) cm^{-1}.

Decomposition of Phosphorane Azide 2 and Characterization of Isocyanate 9. Crude azidophosphorane **2** (2 g) was completely decomposed in acetonitrile solution at room temperature, in 2 days, when evolution of nitrogen stopped. The solution was cooled to −25 °C to give 1.6 g (87%) of isocyanate **9** which precipitated as white crystals: mp 90 °C dec; ^{31}P NMR (CH$_3$CN) +28 ppm (s); IR (KBr) 2320 and 2300 (—N=C=O), 1440 (P–Ph), 1295 (P=O) cm^{-1}; mass spectrum, *m/e* 319 (M$^+$), 291 (M − CO).

9 (1.06 g, 3.3 mmol) in acetonitrile (20 mL) was stirred at room temperature in the presence of a large excess of methanol for 3 h. Evaporation of the solvent furnished **10** (1.15 g, quantitative) as white crystals: mp 144–145 °C; ^{31}P NMR (CDCl$_3$) +36.4 ppm (s); ^{1}H NMR (CDCl$_3$) 3.8 (s, 3 H, OCH$_3$), 6.8–8.6 [m, 14 H, H(aromatic)], 10.5 (s, 1 H, NH); IR (KBr) 1740 (C=O), 1240 (P=O) cm^{-1}. Anal. (C$_{20}$H$_{18}$NO$_3$P) C, H, N.

When the same experimental conditions and the same quantity of **9** are used, treatment with excess water furnished **11** (1.01 g, quantitative) as white crystals: mp 240–242 °C; ^{31}P NMR (CH$_3$CN) +35 (s); IR (KBr) 1730 (C=O), 1440 (P–Ph), 1265 (P=O) cm^{-1}; mass spectrum (CI), 613 (M + 1), 320 (M − C$_{18}$H$_{15}$NOP).

Synthesis of Phosphorane Azide 3. Trimethylsilyl azide (160 mg, 1.4 mmol) was added dropwise to a solution of 1,3,5,7-tetramethyl-1,3,5,7-tetraaza-4-chloro-4λ^5-phosphaspiro[3.3]heptane-2,6-dione[16] (238 mg, 1 mmol) in 10 mL of benzene. The solution was stirred at room temperature for 2 h. Benzene and the silylated compounds were removed under reduced pressure (15 mm). Crude **3** was obtained as white crystals (208 mg, 85%): mp 100–104 °C; ^{31}P NMR (C$_6$H$_6$) −66.8 ppm (br s); ^{1}H NMR (C$_6$D$_6$) 2.5 (d, *J*(HP) = 14 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$) 27.29 (s, CH$_3$), 155.98 (d, *J*(CP) = 9.25 Hz, CO); IR (KBr) 2170 (P–N$_3$), 1770 (C=O), 930 (P–N) cm^{-1}.

Rearrangement of Phosphorane Azide (3). Irradiation of a solution of **3** (123 mg, 0.5 mmol) in acetonitrile (2 mL) at 254 nm for 18 h at −20 °C produced white crystals which precipitated from the solution. After filtration and repeated rinsing with acetonitrile, 82 mg of **15** was obtained (75% yield): ^{31}P NMR (CDCl$_3$), two singlets at −59.8 and −62.6 ppm in a 95/5 ratio; ^{1}H NMR (CDCl$_3$) 2.5–3.2 (m, NCH$_3$); ^{13}C NMR {^{1}H} (CDCl$_3$) 25.89, 29.54, 30.44, and 38.89 (s, CH$_3$), 155.62 [t-like, *J*(CP) = 14.65 Hz, CO (four-membered ring)], 160.27 [t-like, *J*(CP) = 14.65 Hz, CO (five-membered ring)] for the major isomer and 25.58, 29.98, 31.52, and 39.20 (s, CH$_3$) for the minor isomer; the CO signals were not detected; IR (CDCl$_3$) 1770 and 1710 (C=O), 950 and 890 (P–N) cm^{-1}. The mixture of diastereoisomers melted in the range 275–278 °C; mass spectrum, *m/e* 434 (M$^+$), 217 (M/2, 100%), 118 [P(NCH$_3$)$_2$CO]. Attempted separation of the two diastereoisomers was unsuccessful.

