at 60° gave 1.7 g (53%) of methyl trifluoroacetate, bp 41–43°, δ, CCl_4, 4.00. Removal of trifluoroacetic acid by distillation, extraction with ether–aqueous potassium carbonate, and distillation of the ether layer gave 5-trifluoroacetoxy-2-pentanone (2.3 g 45%), bp 86° (15 mm), identical with a center distillation fraction from trifluoroacetylation of 5-hydroxy-2-pentanone.

Anal. Calcd for $C_7H_9F_3O_3$: C, 42.42; H, 4.54. Found: C, 42.21; H, 4.45.

The nmr spectrum of this fraction showed no nmr evidence for the presence of trifluoroacetates arising from the hemiketal present in 5-hydroxy-2-pentanone.

5-Trifluoroacetoxy-2-pentanone 2,4-Dinitrophenylhydrazone. The derivative melted at 102°.

Anal. Calcd for $C_{13}H_{13}F_3N_4O_6$: C, 41.27; H, 3.43. Found: C, 41.42, H, 3.47.

Reaction of 4-Pentyn-1-yl Acetate with Trifluoroacetic Acid. From the alkyne (12.6 g) in 500 ml of acid maintained at 60° for 110 hr there was obtained 11.2 g of flash distillate and 1.17 g of residue. The distillate contained 5-trifluoroacetoxy-2-pentanone (**22**) and 5-acetoxy-2-pentanone (**17**) in the molar ratio 64:36 (nmr analysis) identified as the 2,4-dinitrophenylhydrazones after separation by gas chromatography. Calculation shows the yields of **22** and **27** to be 40 and 23%, respectively, based on the weight of flash distillate and the observed molar ratio.

5-Acetoxy-2-pentanone 2,4-Dinitrophenylhydrazone. A center distillation fraction (spinning-band column) from acetylation of the alcohol gave the noncyclic acetate as shown by nmr, bp 96–99° (10 mm) [lit.[32] bp 93–95° (10 mm)]. The 2,4-dinitrophenylhydrazone melted at 89–90° (lit.[33] mp 77.6–78°).

Anal. Calcd for $C_{13}H_{16}N_4O_6$: C, 48.15; H, 4.94. Found: C, 48.22; H, 4.82.

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(32) M. A. Volodena, A. P. Terent'ev, L. G. Roshchupkina, and V. G. Mishina, *Zh. Obshch. Khim.*, **34**, 469 (1964); *Chem. Abstr.*, **60**, 13241*c* (1964).

(33) U. S. Patent 2,506,770, U. S. Rubber Co.; *Chem. Abstr.*, **46**, P9, 584*d* (1951).

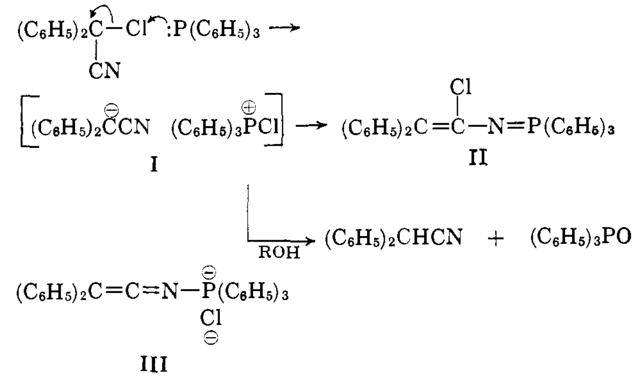
Reactions of Phosphorus Compounds. XIV. The Reactions of Halovinylphosphinimines

R. D. Partos and K. W. Ratts

Contribution from the Monsanto Company, Agricultural Division, Research Department, St. Louis, Missouri 63166. *Received June 30, 1966*

Abstract: The reactions of N-(1-chloro-2,2-diphenylvinyl)triphenylphosphinimine (II) with mercaptans, amines, and benzoic acid are discussed. Mercaptans form isolable phosphonium salts which decompose thermally to diphenylacetonitrile and triphenylphosphine sulfide, probably *via* a thioacylphosphinimine. Amines form amidine-derived phosphonium salts which may be dehydrohalogenated to iminophosphinimines. Benzoic acid yields triphenylphosphine oxide, diphenylacetonitrile, and benzoyl chloride, probably *via* a pentacovalent phosphorus intermediate.

A recent publication[1] from these laboratories described the reaction of chlorodiphenylacetonitrile and triphenylphosphine. Nucleophilic displacement of phosphorus on halogen led to the ion pair I. In the presence of a prototropic solvent, I was converted to diphenylacetonitrile and triphenylphosphine oxide, whereas, in the absence of a protropic solvent, ion pair I was transformed to the halovinylphosphinimine II. (An alternate structure, III, seems unlikely because of the absence of a ketenimine band in the infrared spectrum.) Treatment of II with methanol led to the acylphosphinimine V, presumably *via* the phosphonium salt IV.



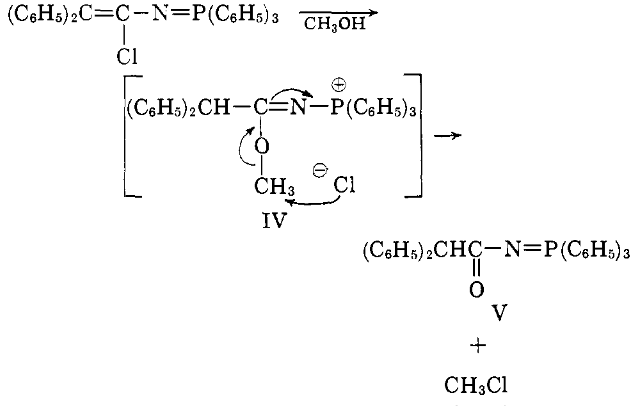
$$(C_6H_5)_2\underset{\displaystyle CN}{\overset{}{C}}{-}Cl\;{:}P(C_6H_5)_3 \longrightarrow \left[(C_6H_5)_2\overset{\ominus}{C}CN\quad (C_6H_5)_3\overset{\oplus}{P}Cl\right] \longrightarrow (C_6H_5)_2C{=}\overset{\displaystyle Cl}{C}{-}N{=}P(C_6H_5)_3$$

