through Celite and extraction of the solution with five 50-ml portions of methylene chloride, the combined organic phase was dried and evaporated *in vacuo*. The semicrystalline residue recrystallized from hexane to give 500 mg (70%) of the nearly pure product.

This compound displayed the following absorption maxima: λ_{H_2O} (pH 8) 232 mμ (ε 4200), 451 (1050); λ_{H_2O} (pH 1) 233 mμ (ε 3920), 383 (1070); λ_{DMSO} (KO-*tert*-bu) 668 mμ (ε 590).

2-Dimethylamino-4,4,5,5-tetramethylimidazoline-1-oxyl [2, R = $N(CH_3)_2$].—2-Bromo-4,4,5,5-tetramethylimidazoline-1-oxyl (**2**, R = Br) (500 mg) was heated under gentle reflux with 20 ml of 40% aqueous dimethylamine. After 90 min the solution was almost colorless. Most of the excess amine was removed by evaporation *in vacuo* and the residual solution was reoxidized by stirring for 15 min with 10 g of PbO_2. After filtration through Celite and extraction with three 50-ml portions of CH_2Cl_2, the combined extracts were dried over Na_2SO_4 and evaporated to leave 230 mg of the brown liquid radical. An analytical sample was obtained by molecular distillation at 0.05 mm.

This compound displayed absorption maxima at: λ_{H_2O} (pH 8) 246 mμ (ε 4200), 475 (600); λ_{H_2O} (pH 1) 244 mμ (ε 3800), 427 (900).

2-Isopropylamino-4,4,5,5-tetramethylimidazoline-1-oxyl [2, R = $NHCH(CH_3)_2$].—2-Bromo-4,4,5,5-tetramethylimidazoline-1-oxyl (**2**, R = Br) (250 mg) dissolved in 25 ml of isopropylamine and 25 ml of water were heated under gentle reflux (55–60°) for 4 hr. The almost colorless solution showed only a very weak esr signal. After cooling to room temperature the solution was concentrated *in vacuo* and then stirred for a few minutes with 10 g of PbO_2. The solution was filtered through Celite and the filtrate extracted with five 50-ml portions of CH_2Cl_2. The combined organic phases were dried and evaporated *in vacuo* to leave a brown oil. Chromatography of this residue on silica gel with ether yielded 100 mg (44%) of the pure radical.

This compound displayed absorption maxima at: λ_{H_2O} (pH 8) 233 mμ (ε 5250), 268 (sh) (2200), 480 (1020); λ_{H_2O} (pH 1) 235 mμ (ε 5670), 270 (sh) (1970), 401 (1270); λ_{DMSO} (KO-*tert*-bu) 698 mμ (ε 430).

2-Amino-1-hydroxy-4,4,5,5-tetramethylimidazoline (17, R = NH_2).—2-Amino-4,4,5,5-tetramethylimidazoline-1-oxyl (**2**, R = NH_2) (70 mg) in 50 ml of methanol containing 5 mg of platinum oxide was stirred under a hydrogen atmosphere at room temperature until the solution became colorless. It was then filtered through Celite and evaporated *in vacuo*. The slightly yellow residue was recrystallized from methanol–acetone to give 20 mg of the product, mp 141–144°. The compound reoxidized slowly to the starting radical on standing in air. A satisfactory analysis was not obtained.

2-Dimethylamino-1-hydroxy-4,4,5,5-tetramethylimidazoline [17, R = $N(CH_3)_2$].—2-Dimethylamino-4,4,5,5-tetramethylimidazoline-1-oxyl [**2**, R = $N(CH_3)_2$] (50 mg) in 50 ml of methanol containing 5 mg of platinum oxide was stirred under a hydrogen atmosphere at room temperature until the solution became colorless. The solution was then rapidly filtered through Celite and evaporated *in vacuo*. The residue was recrystallized from acetone to give 15 mg of product (sublimes without melting above 190°). The compound displayed characteristic infrared absorption at ν_{KBr} 3100 (OH) and 1605 cm^{-1} (C=N).

Anal. Calcd for $C_9H_{19}N_3O$: C, 58.34; H, 10.34; N, 22.68. Found: C, 58.33; H, 10.27; N, 22.47.

2-Cyano-4,4,5,5-tetramethyl-2-imidazoline-1-oxyl (2, R = CN).—A finely ground mixture of 300 mg of sodium cyanide and 300 mg of 2-bromo-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide[3b] was heated in 3 ml of dry dimethylformamide at 70° for 15 min. The solution was then diluted with ether, filtered, and evaporated *in vacuo*. The residue was purified by preparative tlc (silica gel–ether) to give 66 mg (31%) of the radical.

Registry No.—**2** (R = NH_2), 26682-07-5; **2** [R = $N(CH_3)_2$], 26682-08-6; **2** [R = $NHCH(CH_3)_2$], 26682-09-7; **2** (R = OCH_3), 26682-10-0; **2** [R = $C(CH_3)_3$], 26682-11-1; **2** (R = CH_3), 26682-12-2; **2** [R = $CH_2CH(CH_3)_3$], 26682-13-3; **2** [R = $CH(CH_3)_2$], 26682-14-4; **2** (R = C_6H_5), 26731-64-6; **2** (R = H), 26682-15-5; **2** (R = I), 26682-16-6; **2** (R = Br), 26682-17-7; **2** (R = $COOCH_3$), 26682-18-8; **2** (R = C≡N), 26682-19-9; **4**, 26682-20-2; **5**, 26682-21-3; **9**, 26682-22-4; **17** (R = NH_2), 26682-23-5; **17** [R = $N(CH_3)_2$], 26682-24-6; **17b** (R = C_6H_5), 18390-03-0.

Iminophosphoranes from the Reaction of Ylides with Nitriles

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Benzonitrile and α-(triphenylphosphoranylidene)toluene react to give the stable iminophosphorane α-[(triphenylphosphoranylidene)amino]stilbene (**3**) which was also prepared by reaction of *cis*- or *trans*-α-azidostilbene with triphenylphosphine. A wide variety of resonance-stabilized phosphoranes and iminophosphoranes, while not reacting with unactivated nitriles, undergo the analogous reaction with cyanogen and trifluoroacetonitrile. The resulting iminophosphoranes (*e.g.*, **4** and **20**) are air stable and quite resistant to hydrolysis. Two isomers are formed in a number of cases. The reaction of nitriles with phosphoranes is believed to proceed by a mechanism analogous to that of the reaction of phosphoranes with activated acetylenes.

