Reactions of Phosphorus Compounds. X. The Reactions of α-Halo Ketones and Nitriles with Tertiary Phosphines and Phosphites

R. D. Partos and A. J. Speziale

Contribution from Monsanto Company, Agricultural Division, Research
Department, St. Louis, Missouri 63166. Received July 28, 1965

Stable enol phosphonium salts were isolated from the reaction of certain α-haloacetophenones and triphenylphosphine. Pyrolysis and solvolysis of the enol phosphonium salts were also studied. The stereochemistry of the pyrolysis of IIb is discussed. Treatment of chlorodiphenylacetonitrile with triphenylphosphine led to the formation of an intermediate which, upon being treated with methanol, afforded the N-acylphosphinimine XIV. Treatment of chlorodiphenylacetonitrile with triethyl phosphite led to ketene imine XXIV and tetraphenylsuccinonitrile as a by-product. The formation of stable enol phosphonium salts, N-acylphosphinimine, ketenimine, and tetraphenylsuccinonitrile is interpreted mechanistically as involving the initial attack of the phosphorus compound at halogen in the halo ketone or nitrile. The reactions are discussed in terms of an intermediate ion pair.

The reaction of trihaloacetamides with tertiary phosphines and phosphites has been shown to lead to trihalovinylamines *via* the halogenm igration reaction.[1,2] This paper deals with the extension of this reaction to α-haloacetophenones and nitriles.

Enol phosphonium salts have been postulated[1-4] as intermediates in the Perkow[5] and halogen migration reactions.[1,2] Although these intermediates could be formed by attack of the phosphorus compound at carbonyl carbon[3] or oxygen,[1,6] it seems most likely that they are formed *via* a mechanism involving halogen attack.[2,7,8]

Enol phosphonium salts have been reported previously[6,7] but little physical data have been given in their support. In a recent communication[9] we reported the first isolation and characterization of an enol phosphonium salt—that obtained by treatment of chlorodiphenylacetophenone (Ia) with triphenylphosphine.

Treatment of chlorodiphenylacetophenone (Ia), dichlorophenylacetophenone (Ib), and trichloroacetophenone (Ic) with triphenylphosphine leads to the formation in good yield (62–78%), of enol phosphonium salts IIa, b, and c, respectively. Correct elemental analyses were obtained on all three hygroscopic salts. The infrared spectra showed only trace carbonyl ab-

(1) A. J. Speziale and R. C. Freeman, *J. Am. Chem. Soc.*, 82, 903 (1960).
(2) A. J. Speziale and L. R. Smith, *ibid.*, 84, 1868 (1962).
(3) M. S. Kharasch and I. S. Bengelsdorf, *J. Org. Chem.*, 20, 1356 (1955).
(4) I. J. Borowitz and L. I. Grossman, *Tetrahedron Letters*, 471 (1962).
(5) W. Perkow, *Ber.*, 87, 755 (1954); W. Perkow, E. W. Krockow, and K. Knoevenagel, *ibid.*, 88, 662 (1955).
(6) S. Trippett, *J. Chem. Soc.*, 2337 (1962).
(7) H. Hoffmann and H. J. Diehr, *Tetrahedron Letters*, 583 (1962).
(8) I. J. Borowitz and R. Virkhaus, *J. Am. Chem. Soc.*, 85, 2183 (1963).
(9) A. J. Speziale and R. D. Partos, *ibid.*, 85, 3312 (1963).

a, R¹ = R² = C₆H₅
b, R¹ = C₆H₅; R² = Cl
c, R¹ = R² = Cl
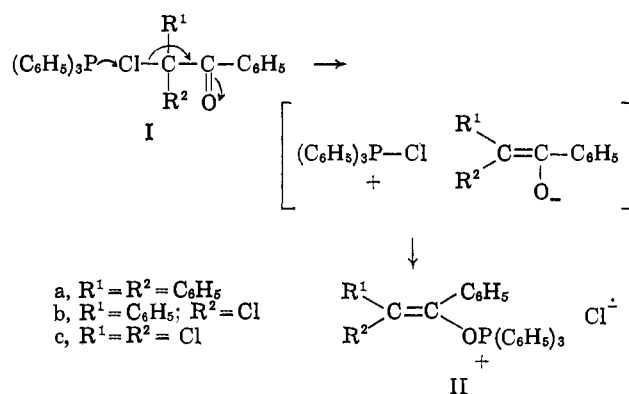
sorption, probably as a result of slight hydrolysis during transfers. Proton magnetic resonance analysis (n.m.r.) of salt IIa showed a multiplet centered at about τ 2.6. The P^{31} magnetic resonance spectrum exhibited a single peak at −63 p.p.m. relative to 85% phosphoric acid.

