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); $n^{25}\text{D}$ 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 δ 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 resinified on standing. The nmr spectrum showed aromatic peaks at δ 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 ϵ 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.[8] mp 117–118.5°). The infrared spectrum was identical with that reported by White.[8] The nmr spectrum ($CDCl_3$) contains a triplet at δ 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); $n^{25}\text{D}$ 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

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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 α to a carbonyl[1] or a di- or polysulfide[2] 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.[3] 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.[4]

Results and Discussion

Difluorodiazirine reacts, in many cases at temperatures below −78°, 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,

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(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).

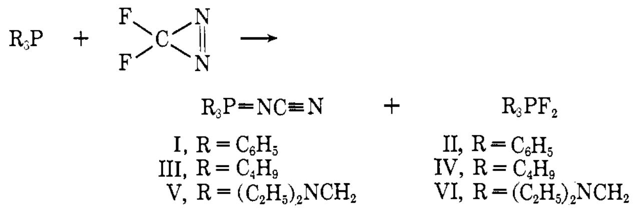
(2) W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Org. Chem.*, 30, 1375 (1965).

(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).

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

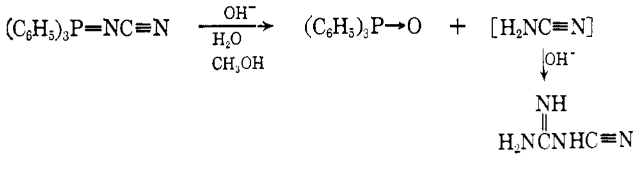
the stoichiometry of the reaction requires 2 moles of organophosphorus compound per mole of difluorodiazirine. The generality of the reaction has been demonstrated with phosphines, phosphites, thiophosphites, phosphorus triamides, and mixed systems. In some cases the rapidity of the reaction permitted the utilization of a flow system in which CF_2N_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 μ assigned to the cyano group and 7.70–7.87 μ due to the $>P{=}N—$ moiety. As a class, the N-cyanophosphorus imides exhibit quite unexpected hydrolytic stability.

Phosphines. The reaction of CF_2N_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



$$(C_6H_5)_3P{=}NC{\equiv}N \xrightarrow[CH_3OH]{\overset{OH^-}{H_2O}} (C_6H_5)_3P{\rightarrow}O + [H_2NC{\equiv}N] \xrightarrow{OH^-} H_2N\overset{NH}{\overset{\|}{C}}NHC{\equiv}N$$

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 N_3CN with triphenylphosphine to form N-cyanotriphenylphosphinimide, mp 193–195°.[5] We have confirmed the synthesis of $(C_6H_5)_3P{=}NC{\equiv}N$ *via* the N_3CN technique and have found that the product is spectroscopically identical with I. The characteristic infrared absorptions for the $—C{\equiv}N$ and $>P{=}N—$ groups in I appear at 4.60 and 7.87 μ, respectively.

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

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

Compound	Position, ϕ*	J_{P-F}, cps
$(C_6H_5)_3PF_2$ (II)	39.8[a]	664
$(C_4H_9)_3PF_2$ (IV)	34.2[b]	588
$[(C_2H_5)_2NCH_2]_3PF_2$ (VI)	51.0	688
$(CH_3O)_3PF_2$ (VIII)	72.8[c]	706
$(C_6H_5O)_3PF_2$ (X)	73.0	721
$(C_4H_9S)_3PF_2$ (XII)	72.3	713
$[(CH_3)_2N]_3PF_2$ (XIV)	53.5[d]	707
$[(CH_3)_2N]_2PF_2OCH_3$ (XVI)	55.5	715

[a] Lit.[6] ϕ*37.5 (−39 ppm from CF_3CO_2H) and J_{PF} = 695 cps; lit.[7] ϕ*37.3 (−39.2 ppm from CF_3CO_2H) and J_{PF} = 667 cps. [b] Lit.[6] ϕ*32.5 (−44 ppm from CF_3CO_2H) and J_{PF} = 585 cps. [c] H^1 nmr absorption is a double (J_{HP} = 15.2 cps) triplet (J_{HF} = 1.0 cps) centered at τ 6.35. [d] H^1 nmr absorption is a double (J_{HP} = 10.6 cps) triplet (J_{HF} = 2.8 cps) at τ 7.37. Lit.[1b] ϕ*51.4 (−25.1 ppm from CF_3CO_2H) and J_{PF} = 700 cps and a H^1 nmr absorption appearing as a doublet (J_{HP} = 10.5 cps) triplet (J_{HF} = 2.8 cps) at τ 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.[8]

