

of VII (1.05 g) in dry ether (60 ml) under argon. After 3 hr at room temperature, the mixture was boiled under reflux for 0.5 hr and extracted with water, and the ethereal layer was distilled, giving X (1.12 g) as a colorless oil; bp 136° (0.4 mm);  $n_D^{25}$  1.5745.

*Anal.* Calcd for  $C_{17}H_{20}BN$ : C, 81.95; H, 8.09; B, 4.34; N, 5.62; mol wt, 249. Found: C, 81.86; H, 7.95; B, 4.12; N, 5.80; mol wt (mass spectrum), 249.

The infrared spectrum showed bands at 3060, 3040, 2980, 2855 (CH), 1600 (C—C), and 1500 K (B—N). The ultraviolet spectrum showed end absorption below 275 nm. The nmr spectrum ( $CDCl_3$ ) showed a broad aromatic multiplet at  $\delta$  7.3, a sharp singlet at 4.3 ( $PhCH_2$ ), and broad multiplets at 3.6, 2.9, and 1.7 (aliphatic protons in the tetrahydroborazarene ring).

**1-Benzyl-2-phenylborazarene (IIIg).** A. From II. Sodium hydride (0.18 g, 55% emulsion in heavy oil) was added to a stirred solution of II (0.15 g) in dry tetrahydrofuran under argon. After 1 hr at room temperature, the mixture was heated to 65° for 0.5 hr, benzyl bromide (0.3 ml) was then added, and the mixture was allowed to cool to room temperature. Ethereal phenylmagnesium bromide (1 ml of 3 M) was then added, mixture heated to 60° for 0.5 hr, cooled, and treated with water, and the organic layer dried and evaporated. Chromatography of the residue from pentane on neutral alumina gave a crystalline solid (200 mg) which after repeated sublimation at 28° (0.4 mm) had mp 58–60°, but resolidified on standing. The nmr spectrum showed aromatic peaks at  $\delta$  7.2–7.7 and a sharp singlet at 2.95. The mass spectrum showed strong peaks at  $m/e$  154 (IIIb — H) and 91 ( $PhCH_2$ ). The infrared spectrum (KBr disks) showed peaks at 1435, 1480, 1600, 1625, 1645, 2930, and 3030–3060 K. The ultraviolet spectrum in

hexane showed a peak at 244 nm ( $\log \epsilon$  4.39). The molecular weight (Rast) was 291.

**B. From X.** An intimate mixture of X (0.5 g) and 10% palladized charcoal (0.5 g) was heated in a stream of argon in a sublimator to 210–220° for 6 hr. Extraction with methylene chloride and chromatography from pentane on alumina gave IIIg which after sublimation at room temperature had mp 58–61.5°, mmp 58–60.5°; the ultraviolet, infrared, and nmr spectra were identical with those of the material described above. The alumina column was then eluted with hexane–methylene chloride (3:1), giving IIIb which, after sublimation at 80° (0.5 mm), had mp 115–115.5° (lit.<sup>8</sup> mp 117–118.5°). The infrared spectrum was identical with that reported by White.<sup>8</sup> The nmr spectrum ( $CDCl_3$ ) contains a triplet at  $\delta$  6.3 ( $J = 6$  Hz), signals at 7.06, 7.15, and 7.19, three unresolved peaks at 7.32–7.38, and a broad structureless line at 8.1 (NH).

**1-Benzyl-2-methoxytetrahydroborazarene (VIII).** Addition of VII (1.45 g) to dry methanol (5 ml) led to an exothermic reaction with evolution of hydrogen. Distillation gave VIII (1.42 g) as an oil; bp 99° (0.5 mm);  $n_D^{25}$  1.5188.

*Anal.* Calcd for  $C_{12}H_{18}BNO$ : C, 70.97; H, 8.93; N, 5.32; mol wt, 203. Found: C, 70.92; H, 8.90; B, 5.16; mol wt (mass spectrum), 203.

**1-Benzyl-2-hydroxytetrahydroborazarene (IX).** Aerial oxidation of VII gave IX as a colorless crystalline solid which after recrystallization from hexene had mp 107.5–109°.

*Anal.* Calcd for  $C_{11}H_{16}BNO$ : B, 5.72; N, 7.41; mol wt, 189. Found: B, 6.02; N, 7.85; mol wt (mass spectrum), 189, (Rast) 185.

## Difluorodiazirine. VII. N-Cyanophosphorus Imides and Difluorophosphoranes

Ronald A. Mitsch

Contribution No. 380 from the Central Research Laboratories,  
Minnesota Mining and Manufacturing Company, Saint Paul, Minnesota 55119.  
Received May 10, 1967

**Abstract:** Difluorodiazirine reacts with trivalent organophosphorus derivatives to form N-cyanophosphorus imides and difluorophosphoranes. The generality of the reaction has been demonstrated with phosphines, phosphites, thiophosphites, and aminophosphines. The mechanism of the reaction is discussed in terms of primary nucleophilic attack of the phosphorus on a nitrogen atom in  $CF_2N_2$ . The N-cyanophosphorus imides undergo reaction with  $HN_3$  to form N-(5-tetrazoyl)phosphorus imides. The stereochemistry of the difluorophosphoranes is examined by  $F^{19}$  nmr spectroscopy.

A limited number of recent publications have described the unique ability of trivalent phosphorus derivatives to effect low-temperature defluorination of fluorine bonded to carbon. In the systems in which this rather unusual defluorination has been observed, removal of fluorine from carbon occurs at the position  $\alpha$  to a carbonyl<sup>1</sup> or a di- or polysulfide<sup>2</sup> moiety with formation of a phosphorus–fluorine bond. In large part, the chemistry of difluorodiazirine,  $CF_2N_2$ , which has appeared in the literature has been that of difluorocarbene generated by photolysis or pyrolysis of this fluorocarbon heterocycle.<sup>3</sup> As a part of our

continuing exploratory investigation into the reactions of fluorodiazirines, we would like to report an unprecedented diazirine ring-opening defluorination reaction which is effected by trivalent organophosphorus derivatives. It is appropriate to note that bis(trifluoromethyl)diazirine does not react with triphenylphosphine even under forcing conditions.<sup>4</sup>

### Results and Discussion

Difluorodiazirine reacts, in many cases at temperatures below  $-78^\circ$ , with trivalent organophosphorus compounds to give N-cyanophosphorus imides,  $R_3P=NC\equiv N$ , and difluorophosphoranes,  $R_3PF_2$ . In this reaction the phosphorus compound is apparently reacting primarily as a reducing agent yielding the difluorophosphorane as the major by-product. Thus,

(4) D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, **88**, 3617 (1966).