Part A

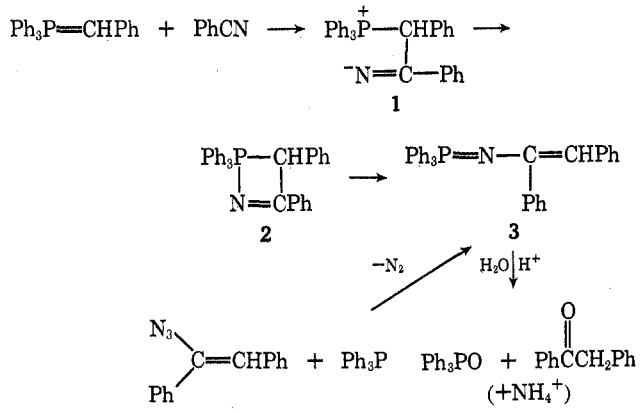
The nucleophilic character of phosphorus ylides has long been recognized and reactions of this class of compounds with a wide variety of electrophilic reagents have been reported.[1] Among these, however, reactions with nitriles have received less attention. McEwen and coworkers[2] found that nonresonance-stabilized ylides[1a,b] react with aliphatic and aromatic nitriles to give ketones after hydrolysis of the unidentified intermediates. We have isolated and characterized the intermediate in one such case and extended the scope to include reactions between resonance-stabilized[1a,b] ylides and the activated nitriles, cyanogen and trifluoroacetonitrile.

α-(Triphenylphosphoranylidene)toluene and benzonitrile reacted slowly in refluxing ether–benzene to give a 1:1 adduct in 68% yield. It was identified as α-[(triphenylphosphoranylidene)amino]stilbene (**3**) by independent synthesis from triphenylphosphine and either *cis*- or *trans*-α-azidostilbene. On hydrolysis, **3** gave deoxybenzoin and triphenylphosphine oxide as reported previously.[2] Attempts to add nitriles to resonance-stabilized ylides, *i.e.*, those carrying electron-withdrawing groups on the ylide carbon, were unsuccessful. How-

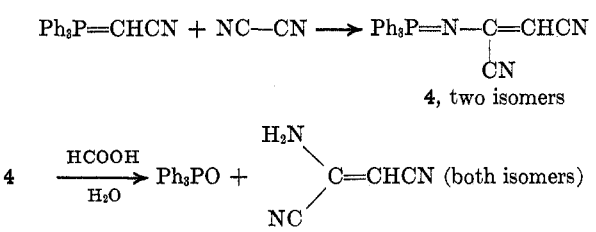
(1) (a) A. Maercker, *Org. React.*, **14**, 270 (1965); (b) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966; (c) H. J. Bestmann, *Angew. Chem.*, **77**, 850 (1965), and preceding reviews.

(2) (a) R. G. Barnhardt, Jr., and W. E. McEwen, *J. Amer. Chem. Soc.*, **89**, 7009 (1967); (b) A. Bladé-Font, W. E. McEwen, and C. A. VanderWerf, *ibid.*, **82**, 2646 (1960); (c) A. Bladé-Font, Ph.D. Thesis, University of Kansas, 1960.

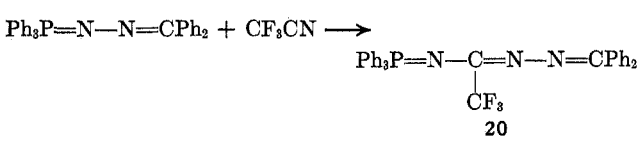
ever, the much more strongly electrophilic nitriles, cyanogen and trifluoroacetonitrile, reacted readily under mild conditions with a large number of such ylides to give iminophosphoranes analogous to **3** in high yields, as



exemplified by the reaction of (triphenylphosphoranylidene)acetonitrile with cyanogen. Hydrolysis of **4**

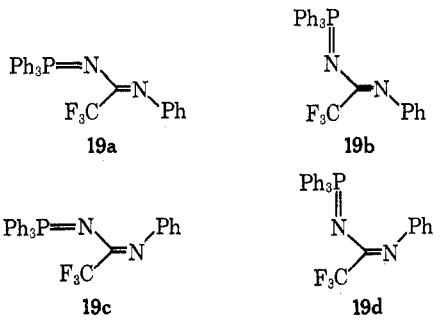


gave a mixture of aminomaleonitrile and aminofumaronitrile, the enamines in this case being resistant to further hydrolysis. Iminophosphoranes, including phosphazines, also reacted readily with cyanogen and trifluoroacetonitrile to give compounds such as **20**.[3] The

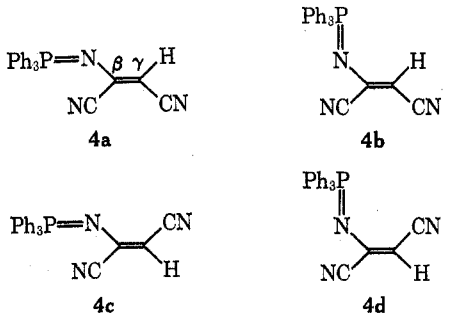


reactions are summarized in Table I. No pure products could be isolated from the reactions of cyanogen or trifluoroacetonitrile with the more strongly basic nonresonance stabilized ylides, polymerization of the nitriles probably occurring to the exclusion of formation of simple adducts. Attempts to add these nitriles to selected nitrogen, arsenic, and sulfur[4] ylides also were unsuccessful.