A solution of **3** (123 mg, 0.5 mmol) in toluene (8 mL) was heated in a sealed tube at 130 °C for 16 h. After evaporation of the solvent, the residue was dissolved in hot acetonitrile. The solution was cooled to −30 °C, causing precipitation of **15** (57 mg, 52%) as white crystals. The ^{31}P NMR spectrum showed the presence of the two isomers (95/5).

(16) (a) Hormuth, P. B. Ph.D. Thesis, University of Heidelberg, 1968. (Latscha, H. P. private communication to R. S., 1970.) (b) Latscha, H. P.; Hormuth, P. B.; Vollmer, H. *Z. Naturforsch., B* **1969**, *24B*, 1237. (c) Dunmur, R. E. Ph.D. Thesis, University of Technology, Loughborough Leics., England, 1970.

Chemical Characterization of the Dimer 15. A solution of **15** in toluene was stirred under reflux for 2 days in the presence of a large excess of methanol. Trimethyl phosphate was identified by ¹H, ¹³C, and ³¹P NMR spectroscopy and by comparison of the spectroscopic data to those of an authentic sample. *N,N′*-Dimethylurea **17** and semicarbazide **18** were isolated by TLC (CHCl₃/EtOH 50/50, and CHCl₃/MeOH 66/33, respectively) and their spectra (¹H NMR, IR) compared with those of authentic samples.

Synthesis of Phosphorane Azide 4. Trimethylsilyl azide (1 g, 9 mmol) was added dropwise to a solution of 2-chloro-2,2′-spirobi[1,3,2-benzo-dioxaphosphole]¹⁵ in 40 mL of benzene. The solution was stirred for 2 h at room temperature. Volatile materials were removed at reduced pressure (15 mmHg). Crude **4** was obtained as highly deliquescent white crystals (1.09 g, 95%); ³¹P NMR (C₆H₆) –27 ppm (s); ¹H NMR (C₆D₆) 6.9 [m, H (aromatic)]; IR (C₆D₆) 2140 (P–N₃), 1490 (P–O–C) cm⁻¹.

Photolysis of 4. A solution of **4** (289 mg, 1 mmol) in benzene (4 mL) was irradiated at 254 nm for 48 h. Removal of the solvent furnished the aminophosphorane **19** as white crystals (255 mg, 96%), mp 94–95 °C; ³¹P NMR (C₆D₆) –27.1 ppm (s); ¹H NMR (C₆D₆) 3.0 (br d, *J*(HP) = 15 Hz, 2 H, NH₂); 6.9 [m, 8 H, H(aromatic)]; IR (C₆D₆) 3520 and 3405 cm⁻¹ (NH₂). Characterization of **19** was confirmed by comparison of its ³¹P and IR data to those of an authentic sample prepared as indicated below.

Preparation of 2-Amino-2,2′-spirobi[1,3,2-benzodioxa-λ⁵-phosphole] (19). Ammonia was bubbled into a solution of 1.1 g (3.9 mmol) of

2-chloro-2,2′-spirobi[1,3,2-benzodioxa-λ⁵-phosphole] in 20 mL of dichloroethane during 30 min at 0 °C. The course of the reaction was monitored by ³¹P NMR spectroscopy. The precipitate of ammonium chloride was filtered off, and the solvent was stripped off. A viscous residue remained which was washed with 10-mL portions of ether several times. The aminophosphorane **19** was finally obtained as a white powder (0.93 g, 90%). Anal. C, H, N, P. The spectroscopic properties of **19** obtained by this procedure were identical with those of the product formed in the photolysis of **4**.

Registry No. 1, 66436-22-4; **2**, 89982-26-3; **3**, 89982-28-5; **4**, 72434-50-5; *cis*-**6**, 92269-73-3; *trans*-**6**, 92344-04-2; **9**, 89982-27-4; **10**, 92269-74-4; **11**, 92269-75-5; **13**, 79184-77-3; **15** (isomer 1), 92269-76-6; **15** (isomer 2), 92344-05-3; **19**, 89982-30-9; Me₃SiN₃, 4648-54-8; 1,3,5,7-tetramethyl-1,3,5,7-tetraaza-4-chloro-4λ⁵-phosphaspiro[3.3]heptane-2,6-dione, 77507-70-1; 2-chloro-2,2′-spirobi[1,3,2-benzodioxaphosphole], 6857-81-4.