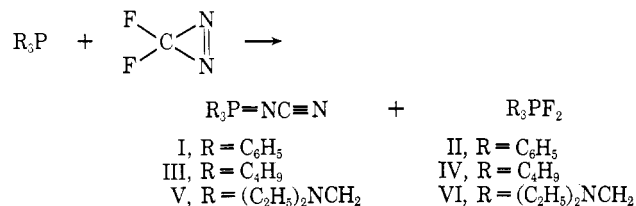
(1) (a) F. Ramirez, C. P. Smith, A. S. Gulati, and A. V. Palwardhan, *Tetrahedron Letters*, 2151 (1966); (b) F. Ramirez, C. P. Smith, and S. Meyerson, *ibid.*, 3651 (1966); (c) V. Mark, *ibid.*, 3139 (1964).

(2) W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Org. Chem.*, **30**, 1375 (1965).

(3) (a) R. A. Mitsch and J. E. Robertson, *J. Heterocyclic Chem.*, **2**, 152 (1965), and references cited therein; (b) R. A. Mitsch, *ibid.*, **3**, 245 (1966).

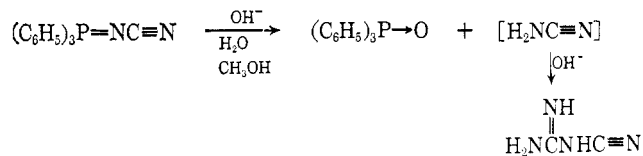
the stoichiometry of the reaction requires 2 moles of organophosphorus compound per mole of difluorodiazirine. The generality of the reaction has been demonstrated with phosphines, phosphites, thiophosphites, phosphorus triamides, and mixed systems. In some cases the rapidity of the reaction permitted the utilization of a flow system in which  $\text{CF}_2\text{N}_2$  was bubbled through a solution of the organophosphorus compound in methylene chloride. The identities of the N-cyanophosphorus imides have been established by chemical, elemental, and spectroscopic means as well as independent synthesis. In the infrared spectra, the N-cyanophosphorus imides exhibit characteristic absorptions at 4.46–4.62  $\mu$  assigned to the cyano group and 7.70–7.87  $\mu$  due to the  $\text{>P=N-}$  moiety. As a class, the N-cyanophosphorus imides exhibit quite unexpected hydrolytic stability.

**Phosphines.** The reaction of  $\text{CF}_2\text{N}_2$  with phosphines was observed to proceed quite readily below room temperature. Although the reactions were generally stirred overnight or longer, certain solvent systems, as well as infrared spectral examination of the volatiles, permitted the observation that the reaction was usually complete before the mixture had warmed to room temperature.



The reaction of triphenylphosphine, in a wide variety of solvents, was found to occur below room temperature. In benzene, a 69.5% yield of N-cyanotriphenylphosphinimide (I), mp 194–196°, precipitated, as colorless needles, from the reaction mixture upon warm-up. At the time this work was in progress, the chemical literature did not contain an example of an N-cyanophosphorus imide. Thus, the structure of I was established by elemental and spectral analysis, hydrolysis studies, and more recently by independent synthesis.

Hydrolysis of N-cyanotriphenylphosphinimide (I) with dilute sodium hydroxide in refluxing methanol proceeds as shown below and represents good evidence



for the N-cyanoimide structure as written. The isolated yields of triphenylphosphine oxide and cyanoguanidine from the hydrolysis of I were 83 and 74%, respectively.

It is interesting to note that although N-alkylphosphinimides are reported to be quite susceptible to hydrolysis (some hydrolyze on exposure to moist air), apparently the resonance stabilization of the imide (I) by the cyano group imparts considerable hydrolytic stability. Samples of I, dissolved in acetic acid, have been heated on a steam bath and recovered unchanged by reprecipitation with water. N-Cyanotriphenylphosphinimide was also recovered essentially unchanged after heating at 40°, for 15 min, with vigorous stirring in 10% NaOH in a mixture of water and methanol.

A recent publication, describing the synthesis and some of the chemistry of cyanogen azide, reported the reaction of  $\text{N}_3\text{CN}$  with triphenylphosphine to form N-cyanotriphenylphosphinimide, mp 193–195°. We have confirmed the synthesis of  $(\text{C}_6\text{H}_5)_3\text{P=NC}\equiv\text{N}$  via the  $\text{N}_3\text{CN}$  technique and have found that the product is spectroscopically identical with I. The characteristic infrared absorptions for the  $\text{—C}\equiv\text{N}$  and  $\text{>P=N—}$  groups in I appear at 4.60 and 7.87  $\mu$ , respectively.

The identity of triphenyldifluorophosphorane (II), obtained after recrystallization from benzene, was established by infrared and  $\text{F}^{19}$  nmr spectral (Table I) comparisons to reported values.<sup>6,7</sup> Hydrolysis of II yields triphenylphosphine oxide.

Table I.  $\text{F}^{19}$  Nmr Data for Difluorophosphoranes

Compound	Position, $\phi^*$	$J_{\text{P-F}}$ , cps
$(\text{C}_6\text{H}_5)_3\text{PF}_2$ (II)	39.8 <sup>a</sup>	664
$(\text{C}_4\text{H}_9)_3\text{PF}_2$ (IV)	34.2 <sup>b</sup>	588
$[(\text{C}_2\text{H}_5)_2\text{NCH}_2]_3\text{PF}_2$ (VI)	51.0	688
$(\text{CH}_3\text{O})_3\text{PF}_2$ (VIII)	72.8 <sup>c</sup>	706
$(\text{C}_6\text{H}_5\text{O})_3\text{PF}_2$ (X)	73.0	721
$(\text{C}_4\text{H}_9\text{S})_3\text{PF}_2$ (XII)	72.3	713
$[(\text{CH}_3)_2\text{N}]_3\text{PF}_2$ (XIV)	53.5 <sup>d</sup>	707
$[(\text{CH}_3)_2\text{N}]_2\text{PF}_2\text{OCH}_3$ (XVI)	55.5	715

<sup>a</sup> Lit.<sup>6</sup>  $\phi^*37.5$  (–39 ppm from  $\text{CF}_3\text{CO}_2\text{H}$ ) and  $J_{\text{PF}} = 695$  cps; lit.<sup>7</sup>  $\phi^*37.3$  (–39.2 ppm from  $\text{CF}_3\text{CO}_2\text{H}$ ) and  $J_{\text{PF}} = 667$  cps.

<sup>b</sup> Lit.<sup>6</sup>  $\phi^*32.5$  (–44 ppm from  $\text{CF}_3\text{CO}_2\text{H}$ ) and  $J_{\text{PF}} = 585$  cps.