N-Cyanotri-*n*-butylphosphinimide (III) was quite readily purified by column chromatography on neutral alumina. Elution with chloroform removed any residual $(C_4H_9)_3P$ and $(C_4H_9)_3PF_2$ with the solvent front. The N-cyanophosphorus imide III is a colorless oil exhibiting infrared absorptions at 4.62 and 7.83 μ due to the $—C{\equiv}N$ and $>P{=}N—$ groups, respectively.

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

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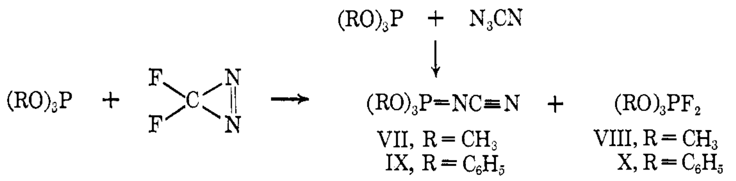
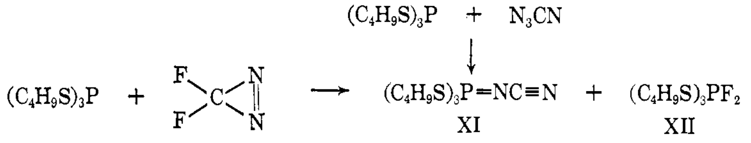
(5) F. O. Marsh and M. E. Hermes, *J. Am. Chem. Soc.*, **86**, 4506 (1964).

(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 (—C≡N) and 7.71–7.85 ($>$P=N—) μ. Tris(diethylaminomethyl)phosphine was the most reactive of the phosphines studied. High yields of V were also obtained by bubbling undiluted CF_2N_2 through a solution of the phosphine in CH_2Cl_2 at room temperature. The bubbles of CF_2N_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 CF_2N_2 and N_3CN techniques were employed in order to obtain sufficient amounts of products for complete identification and further chemical reactions.

The reaction of difluorodiazirine wih trimethyl phosphite to form the desired $(CH_3O)_3P$=NC≡N (VII) and $(CH_3O)_3PF_2$ (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 $(CH_3O)_3P$ and $(CH_3O)_3PF_2$ (VIII) from the higher boiling VII. A second technique which was also useful for the removal of $(CH_3O)_3P$ 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-cyanophosphoroimidate (VII) boiling at 69° (0.16 mm) and exhibiting infrared absorptions at 4.46 (—C≡N) and 7.73 ($>$P=N—) μ. 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 $(CH_3O)_3P$ 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 $(CH_3O)_3P$, the reaction of triphenyl phosphite with difluorodiazirine is quite slow, proceeding to only about 60% completion in 1 week at room temperature. Increasing the CF_2N_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 F^{19} nmr spectral data reported in Table I. It should be noted that difluorophosphoranes represented by the formulas $(RO)_3PF_2$ or $(RS)_3PF_2$ 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* CF_2N_2) of colorless crystals of O,O,O-triphenyl N-cyanophosphoroimidate (IX). Pure IX melts at 92.5–93.5° and shows the cyano absorption as a doublet at 4.51 and 4.59 μ in its infrared spectrum. Compound IX was prepared more conveniently and in a more readily purified form from triphenyl phosphite and cyanogen azide.

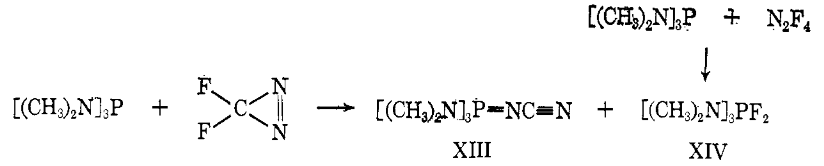
As in the case of phosphites, both the difluorodiazirine and cyanogen azide techniques were used with tributyl trithiophosphite. The reaction of $(C_4H_9S)_3P$ with CF_2N_2 followed the expected course, yielding $(C_4H_9S)_3P$=NC≡N and $(C_4H_9S)_3PF_2$. The difluorophosphorane (XII) could be distilled readily from the crude reaction mixture and was identified by infrared and 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 $(C_4H_9S)_3P$ and N_3CN. A 63% yield of pure $(C_4H_9S)_3P$=NC≡N, spectroscopically identical with that obtained from CF_2N_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 μ.