I II

$$\xrightarrow[\text{ROH}]{} (C_6H_5)_2CHCN + (C_6H_5)_3PO$$

$$(C_6H_5)_2C{=}C{=}N{-}\overset{\ominus}{\underset{\displaystyle \underset{\ominus}{Cl}}{P}}(C_6H_5)_3$$

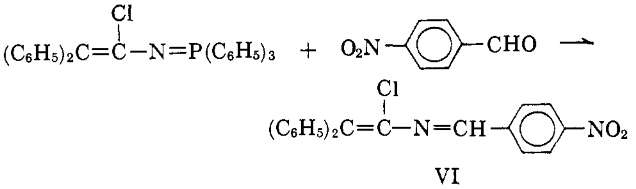
III



$$(C_6H_5)_2C{=}\underset{\displaystyle Cl}{C}{-}N{=}P(C_6H_5)_3 \xrightarrow[\text{CH}_3\text{OH}]{} \left[(C_6H_5)_2CH{-}\underset{\displaystyle \underset{\displaystyle CH_3}{O}}{C}{=}N{-}\overset{\oplus}{P}(C_6H_5)_3 \quad \overset{\ominus}{Cl}\right] \longrightarrow (C_6H_5)_2CH\underset{\displaystyle \| \atop O}{C}{-}N{=}P(C_6H_5)_3 + CH_3Cl$$

IV V

Since the favored structure, II, is that of an ylide, its reaction as a Wittig reagent was investigated. Indeed, treatment of II with *p*-nitrobenzaldehyde afforded N-(1-chloro-2,2-diphenylvinyl)-*p*-nitrobenzaldimine (VI). The nuclear magnetic resonance (nmr)



$$(C_6H_5)_2C{=}\overset{\displaystyle Cl}{C}{-}N{=}P(C_6H_5)_3 + O_2N{-}C_6H_4{-}CHO \longrightarrow (C_6H_5)_2C{=}\overset{\displaystyle Cl}{C}{-}N{=}CH{-}C_6H_4{-}NO_2$$

VI

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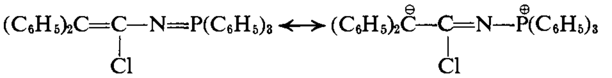
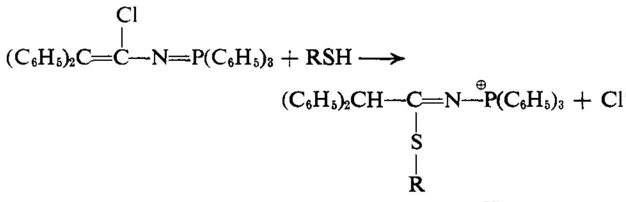
[1] R. D. Partos and A. J. Speziale, *J. Am. Chem. Soc.*, **87**, 5068 (1965).

spectrum of VI exhibited a peak at τ 1.28 for the aldimino hydrogen. The low yield of VI, about 8%, was probably due to deactivation of the ylide II by the diphenylvinyl group.



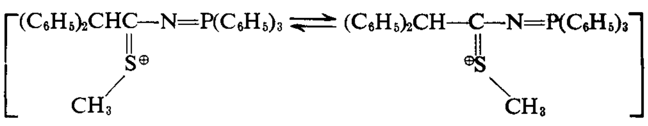
$$(C_6H_5)_2C{=}C(Cl){-}N{=}P(C_6H_5)_3 \longleftrightarrow (C_6H_5)_2\overset{\ominus}{C}{-}C(Cl){=}N{-}\overset{\oplus}{P}(C_6H_5)_3$$

The bulk of the present paper deals with the interaction of II with nucleophiles other than alcohols. Treatment of II with mercaptans led to the formation of phosphonium salts VII. The isolation and characterization of VIIa supports the intermediacy of IV in the formation of phosphinimine V. The nmr spectrum of VIIa showed the protons on the methyl group as two peaks, at τ 7.20 and 7.72; the ratio of the peak areas was 1.7:1. Restricted rotation due to considerable double-bond character in the carbon–sulfur bond of VIIa gives rise to two geometrical isomers.



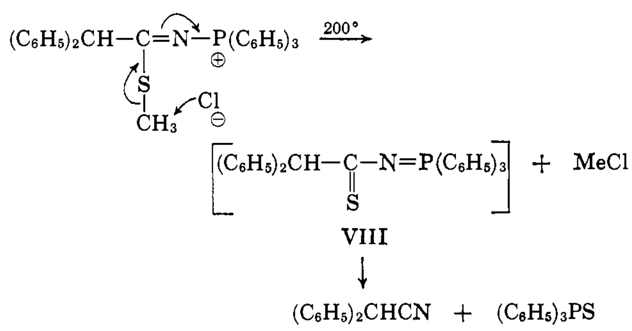
$$(C_6H_5)_2C{=}C(Cl){-}N{=}P(C_6H_5)_3 + RSH \longrightarrow (C_6H_5)_2CH{-}C(SR){=}N{-}\overset{\oplus}{P}(C_6H_5)_3 + Cl^{\ominus}$$

VIIa, R = CH_3
b, R = $C(CH_3)_3$

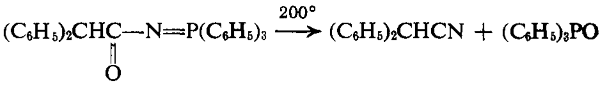


At elevated temperatures (about 120°) the two peaks coalesced to one broad peak.

An attempt was made to convert VIIa to the thioacylphosphinimine VIII by heating at 200°.



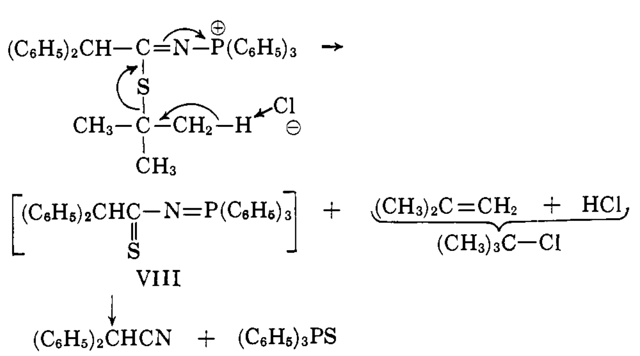
Only triphenylphosphine sulfide, diphenylacetonitrile, and methyl chloride were isolated from the pyrolysis. It was shown previously[1] that V could be pyrolyzed to diphenylacetonitrile and triphenylphosphine oxide.