Two isomers were formed in most but not all cases (Table I). These can differ in the arrangement of the substituents on the phosphorus–nitrogen or carbon–carbon double bonds as exemplified for **4**; the four possible isomers of the iminophosphorane adducts are illustrated for the case of compound **19**. Existence of four isomers presupposes restricted rotation around the



N–C_β bond, since **4a–4b** and **4c–4d** are pairs of rotamers. Restricted rotation around the C_α–C_β bond has been observed in the case of alkoxycarbonylmethylenetriphenylphosphoranes[5] with rotation barriers as high as 18 kcal/mol.[5b] Substituents on C_γ capable of delocalizing a negative charge (*e.g.*, the cyano group in **4**) should increase the double bond character of the N–C_β bond and consequently increase the barrier of rotation around that bond. The data available do not allow a choice of which of these isomers are present in the products **4–20**. The isomer ratios seemed to be dependent on minor changes in reaction conditions since the values listed in the Table were not always exactly reproducible. In most cases the isomer predominating in the crude sample was also the major component of the purified material, although there were some exceptions. Thus, crystallization of the crude isomer mixture **7** from hot ethyl acetate produced the minor isomer exclusively; similarly, the adduct **10** consisted mainly of the less stable isomer, since heating of the crude reaction product in isopropyl alcohol gave a product in which the isomer ratio was reversed (both in the crystals and in the mother liquor); this ratio remained unchanged on further crystallization. Isomerization on crystallization was observed in other but not all cases. Thus, the major and minor isomers in adduct **4** could be almost completely separated by crystallization from hot isopropyl alcohol or acetonitrile. Since conditions for isomerization were determined for only three sets of isomers (**5** in addition to **7** and **10**), a statement as to which isomers are the thermodynamically more stable ones cannot be made in most cases. The isomer ratio in the formation of **5** from methyl (triphenylphosphoranylidene)acetate and cyanogen was solvent dependent; the equilibrium mixture (*ca.* 80:20) was formed in acetonitrile, toluene, and acetone whereas a mixture containing the two isomers in equal amounts was obtained in methylene chloride. A rationalization of this



(3) The reaction of activated nitriles with $Ph_3P{=}NH$ to give iminophosphoranes, $Ph_3P{=}N{-}C(R){=}NH$, has recently been reported: A. S. Shtepanek, E. N. Tkachenko, and A. V. Kirsanov, *Zh. Obshch. Khim.*, **39**, 1475 (1969). Although these products are probably formed by simple addition of the phosphineimine across the nitrile triple bond as suggested by these authors, the possibility that a four-membered ring intermediate analogous to **2** is involved cannot be ruled out completely.

(4) The reaction of trichloroacetonitrile with carboethoxymethylenedimethylsulfurane has been reported to give a complex mixture of products, neither of which was an iminosulfurane analagous to **3**: G. B. Payne, *J. Org. Chem.*, **33**, 3517 (1968).

(5) (a) For a brief summary see "Organophosphorus Chemistry," S. Trippett, Ed., Vol. 1, The Chemical Society, London, 1970, pp 288–289. (b) H. I. Zelinger, J. P. Snyder, and H. J. Bestmann, *Tetrahedron Lett.*, 2199 (1969).

TABLE I[a]

$$R^1CN + Ph_3P{=}YR^2R^3 \longrightarrow Ph_3P{=}N{-}\underset{\displaystyle R^1}{\underset{|}{C}}{=}YR^2R^3$$

No.	Y	R^1	R^2	R^3	Conditions[b]	Yield, %	Mp, °C[c]	Isomer ratio (crude product)	δ_H[d,e]	J_{PH}[e,f]
4	C	CN	CN	H	25 (16)	87[g]	228–230	72:28	5.2, 5.3	6.1, 0.6
5	C	CN	COOMe	H	25 (16)	90[g]	173–174	77:23	4.5, 4.5	0.5, 5.0
6	C	CN	COPh	H	25 (16)	77[g]	198–200	...[i]	3.6	<1
7	C	CN	COOMe	Me	25 (16)	100[h]	178–179[k]	76:24	7.9, 7.8[j]	1.9, 0.7[j]
8	C	CN	$-COOCH_2CH_2CH_2-$		80 (0.5)	100[h]	218–200	?		
9	C	CN	9-fluorenylidene		106 (1)	63[g]	272–273	?		
10	C	CF_3	CN	H	25 (16)	84[g]	162–166[l]	80:20	6.1, 5.2	<1, <1
11	C	CF_3	COOMe	H	25 (90)	94[g]	114–115	...[i]	4.5	<1
12	C	CF_3	COPh	H	70 (1)	81[g]	163–165	...[i]	3.6	<1
13	C	CF_3	COOMe	Me	25 (18)	100[h]	88–90[m]	71:29	6.7, 6.3[n]	
14	C	CF_3	$-COOCH_2CH_2CH_2-$		80 (0.5)	97[h]	165–169	93:7		
15	C	CF_3	9-fluorenylidene		82 (68)	98[h]	253–254	?		
16	N	CN	Ph		25 (1)	82[g]	197–198	...[i,o]		
17	N	CN	*tert*-Bu		25 (16)	90[h]	150–151	50:50	8.5, 8.9[p]	
18	N	CN	$N{=}CPh_2$		25 (70)	60[g]	219–221	?		
19	N	CF_3	Ph		40 (3)	81[h]	122–124	80:20		
20	N	CF_3	$N{=}CPh_2$		90 (6)	47[g]	223–224[m]	82:18		

[a] Satisfactory analytical data (±0.3% for C, H, N) were reported for all compounds in the table; analyses for P were reported for **4**, **5**, **11**, and **17**. Ed. [b] Solvent CH_3CN in all cases except for **9**, which was run in CH_2Cl_2; numbers are temperature and time (hr) in that order; see Experimental Section (Part B) for typical procedures. [c] Melting point of analytical sample of isomer mixture unless indicated otherwise. [d] Chemical shift of vinyl proton (R^3) in τ units, measured in $CDCl_3$ solution with TMS as externally substituted standard. [e] Parameters for the major isomer are listed first. [f] Coupling constant between phosphorus and the vinylic proton (R^3) from the splitting of the proton nmr spectra. [g] Yield of crystallized product. [h] Yield of crude product. [i] Only one isomer formed. [j] Parameters for the methyl group (R^2). [k] Melting point of pure minor isomer which is obtained on crystallization of the crude product mixture. [l] Melting point of a mixture containing 78% of the previously minor isomer and 22% of the major isomer obtained on crystallization from isopropyl alcohol. [m] Melting point of the pure major isomer. [n] Parameters for the COOMe group (R^2). [o] Only one phosphorus resonance at −19.7 ppm from H_3PO_4 was observed. [p] Parameters for the *tert*-butyl groups (R^2).

solvent effect requires knowledge of the as yet unknown stereochemistry of the isomers. However, the fact that of the four solvents tried only methylene chloride produced a different isomer mixture indicates that the ability of the latter to form strong hydrogen bonds may be of importance.