<sup>c</sup>  $\text{H}^1$  nmr absorption is a double ( $J_{\text{HP}} = 15.2$  cps) triplet ( $J_{\text{HF}} = 1.0$  cps) centered at  $\tau$  6.35. <sup>d</sup>  $\text{H}^1$  nmr absorption is a double ( $J_{\text{HP}} = 10.6$  cps) triplet ( $J_{\text{HF}} = 2.8$  cps) at  $\tau$  7.37. Lit.<sup>1b</sup>  $\phi^*51.4$  (–25.1 ppm from  $\text{CF}_3\text{CO}_2\text{H}$ ) and  $J_{\text{PF}} = 700$  cps and a  $\text{H}^1$  nmr absorption appearing as a doublet ( $J_{\text{HP}} = 10.5$  cps) triplet ( $J_{\text{HF}} = 2.8$  cps) at  $\tau$  7.40.

The reactions of the other two phosphines studied, tri-*n*-butylphosphine and tris(diethylaminomethyl)phosphine, were both conveniently carried out in methylene chloride solvent at room temperature. The work-up procedures, on the other hand, were quite dissimilar.

Vacuum distillation of the crude mixture from the tri-*n*-butylphosphine–difluorodiazirine reaction afforded a 74% yield of tri-*n*-butyldifluorophosphorane (IV). It was found, however, that attempted distillation of difluorophosphoranes boiling higher than IV was generally not a satisfactory technique for initial purification. In accordance with previously reported studies, IV is quite satisfactorily stored and manipulated in glass equipment without special protection from moisture.<sup>8</sup>

N-Cyanotri-*n*-butylphosphinimide (III) was quite readily purified by column chromatography on neutral alumina. Elution with chloroform removed any residual  $(\text{C}_4\text{H}_9)_3\text{P}$  and  $(\text{C}_4\text{H}_9)_3\text{PF}_2$  with the solvent front. The N-cyanophosphorus imide III is a colorless oil exhibiting infrared absorptions at 4.62 and 7.83  $\mu$  due to the  $\text{—C}\equiv\text{N}$  and  $\text{>P=N—}$  groups, respectively.

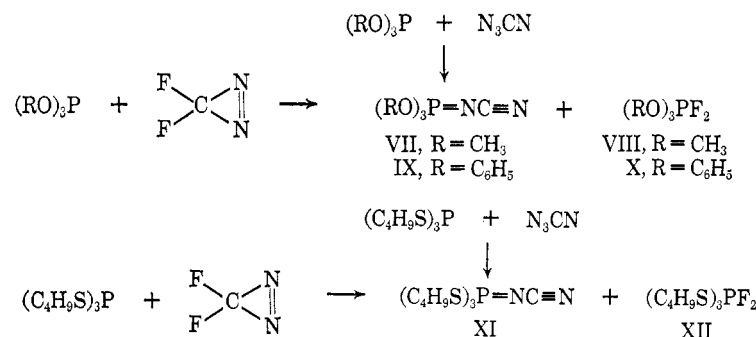
N-Cyanotris(diethylaminomethyl)phosphinimide (V), on the other hand, is a colorless solid which could not be separated effectively from the difluorophosphorane

(5) F. O. Marsh and M. E. Hermes, *J. Am. Chem. Soc.*, **86**, 4506 (1964).

(6) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

(7) W. C. Firth, S. Frank, M. Garber, and V. P. Wystrach, *ibid.*, **4**, 765 (1965).

(8) R. Schmutzler, *ibid.*, **3**, 421 (1964).



by-product (VI) by column chromatography. However, the ability of warm heptane (60°) to differentiate between V and VI according to solubilities permitted the utilization of a simple extraction and recrystallization technique to afford a 60% yield of pure N-cyanotris(diethylaminomethyl)phosphinimide melting at 90–92°. The characteristic infrared absorptions appear at 4.62 ( $-\text{C}\equiv\text{N}$ ) and 7.71–7.85 ( $>\text{P}=\text{N}-$ )  $\mu$ . Tris(diethylaminomethyl)phosphine was the most reactive of the phosphines studied. High yields of V were also obtained by bubbling undiluted  $\text{CF}_2\text{N}_2$  through a solution of the phosphine in  $\text{CH}_2\text{Cl}_2$  at room temperature. The bubbles of  $\text{CF}_2\text{N}_2$  disappeared before reaching the surface of the solution.

**Phosphites and Thiophosphites.** The two phosphites studied in the work showed widely differing reactivities with difluorodiazirine. Consequently, both the  $\text{CF}_2\text{N}_2$  and  $\text{N}_3\text{CN}$  techniques were employed in order to obtain sufficient amounts of products for complete identification and further chemical reactions.

The reaction of difluorodiazirine with trimethyl phosphite to form the desired  $(\text{CH}_3\text{O})_3\text{P}=\text{NC}\equiv\text{N}$  (VII) and  $(\text{CH}_3\text{O})_3\text{PF}_2$  (VIII) is extremely exothermic. Explosions occurred in two cases in which the reaction mixture was allowed to warm rapidly to room temperature. Increasing the amount of solvent and running the reaction at Dry Ice temperature were necessary to maintain adequate control. Vacuum fractionation of the crude mixture, after solvent removal, was suitable for the separation of unreacted  $(\text{CH}_3\text{O})_3\text{P}$  and  $(\text{CH}_3\text{O})_3\text{PF}_2$  (VIII) from the higher boiling VII. A second technique which was also useful for the removal of  $(\text{CH}_3\text{O})_3\text{P}$  and VIII was to wash the methylene chloride reaction mixture with water. Trimethyl phosphite and trimethyl phosphate (the hydrolysis product of VIII) are both water soluble. Vacuum distillation of the residue remaining after fractionation of water wash afforded a relatively low yield of O,O,O-trimethyl N-cyanophosphoroimide (VII) boiling at 69° (0.16 mm) and exhibiting infrared absorptions at 4.46 ( $-\text{C}\equiv\text{N}$ ) and 7.73 ( $>\text{P}=\text{N}-$ )  $\mu$ . It should be noted that the relatively low yield of VII isolated pure is due primarily to the fact that the distillation is accompanied by a large amount of resin formation. The infrared spectrum of the crude product (ca. 66% yield), after removal of  $(\text{CH}_3\text{O})_3\text{P}$  and VIII, is essentially the same as that of the purified product.

A spectroscopically identical product was obtained in a 24% yield from the reaction of trimethyl phosphite with cyanogen azide.

In contrast to the rapid reaction with  $(\text{CH}_3\text{O})_3\text{P}$ , the reaction of triphenyl phosphite with difluorodiazirine is quite slow, proceeding to only about 60%

completion in 1 week at room temperature. Increasing the  $\text{CF}_2\text{N}_2$ :phosphite ratio or the reaction temperature or changing solvents did not improve the yields markedly.