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 $[(CH_3)_2N]_3P$. When CF_2N_2 was allowed to react with a methylene chloride solution of $[(CH_3)_2N]_3P$ at $-78°$, 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%

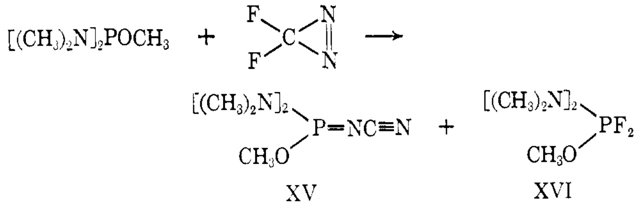


yield of pure $[(CH_3)_2N]_3PF_2$ (XIV) which was identified by infrared and F^{19} and H^1 nmr spectroscopy and independent synthesis.

The difluorophosphorane (XIV) prepared from $[(CH_3)_2N]_3P$ and either CF_2N_2 or N_2F_4 was spectroscopically identical with that reported by Ramirez, *et al.*[1b]

Column chromatography of the residue after removal of XIV was used to isolate XIII in a relatively pure state. Pure N-cyanotris(dimethylamino)phosphinimide (XIII) was isolated as long colorless needles after a final recrystallization from *n*-butyl ether. It is essential in the recrystallization of XIII that the solution is not heated above 60° or an oily, difficulty removed residue is formed during crystallization. The infrared spectrum of XIII shows absorptions at 4.59 and 7.71 μ.

The preparation, isolation, and identification of bis(dimethylamino)methoxydifluorophosphorane (XVI) and N-cyanobis(dimethylamino)methoxyphosphinimide (XV) deserve little comment, other than that the hydrolytic stability of the $\geqslant P{=}NC{\equiv}N$ moiety is again indicated by the fact that a 5% aqueous HCl wash was utilized effectively during purification without decomposition of XV. The infrared spectrum of XV exhibits absorptions at 4.57 ($-C{\equiv}N$) and 7.70 ($\geqslant P{=}N-$) μ.



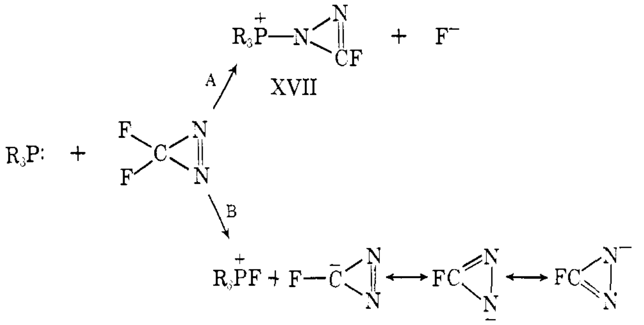
XV XVI

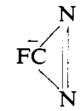
Not all trivalent phosphorus compounds react with difluorodiazirine. It is obvious from the foregoing discussion that the reaction is enhanced by electron-donating substituents. Thus, CF_2N_2 can react explosively with $[(CH_3)_2N]_3P$ and $(CH_3O)_3P$, at a convenient rate with phosphines and quite slowly with $(C_6H_5O)_3P$ and $(C_4H_9S)_3P$. Conversely, electron-withdrawing substituents decrease the reactivity of trivalent phosphorus compounds with CF_2N_2, and N_3CN as well. In this regard, little reaction occurred between CF_2N_2 and $(CH_3O)_2PCl$ and no reaction was observed with PCl_3.

Although no detailed mechanistic study was undertaken, it is possible to formulate a reasonable reaction path based upon mechanisms postulated previously for other systems. As discussed in some detail by Miller[9] and Ramirez, *et al.*,[1a] the factors responsible for the enhanced nucleophilicity of phosphorus toward halogens are the energy of the bond being formed (117–123 kcal/mole in the case of the P–F bond), the polarizability of the nucleophile, and the nature of the leaving group.