α-Benzoyl-α-chlorobenzyltriphenylphosphonium chloride (IIIa) and the corresponding perchlorate IIIb
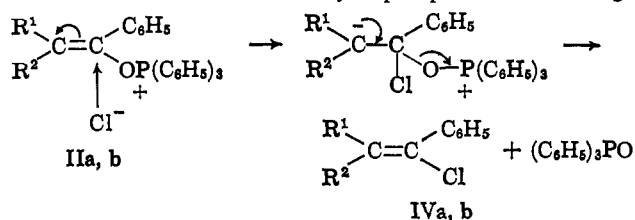

IIIa, X = Cl
b, X = ClO₄
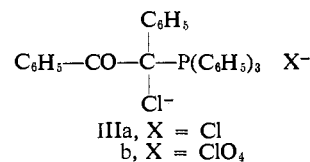
were prepared in order to compare the enol phosphonium salt IIb with its corresponding C-phosphonium salt. Salts IIIa and IIIb exhibited strong carbonyl absorption at 6.80 and 6.79 μ, respectively. They were considerably more stable to prototropic solvents than the enol phosphonium salts.

Solvolysis of salts IIa, b, and c in aqueous methanol yielded the corresponding dehalogenated ketones in excellent yield (67–81%).
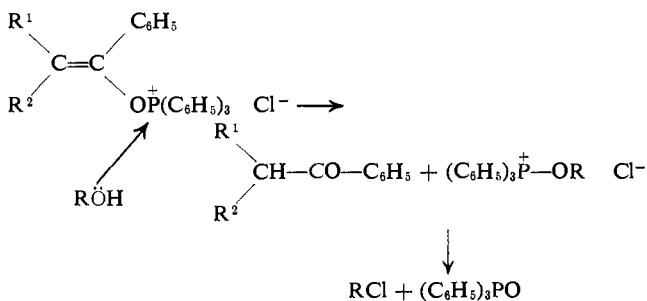
The pyrolysis of salts IIa and IIb at about 200° led to the expected products of the halogen migration reaction, triphenylchloroethylene (IVa) and dichlorostilbene (IVb). The pyrolysis of IIb was especially interesting since either *cis*- or *trans*-dichlorostilbene

could be formed. The pyrolysis product consisted of 73% *cis-* and 27% *trans*-dichlorostilbene. The isomer distribution was determined by vapor phase chromatog-
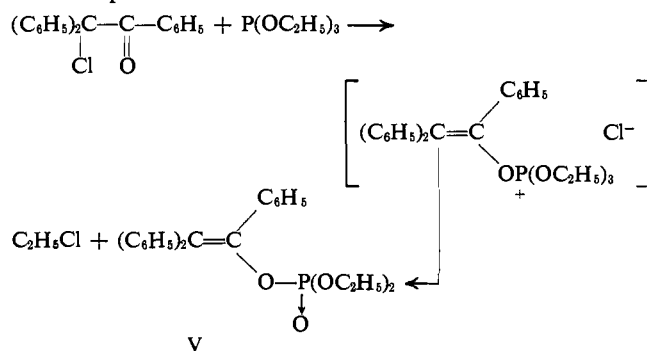
$$R^1\diagdown C\!\!=\!\!C\diagup C_6H_5 \quad\to\quad R^1\diagdown C\!-\!C\diagup C_6H_5 \quad\to$$
$$R^2\diagup \uparrow OP(C_6H_5)_3 \qquad R^2\diagup \underset{Cl}{|}\ O\!-\!P(C_6H_5)_3$$
$$\underset{Cl^-}{+} \qquad\qquad\qquad +$$
$$\textbf{IIa, b}$$

$$R^1\diagdown C\!\!=\!\!C\diagup C_6H_5 + (C_6H_5)_3PO$$
$$R^2\diagup \diagdown Cl$$
$$\textbf{IVa, b}$$