Removal of the solvent, followed by filtration, gave a small amount of triphenoxydifluorophosphorane (X) as a colorless solid which was used to obtain the  $\text{F}^{19}$  nmr spectral data reported in Table I. It should be noted that difluorophosphoranes represented by the formulas  $(\text{RO})_3\text{PF}_2$  or  $(\text{RS})_3\text{PF}_2$  have not been reported previously.

Column chromatography of the above filtrate, followed by recrystallization from *n*-butyl acetate, afforded a 38% yield (based on reacted  $\text{CF}_2\text{N}_2$ ) of colorless crystals of O,O,O-triphenyl N-cyanophosphoroimide (IX). Pure IX melts at 92.5–93.5° and shows the cyano absorption as a doublet at 4.51 and 4.59  $\mu$  in its infrared spectrum. Compound IX was prepared more conveniently and in a more readily purified form from triphenyl phosphite and cyanogen azide.

As in the case of phosphites, both the difluorodiazirine and cyanogen azide techniques were used with tributyl trithiophosphite. The reaction of  $(\text{C}_4\text{H}_9\text{S})_3\text{P}$  with  $\text{CF}_2\text{N}_2$  followed the expected course, yielding  $(\text{C}_4\text{H}_9\text{S})_3\text{P}=\text{NC}\equiv\text{N}$  and  $(\text{C}_4\text{H}_9\text{S})_3\text{PF}_2$ . The difluorophosphorane (XII) could be distilled readily from the crude reaction mixture and was identified by infrared and  $\text{F}^{19}$  nmr spectral means. However, at the distillation temperatures necessary to remove XII, the N-cyanophosphorus imide (XI) underwent considerable decomposition. Recourse to repeated column chromatography on fractions separated from the crude reaction mixture was not very satisfactory but did permit the isolation of a 40% yield of pure XI.

A more readily separable mixture and better yields of XI were obtained from  $(\text{C}_4\text{H}_9\text{S})_3\text{P}$  and  $\text{N}_3\text{CN}$ . A 63% yield of pure  $(\text{C}_4\text{H}_9\text{S})_3\text{P}=\text{NC}\equiv\text{N}$ , spectroscopically identical with that obtained from  $\text{CF}_2\text{N}_2$ , was isolated as a nearly colorless oil, after column chromatography on silica gel. The infrared spectrum of XI shows absorptions at 4.57 and 7.87  $\mu$ .

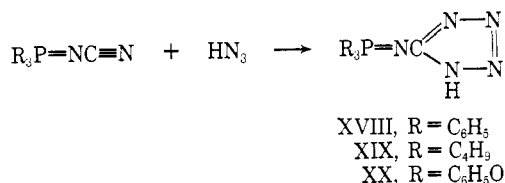
Trilauryl trithiophosphite also reacted quite readily with difluorodiazirine; however, purification of this mixture was not attempted.

**Aminophosphines.** Unequivocally, the most reactive trivalent phosphorus compound studied in this investigation was the highly nucleophilic  $[(\text{CH}_3)_2\text{N}]_3\text{P}$ . When  $\text{CF}_2\text{N}_2$  was allowed to react with a methylene chloride solution of  $[(\text{CH}_3)_2\text{N}]_3\text{P}$  at  $-78^\circ$ , the heat of reaction caused the methylene chloride to reflux. The reaction was obviously complete in less than 2 min.

Vacuum-line fractional distillation–condensation of the crude reaction mixture was used to isolate a 75%



in the formation of the N-(5-tetrazoyl)phosphorus imides in 40–70% yields. The tetrazoles XVIII, XIX, and XX are colorless solids which precipitate from the benzene–diethyl ether solvent system during the reaction. They generally melt with decomposition above 160° and were identified by elemental and spectral analyses.



In contrast to the N-cyanophosphorus imide forming reaction discussed above, the cycloaddition of HN<sub>3</sub> to the cyano moiety appears to be facilitated by electron-withdrawing substituents on the phosphorus atom. Stirring at room temperature resulted in good yields of the tetrazoles when the phosphorus substituents are alkyl or aryl groups, whereas heating at steam bath temperature was necessary in the case of phenoxy substituents. The reaction of (CH<sub>3</sub>O)<sub>3</sub>P=NC≡N with HN<sub>3</sub> did not result in the isolation of any of the desired tetrazole derivative.

**Stereochemistry of Difluorophosphoranes.** As an interesting side light to the preparation of the N-cyanophosphorus imides described herein, the stereochemistry of the difluorophosphorane by-products II, IV, VI, VIII, X, XII, XIV, and XVI was examined by F<sup>19</sup> nmr spectroscopy. Previous investigations in the field have shown that phosphorus (V) fluorides of the formula R<sub>3</sub>PF<sub>2</sub> have spectroscopically equivalent sets of fluorine atoms and equivalent sets of R groups. Thus, the nmr spectra of these compounds can be interpreted in terms of the trigonal bipyramid model, XXI, with both



fluorine atoms in the axial positions. The axial phosphorus–fluorine splitting is generally about 500–700 cps.<sup>6,7</sup> On the other hand, R<sub>2</sub>PF<sub>3</sub> derivatives have two distinct fluorine atom environments and exist in the trigonal bipyramid geometry shown by XXII. The axial phosphorus–fluorine coupling constants are less than the equatorial (the ratio being about 0.8 to 0.95) and the axial resonance is downfield relative to the equatorial P–F absorption.<sup>6,10</sup>

In agreement with previous investigations, the positions and phosphorus–fluorine coupling constants (Table I) suggest that all of the difluorophosphoranes prepared in this work, II, IV, VI, VIII, X, XII, XIV, and XVI, can best be represented by the trigonal bipyramid model, XXI, with both fluorine atoms in the axial positions.

(10) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, **3**, 1298 (1964); J. F. Nixon and R. Schmutzler, *Spectrochim. Acta*, **20**, 1835 (1964); R. Schmutzler, *Angew. Chem.*, **76**, 893 (1964); R. Schmutzler, *Angew. Chem. Intern. Ed. Engl.*, **3**, 753 (1964); R. Schmutzler and G. S. Reddy, *Inorg. Chem.*, **4**, 191 (1965); R. Schmutzler, *J. Chem. Soc.*, 5630 (1965).