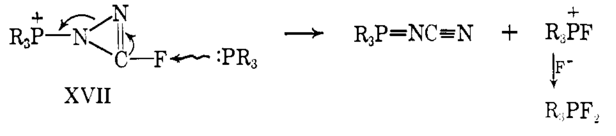
In order to distinguish between an ionic and a radical mechanism involving cyanonitrene and fluorine atoms in the reaction of CF_2N_2 with trivalent phosphorus compounds, a reaction was carried out in isobutylene solvent. No change in products was observed. In fact, the yields of N-cyanophosphorus imide (I) and difluorophosphorane (II) were 91 and 82%, respectively. Similarly, in methanol the yields of I and II were 88 and 86.5%. On the basis of the isobutylene and methanol experiments it is concluded that the reaction is ionic rather than radical.

Although there appears to be some precedent in the literature for initial attack on fluorine by trivalent phosphorus derivatives,[2] Ramirez and co-workers[1a,b] have shown quite conclusively that with fluoro ketones initial attack occurs at the oxygen of the carbonyl group. In the case of the reaction of CF_2N_2 with phosphorus derivatives, initial nucleophilic attack could occur at a nitrogen atom (path A) or a fluorine (path B). Of the two, path A appears to be the most plausible at this time because of the excellent leaving-group nature of a fluoride ion and the reported reluctance of phosphorus to attack fluorine.[1a] However, path B cannot be completely eliminated from consideration, for the nature of





as a leaving group is unknown. Further nucleophilic attack at the fluorine atom of XVII may be expected because the N-cyanophosphorus imides (being quite similar to $R_3P{=}O$ and $R_3P{=}S$) are apparently excellent leaving groups.



N-(5-Tetrazoyl)phosphorus Imides. It was of considerable interest to determine the ease with which nucleophilic addition reactions occurred at the cyano group of N-cyanophosphorus imides. Thus, the cycloaddition of HN_3 was examined because of experimental simplicity and evidence to suggest that the N-tetrazoylphosphorus imides would be stable compounds.

The cycloaddition of HN_3 to N-cyanophosphorus imides has been found to be a clean reaction, resulting

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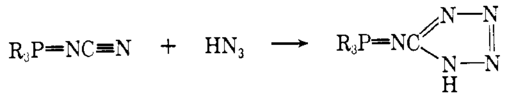
(9) B. Miller in "Topics in Phosphorus Chemistry," M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, pp 133–195.

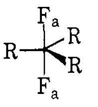
in the formation of the N-(5-tetrazoyl)phosphorus imides in 40–70% yields. The tetrazoles XVIII, XIX, and XX are colorless solids which precipitate from the benzene–diethyl ether solvent system during the reaction. They generally melt with decomposition above 160° and were identified by elemental and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



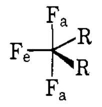
XVIII, R = C_6H_5
XIX, R = C_4H_9
XX, R = C_6H_5O

In contrast to the N-cyanophosphorus imide forming reaction discussed above, the cycloaddition of HN_3 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 $(CH_3O)_3P{=}NC{\equiv}N$ with HN_3 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^{19} nmr spectroscopy. Previous investigations in the field have shown that phosphorus (V) fluorides of the formula R_3PF_2 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



XXI



XXII

fluorine atoms in the axial positions. The axial phosphorus–fluorine splitting is generally about 500–700 cps.[6,7] On the other hand, R_2PF_3 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.[6,10]

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.

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.[11] 174–180° (15 mm)).

Anal. Calcd for $C_{12}H_{27}PS_3$: 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.[12] Bis(dimethylamino)phosphorus chloride, $[(CH_3)_2N]_2PCl$, used in the preparation of $[(CH_3)_2N]_2POCH_3$, was prepared in 90% yield, bp 63–64° (9 mm) (lit.[13] 29° (1 mm)), from hexamethylphosphorus triamide and phosphorus trichloride according to Nöth and Vetter.[13] Bis(dimethylamino)methoxyphosphine was prepared by the addition of an ethereal solution of 9.27 g (6×10^{-2} mole) of $[(CH_3)_2N]_2PCl$ to a stirred, cooled solution of 1.92 g (6×10^{-2} mole) of methanol and 6.06 g (6×10^{-2} mole) of triethylamine in 50 ml of dry ether. Filtration of the amine salt followed by distillation afforded 5.48 g (61%) of $[(CH_3)_2N]_2POCH_3$ as a colorless liquid boiling at 53–54° (24 mm), $n^{23}\text{D}$ 1.4474.