raphy and the authentic dichlorostilbenes were prepared for purposes of comparison. The *cis–trans* isomer distribution corresponds to the composition of the equilibrium mixture of the two dichlorostilbenes (75% *cis* and 25% *trans*). Their isomerization is slow at 200°.[10]
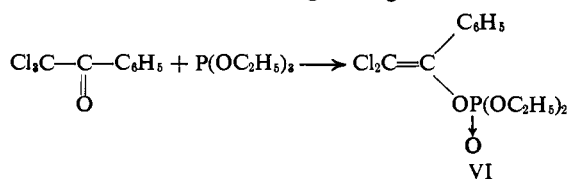
Enol phosphonium salt IIb was also pyrolyzed in the presence of excess *trans*-dichlorostilbene. Isomerization of the *trans* olefin was extremely slow. After 5 min. the product distribution was 60% *trans*, and this changed to only 57% *trans* after an additional 30 min. Since the original pyrolysis had been carried out for only 5 min., equilibration of the product olefins could not have occurred.

The formation of an equilibrium mixture of olefins must therefore be attributed to a similarity of the pyrolysis transition states to the final product olefins. That is, whatever causes *cis*-dichlorostilbene to predominate in equilibrium also causes the transition state leading to *cis* olefin in pyrolysis to be of lower energy than that leading to *trans*. Taylor and Murray[10] have attributed this to attractive London forces between the chlorine atoms.

The reaction of chlorodiphenylacetophenone with a tertiary phosphite was also investigated. Treatment of chlorodiphenylacetophenone with triethyl phosphite yielded diethyl triphenylvinyl phosphate (V), the normal Perkow product. No intermediate was isolated. The
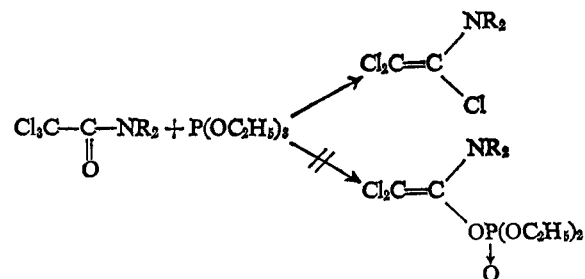
$$(C_6H_5)_2C\!-\!C\!-\!C_6H_5 + P(OC_2H_5)_3 \longrightarrow$$
$$\underset{Cl}{|}\ \underset{O}{\|}$$

$$\left[(C_6H_5)_2C\!\!=\!\!C\diagup C_6H_5\quad Cl^-\right]$$
$$\diagdown OP(OC_2H_5)_3$$
$$+$$

$$C_2H_5Cl + (C_6H_5)_2C\!\!=\!\!C\diagup C_6H_5$$
$$\diagdown O\!-\!P(OC_2H_5)_2 \longleftarrow$$
$$\downarrow$$
$$O$$
$$\textbf{V}$$

reaction of trichloroacetophenone with triethyl phosphite is also known[11] to yield the corresponding enol phosphate (VI). Thus α-halo acetophenones undergo the Perkow reaction with trialkyl phosphites, whereas α-haloamides react *via* the halogen migration reaction.[1,2]

$$Cl_3C\!-\!C\!-\!C_6H_5 + P(OC_2H_5)_3 \longrightarrow Cl_2C\!\!=\!\!C\diagup C_6H_5$$
$$\underset{O}{\|} \qquad\qquad\qquad\qquad \diagdown OP(OC_2H_5)_2$$
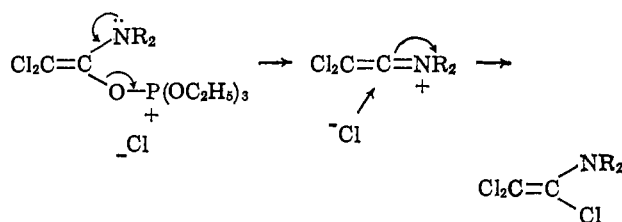$$\downarrow$$
$$O$$
$$\textbf{VI}$$

(10) T. S. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938).
(11) A. N. Pudovik and L. G. Biktimerova, *Zh. Obsch. Khim.*, 27, 1708 (1957).