## Experimental Section

**General.** Most of the trivalent phosphorus compounds which were used in this investigation were available commercially and were used as received. The sources were as follows: triphenylphosphine (Eastman Organic Chemicals), tri-*n*-butylphosphine (K and K Laboratories), tris(diethylaminomethyl)phosphine (Aldrich Chemical Co.), trimethyl phosphite (Matheson Coleman and Bell), triphenyl phosphite (Eastman Organic Chemicals), and trilauryl trithiophosphite (Hooker Chemical Corp.). Tri-*n*-butyl trithiophosphite was obtained from Virginia-Caroline Chemical Corp. (sold as "Merphos") and was distilled before use, bp 124° (0.08 mm) (lit.<sup>11</sup> 174–180° (15 mm)).

*Anal.* Calcd for C<sub>12</sub>H<sub>27</sub>PS<sub>3</sub>: C, 48.3; H, 9.1. Found: C, 48.2; H, 9.2.

Tris(dimethylamino)phosphine (hexamethylphosphorus triamide) was prepared in 68% yield, bp 164° (740 mm), from phosphorus trichloride and dimethylamine according to the method of Burg and Slota.<sup>12</sup> Bis(dimethylamino)phosphorus chloride, [(CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>P-Cl, used in the preparation of [(CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>POCH<sub>3</sub>, was prepared in 90% yield, bp 63–64° (9 mm) (lit.<sup>13</sup> 29° (1 mm)), from hexamethylphosphorus triamide and phosphorus trichloride according to Nöth and Vetter.<sup>13</sup> Bis(dimethylamino)methoxyphosphine was prepared by the addition of an ethereal solution of 9.27 g (6 × 10<sup>-2</sup> mole) of [(CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>P-Cl to a stirred, cooled solution of 1.92 g (6 × 10<sup>-2</sup> mole) of methanol and 6.06 g (6 × 10<sup>-2</sup> mole) of triethylamine in 50 ml of dry ether. Filtration of the amine salt followed by distillation afforded 5.48 g (61%) of [(CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>POCH<sub>3</sub> as a colorless liquid boiling at 53–54° (24 mm), *n*<sub>D</sub><sup>20</sup> 1.4474.

*Anal.* Calcd for C<sub>6</sub>H<sub>18</sub>N<sub>2</sub>PO: C, 40.0; H, 10.1. Found: C, 39.8; H, 10.2.

Infrared spectra were obtained on a Perkin-Elmer Model 21 double-beam instrument using NaCl windows. Fluorine nuclear magnetic resonance spectra were measured with a Varian V-4300-2 instrument operating at 40.0 mc; utilizing an internal standard of CFCl<sub>3</sub> for the determination of chemical shifts. The values are reported in  $\phi^*$  values<sup>14</sup> at dilutions of about 20–30%. Trifluoroacetic acid is  $\phi^*$  76.5 on this scale. Proton magnetic resonance spectra were obtained with a Varian A-60 nmr spectrometer. Chemical shifts are given in  $\tau$  units<sup>15</sup> relative to tetramethylsilane. Molecular weights were determined by the method of Neumayer.<sup>16</sup>

**N-Cyanotriphenylphosphinimide (I).** A 7.86-g (3 × 10<sup>-2</sup> mole) sample of triphenylphosphine, followed by 25 ml of benzene, was placed in a 50-ml glass reactor fitted with a Teflon needle valve and containing a magnetic stirring bar. The solution was cooled to liquid nitrogen temperature and degassed, and 1.17 g (1.5 × 10<sup>-2</sup> mole) of difluorodiazirine was added by condensation. The mixture was allowed to warm to room temperature and stirred for 24 hr. The resulting colorless solid was filtered and recrystallized twice from benzene to afford 3.146 g (69.5%) of colorless needles, mp 194–196° (lit.<sup>5</sup> 193–195°).

*Anal.* Calcd for C<sub>18</sub>H<sub>15</sub>N<sub>2</sub>P: C, 75.5; H, 4.97; N, 9.3; P, 10.3; mol wt, 302. Found: C, 75.7; H, 5.0; N, 9.7; P, 10.2; mol wt, 308.

Evaporation of the filtrate of the reaction mixture and repeated recrystallization from benzene afforded a 45% yield of difluorotriphenylphosphorane (II). The infrared spectrum was identical with that which has been reported.<sup>7</sup> The F<sup>19</sup> nmr is recorded in Table I.

In a separate experiment in which isobutylene (0.1 mole) was used as a solvent, a 91.3% yield of I was obtained from 1.31 g (5 × 10<sup>-3</sup> mole) of triphenylphosphine and 0.39 g (5 × 10<sup>-3</sup> mole) of difluorodiazirine after removal of the solvent and trituration with benzene. The benzene extract afforded an 82% yield of II after recrystallization.

In another experiment, 1.31 g (5 × 10<sup>-3</sup> mole) of triphenylphosphine was treated with 0.39 g (5 × 10<sup>-3</sup> mole) of difluorodiazirine in 0.5 ml of benzene and 10 ml of methanol. The colorless solid which precipitated during 3 hr of stirring at room temperature was filtered, dried, and identified as difluorotriphenylphosphorane (0.649 g, 86.5%). The filtrate was dried, trituated with benzene,

(11) A. Lippert and E. M. Reid, *J. Am. Chem. Soc.*, **60**, 2370 (1938).

(12) A. B. Burg and P. J. Slota, Jr., *ibid.*, **80**, 1107 (1958).

(13) H. Nöth and J. Vetter, *Chem. Ber.*, **94**, 1505 (1961).

(14) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

(15) G. V. D. Tiers, *ibid.*, **62**, 1151 (1958).

(16) J. J. Neumayer, *Anal. Chim. Acta*, **20**, 519 (1959).

and filtered. The yield of pure N-cyanotriphenylphosphinimide (I) was 0.664 g (88.0%).

A spectroscopically identical sample of I was also obtained from the reaction of triphenylphosphine with cyanogen azide.

**Hydrolysis of N-Cyanotriphenylphosphinimide (I).** A 0.290-g ( $9.6 \times 10^{-4}$  mole) sample of N-cyanotriphenylphosphinimide (I) was dissolved in a mixture of 7 ml of methanol and 2 ml of 10% aqueous sodium hydroxide. The solution was heated at refluxing methanol temperature for 15 min and then evaporated to dryness under vacuum. The resulting colorless solid was extracted with 15 ml of hot benzene in three portions. The benzene extract was evaporated to dryness to afford 0.222 g (83.2%) of a colorless solid, identified as triphenylphosphine oxide by infrared spectroscopy.

The solid, benzene-insoluble residue was dissolved in water, neutralized with dilute HCl, and evaporated to dryness. Infrared examination of the resulting colorless solid identified cyanoguanidine as the major organic component. Extraction with 13 ml of hot anhydrous ethanol in three portions and evaporation of the extract afforded 0.030 g (74.3%) of a slightly tan solid identified as cyanoguanidine by comparison of its infrared spectrum to that of an authentic sample.