Anal. Calcd for $C_5H_{15}N_2PO$: 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 $CFCl_3$ for the determination of chemical shifts. The values are reported in ϕ^* values[14] at dilutions of about 20–30%. Trifluoroacetic acid is ϕ^* 76.5 on this scale. Proton magnetic resonance spectra were obtained with a Varian A-60 nmr spectrometer. Chemical shifts are given in τ units[15] relative to tetramethylsilane. Molecular weights were determined by the method of Neumayer.[16]

N-Cyanotriphenylphosphinimide (I). A 7.86-g (3×10^{-2} 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^{-2} 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.[5] 193–195°).

Anal. Calcd for $C_{19}H_{15}N_2P$: 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.[7] The F^{19} 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^{-3} mole) of triphenylphosphine and 0.39 g (5×10^{-3} 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^{-3} mole) of triphenylphosphine was treated with 0.39 g (5×10^{-3} 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, triturated with benzene,

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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 (9.6×10^{-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 (3.84×10^{-2} mole) of tri-*n*-butylphosphine dissolved in 25 ml of methylene chloride was allowed to react with 1.5 g (1.92×10^{-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 CF_2N_2 had reacted. Distillation through a short-path apparatus afforded 3.581 g (74.1%) of tri-*n*-butyldifluorophosphorane (IV) boiling at 63° (0.155 mm), n^{24}_{D} 1.4332 (lit.[6] bp 71–72° (0.4 mm), n^{25}_{D} 1.4320). The 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^{24}_{D} 1.4813.

Anal. Calcd for $C_{13}H_{27}PN_2$: 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 (4.0×10^{-2} mole) sample of tris(diethylaminomethyl)phosphine, followed by 40 ml of CH_2Cl_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 (2.56×10^{-2} mole) of difluorodiazirine was added by condensation. The mixture was allowed to warm slowly to −78° and then stirred at that temperature for 24 hr. There was little, if any, unreacted CF_2N_2. The solvent was removed by vacuum distillation to give 13.76 g of a semisolid product. Two extractions with heptane at 60°, followed by cooling the extract to initiate crystallization, resulted in the collection of 3.97 g (60.4% yield) of a colorless solid, mp 90–92°, identified as N-cyanotris(diethylaminomethyl)phosphinimide (V).

Anal. Calcd for $C_{16}H_{36}N_5P$: 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 CH_2Cl_2 and $CFCl_3$ for nmr measurements. The reslts are shown in Table I.

O,O,O-Trimethyl N-Cyanophosphoroimidate (VII) from CF_2N_2. A mixture of 5.124 g (4.13×10^{-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°, 2.0 g (2.56×10^{-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 $(CH_3O)_3P$ under partial vacuum, followed by fractional distillation on a vacuum system through −35 and −196° receivers afforded 1.038 g (25.0%) of difluorotrimethoxyphosphorane (VIII), containing 20–50% of dimethyl phosphorofluoridate (F^{19} nmr spectrum; ϕ^* 86.1, $J_{PF} = 972$ 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° (0.160 mm) (20%) was identified as O,O,O-trimethyl N-cyanophosphoroimidate (VII) by infrared and elemental analyses.

Anal. Calcd for $C_4H_9N_2O_3P$: 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-Cyanophosphoroimidate (VII) from Cyanogen Azide. To a solution of 6.8 g (0.1 mole) of cyanogen azide, prepared 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-cyanophosphoroimidate (VII), bp 80–83° (0.5 mm), which was spectroscopically identical with VII prepared from $(CH_3O)_3P$ and CF_2N_2.

O,O,O-Triphenyl N-Cyanophosphoroimidate (IX) from Difluorodiazirine. A 7.91-g (2.55×10^{-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°, 1.0 g (1.28×10^{-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° receivers was employed to recover 5.17×10^{-3} mole (40.5%) of unreacted CF_2N_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 CF_2N_2) of pure IX, mp 92.5–93.5°.