The mechanism of the addition of nitriles to ylides probably involves initial formation of an adduct such as **1** followed by ring closure to the dihydrophosphazete **2**; the final product (**3**) then results by opening of the four-membered ring. Such a mechanism has been proposed for the addition of activated acetylenes to ylides,[6–8] in which products exactly analogous to the nitrile adducts are formed. The formation of isomers was also noted in these reactions.[6]

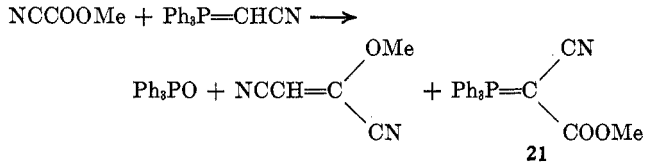
The phosphoranes **4** to **20** are stable to air and quite resistant to hydrolysis. Their diminished nucleophilic character is demonstrated by their reluctance to react with alkylating and acylating agents and to undergo further reaction with activated nitriles or a normal Wittig reaction with aldehydes or ketones.

Part B

Scope of the Reaction of Nitriles with Ylides.—The results presented above make it likely that iminophosphoranes corresponding to **3** are formed in all the reactions of trialkyl- and triarylphosphoranes with aromatic and aliphatic nitriles studied by McEwen and coworkers.[2] It appears that resonance-stabilized ylides do not react with unactivated nitriles, since (triphenylphosphoranylidene)acetonitrile was recovered unchanged after heating in neat acetonitrile, benzonitrile, and phthalonitrile to 200° for 8 hr. Addition of lithium iodide[2a] failed to promote the reaction. Similarly, *N*-(triphenylphosphoranylidene)aniline and acetonitrile did not react at 150° during 3 days. Cyanogen and perfluoroalkylnitriles will probably form adducts of type **4**–**20** with most resonance-stabilized phosphoranes provided that the nucleophilic character of the latter is not too drastically diminished by the presence of two electron-withdrawing substituents on the ylide carbon. Thus, methyl (triphenylphosphoranylidene)cyanoacetate gave no adduct with cyanogen at 120°; *N*-(triphenylphosphoranylidene)benzamide also failed to react under these conditions. In the following combinations, reaction did occur but pure products could not be isolated: (triphenylphosphoranylidene)methane with cyanogen or trifluoroacetonitrile; α-(triphenylphosphoranylidene)toluene, (triphenylphosphoranylidene)cyclopentadiene, pyridinium benzoylmethylide, and (methoxycarbonylmethylene)triphenylarsenic with cyanogen; and methyl (triphenylphosphoranylidene)acetate with trichloroacetonitrile. Methyl (triphenylphosphoranylidene)acetate catalyzed the trimerization[9] of malononitrile. Methyl cyanoformate underwent a normal Wittig reaction with (triphenylphosphoranyli-

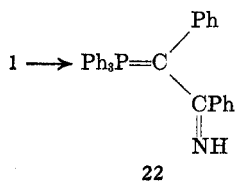
(6) H. J. Bestmann and O. Rothe, *Angew. Chem.*, **76**, 569 (1964).
(7) G. W. Brown, R. C. Cookson, and I. D. R. Stevens, *Tetrahedron Lett.*, 1263 (1964).
(8) J. B. Hendrickson, R. Rees, and J. F. Templeton, *J. Amer. Chem. Soc.*, **86**, 107 (1964); J. B. Hendrickson, C. Hall, R. Rees, and J. F. Templeton, *J. Org. Chem.*, **30**, 3312 (1965).
(9) Various structures have been assigned to the trimer of malononitrile; *cf.* J. D. Atkinson and M. C. Johnson, *J. Chem. Soc. C*, 2181 (1969).

dene)acetonitrile; a small amount of the acylation product **21** was also isolated.



21

Structures.—Only one isomer of **3** was isolated from the addition of benzonitrile to α-(triphenylphosphoranylidene)toluene as well as from the reaction of either *cis*- or *trans*-α-azidostilbene with triphenylphosphine. This probably indicates that the barrier for interconversion between the four possible isomers of **3** is lower than in the case of the phosphoranes **4–20.** Phosphorane **3** exists in two crystal forms having slightly different infrared spectra in the solid but identical infrared and nmr spectra in solution. The previous workers[2] suggested structure **22** for the intermediate of the reaction between benzonitrile and α-(triphenylphosphoranylidene)toluene, although the correct structure **3** was also mentioned[2c] as a possibility.



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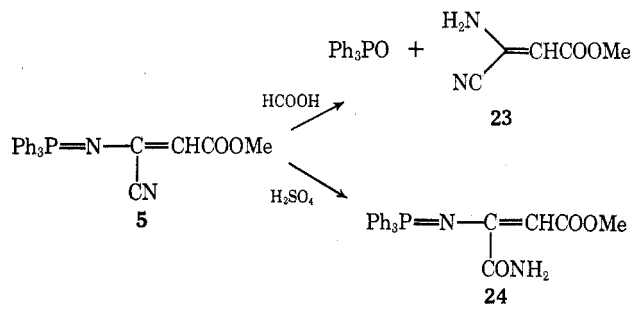
Although only one or two isomers were formed in most reactions of activated nitriles with phosphoranes, there were indications in two cases for the presence of three isomeric species in the products: the nmr spectra of the crude adduct of trifluoroacetonitrile to *N*-(triphenylphosphoranylidene)-*tert*-butylamine showed three trifluoromethyl groups and three *tert*-butyl groups. Similarly, three carbomethoxy peaks were observed in the nmr spectrum of the crude adduct of cyanogen to methyl (triphenylphosphoranylidene)phenylacetate. No attempts were made to isolate these isomers. The isomers listed in Table I could in some cases be separated by chromatography on Florisil (*e.g.*, **10**); others either isomerized (*e.g.*, **5**) or hydrolyzed (*e.g.*, **7**) under these conditions. The only case where the position of the equilibrium was determined is that of **5**. Slow room temperature crystallization from ethyl acetate of the 1:1 mixture of isomers obtained on carrying out the reaction in methylene chloride (see above) gave crystals containing a 77:23 mixture of the major and minor isomers of **1**. The mother liquor contained these isomers in the ratio of 25:75, but on chromatography on Florisil the 77:23 equilibrium mixture was again obtained. A pure sample of the major isomer was accidentally obtained when the isomer mixture was treated with acetyl chloride and triethylamine in an abortive attempt at acetylation. Crystallization from hot acetonitrile again resulted in formation of the 77:23 equilibrium mixture.