**N-Cyanotri-*n*-butylphosphinimide (III).** Following the procedure for the preparation of I, 7.75 g ( $3.84 \times 10^{-2}$  mole) of tri-*n*-butylphosphine dissolved in 25 ml of methylene chloride was allowed to react with 1.5 g ( $1.92 \times 10^{-2}$  mole) of difluorodiazirine for 2 days at room temperature with stirring. Infrared examination of the volatiles at the end of this time showed that all of the  $\text{CF}_2\text{N}_2$  had reacted. Distillation through a short-path apparatus afforded 3.581 g (74.1%) of tri-*n*-butyldifluorophosphorane (IV) boiling at  $63^\circ$  (0.155 mm),  $n_D^{25}$  1.4332 (lit.<sup>6</sup> bp  $71\text{--}72^\circ$  (0.4 mm),  $n_D^{25}$  1.4320). The  $\text{F}^{19}$  nmr spectrum of IV is recorded in Table I.

The brown distillation residue was purified by column chromatography on a neutral alumina column using chloroform as the eluent to give 3.39 g (70%) of pure III as a colorless oil,  $n_D^{25}$  1.4813.

*Anal.* Calcd for  $\text{C}_{13}\text{H}_{27}\text{PN}_2$ : C, 64.5; H, 11.2; N, 11.6; mol wt, 242. Found: C, 64.2; H, 11.2; N, 11.4; mol wt, 234.

**N-Cyanotris(diethylaminomethyl)phosphinimide (V).** A 11.56-g ( $4.0 \times 10^{-2}$  mole) sample of tris(diethylaminomethyl)phosphine, followed by 40 ml of  $\text{CH}_2\text{Cl}_2$ , was placed in a 75-ml reactor containing a magnetic stirring bar. The solution was cooled to liquid nitrogen temperature and degassed, and 2.0 g ( $2.56 \times 10^{-2}$  mole) of difluorodiazirine was added by condensation. The mixture was allowed to warm slowly to  $-78^\circ$  and then stirred at that temperature for 24 hr. There was little, if any, unreacted  $\text{CF}_2\text{N}_2$ . The solvent was removed by vacuum distillation to give 13.76 g of a semisolid product. Two extractions with heptane at  $60^\circ$ , followed by cooling the extract to initiate crystallization, resulted in the collection of 3.97 g (60.4% yield) of a colorless solid, mp  $90\text{--}92^\circ$ , identified as N-cyanotris(diethylaminomethyl)phosphinimide (V).

*Anal.* Calcd for  $\text{C}_{16}\text{H}_{36}\text{N}_5\text{P}$ : C, 58.4; H, 10.9; N, 21.3; mol wt, 329. Found: C, 57.2; H, 10.9; N, 21.4; mol wt, 320.

The residue from the extraction was dissolved in a mixture of  $\text{CH}_2\text{Cl}_2$  and  $\text{CFCl}_3$  for nmr measurements. The results are shown in Table I.

**O,O,O-Trimethyl N-Cyanophosphorimidate (VII) from  $\text{CF}_2\text{N}_2$ .** A mixture of 5.124 g ( $4.13 \times 10^{-2}$  mole) of redistilled trimethyl phosphite and 20 ml of methylene chloride was added to a 75-ml glass reactor containing a magnetic stirring bar. After degassing at  $-196^\circ$ , 2.0 g ( $2.56 \times 10^{-2}$  mole) of difluorodiazirine was added by condensation. The mixture was warmed slowly to room temperature and stirred for 3 days. Removal of the solvent and unreacted  $(\text{CH}_3\text{O})_3\text{P}$  under partial vacuum, followed by fractional distillation on a vacuum system through  $-35$  and  $-196^\circ$  receivers afforded 1.038 g (25.0%) of difluorotrimethoxyphosphorane (VIII), containing 20–50% of dimethyl phosphorofluoridate ( $\text{F}^{19}$  nmr spectrum;  $\delta^*$  86.1,  $J_{\text{PF}}$  = 972 cps). An alternate procedure to remove VIII involves washing the methylene chloride solution with four 10-ml portions of water.

The 4.49-g (66%) residue from the above fractionation (identified as nearly pure VII by infrared spectroscopy) was distilled through a short-path apparatus. The fraction boiling at  $69^\circ$  (0.160 mm) (20%) was identified as O,O,O-trimethyl N-cyanophosphorimidate (VII) by infrared and elemental analyses.

*Anal.* Calcd for  $\text{C}_3\text{H}_9\text{N}_2\text{O}_3\text{P}$ : C, 29.3; H, 5.5; mol wt, 164. Found: C, 28.8; H, 5.6; mol wt, 164.

A considerable amount of viscous residue remained in the distillation flask. This material did not exhibit the characteristic cyano absorption in the infrared.

**O,O,O-Trimethyl N-Cyanophosphorimidate (VII) from Cyanogen Azide.** To a solution of 6.8 g (0.1 mole) of cyanogen azide, pre-

pared in 50 ml of anhydrous acetonitrile from 10.5 g (0.1 mole) of cyanogen bromide and 6.5 g (0.1 mole) of sodium azide, was added dropwise 12.4 g (0.1 mole) of trimethyl phosphite dissolved in 50 ml of benzene. After the addition was complete, the mixture was allowed to stir at room temperature for an additional 2 hr and filtered. Removal of the solvent, followed by distillation, afforded 3.97 g (24.2%) of pure trimethyl N-cyanophosphorimidate (VII), bp  $80\text{--}83^\circ$  (0.5 mm), which was spectroscopically identical with VII prepared from  $(\text{CH}_3\text{O})_3\text{P}$  and  $\text{CF}_2\text{N}_2$ .

**O,O,O-Triphenyl N-Cyanophosphorimidate (IX) from Difluorodiazirine.** A 7.91-g ( $2.55 \times 10^{-2}$  mole) sample of triphenyl phosphite and 10 ml of benzene were added to a 75-ml glass reactor containing a magnetic stirring bar. After degassing at  $-196^\circ$ , 1.0 g ( $1.28 \times 10^{-2}$  mole) of difluorodiazirine was added by condensation. The mixture was allowed to warm to room temperature and stir for 1 week. At the end of this time, fractional distillation–condensation through  $-78$  and  $-196^\circ$  receivers was employed to recover  $5.17 \times 10^{-3}$  mole (40.5%) of unreacted  $\text{CF}_2\text{N}_2$ . The yellow colored residue was extracted with three 10-ml portions of pentane. Evaporation of the pentane extract gave 3.48 g (44%) of unreacted triphenyl phosphite identified by infrared spectral comparisons.