Anal. Calcd for $C_{19}H_{15}N_2O_3P$: 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-Cyanophosphoroimidate (IX) from Cyanogen Azide. The cyanogen azide technique outlined for VII with redistilled cyanogen bromide and employing 1.36 g (2×10^{-2} mole) of cyanogen azide and 6.82 g (2.2×10^{-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-Cyanotrithiophosphoroimidate (XI) from Difluorodiazirine. Using the procedure outlined above for I, 11.92 g (4.0×10^{-2} mole) of tributyl trithiophosphite dissolved in 40 ml of methylene chloride was allowed to react with 2.0 g (2.56×10^{-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 $(BuS)_3P$, $(BuS)_3P=NCN$, and $(BuS)_3PF_2$ by infrared spectroscopy.

Distillation could be used to remove the unreacted $(BuS)_3P$ and $(BuS)_3PF_2$, bp 123° (0.05 mm), n^{24}_{D} 1.5232. Infrared and F^{19} nmr were utilized to identify the $(BuS)_3PF_2$ by-product (see Table I). Under the distillation conditions, however, the desired N-cyanophosphoroimidate (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-cyanotrithiophosphoroimidate (XI) as a nearly colorless oil.

Anal. Calcd for $C_{13}H_{27}N_2PS_3$: C, 46.2. Found: C, 46.6.

S,S,S-Tributyl N-Cyanotrithiophosphoroimidate (XI) from Cyanogen Azide. To a solution of 2.72 g (4.0×10^{-2} mole) of cyanogen azide, prepared in 20 ml of anhydrous acetonitrile from 4.2 g (4×10^{-2} mole) of cyanogen bromide and 2.6 g (4×10^{-2} mole) of sodium azide, was added dropwise 11.92 g (4.0×10^{-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 ($CHCl_3$–EtOAc) and resulted in a recovery of 63.8% of the theoretical of purified $(BuS)_3P{=}NCN$ which was spectroscopically identical with that described above.

N-Cyanotris(dimethylamino)phosphinimide (XIII). According to the procedure outlined for I, 6.52 g (4.0×10^{-2} mole) of tris(dimethylamino)phosphine in 25 ml of methylene chloride was treated with 2.0 g (2.56×10^{-3} mole) of difluorodiazirine at −78° 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, $[(CH_3)_2N]_3PF_2$ was distilled from the crude product mixture by fractionation under vacuum through −40 and −196° receivers. The −40° receiver contained a 75% yield of essentially pure tris(dimethylamino)difluorophosphorane (XIV) which was identified by infrared, F^{19}, and 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[7] for the preparation of difluorotriphenylphosphorane. A 0.489-g (3×10^{-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° and degassed and 0.416 g (4×10^{-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_2N_2–$[(CH_3)_2N]_3P$ reaction described above.

N-Cyanobis(dimethylamino)methoxyphosphinimide (XV). Using the procedure outlined for XIII, 5.05 g (3.36×10^{-2} mole) of $[(CH_3)_2N]_2POCH_3$ and 2.0 g (2.56×10^{-2} mole) of difluorodiazirine in 25 ml of methylene chloride were allowed to react, with stirring, at −78°. The reactor was warmed to room temperature; methylene chloride was removed under partial vacuum. Fractional distillation–condensation through −40 and −196° traps was used to remove the difluorophosphorane by-product (XVI). Distillation of the contents of the −40° trap gave 1.5 g (47.5%) of pure difluorobis(dimethylamino)methoxyphosphorane (XVI), bp 39–40° (4 mm), $n^{23}\text{D}$ 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, $n^{23}\text{D}$ 1.4797.

Anal. Calcd for $C_6H_{15}N_4OP$: 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 (3.95×10^{-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 (6.0×10^{-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°. Unreacted N-cyanoimide 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 (5.0×10^{-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 (6.0×10^{-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°.

Anal. Calcd for $C_{13}H_{28}N_5P$: 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)phosphoroimidate (XX). To 0.35 g (1.0×10^{-3} mole) of triphenyl N-cyanophosphoroimidate (IX), dissolved in 5 ml of benzene, was added 2 ml of a 0.545 *N* HN_3 solution (1.09×10^{-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°, was obtained.

Anal. Calcd for $C_{19}H_{16}N_5O_3P$: 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.

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Pivaloylnitrene

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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.[3–7] 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 α-elimination route was developed for carbalkoxynitrenes[8,9] and the deoxygenation of aromatic nitro and nitroso compounds served in the case of arylni-

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