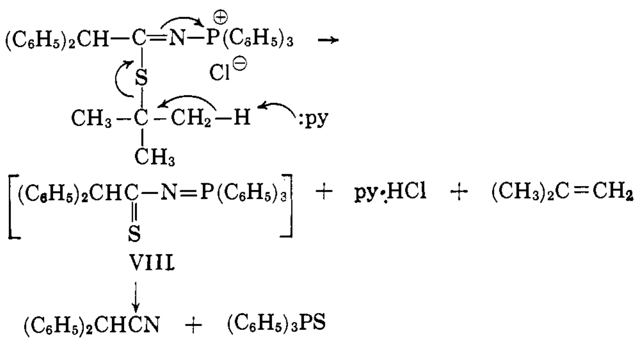
$$(C_6H_5)_2CHC({=}O){-}N{=}P(C_6H_5)_3 \xrightarrow{200°} (C_6H_5)_2CHCN + (C_6H_5)_3PO$$

V

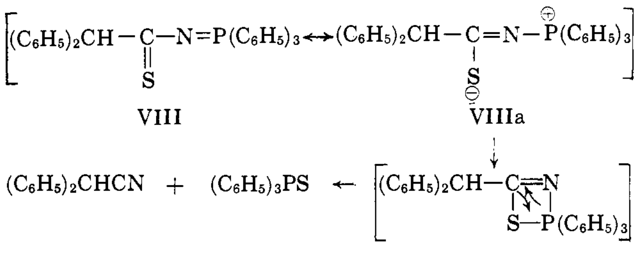
In hope of isolating VIII, the salt VIIb was prepared. It was more easily pyrolyzed, decomposing at 80°, but again only diphenylacetonitrile and triphenylphosphine sulfide were isolated. The nmr spectrum of the gases evolved indicated the presence of isobutylene and *t*-butyl chloride; hydrogen chloride was also evolved.



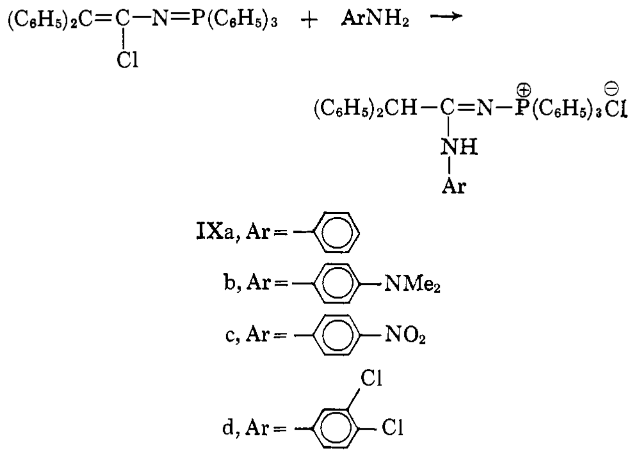
Treatment of VIIb with pyridine at 10° again afforded only the decomposition products of VIII.

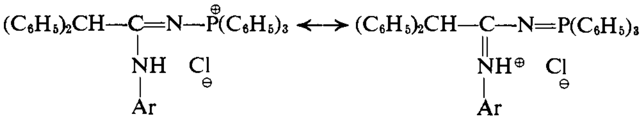


The instability of VIII relative to the oxygen analog V may be due to the greater contribution of the dipolar structure VIIIa to the resonance hybrid.



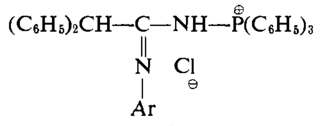
Treating II with aromatic amines led to the formation of phosphonium salts IXa–d. The nmr spectra of the salts clearly exhibited the $(C_6H_5)_2CH$ proton at about τ 4.1 (see Table I). The -N*H* proton appeared at τ −2.9 to 1.4, indicating a significant contribution of an iminium structure to the resonance hybrid.



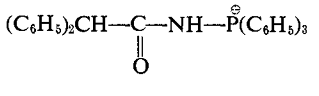


$$(C_6H_5)_2CH{-}C(NHAr){=}N{-}\overset{\oplus}{P}(C_6H_5)_3\ Cl^{\ominus} \longleftrightarrow (C_6H_5)_2CH{-}C({=}\overset{\oplus}{N}HAr){-}N{=}P(C_6H_5)_3\ Cl^{\ominus}$$

An alternative structure, X, would satisfy the observed chemical shift of the -N*H* proton [the nmr absorption of the -N*H* proton in XI[1] (see Table I) occurs at τ −3.3]. However, it can be seen from the data in Table I that there is a downfield shift in the position of absorption of the -N*H* proton as the ring substituent becomes more electron withdrawing, whereas the position of the $(C_6H_5)_2CH$ proton does not change. This difference is most consistent with structure IX, in which the -N*H* proton is α to the substituted ring.[2]

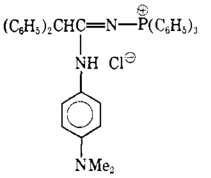
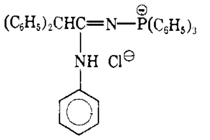
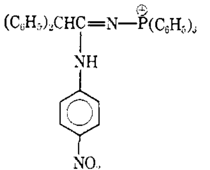
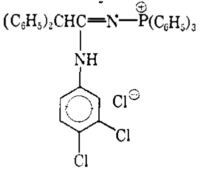
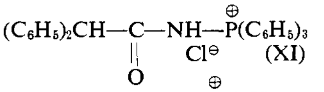
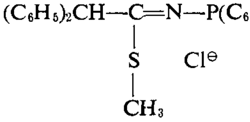