The residue from the pentane extraction (4.80 g, 53.8%) was purified by column chromatography on a silica gel column using chloroform and ethyl acetate as eluents. Recrystallization of the waxy solid obtained from chromatography from butyl acetate gave 0.8 g (38% based on reacted  $\text{CF}_2\text{N}_2$ ) of pure IX, mp  $92.5\text{--}93.5^\circ$ .

*Anal.* Calcd for  $\text{C}_{19}\text{H}_{15}\text{N}_2\text{O}_3\text{P}$ : C, 65.2; H, 4.3; N, 8.0; mol wt, 350. Found: C, 65.2; H, 4.5; N, 8.0; mol wt, 345.

**O,O,O-Triphenyl N-Cyanophosphorimidate (IX) from Cyanogen Azide.** The cyanogen azide technique outlined for VII with redistilled cyanogen bromide and employing 1.36 g ( $2 \times 10^{-2}$  mole) of cyanogen azide and 6.82 g ( $2.2 \times 10^{-2}$  mole) of triphenyl phosphite afforded 3.56 g (50%) of IX after column chromatography. Analytically pure IX (22% yield) was obtained after washing the solid with 5 ml of butyl acetate and recrystallization.

**S,S,S-Tributyl N-Cyanotrithiophosphorimidate (XI) from Difluorodiazirine.** Using the procedure outlined above for I, 11.92 g ( $4.0 \times 10^{-2}$  mole) of tributyl trithiophosphite dissolved in 40 ml of methylene chloride was allowed to react with 2.0 g ( $2.56 \times 10^{-2}$  mole) of difluorodiazirine. Removal of the solvent after 5 days stirring afforded 13.58 g of crude product which was identified as a mixture of  $(\text{BuS})_3\text{P}$ ,  $(\text{BuS})_3\text{P}=\text{NCN}$ , and  $(\text{BuS})_3\text{PF}_2$  by infrared spectroscopy.

Distillation could be used to remove the unreacted  $(\text{BuS})_3\text{P}$  and  $(\text{BuS})_3\text{PF}_2$ , bp  $123^\circ$  (0.05 mm),  $n_D^{25}$  1.5232. Infrared and  $\text{F}^{19}$  nmr were utilized to identify the  $(\text{BuS})_3\text{PF}_2$  by-product (see Table I). Under the distillation conditions, however, the desired N-cyanophosphorimidate (XI) underwent considerable decomposition.

On the other hand, repeated column chromatography of the crude reaction mixture on silica gel using chloroform and ethyl acetate as eluents, afforded a 40% yield of pure S,S,S-tributyl N-cyanotrithiophosphorimidate (XI) as a nearly colorless oil.

*Anal.* Calcd for  $\text{C}_{13}\text{H}_{27}\text{N}_2\text{PS}_3$ : C, 46.2. Found: C, 46.6.

**S,S,S-Tributyl N-Cyanotrithiophosphorimidate (XI) from Cyanogen Azide.** To a solution of 2.72 g ( $4.0 \times 10^{-2}$  mole) of cyanogen azide, prepared in 20 ml of anhydrous acetonitrile from 4.2 g ( $4 \times 10^{-2}$  mole) of cyanogen bromide and 2.6 g ( $4 \times 10^{-2}$  mole) of sodium azide, was added dropwise 11.92 g ( $4.0 \times 10^{-2}$  mole) of tributyl trithiophosphite dissolved in 10 ml of benzene. After the addition was complete, the mixture was stirred at room temperature for an additional 2 hr, followed by filtration. Evaporation of the filtrate afforded 12.69 g of impure XI.

Purification was accomplished by column chromatography on silica gel ( $\text{CHCl}_3\text{--EtOAc}$ ) and resulted in a recovery of 63.8% of the theoretical of purified  $(\text{BuS})_3\text{P}=\text{NCN}$  which was spectroscopically identical with that described above.

**N-Cyanotris(dimethylamino)phosphinimide (XIII).** According to the procedure outlined for I, 6.52 g ( $4.0 \times 10^{-2}$  mole) of tris(dimethylamino)phosphine in 25 ml of methylene chloride was treated with 2.0 g ( $2.56 \times 10^{-2}$  mole) of difluorodiazirine at  $-78^\circ$  with stirring. The low temperature is extremely important in this reaction due to the high reactivity of the tris(dimethylamino)phosphine. After removal of the solvent,  $[(\text{CH}_3)_2\text{N}]_3\text{PF}_2$  was distilled from the crude product mixture by fractionation under vacuum through  $-40$  and  $-196^\circ$  receivers. The  $-40^\circ$  receiver contained a 75% yield of essentially pure tris(dimethylamino)difluorophosphorane (XIV) which was identified by infrared,  $\text{F}^{19}$ , and  $\text{H}^1$  nmr spectroscopy (Table I) and independent synthesis.

Column chromatography of the residue after distillation employing chloroform, ethyl acetate, and methanol as eluents on silica gel gave about 5 g of a light yellow-brown semisolid which crystallized overnight under vacuum. This material was extracted with diethyl ether in a Soxhlet extractor. The resultant colorless solid recrystallized from di-*n*-butyl ether (100:1 ratio of ether to solid heated to 60°) to afford 2.1 g (52%) of colorless needles (some as long as 1.5–2 in.) of pure N-cyanotris(dimethylamino)phosphinimide (XIII), mp 77.8–79°.

*Anal.* Calcd for  $C_7H_{18}N_5P$ : C, 41.4; H, 8.9; N, 34.5. Found: C, 41.5; H, 8.8; N, 34.0.

**Tris(dimethylamino)difluorophosphorane (XIV).** The difluorophosphorane (XIV) was prepared by the procedure described by Firth and co-workers<sup>7</sup> for the preparation of difluorotriphenylphosphorane. A 0.489-g ( $3 \times 10^{-3}$  mole) sample of  $[(CH_3)_2N]_3P$  and 20 ml of diethyl ether were placed in a 50-ml glass reactor fitted with a Teflon needle valve and a magnetic stirring bar. The reactor was cooled to  $-196^\circ$  and degassed and 0.416 g ( $4 \times 10^{-3}$  mole) of  $N_2F_4$  was added by condensation. The mixture was warmed very slowly to room temperature and stirred overnight. After removal of the solvent and excess  $N_2F_4$  under partial vacuum, the residue was fractionally distilled to give 0.37 g (61.4%) of tris(dimethylamino)difluorophosphorane (XIV). This material was spectroscopically identical with that obtained from the  $CF_3N_2-[(CH_3)_2N]_3P$  reaction described above.