One-Bond ¹³C–¹³C NMR Coupling Constants in Substituted Acetophenones and Benzaldehydes and Their O-Protonated Carboxonium Ions[1]

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Abstract: One-bond ¹³C–¹³C NMR coupling constants in a series of substituted acetophenones and benzaldehydes and their O-protonated carboxonium ions were measured by natural-abundance ¹³C NMR spectroscopy, using the INADEQUATE pulse sequence. These studies are of particular interest in regard to the effect of substituents on the nature of the electron-deficient carbonyl group. The measured $J_{C_{ipso}-C_{carbonyl}}$ values seemingly reflect the increased double bond character of the $C_{ipso}-C_{carbonyl}$ bond, and the substituent effects on these coupling constant values were analyzed in terms of inductive, resonance, and electronegativity effect of the substituent. We observed good linearity in the substituent effects on $J_{C_{ipso}-C_{carbonyl}}$ values within the acetophenone–benzaldehyde series as well as in their O-protonated carboxonium ions, indicating similarities of the closely related systems.

The coupling interaction between ¹³C nuclei have not yet been extensively examined because of experimental difficulties. The 1.1% natural abundances of ¹³C means that the probability for two ¹³C nuclei to be neighbors is very low (10⁻⁴). Initial efforts were made in different laboratories notably by Frei and Bernstein[3] to obtain the necessary data using doubly labeled materials.[2–4] The limited number of examples of one-bond ¹³C–¹³C coupling constants of each of the six combinations of hybridized carbons (sp³–sp³, sp³–sp², sp³–sp, sp²–sp², sp²–sp, and sp–sp) led to the conclusion that J_{CC} values are approximately correlated to the % s character of the orbitals making up the bond. The major limitation of these studies was the difficulty in obtaining a wider variety of doubly labeled compounds.

Theoretical descriptions of coupling between nuclear spins are based on Ramsey's theory[5] that coupling via electrons originates from three types of interaction between the magnetic moments due to the nuclear and electron spins. The three types are as follows: (a) orbital interaction with the magnetic field due to the orbital motion of electrons, (b) dipolar interaction with the electron spin, and (c) Fermi contact interaction with the electron spin. While these three contributions may vary in sign as well as in magnitude, calculations indicate that coupling between the majority of first-row elements is dominated by the Fermi contact[6–12] and, as a result, would be expected to correlate with the product

(1) Presented at the ACS National Meeting held at Seattle, March 1983, Organic Division, Abstract No. 198. Considered Stable Carbocations, Part 253. For part 252, see: Olah, G. A.; Prakash, G. K. S.; Krishnamurthy, V. V. *J. Org. Chem.* **1983**, *48*, 5116.
(2) Graham, D. M.; Holloway, C. E. *Can. J. Chem.* **1963**, *41*, 2114.
(3) Frei, K.; Bernstein, H. J. *J. Chem. Phys.* **1963**, *38*, 1216.
(4) Lynden-Bell, R. M.; Sheppard, N. A. *Proc. R. Soc. London, Ser. A* **1962**, *269*, 385.

(5) Ramsey, N. F. *Phys. Rev.* **1953**, *91*. 303.
(6) Blizzard, A. C.; Santry, D. P. *J. Chem. Phys.* **1971**, *55*, 1950.
(7) Towl, A. D. C.; Schaumberg, K. *Mol. Phys.* **1971**, *22*, 49.
(8) Schulman, J. M.; Newton, M. D. *J. Am. Chem. Soc.* **1974**, *96*, 6295.
(9) Wasylishen, R. E. "Annual Reports in NMR Spectroscopy", Webb, G. A., Ed.; Academic Press: London, 1977; Vol. 7, p 245.
(10) Axenrod, T.; Webb, G. A., Eds. "NMR Spectroscopy of Nuclei Other Than Protons"; Wiley-Interscience: New York, 1974; Chapters 6, 8, and 13.
(11) Pachler, K. G. R.; Chalmers, A. A. "Specialist Periodical Reports: Nuclear Magnetic Resonance", Abraham, R. J. Ed.; Chemical Society: London, 1979, Chapter 3.
(12) Egli, H.; Phillipsborn, W.U. *Tetrahedron Lett.* **1979**, 4265.