The two isomers of **4**, each containing about 10% of the other, were obtained by fractional crystallization. Their ultraviolet spectra are very similar but they differ in their infrared and proton and phosphorus nmr spectra. Thus, the long-range coupling between the vinylic proton (R^3) and phosphorus is 0.5 Hz in the major, and 5.0 Hz in the minor isomer (Table I); the phosphorus resonances occur at −13.7 and −15.1 ppm (from 85% H_3PO_4). Interestingly, the magnitude of the P–H coupling constants is reversed in the case of the isomers **5**, whereas both isomers of **10** have $J_{HP} < 1$ Hz. The phosphorus resonances in **10** are found at −13.4 (major isomer) and −8.5 ppm; the ^{19}F nmr spectrum shows P–F coupling of 5 Hz in the major and of 1 Hz in the minor isomer, but little or no H–F coupling. On the other hand, the fluorines in both isomers of **13** are coupled to the methyl protons (3 and 2 Hz, respectively) but very little to phosphorus; the methyl protons of the major isomer of **13**, however, are coupled to phosphorus (5 Hz); this parameter could not be determined in the minor isomer of **13**. The phosphorus resonances in the two isomers of the iminophosphorane adduct **19** occur at −1.5 and −19.7 ppm, that of the single isomer of **16** at −19.7 ppm. The somewhat conflicting nmr data seem to indicate that different combinations of the four possible types of isomers (*e.g.*, **4a–4d** and **19a–19d**) may occur in the adducts **4–20.**

Reactions.—The iminophosphoranes **4–20** are quite resistant to hydrolysis as evidenced by the fact that **5** was recovered unchanged on heating in methanol to 150°, on refluxing in 20% aqueous acetonitrile, and on stirring with potassium carbonate or potassium hydroxide in methanol at room temperature. Some hydrolysis to triphenylphosphine oxide and methyl 3-amino-3-cyanoacrylate (**23**) occurred on heating **5** to



23

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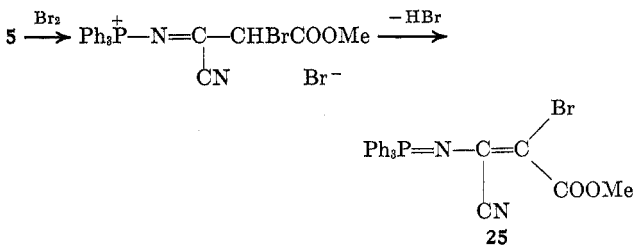
160° in 80% aqueous methanol for 6 hr, but hydrolysis to **23** was much more readily and conveniently carried out with 90% formic acid at room temperature. Only a single isomer of **23** was obtained whereas both aminomaleonitrile and aminofumaronitrile were obtained from **4** under similar conditions. Quenching a solution of **5** in concentrated sulfuric acid with base resulted mainly in conversion of the cyano to an amide group to give **24.** Bromination of **5** followed by treatment with base gave a single isomer of **25.** Unchanged **5** was re-



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covered after heating with neat methyl iodide to 70°; reaction did occur at 100° but no pure products could be isolated. Adduct **5** did not react with acetyl chloride and base at room temperature, or with cyanogen chloride at 70°, nor could it be hydrogenated with a palladium catalyst at room temperature. Pyrolysis of **5** at

275° gave a complex mixture of products. No reaction occurred between **5** and acetone at 120° or between **5** and a large excess of cyanogen at room temperature.

Experimental Section

Reaction of (Triphenylphosphoranylidene)acetonitrile with Cyanogen.—Cyanogen (7.38 g) was transferred at liquid nitrogen temperature to a Carius tube containing 20.27 g of (triphenylphosphoranylidene)acetonitrile[10] and 70 ml of acetonitrile. The tube was sealed under vacuum and the contents were allowed to come to room temperature with magnetic stirring. On reaching room temperature, the phosphorane dissolved and a new precipitate formed. It was collected after standing at room temperature overnight, washed with acetonitrile, and dried to give 17.33 g of a product (A) containing 82% of the major isomer and 18% of the minor isomer of 1-[(triphenylphosphoranylidene)-amino]-1,2-dicyanoethylene (**4**) as indicated by nmr spectroscopy. The mother liquors, on concentration to dryness gave 3.46 g of a solid (B) containing 77% of the minor and 23% of the major isomer, combined yield 20.77 g (87%). Two crystallizations of A from acetonitrile gave a sample of the major isomer, still containing 10% of the minor isomer: mp 228–230°; ^{1}H nmr ($CDCl_3$) τ 1.9–2.8 (m, 15, Ph) and 5.2 (d, J = 6.0 Hz, 1, CH); ^{31}P nmr (CH_2Cl_2, shift from internally substituted 85% H_3PO_4) −13.7 ppm; uv max (MeCN) 314 mμ (ϵ 18,300), 275 (8300), 268 (7500), and 225 (sh, 23,100); ir max (KBr) 2205, 1545 cm^{-1} (vs), among others.