$(C_6H_5)_2CH{-}C({=}N{-}Ar){-}NH{-}\overset{\oplus}{P}(C_6H_5)_3\ Cl^{\ominus}$

X


$(C_6H_5)_2CH{-}C({=}O){-}NH{-}\overset{\oplus}{P}(C_6H_5)_3$

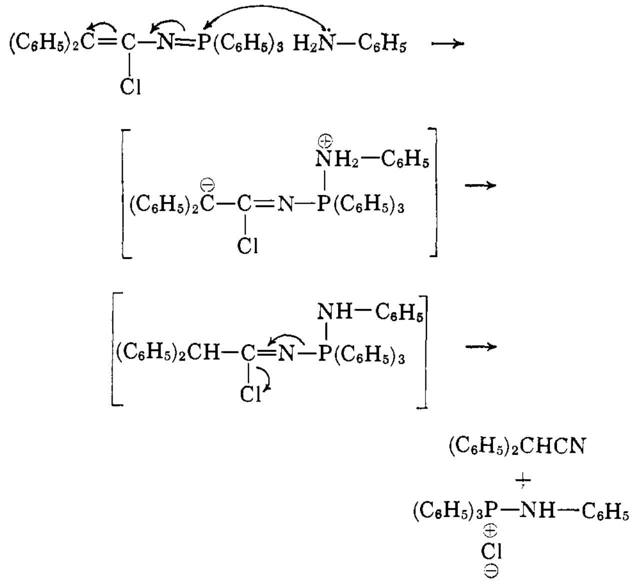
XI

Table I. Nuclear Magnetic Resonance Spectra of Phosphonium Salts

Phosphonium salt		Chemical shifts, τ $(C_6H_5)_2CH$-	 -NH-
	(IXb)	4.0 ($J_{P^{31}-H}$ = 2.2 cps)	−1.4
	(IXa)	4.0 (broad)	−2.0
	(IXc)	4.1 (broad)	−2.8
	(IXd)	4.0 ($J_{P^{31}-H}$ = 2.5 cps)	−2.9
 $(C_6H_5)_2CH{-}C({=}O){-}NH{-}\overset{\oplus}{P}(C_6H_5)_3\ Cl^{\ominus}$	(XI)	3.3 (broad)	−3.3
 $(C_6H_5)_2CH{-}C(SCH_3){=}N{-}\overset{\oplus}{P}(C_6H_5)_3\ Cl^{\ominus}$	(VIIa)	4.1 (broad)	. . .

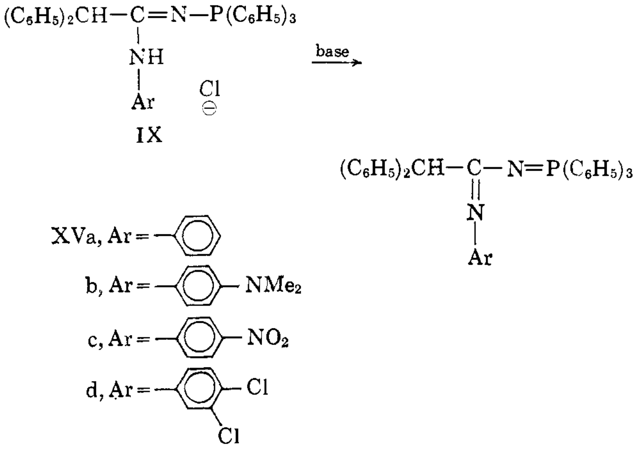
If water is not carefully excluded from the reaction mixture, the hydrate of the phosphonium salt is likely to be obtained. The hydrate of IXa was indeed prepared by recrystallization from aqueous acetonitrile. It was stable to subsequent recrystallization from nonaqueous solvents but could be reconverted to the anhydrous material by heating for 5 min in refluxing xylene.

If the reaction mixture was not cooled during the addition of aniline, a significant amount of attack at phosphorus occurred. When aniline was added at room temperature, about one-third of the isolated product was XIVa.[3] This was not observed when the addition was carried out at 0°. Apparently, attack at carbon to give IX is favored but at higher temperatures selectivity is lost.



XIVa

Treating salts IXa–d with aqueous base yields the iminophosphinimines XVa–d.[4] These materials exhibited infrared spectra similar to the acylphosphinimine V[1] (see Table II), *i.e.*, three strong peaks in the


IX

XVa, Ar = C_6H_5

b, Ar = C_6H_4–NMe$_2$

c, Ar = C_6H_4–NO$_2$

d, Ar = $C_6H_3Cl_2$

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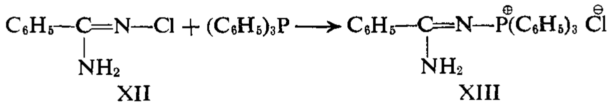
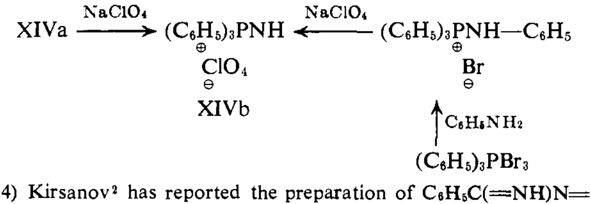
[2] Kirsanov [G. I. Derkach and A. V. Kirsanov, *J. Gen. Chem. USSR*, **32**, 2221 (1962)] has reported the preparation of XIII from the treatment of XII with triphenylphosphine. No evidence for this structure was given.


$C_6H_5{-}C(NH_2){=}N{-}Cl + (C_6H_5)_3P \longrightarrow C_6H_5{-}C(NH_2){=}N{-}\overset{\oplus}{P}(C_6H_5)_3\ \overset{\ominus}{Cl}$

XII XIII

[3] Phosphonium salt XIVa was identified by conversion to the perchlorate which was prepared independently from the corresponding bromide.

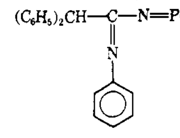
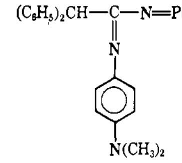
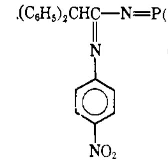
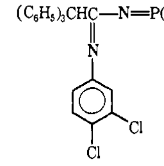

$$\text{XIVa} \xrightarrow{NaClO_4} (C_6H_5)_3\overset{\oplus}{P}NH\ \overset{\ominus}{ClO_4} \xleftarrow{NaClO_4} (C_6H_5)_3\overset{\oplus}{P}NH{-}C_6H_5\ \overset{\ominus}{Br} \xleftarrow{C_6H_5NH_2} (C_6H_5)_3PBr_2$$

XIVb

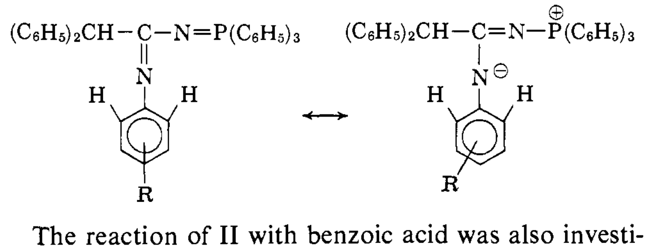
[4] Kirsanov[2] has reported the preparation of $C_6H_5C({=}NH)N{=}P(C_6H_5)_3$ from the corresponding hydrochloride.

region of 6.4, 7.5, and 9.0 μ. The nmr spectra of XV showed the $(C_6H_5)_2CH$ proton to be split by 6–7 cps. This splitting, due to long-range coupling with phosphorus, was either greatly reduced or not observed at all in the corresponding hydrochlorides IXa–d (Table I). This effect was also observed in the case of V[1] (see Tables I and II).