**N-Cyanobis(dimethylamino)methoxyphosphinimide (XV).** Using the procedure outlined for XIII, 5.05 g ( $3.36 \times 10^{-2}$  mole) of  $[(CH_3)_2N]_3POCH_3$  and 2.0 g ( $2.56 \times 10^{-2}$  mole) of difluorodiazirine in 25 ml of methylene chloride were allowed to react, with stirring, at  $-78^\circ$ . The reactor was warmed to room temperature; methylene chloride was removed under partial vacuum. Fractional distillation–condensation through  $-40$  and  $-196^\circ$  traps was used to remove the difluorophosphorane by-product (XVI). Distillation of the contents of the  $-40^\circ$  trap gave 1.5 g (47.5%) of pure difluorobis(dimethylamino)methoxyphosphorane (XVI), bp  $39-40^\circ$  (4 mm),  $n_D^{20}$  1.4069, which was identified by infrared and nmr spectroscopy (Table I).

The residue from the solvent removal and fractionation was dissolved in chloroform, washed with 5% HCl, dried, and purified by column chromatography on silica gel, using chloroform and methanol as eluents. Evaporation of the solvents afforded a 61.5% yield of N-cyanobis(dimethylamino)methoxyphosphinimide (XV) as a colorless, viscous liquid,  $n_D^{20}$  1.4797.

*Anal.* Calcd for  $C_6H_{11}N_4OP$ : C, 37.9; H, 7.9; N, 29.5. Found: C, 38.0; H, 7.9; N, 29.2.

**Triphenyl-N-(5-tetrazoyl)phosphinimide (XVIII).** To 1.193 g ( $3.95 \times 10^{-3}$  mole) of N-cyanotriphenylphosphinimide (I) in 12 ml of  $CH_2Cl_2$  was added 11 ml of a 0.545 *N*  $HN_3$  solution ( $6.0 \times 10^{-3}$  mole) in diethyl ether. The mixture was stirred overnight and filtered and the colorless solid was recrystallized from methanol. The yield of XVIII was 0.702 g (51.5%) melting with decomposition at  $225-226^\circ$ . Unreacted N-cyanimide was also recovered.

*Anal.* Calcd for  $C_{19}H_{16}N_5P$ : C, 66.1; H, 4.7; N, 20.3; mol wt, 345. Found: C, 66.0; H, 4.9; N, 20.1; mol wt, 347.

**Tributyl-N-(5-tetrazoyl)phosphinimide (XIX).** To a 1.21-g ( $5.0 \times 10^{-3}$  mole) sample of N-cyanotributylphosphinimide (III) dissolved in 12 ml of benzene was added 11 ml of a 0.545 *N* solution of  $HN_3$  ( $6.0 \times 10^{-3}$  mole) in diethyl ether. The mixture was stirred overnight at room temperature during which a colorless solid precipitated. Filtration (two crops) and recrystallization from ethyl acetate afforded 0.915 g (64.2%) of colorless needles of XIX melting with decomposition at  $169-170^\circ$ .

*Anal.* Calcd for  $C_{15}H_{28}N_5P$ : C, 54.7; H, 9.9; N, 24.5; mol wt, 285. Found: C, 54.9; H, 9.9; N, 24.2; mol wt, 300.

**O,O,O-Triphenyl N-(5-Tetrazoyl)phosphorimidate (XX).** To 0.35 g ( $1.0 \times 10^{-3}$  mole) of triphenyl N-cyanophosphorimidate (IX), dissolved in 5 ml of benzene, was added 2 ml of a 0.545 *N*  $HN_3$  solution ( $1.09 \times 10^{-3}$  mole) in diethyl ether. The reactor was sealed and heated on a steam bath for 18 hr. The colorless precipitate was removed by filtration and recrystallized from ethyl acetate. A 37% yield of the desired tetrazoyl derivative, melting at  $162-163^\circ$ , was obtained.

*Anal.* Calcd for  $C_{18}H_{16}N_5O_3P$ : C, 58.0; H, 4.1; N, 17.8; mol wt, 393. Found: C, 57.7; H, 4.4; N, 17.6; mol wt, 391.

**Acknowledgments.** The author is deeply indebted to Mr. Albert H. Stoskopf, without whose assistance and helpful experimental innovations this work would not have been completed. The author also wishes to express his appreciation to Mr. D. L. Wood for technical assistance, Dr. J. J. McBrady for infrared and nuclear magnetic resonance measurements and interpretation, Mr. P. B. Olson for analytical determinations, and Mr. J. J. Neumayer for molecular weight determinations.

## Pivaloylnitrene

G. Thomas Tissue,<sup>1</sup> Siegfried Linke, and Walter Lwowski<sup>2</sup>

*Contribution from the Chemistry Department and the Research Center, New Mexico State University, Las Cruces, New Mexico, and the Department of Chemistry, Yale University, New Haven, Connecticut. Received June 12, 1967*

**Abstract:** The photolysis of pivaloyl azide gives pivaloylnitrene and *t*-butyl isocyanate. The nitrene behaves similar to carbethoxynitrene; it adds to C=C double bonds, inserts into C–H bonds selectively, and dissociates. With cyclohexene, the yield of nitrene products is 46%, based on azide.

Nitrenes are often invoked as short-lived intermediates in the decomposition of azides, but in many cases it has been difficult to prove that the reaction in question is not one of the undecomposed azide, followed by loss of nitrogen.<sup>3–7</sup> Convincing proof for

nitrene intermediates in reactions of decomposing azides has been furnished by creating the same species from a precursor other than the azide. To this end, an  $\alpha$ -elimination route was developed for carbalkoxynitrenes<sup>8,9</sup> and the deoxygenation of aromatic nitro and nitroso compounds served in the case of arylni-

(1) National Institutes of Health Predoctoral Fellow, 1962–1965.

(2) To whom correspondence should be addressed: Chemistry Department, New Mexico State University, Las Cruces, N. M. 88001.

(3) For a review see R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

(4) P. Walker and W. A. Waters, *J. Chem. Soc.*, 1632 (1962).

(5) P. A. S. Smith and J. H. Hall, *J. Am. Chem. Soc.*, **84**, 480 (1962).

(6) M. F. Sloan, W. B. Renfrow, and D. S. Breslow, *Tetrahedron*

*Letters*, 2905 (1964); D. S. Breslow, T. J. Prosser, A. F. Marcantonio, and C. A. Genge, *J. Am. Chem. Soc.*, **89**, 2384 (1967).

(7) W. Lwowski and T. W. Mattingly, Jr., *ibid.*, **87**, 1947 (1965); *Tetrahedron Letters*, 277 (1962).

(8) W. Lwowski, T. Maricich, and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **85**, 1200 (1963).

(9) W. Lwowski and T. J. Maricich, *ibid.*, **87**, 3630 (1965).