One crystallization of B from acetonitrile gave a sample composed of 82% of the minor and 18% of the major isomer of **4**: mp 162–166° (a small amount remained solid to 210°); ^{1}H nmr ($CDCl_3$) τ 2.0–2.7 (m, 15, Ph) and 5.3 (d, J = 0.6 Hz, 1, CH); ^{31}P nmr (CH_2Cl_2, shift from internally substituted 85% H_3PO_4) −15.1 ppm; uv max (MeCN) 314 mμ (ϵ 18,100), 275 (8000), 268 (7300), and 225 (sh, 24,600); ir max (KBr) 2200, 1550 (vs), 930 cm^{-1} (s), among others; the band at 930 cm^{-1} is absent in the spectrum of the major isomer.

Anal. Calcd for $C_{22}H_{16}N_3P$: C, 74.78; H, 4.57; N, 11.89. Found: C, 74.42; H, 4.22; N, 12.09.

Hydrolysis of 1-[(Triphenylphosphoranylidene)amino]-1,2-dicyanoethylene (4).—A mixture of 2.00 g of 1-[(triphenylphosphoranylidene)amino]-1,2-dicyanoethylene (product A, above) and 10 ml of 90% formic acid was stirred at room temperature for 1 hr. The solvent was removed under vacuum and the residue was sublimed at 90° bath temperature (0.1 μ) to give 0.19 g (39%) of a mixture of aminomaleonitrile and aminofumaronitrile in the ratio of 55:45 as judged by the nmr spectrum (in CD_3CN): broad band at τ 4.5 (2 H) and singlets at 5.2 and 5.5 (1 H) in the ratio of 45:55. The infrared spectrum was identical with that of a mixture of aminomaleonitrile and aminofumaronitrile (see below).

Aminomaleonitrile from Ammonia and Dicyanoacetylene.—To a mixture of 1.36 g of anhydrous ammonia and 150 ml of ethyl ether was added, at −80° over 30 min, a solution of 5.35 g of dicyanoacetylene[11] in 100 ml of ether. The mixture was allowed to come to room temperature slowly. Removal of the solvent from the filtered solution gave 6.08 g of a tan solid. Sublimation of 5.51 g of this material at 80° (0.1 mm) overnight gave 5.20 g of colorless crysals. Crystallization from 10 ml of isopropyl alcohol gave 3.86 g of aminomaleonitrile: mp 135–136° (lit.[12] mp 131°); nmr (CD_3CN) τ 4.4 (broad, 2) and 5.5 (s, 1). The stereochemical assignment is based on the chemical shift of the vinylic proton, which in aminomaleonitrile might be expected to occur at higher field, and on the fact that amines add to activated acetylenes predominantly in a cis fashion.[13] Concentration of the mother liquors and crystallization of the residue from dichloroethane gave 0.67 g of tan crystals, mp 121–124°, the nmr spectrum of which showed it to be a mixture of 75% aminomaleonitrile and 25% aminofumaronitrile (singlets at τ 5.5 and 5.2 in a ratio of 3:1). Since the latter was absent in the nmr spectrum of the crude reaction product, the isomerization must have occurred during the crystallization.

Reaction of Methyl (Triphenylphosphoranylidene)acetate with Cyanogen.—In a Carius tube was placed 22.02 g of methyl (triphenylphosphoranylidene)acetate and 80 ml of acetonitrile. Cyanogen (6.0 g) was distilled in at liquid nitrogen temperature. The tube was sealed under vacuum and placed in a Dry Ice–acetone bath which was allowed to come to room temperature slowly overnight. The tube was cooled to −10° and opened. The precipitate was collected by filtration, washed with acetonitrile, and dried to give 22.81 g (90% yield) of methyl 3-[(triphenylphosphoranylidene)amino]-3-cyanoacrylate (**5**, two isomers, the ratio of the two isomers was 77:23 as determined by nmr spectroscopy). An analytical sample, prepared by recrystallization from acetonitrile, had mp 173–174°. The nmr spectrum showed the ratio of the two isomers to be unchanged: uv max (MeCN) 322 mμ (ϵ 18,700), 375 (6500), 268 (6000), and 225 (sh) (23,300); ir max (KBr) COOMe at 1710 cm^{-1}, CN very weak; nmr ($CDCl_3$) major isomer [τ 1.9–2.7 (m, 15), 4.5 (d, J = 0.5 Hz, 1), and 6.3 (s, 3)], minor isomer [1.9–2.6 (m, 15), 4.5 (d, J = 5 Hz, 1), and 6.2 (s, 3)].

Hydrolysis of Methyl 3-[(Triphenylphosphoranylidene)amino]-3-cyanoacrylate (5) with Formic Acid.—A solution of 5.19 g of methyl 3-[(triphenylphosphoranylidene)amino]-3-cyanoacrylate in 33 ml of 90% formic acid was allowed to stand at room temperature for 50 min. Removal of the solvent at room temperature under high vacuum left a semisolid which on addition of acetonitrile deposited 0.39 g of methyl 3-amino-3-cyanoacrylate (**23**). Concentration of the mother liquor and addition of methylene chloride gave another 0.32 g of the product, combined yield 0.71 g (42%). Crystallization from ethyl acetate gave an analytical sample: mp 163–164°; uv max (MeCN) 289 mμ (ϵ 13,400);[14] ir max (KBr) 3400, 3320, 2240, 1670, 1625, and 1575 cm^{-1} among others; nmr (CD_3CN) τ 3.0–4.5 (broad, s, 2), 5.0 (s, 1), and 6.5 (s, 3).

Anal. Calcd for $C_5H_6N_2O_2$: C, 47.62; H, 4.80; N, 22.21. Found: C, 47.61; H, 4.77; N, 22.57.