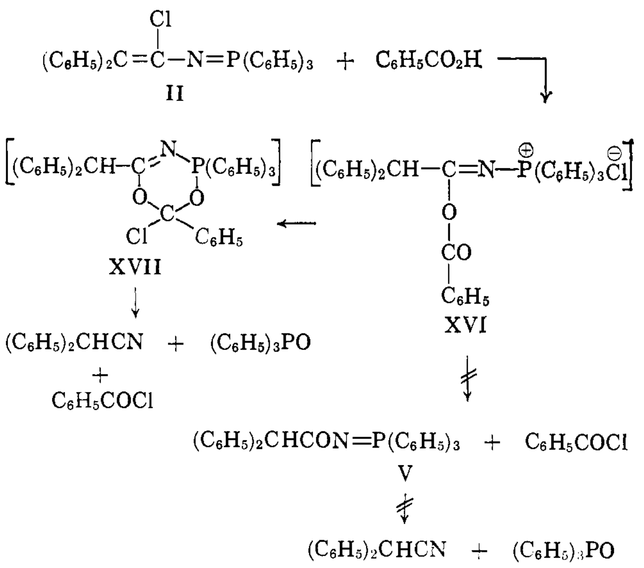
Table II. Nuclear Magnetic Resonance and Infrared Spectra of Phosphinimines

Phosphinimine	Infrared max, μ	Nmr chemical shift of $(C_6H_5)_2CH$ proton, τ
$(C_6H_5)_2CHCON{=}P(C_6H_5)_3$ (V)[1]	6.35, 7.56, 9.06	4.77 ($J_{P^{31}-H}$ = 3.2 cps)
 (XVa)	6.40, 7.45, 9.00	4.85 ($J_{P^{31}-H}$ = 7.5 cps)
 (XVb)	6.45, 7.50, 9.02	4.83 ($J_{P^{31}-H}$ = 7 cps)
 (XVc)	6.50, 7.60, 9.07	5.01 ($J_{P^{31}-H}$ = 6 cps)
 (XVd)	6.43, 7.38, 8.99	4.97 ($J_{P^{31}-H}$ = 7 cps)

An upfield shift of the protons *ortho* to the imino nitrogen atom was observed in the phosphinimines. [The chemical shift occurred at τ 3.62–3.84.] This upfield shift can be attributed to the presence of a significant amount of negative charge on the nitrogen atom adjacent to the aromatic ring.



The reaction of II with benzoic acid was also investigated. The reaction products were diphenylacetonitrile, triphenylphosphine oxide, and benzoyl chloride (contaminated with benzoic anhydride). Addition of benzoic acid to II was expected to give rise to intermediate XVI which should fragment to yield benzoyl chloride and V. The latter compound, however, which should be stable under the reaction conditions (refluxing benzene), was *not* isolated from the reaction. It thus appears that a pentacovalent phosphorus intermediate such as XVII is probably formed; this decomposes directly to the observed products. Formation of benzoic anhydride is due to reaction of benzoyl chloride with residual benzoic acid. Further evidence for the intermediacy of XVII was obtained by adding the phosphinimine V to the reaction mixture before the addition of benzoic acid. It was completely converted to the corresponding hydrochloride XI. Since none of salt XI was isolated when V was not initially present, V could not be an intermediate in the reaction.



$$C_6H_5COCl + C_6H_5CO_2H \longrightarrow (C_6H_5CO)_2O + HCl \xrightarrow{V} \underset{XI}{(C_6H_5)_2CHCONH\overset{\oplus}{P}(C_6H_5)_3\ Cl^{\ominus}}$$

Experimental Section[5]

N-(1-Chloro-2,2-diphenylvinyl)-*p*-nitrobenzaldimine (VI). To a solution of 3.5 g (13.4 mmoles) of triphenylphosphine in 15 ml of benzene was slowly added 3.0 g (13.4 mmoles) of chlorodiphenylacetonitrile.[6] After 15 min a solution of 2 g (13.3 mmoles) of *p*-nitrobenzaldehyde in 10 ml of tetrahydrofuran was added. The mixture was stirred 1.5 hr at room temperature and then refluxed 1 hr. The solution was evaporated and the residue (9 g) chromatographed first on silica gel and then on alumina. There was obtained 400 mg (8.1%) of aldimine VI. Recrystallization from methylcyclohexane yielded material having mp 165–168°; nmr ($CDCl_3$, τ): singlet at 1.28, quartet centered at 1.9, doublet at 2.6, peak areas in the ratio 1.3 : 4.5 : 10.

Anal. Calcd for $C_{21}H_{15}ClN_2O_2$: C, 69.52; H, 4.17; Cl, 9.76; N, 7.72. Found: C, 69.52; H, 4.30; Cl, 9.69; N, 7.57.

Treatment of II with Methyl Mercaptan. To a solution of 5.8 g (22 mmoles) of triphenylphosphine in 30 ml of xylene was added 5 g (22 mmoles) of chlorodiphenylacetonitrile in 10 ml of xylene. The mixture was stirred 15 min at room temperature; then 1.5–2 ml of condensed methyl mercaptan in 5 ml of xylene was added. The mixture was refluxed 15 min. There was collected (in a drybox) 5 g (46%) of salt VIIa; nmr ($CDCl_3$, τ): multiplet at 2.6, singlets at 4.06, 7.20, 7.72, peak area ratios 25 : 0.7 : 1.9 : 1.1.