It is apparent that an electron-donating group such as amino must be adjacent to the carbonyl group to

$$Cl_3C\!-\!C\!-\!NR_2 + P(OC_2H_5)_3 \nearrow\!\!\!\!\nearrow \begin{array}{c} Cl_2C\!\!=\!\!C\diagup NR_2 \\ \diagdown Cl \end{array}$$
$$\underset{O}{\|} \qquad\qquad\qquad /\!\!\!\!/ \begin{array}{c} Cl_2C\!\!=\!\!C\diagup NR_2 \\ \diagdown OP(OC_2H_5)_2 \\ \downarrow \\ O \end{array}$$
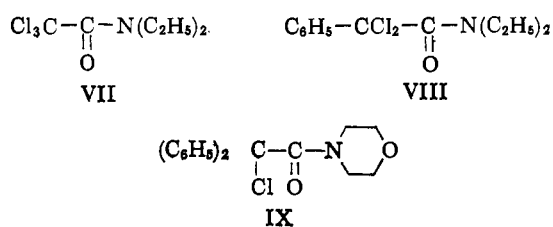
facilitate the collapse of the intermediate enol phosphonium salt to halo olefin instead of enol phosphate. This supports the mechanism postulated by Speziale and Smith,[2] in which the enol phosphonium salt fragments prior to attack of chloride ion.

$$Cl_2C\!\!=\!\!C\overset{\curvearrowleft}{\diagdown}NR_2 \longrightarrow Cl_2C\!\!=\!\!C\!\!=\!\!\overset{+}{N}R_2 \longrightarrow$$
$$\diagdown O\!-\!P(OC_2H_5)_3 \qquad\qquad \diagup$$
$$+ \qquad\qquad\qquad -Cl$$
$$-Cl$$

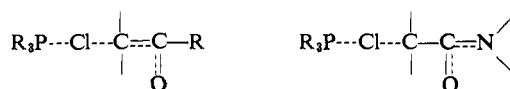$$Cl_2C\!\!=\!\!C\diagup NR_2$$
$$\diagdown Cl$$

The enol phosphonium salts II, however, can only collapse *via* an addition–elimination mechanism as shown earlier. It is to this difference that the relative stability of these enol phosphonium salts is due.

Although N,N-diethyltrichloroacetamide (VII) and N,N-diethyldichlorophenylacetamide (VIII) react readily with triphenylphosphine[1,2] to give the corresponding vinylamines, chlorodiphenylacetmorpholide (IX) was recovered unchanged after treatment with triphenylphosphine. The ketones Ia–c, corresponding to amides IX, VIII, and VII, all reacted readily with triphenylphosphine, however. Thus, the α-halo ketones are more reactive than the corresponding amides with respect to halogen attack. This difference is attributable to the greater facility of the

$$Cl_3C\!-\!C\!-\!N(C_2H_5)_2 \qquad C_6H_5\!-\!CCl_2\!-\!C\!-\!N(C_2H_5)_2$$
$$\underset{O}{\|} \qquad\qquad\qquad\qquad \underset{O}{\|}$$
$$\textbf{VII} \qquad\qquad\qquad\qquad \textbf{VIII}$$

$$(C_6H_5)_2\ \ C\!-\!C\!-\!N\diagup\diagdown O$$
$$\underset{Cl}{|}\ \underset{O}{\|}$$
$$\textbf{IX}$$

ketone carbonyl to stabilize the negative charge on an adjacent carbon atom in the transition state, as compared to the amide carbonyl, with its electron-donating amino moiety. Furthermore, the order of reactivity
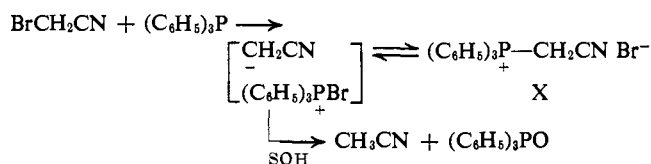
$$R_3P\!\cdots\!Cl\!\cdots\!\underset{|}{C}\!\!=\!\!\underset{|}{C}\!-\!R \qquad R_3P\!\cdots\!Cl\!\cdots\!\underset{|}{C}\!-\!\underset{|}{C}\!\!=\!\!N\diagup$$
$$\underset{O}{\|} \qquad\qquad\qquad\qquad \underset{O}{\|}$$