Hydrolysis of Methyl 3-[(Triphenylphosphoranylidene)amino]-3-cyanoacrylate (5) with Sulfuric Acid.—To a solution of 2.07 g of methyl 3-[(triphenylphosphoranylidene)amino]-3-cyanoacrylate in 10 ml of methylene chloride was added, at room temperature, 2 ml of concentrated sulfuric acid. The mixture became warm and two layers formed; the lower sulfuric acid layer was yellow. The mixture was stirred at room temperature for 5 min and poured into a cold solution of 5.3 g of sodium hydroxide and 25 ml of water. Methylene chloride was added, the layers were separated, and the aqueous layer was extracted twice with methylene chloride. The extracts were washed with concentrated sodium chloride solution and dried. Removal of the solvent gave 2.06 g of a yellow glass. Addition of 5 ml of methanol and filtration gave 1.43 g (66%) of methyl 3-[(triphenylphosphoranylidene)amino]-3-carbamoylacrylate (**24**), mp 163–164°. An analytical sample, prepared by crystallization from isopropyl alcohol, had mp 164–165°: uv max (MeCN) 313 mμ (ϵ 11,200), 274 (6200), 267 (74,000), 225 (sh, 25,200); ir (KBr) 3450, 3400, 3270, 1660, 1625, 1580, 1560, and 1540 cm^{-1}, among others; nmr ($CDCl_3$) τ 1.9–2.7 (m, 17), 4.0 (s, 1), and 6.2 (s, 3).

Anal. Calcd for $C_{23}H_{21}N_2O_3P$: C, 68.30; H, 5.24; N, 6.93. Found: C, 68.31; H, 5.28; N, 7.08.

Bromination of Methyl 3-[(Triphenylphosphoranylidene)amino]-3-cyanoacrylate (5).—Bromine (1.16 g) was added with cooling to a solution of 2.66 g of methyl 3-[(triphenylphosphoranylidene)amino]-3-cyanoacrylate in 30 ml of methylene chloride. The mixture was stirred at room temperature for 5 min. Triethylamine (3 ml) was added, and stirring was continued for another 10 min. Water was added, the layers were separated, and the aqueous layer was extracted once with methylene chloride. The combined extracts were washed with concentrated sodium chloride solution and dried. Removal of the solvent gave a tan solid which was washed several times with water and dried. Crystallization from isopropyl alcohol gave methyl 3-[(triphenylphosphoranylidene)amino]-2-bromo-3-cyanoacrylate (**25**), mp 158–159°, as pale yellow crystals: uv λ_{max} (MeCN) 334 mμ (ϵ 21,300), 275 (5500), 268 (5500), 262 (sh, 4700), 225 (sh, 25,200); ir (KBr) 2220, 1700, 1625 cm^{-1}, among others; nmr τ 1.8–2.6 (m, 15) and 6.1 (s, 3).

Anal. Calcd for $C_{23}H_{18}BrN_2O_2P$: C, 59.37; H, 3.90; N, 6.02. Found: C, 59.53; H, 4.14; N, 6.11.

Reaction of Methyl 2-(Triphenylphosphoranylidene)propionate with Trifluoroacetonitrile.—To a Carius tube containing 10.54 g

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of methyl 2-(triphenylphosphoranylidene)propionate[15] and 40 ml of acetonitrile was transferred 9.70 g of trifluoroacetonitrile. The tube was sealed under vacuum at liquid nitrogen temperature and allowed to come to room temperature with internal agitation (magnetic stirrer). After stirring at room temperature overnight, the tube was cooled in liquid nitrogen, opened, and rinsed out with methylene chloride. Removal of the solvent gave 13.95 g of the crude mixture of isomeric products. To a solution of 6.18 g of this mixture in 50 ml of methanol was added water to the cloud point, followed by sufficient methanol to produce a homogeneous solution. Crystals deposited on standing for 3 hr. They were collected by filtration, washed with aqueous alcohol, and dried, giving 2.87 g of a single isomer of methyl 3-[(triphenylphosphoranylidene)amino]-2-methyl-4,4,4-trifluorocrotonate(**13**), mp 86–89°. An analytical sample, prepared by crystallization from hexane, had mp 88–90°: uv max (MeCN) 295 mμ (sh, ε 6500), 273 (7800), 266 (8100), and 225 (sh, 23,000); ir max (KBr) 1690 and 1560 cm^{-1}, among others; ^{1}H nmr ($CDCl_3$) τ 2.0–2.8 (m, 15, Ph), 6.8 (s, 3, COOMe), and 8.1 [doublet (J = 5 Hz), of quartets (J = 3 Hz), 3, Me]; ^{19}F nmr ($CDCl_3$, shift from external Freon® 11) +62.2 ppm (q, J = 3 Hz, CF_3). The minor isomer had the following nmr data as deduced from the spectra of the crude mixture: ^{1}H nmr ($CDCl_3$) τ 2.0–2.8 (m, 15, Ph), 6.4 (s, 3, COOMe), and 8.1 (m, 3, Me); ^{19}F nmr ($CDCl_3$, shift from external Freon® 11) +63.4 ppm (q, J = 2 Hz, CF_3).

Reaction of (Triphenylphosphoranylidene)aniline with Cyanogen.—To a Carius tube containing 11.12 g of (triphenylphosphoranylidene)aniline[16] and 50 ml of acetonitrile was transferred, at liquid nitrogen temperature, 4.36 g of cyanogen and the tube was sealed under vacuum. The mixture became homogeneous shortly after reaching room temperature whereupon internal stirring was discontinued. Crystals started to form soon. After standing at room temperature for 1 hr, the tube was cooled in ice and opened, and the crystals were collected, washed with cold acetonitrile, and dried to give 11.02 g (82%) of N-(triphenylphosphoranylidene)-N'-phenylcyanoformamidine (**16**), mp 197–198, unchanged on further recrystallization: uv max (MeCN) 310 mμ (ε 7000), 273 (sh, 11,400), 267 (11,900), and 225 (sh, 31,800); ir max (KBr) 2210 (w) and 1575 cm^{-1} (vs), among others.