Anal. Calcd for $C_{33}H_{29}ClNPS$: C, 73.66; H, 5.43; N, 2.60; P, 5.76; S, 5.96. Found: C, 73.48; H, 5.71; N, 2.60; P, 5.94; S, 6.17.

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(5) All melting points were taken on a Mel-Temp capillary melting point apparatus and are uncorrected. Infrared spectra were determined with a Beckman IR-5 spectrophotometer. Nmr spectra were determined on a Varian A-60 spectrophotometer. Elementary analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(6) C. Stevens and C. T. Lenk, *J. Org. Chem.*, **19**, 538 (1954).

The nmr spectrum in nitrobenzene exhibited two singlets at τ 7.0 and 7.43. At 120° these coalesced to a broad peak at τ 7.32. Upon cooling the orginal spectrum was obtained.

Pyrolysis of VIIa. Crude VIIa (3 g) was heated to 200° until bubbling ceased. (The evolved gas was trapped in deuteriochloroform; nmr of this solution exhibited a peak at τ 6.97; authentic methyl chloride was found to exhibit a singlet at τ 7.03). The residual material was chromatographed on silica gel and then alumina. There was obtained 0.7 g (70%) of diphenylacetonitrile, mp 64–68°, undepressed (64–72°) upon admixture of authentic material, and 1.5 g (100%) of triphenylphosphine sulfide, mp 157–162° (from ethyl acetate), undepressed (157–163°) upon admixture of authentic material.

Treatment of II with *t*-Butyl Mercaptan and Pyrolysis of the Salt Formed (VIIb). A solution of 5 g (22 mmoles) of chlorodiphenylacetonitrile in 5 ml of benzene was slowly added to a solution of 5.8 g (22 mmoles) of triphenylphosphine in 25 ml of benzene. The solution was stirred 15 min and then cooled to 5°. A solution of 2 g (22 mmoles) of *t*-butyl mercaptan in 5 ml of benzene was added. The mixture was slowly warmed to reflux; a gas was evolved. The gas was trapped in deuteriochloroform; the nmr of this solution exhibited peaks (τ) at 2.70 (singlet), 5.32 (broad), 8.30 singlet), 8.45 (singlet), and 8.62 (singlet). Reported values[7] (τ) are chloroform, 2.75; $(CH_3)_2C{=}\mathit{CH}_2$, 5.40; $(\mathit{C_3H})_2C{=}CH_2$, 8.30; *t*-butyl mercaptan, 8.61. The ratio of the peak areas at 8.30 and 5.32 was 2.7:1.

The benzene solution was evaporated and the residue chromatographed on alumina. There was obtained 3.5 g (83%) of crude diphenylacetonitrile, mp 63–71°. Recrystallization from aqueous methanol raised the melting point to 63–68°, undepressed (67–71°) upon admixture of authentic material. There was also obtained 5.5 g (84%) of crude triphenylphosphine sulfide, mp (after recrystallization from ethyl acetate) 162–164°, undepressed (160–163°) upon admixture with authentic material.

Treatment of II with *t*-Butyl Mercaptan and Subsequent Base Treatment of the Salt Formed. A solution of 5 g (22 mmoles) of chlorodiphenylacetonitrile in 5 ml of benzene was added to a solution of 5.8 g (22 mmoles) of triphenylphosphine in 25 ml of benzene. The mixture was stirred at room temperature for 15 min and then 2.0 g (22 mmoles) of *t*-butyl mercaptan was added. The mixture was warmed to 45°; at this temperature a second phase separated. The mixture was now cooled to 10° and 1.8 g (23 mmoles) of pyridine was added. The solution was filtered, and the filtrate was evaporated. The residue exhibited an infrared spectrum identical with that of the pyrolysis product above, before chromatography.

Salt IXa. A solution of 5.0 g (22 mmoles) of chlorodiphenylacetonitrile in 5 cc of benzene was added to 5.8 g (22 mmoles) of triphenylphosphine in 25 cc of benzene. The mixture was stirred at room temperature for 15 min and then cooled to *ca.* 0°. A solution of 2.1 g (22.5 mmoles) of aniline was slowly added, and the mixture was then allowed to warm to room temperature and finally refluxed 25 min. There was collected 10.0 g (78%) of crude IXa, mp 198–210°. Repeated recrystallization from acetonitrile–ethyl acetate raised the melting point to 218–220°; nmr absorption ($CDCl_3$, τ): broad singlet at −2.0, multiplet at 2.75, broad singlet at 4.03, peak area ratios 1.1:30:1.2.

Anal. Calcd for $C_{38}H_{32}ClPN_2$: C, 78.27; H, 5.53; N, 4.81. Found: C, 78.26; H, 5.68; N, 4.76.

A small amount of IXa was recrystallized once from aqueous acetonitrile and then once from acetonitrile–ethyl acetate. The material obtained was the monohydrate of IXa, mp 215–218° (undepressed upon admixture of IXa); nmr ($CDCl_3$, τ): very broad peak at −1.5, multiplet at 2.54, singlet at 4.35, and a broad peak at 7.22, peak area ratios 0.6:30:0.9:1.5.

Anal. Calcd for $C_{38}H_{34}ClN_2OP$: C, 75.92; H, 5.70; N, 4.66. Found: C, 76.05; H, 5.69; N, 4.80.

A small amount of IXa monohydrate was heated in refluxing xylene for 5 min. Xylene was distilled until it appeared water free. The solid collected exhibited an nmr spectrum superimposable upon that of IXa.

A solution of 5.0 g (22 mmoles) of chlorodiphenylacetonitrile in 5 cc of benzene was added to 5 g (22 mmoles) of triphenylphosphine in 25 ml of benzene. The mixture was stirred at room temperature for 15 min and then 2.1 g (22.5 mmoles) of aniline was slowly added. No cooling was applied during the addition. The mixture was refluxed 30 min. There was collected 8.7 g of a solid melting at 178–190°. One recrystallization from acetonitrile–ethyl acetate gave 5 g of material with mp 195–214°. This material was again recrystallized from acetonitrile–ethyl acetate; the first crop was about 1 g of crude phosphonium salt XIVa. Recrystallization from acetonitrile–ethyl acetate and then chloroform (ethyl acetate raised the melting point to 230–233°; nmr ($CDCl_3$, τ): broad peak at −1.3, multiplets at 2.27 and 2.87, peak area ratios 0.6:15.5.1.

Anal. Calcd for $C_{24}H_{21}ClNP$: C, 73.93; H, 5.43; N, 3.59. Found: C, 73.75; H, 5.69; N, 3.55. Treatment of an ethanolic solution of XIVa with aqueous sodium perchlorate yielded the corresponding perchlorate, XIVb. Recrystallization from acetonitrile–ethyl acetate gave material with mp 188–190°, undepressed (189–191°) upon admixture of authentic XIVb.

The *second* crop (above, from recrystallization of crude reaction product) consisted of 2.7 g of crude IXa monohydrate; two recrystallizations from acetonitrile–ethyl acetate raised the melting point to 213–216°; nmr ($CDCl_3$) superimposable upon that of authentic IXa monohydrate.

Authentic Anilinotriphenylphosphonium Perchlorate (XIVb). A small amount of anilinotriphenylphosphonium bromide, mp 195–203° from chloroform–ethyl acetate, prepared by the method of Horner,[8] was dissolved in ethanol and treated with aqueous sodium perchlorate. The perchlorate obtained was recrystallized from chloroform–ethyl acetate to give XIVb with mp 188–191°.

Anal. Calcd for $C_{24}H_{21}ClNO_4P$: C, 63.51; H, 4.66; N, 3.09. Found: C, 63.35; H, 4.69; N, 2.90.

Salt IXb. A solution of 5.0 g (22 mmoles) of chlorodiphenylacetonitrile in 5 ml of benzene was slowly added to 5.8 g (22 mmoles) of triphenylphosphine in 25 ml of benzene, and the mixture was stirred 15 min. Ice-bath cooling was applied and 3.0 g (22 mmoles) of N,N-dimethyl-*p*-phenylenediamine in 5 ml of benzene was added. The mixture was allowed to warm to room temperature and then refluxed for 10 min. There was collected 9.5 g (69%) of a yellow solid. Recrystallization from acetonitrile–ethyl acetate and then 2-propanol–ethyl acetate gave material with mp 231–234°, nmr ($CDCl_3$, τ): broad peak at −1.4, multiplet at 2.8, doublet at 3.73, doublet at 4.04 ($J_{P^{31}-H}$ = 2.2 cps), singlet at 7.17, peak area ratios 1.0:27:2.2:1.0:5.9.

Anal. Calcd for $C_{40}H_{37}ClN_3P$: C, 76.72; H, 5.96; Cl, 5.66; N, 6.71; P, 4.95. Found: C, 76.31; H, 6.11; Cl, 5.66; N, 6.67; P, 4.88.

Salt IXc. A solution of 5.0 g (22 mmoles) of chlorodiphenylacetonitrile in 5 ml of benzene was added to 5.8 g (22 mmoles) of triphenylphosphine in 25 ml of benzene. The mixture was stirred 15 min, then 3.1 g (22.5 mmoles) of *p*-nitroaniline in about 50 ml of a benzene–acetonitrile solution was added. The mixture was refluxed 15 min and then evaporated. The residue was recrystallized from acetone–ethyl acetate and then acetonitrile–ethyl acetate, to give 3.8 g of IXc, mp 213–214°, nmr ($CDCl_3$, τ): broad peak at −2.8, multiplet at 2.5, broad peak at 4.12, peak area ratios 0.8:29:0.9.

Anal. Calcd for $C_{38}H_{31}ClN_3O_2P$: C, 72.66; H, 4.98; Cl, 5.65; N, 6.69; P, 4.93. Found: C, 72.45; H, 5.26; Cl, 5.37; N, 6.71; P, 4.65.

Salt IXd. A mixture of 5.8 g (22 mmoles) of triphenylphosphine and 5.0 g (22 mmoles) of chlorodiphenylacetonitrile in 30 ml of benzene was stirred 15 min. A solution of 3.6 g (21 mmoles) of 3,4-dichloroaniline in 30 ml of benzenew as added. The mixture was refluxed 30 min; there was collected 9.0 g (62%) of IXd. Recrystallization from acetonitrile–ethyl acetonitrile gave material with mp 210–216°; nmr ($CDCl_3$, τ): broad peak at −2.9, multiplet at 2.76, doublet at 4.02 ($J_{P^{31}-H}$ = 2.5 cps), peak area ratios 0.9:28:0.9.

Anal. Calcd for $C_{38}H_{30}Cl_3N_2P$: C, 70.00; H, 4.64; Cl, 16.31; N, 4.30; P, 4.75. Found: C, 69.68; H, 4.89; Cl, 16.06; N, 4.28; P, 4.71.

Phosphinimine XVa. A solution of 1 g of sodium bicarbonate in 20 ml of water was added to a solution of 4 g of phosphonium salt IXa in 300 ml of acetone. The mixture was stirred 15 min, diluted with water, and evaporated to 3.3 g (89%) of crude XVa, mp 181–184°. Recrystallization from ethyl acetate and then benzene–hexane raised the melting point to 185–187°; infrared spectrum ($CHCl_3$): 6.40, 7.45, 9.00 μ; nmr ($CDCl_3$, τ): multiplet at 2.7, doublet at 3.62, doublet at 4.85 ($J_{P^{31}-H}$ = 7.5 cps), peak area ratios 28:1.7:0.8.

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(7) G. V. D. Tiers, "The 3M Handy Pocket Guide to Characteristic Nuclear Resonance Shielding Values, τ, for Hydrogen Bonded to Carbon," Minnesota Mining and Manufacturing Co., St. Paul, Minn.

(8) L. Horner and H. Oediger, *Ann.*, **627**, 142 (1959).

Anal. Calcd for $C_{38}H_{31}N_2P$: C, 83.49; H, 5.72; N, 5.13; P, 5.67. Found: C, 83.37; H, 5.78; N, 5.11; P, 5.72.

Phosphinimine XVb. A solution of 1 g of sodium carbonate in 10 ml of water was added to a solution of 2 g of salt IXb in 15 ml of methanol. The mixture was extracted with benzene, and the benzene extracts were washed, dried, and evaporated. There was obtained 1.7 g (90%) of crude XVb, mp 168–173°. Recrystallization from benzene–hexane raised the melting point to 178–181°; infrared spectrum ($CHCl_3$): 6.45, 7.50, 9.02 μ; nmr ($CDCl_3$, τ): multiplet at 2.7, quartet at 3.62, doublet at 4.83 ($J_{P^{31}-H} = 7.0$ cps), singlet at 7.25, peak area ratios 25:4.5:1.1:6.0.