Reaction of Benzophenone Triphenylphosphazine with Trifluoroacetonitrile.—A sealed Carius tube, containing 6.0 g of benzophenone triphenylphosphazine,[17] 6.0 g of trifluoroacetonitrile, and 15 ml of acetonitrile was heated, with internal stirring, to 90° for 6 hr. It was cooled to liquid nitrogen temperature, opened, and rinsed out with methylene chloride. Removal of the solvent gave 7.43 g of a tan semisolid. The ^{19}F nmr spectrum showed a doublet (J = 7.5 Hz) at +69.0 ppm (from Freon® 11) and a broadened singlet at +70.0 ppm in the ratio of 82:18. Crystallization from ethyl acetate gave 3.36 g (47% yield) of the major isomer of N-(triphenylphosphoranylidene)trifluoroacetamide diphenylmethylenehydrazone (**20**), mp 220–224°. An analytical sample (1,2-dichloroethane) had mp 223–224°: uv max (MeCN) 331 mμ (ε 12,300) and 225 (sh, 35,000); ir max (KBr) 1575 cm^{-1} (vs), among others; ^{19}F nmr ($CDCl_3$, shift from external Freon® 11) +69.0 ppm (d, J = 7.5 Hz, CF_3).

Reaction of α-(Triphenylphosphoranylidene)toluene with Benzonitrile.—To a slurry of 23.17 g (49 mmol) of benzyltriphenylphosphonium iodide in 25 ml of anhydrous benzene was added, under nitrogen, 28 ml of a 2.3 M solution of methyllithium (65 mmol) in ether. The clear red solution was heated to reflux; a precipitate formed before the boiling point was reached. Benzonitrile (21.7 g) was added, and the mixture was stirred under reflux for 44 hr. The mixture was cooled and filtered. Removal of the solvents from the filtrate gave 39.0 g of a brown oil. Addition of 20 ml of methanol to 5.1 g of this product, heating the mixture under reflux for a short time, and cooling gave 1.95 g (68% yield) of pale yellow crystals, which according to their infrared spectrum were a mixture of the two crystal forms of α-[(triphenylphosphoranylidene)amino]stilbene (**3**). Crystallization from ethyl acetate gave a mixture of pale yellow cubes (crystal form A) and yellow needles (B), which was separated mechanically. The melting points and mixture melting point of A and B were identical (156–157°). The infrared spectrum (in Nujol) of A was identical with that of the authentic sample prepared by reaction of α-azidostilbene with triphenylphosphine (see below). The spectrum of crystal form B (in Nujol) is quite similar to that of A, the main differences being as follows: A has a doublet at 1240 cm^{-1}, B only a singlet; bands at 1160 and 1100 cm^{-1}, and the region of 690–770 cm^{-1} show differences in the relative intensities; A has a band at 800 cm^{-1}, not present in B; B has a band at 820 cm^{-1}, not present in A. In solution, A and B have identical ir, uv, and nmr spectra (in tetrahydrofuran, cyclohexane, and deuteriochloroform, respectively). The uv spectra of A and B in the solid phase both show maxima at 322 mμ. The two crystal forms could be interconverted by dissolution in hot acetonitrile and seeding with a crystal of pure A or B.

Reaction of α-Azido-*trans*-stilbene with Triphenylphosphine.—To a solution of 8.91 g of α-azido-*trans*-stilbene[18] in 50 ml of ether was added 11.75 g of triphenylphosphine. Nitrogen evolution began after a while, the mixture started to reflux, and a precipitate formed. After heating under reflux for 1 hr, the solvents were removed. There was no evidence for the presence of crystal form B (see above) in the infrared spectrum of the crude product. Crystallization from 50 ml of ethyl acetate gave 11.09 g (61% yield) of α-[(triphenylphosphoranylidene)amino]stilbene (**3**, crystal form A) as yellow crystals, mp 156–156.5°. An analytical sample, obtained by crystallization from ethyl acetate, had mp 157–157.5°: uv max (cyclohexane) 317 mμ (ε 18,500), 275 (sh, 11,500), and 267 (sh, 10,500); ir (KBr) 1595, 1565 and 1390 cm^{-1}, among others; ^{1}H nmr ($CDCl_3$) τ 1.8–3.4 (m, 25, phenyl) and 4.3 (d, 1, J = 4 Hz, β-H); ^{31}P nmr ($CDCl_3$) + 0.3 ppm (from 85% H_3PO_4).

Anal. Calcd for $C_{32}H_{26}NP$: C, 84.37; H, 5.76; N, 3.08; P, 6.81. Found: C, 84.03; H, 5.71; N, 3.05; P, 7.10.

The same product was obtained from the reaction of triphenylphosphine with α-azido-*cis*-stilbene[18]; again, there was no evidence for the presence of crystal form B in the infrared spectrum of the crude product.

Reaction of (Triphenylphosphoranylidene)acetonitrile with Methyl Cyanoformate.—A mixture of 1.78 g of (triphenylphosphoranylidene)acetonitrile, 2.84 g of methyl cyanoformate, and 3 ml of acetonitrile was heated under reflux for 10 min. Removal of the solvent and short-path distillation of the residue at 120° bath temperature (0.5 mm) gave 470 mg (90% yield) of a colorless liquid which according to its infrared and nmr spectra and its gas chromatogram was a 1:1 mixture of methoxymaleonitrile and methoxyfumaronitrile.[19] The residue was crystallized from 4 ml of ethyl acetate to give 0.99 g of triphenylphosphine oxide, identified by its infrared spectrum. The mother liquors were concentrated to dryness and the residue was chromatographed over Florisil. Elution with a mixture of methylene chloride and tetrahydrofuran (98:2) gave 77 mg (4% yield) of methyl (triphenylphosphoranylidene)cyanoacetate, identified by comparison of its infrared spectrum with that of an authentic sample.[20]

Registry No.—**3**, 26740-23-8; **4**, 26740-24-9, 26740-25-0; **5**, 26740-26-1, 26740-27-2; **6**, 26740-28-3; **7**, 26740-30-7, 26740-31-8; **8**, 26740-32-9; **9**, 26740-33-0; **10**, 26740-34-1, 26740-35-2; **11**, 26740-29-4; **12**, 26740-36-3; **13**, 26740-37-4, 26740-38-5; **14**, 26740-39-6, 26740-40-9; **15**, 26740-41-0; **16**, 26740-42-1; **17**, 26740-43-2, 26740-44-3; **18**, 26740-45-4; **19**, 26740-46-5, 26740-47-6; **20**, 26740-48-7, 26740-49-8; **23**, 26740-50-1; **24**, 26740-51-2; **25**, 26740-52-3.

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