Anal. Calcd for $C_{40}H_{36}N_3P$: C, 81.47; H, 6.15; N, 7.13; P, 5.25. Found: C, 81.27; H, 6.14; N, 7.05; P, 5.20.

Phosphinimine XVc. A solution of 0.5 g of sodium bicarbonate in 10 ml of water was added to a solution of 1 g of phosphonium salt IXc in 10 ml of methanol. The mixture was extracted with benzene and the extracts were washed, dried, and evaporated. There was obtained 0.9 g (95%) of crude XVc, mp 187–189°. Recrystallization from benzene–hexane gave yellow prisms with mp 188–190°; infrared spectrum ($CHCl_3$): 6.50, 7.60, 9.07 μ; nmr ($CDCl_3$, τ): multiplet at 2.7, doublet at 3.70, doublet at 5.01 ($J_{P^{31}-B} = 6.0$ cps), peak area ratios 27:2.1:1.2.

Anal. Calcd for $C_{38}H_{30}N_3O_2P$: C, 77.14; H, 5.11; N, 7.10; P, 5.24. Found: C, 77.06; H, 5.17; N, 6.97; P, 5.21.

Phosphinimine XVd. A solution of 1.5 g of sodium bicarbonate in 20 ml of water was added to a solution of 3 g of salt IXd in 20 ml of methanol. The mixture was diluted with water and extracted with benzene. There was obtained 2.3 g (82%) of the phosphinimine, mp 143–146°. Recrystallization from benzene–hexane yielded XVd having mp 144–146°; infrared spectrum ($CHCl_3$): 6.43, 7.38, 8.99 μ; nmr ($CDCl_3$, τ): multiplet at 2.6, doublet at 3.56, quartet at 3.84, doublet at 4.97 ($J_{P^{31}-H} = 7.0$ cps), peak area ratios 26:0.9:1.1:1.0.

Anal. Calcd for $C_{38}H_{29}Cl_2N_2P$: C, 74.15; H, 4.75; Cl, 11.52; N, 4.55. Found: C, 73.98; H, 4.66; Cl, 11.70; N, 4.70.

Treatment of II with Benzoic Acid. A solution of 5.0 g (22 mmoles) of chlorodiphenylacetonitrile in 10 ml of benzene was added to 5.8 g (22 mmoles) of triphenylphosphine in 30 ml of benzene. The mixture was stirred 15 min and then 2.7 g (22 mmoles) of benzoic acid was added. The mixture was refluxed 15 min and then evaporated. The residue was triturated with pentane. The solid residue was chromatographed on silica gel; there was obtained 4.3 g (100%) of crude diphenylacetonitrile, mp 58–65°. Recrystallization from aqueous methanol raised the melting point to 68–71°, undepressed upon addition of authentic diphenylacetonitrile. There was also obtained 4.9 g (80%) of triphenylphosphine oxide, mp 151–153°; the mixture melting point with authentic material was 152–154°. The pentane triturate was evaporated to 3.1 g of colorless oil, smelling strongly of benzoyl chloride. The infrared spectrum was almost identical with that of benzoyl chloride; a peak at 5.80 μ indicated the probable presence of benzoic anhydride.

A solution of 5 g of chlorodiphenylacetonitrile in 10 ml of benzene was added to 5.8 g of triphenylphosphine in 30 ml of benzene. After 15 min 3 g of phosphinimine V was added and then after 1 min, 2.7 g of benzoic acid. The mixture was refluxed 15 min and then evaporated. The residue was triturated with pentane. The remaining solid was washed with benzene. There remained 3.1 g of salt XI, mp 177–178°. Recrystallization raised the melting point to 181–184°, undepressed upon admixture of authentic material. The benzene washings were evaporated, and the residue was chromatographed on silica gel and alumina. There was obtained 2.9 g (69%) of diphenylacetonitrile, mp 65–70°, undepressed upon admixture of authentic material. There was also obtained 4.5 g (73%) of triphenylphosphine oxide, mp 139–152°; recrystallization from benzene–hexane raised the melting point to 145–153°, the mixture melting point with authentic material was 150–156°. There was also obtained 0.7 g of phosphinimine V, mp 139–147°. Recrystallization from benzene–hexane gave material with mp 148–151°, undepressed upon admixture of authentic material. The pentane triturate was evaporated to 2.8 g of oil having an infrared spectrum essentially identical with that of the benzoyl chloride–benzoic anhydride mixture obtained above.

Isoimides. A Kinetic Study of the Reactions of Nucleophiles with N-Phenylphthalisoimide[1a,b]

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Abstract: The pH–rate profile of the hydrolysis of N-phenylphthalisoimide (I) has been investigated in the pH range 0–11 (30°) and has been explained in terms of specific acid and specific base catalyzed pathways of hydrolysis, together with a small contribution by an uncatalyzed water reaction. A detailed kinetic study of the reactions of nucleophiles with I has revealed that nucleophilic agents may react with either neutral or protonated isoimide; in the former case, extensive rearrangement to N-phenylphthalimide (II) generally occurs. The reactivity of nine nucleophiles to the carbonyl group of I has been found to parallel closely the reactivity of the same nucleophiles to *p*-nitrophenyl acetate.

Since the initial report[2] of the isolation of an isoimide in 1893, isoimide intermediates have been proposed to occur in a wide array of reactions. Recent examples include the conversion of amides to nitriles (by means of mixed carboxylic–sulfonic anhydrides,[3] arylsulfonyl chlorides,[4] or N,N′-dicyclohexylcarbodiimide[4,5]), the Beckmann rearrangement of an oxime tosylate,[6] the reaction of amides with acid chlorides,[7] the photooxidation of substituted oxazoles,[8] and the reaction of the N-ethylbenzisoxazolium cation with carboxylate

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[1] (a) Taken from a dissertation to be presented by M. L. E. in partial fulfillment of the requirements for the Ph.D. degree, Yale University. (b) Financial support by the National Institutes of Health (Grant No. AM-04288) is gratefully acknowledged. (c) Trainee of the U. S. Public Health Service, 1963–1965; Postdoctoral Fellow of the National Institutes of Health, 1965–1966.

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