of the α-halo ketones was Ic > Ib > Ia. Halogen atoms are better able to stabilize the carbanion formed by halogen attack than are phenyl groups.
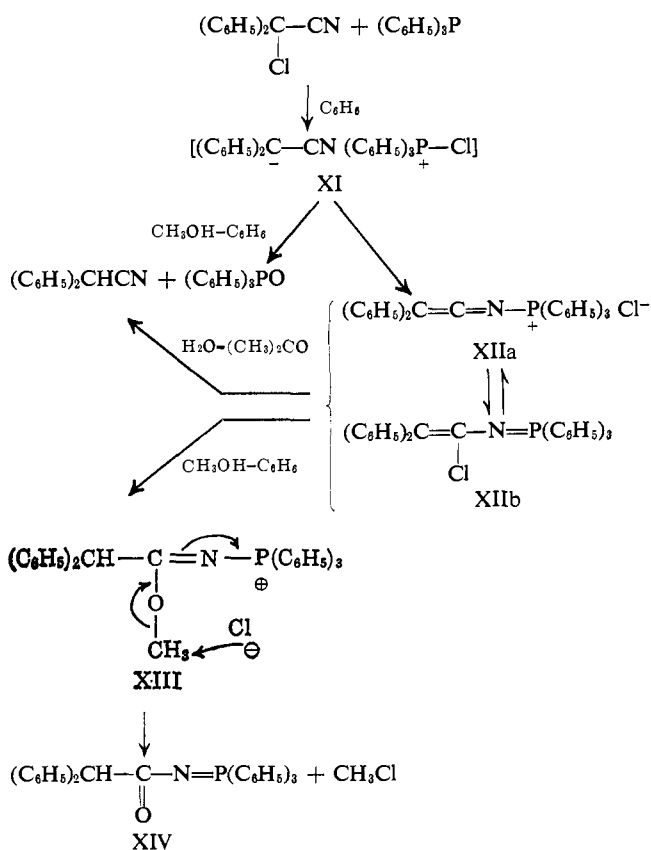
Schiemenz and Engelhard[12] have reported that bromoacetonitrile and triphenylphosphine reacted in anhydrous benzene to give the usual C-phosphonium

(12) G. P. Schiemenz and H. Engelhard, *Ber.*, 94, 578 (1961).

salt, X, but in the presence of aqueous methanol the main products were triphenylphosphine oxide and acetonitrile. Since X was found to be stable in boiling water, it seems probable that the reaction proceeds through halogen attack. The ion pair recombines to X under anhydrous conditions, but is "trapped" by prototropic solvents and converted to acetonitrile and triphenylphosphine oxide.[2]

$$BrCH_2CN + (C_6H_5)_3P \longrightarrow$$

$$\begin{bmatrix} CH_2CN \\ \overset{-}{} \\ (C_6H_5)_3PBr \\ \overset{+}{} \end{bmatrix} \rightleftharpoons (C_6H_5)_3\overset{+}{P}-CH_2CN\ Br^- \qquad X$$

$$\overset{\displaystyle\longmapsto}{\underset{SOH}{}} CH_3CN + (C_6H_5)_3PO$$

When chlorodiphenylacetonitrile was treated first with triphenylphosphine in benzene and then with methanol, the major product (49%) was acylphosphinimine XIV, presumably via XI → XII → XIII. Steric hindrance may prevent recombination of ion pair XI at carbon to form a C-phosphonium salt; instead

$$(C_6H_5)_2\overset{|}{\underset{Cl}{C}}-CN + (C_6H_5)_3P$$

$$\downarrow C_6H_6$$

$$[(C_6H_5)_2\overset{-}{C}-CN\ (C_6H_5)_3\overset{+}{P}-Cl]$$
XI

CH₃OH–C₆H₆ ↙ ↘

$(C_6H_5)_2CHCN + (C_6H_5)_3PO$

$(C_6H_5)_2C=C=N-\overset{+}{P}(C_6H_5)_3\ Cl^-$
XIIa

↕

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

H₂O–(CH₃)₂CO

CH₃OH–C₆H₆

$$(C_6H_5)_2CH-\underset{\underset{\underset{XIII}{CH_3\leftarrow\ominus}}{\overset{|}{\underset{O}{\overset{|}{\ominus}}}}{C}\overset{\frown}{=N}-\overset{\oplus}{P}(C_6H_5)_3$$

$$\downarrow$$

$$(C_6H_5)_2CH-\underset{O}{\overset{\|}{C}}-N=P(C_6H_5)_3 + CH_3Cl$$
XIV

recombination occurs at nitrogen. When methanol was present in the *original* reaction mixture, the main products were triphenylphosphine oxide and diphenylacetonitrile (presumably formed by the trapping of ion pair XI). Only a very small amount of XIV could be isolated. (An alternate mechanism for the formation of XIIa would involve nitrogen attack. In this instance the ion pair would not be an intermediate but XIIa would be formed directly.) In order to trap XI, a 50% methanol–

$$(C_6H_5)_2C\overset{\frown}{\underset{Cl}{\overset{|}{\smile}}}C\equiv N\overset{\frown}{}:P(C_6H_5)_3 \longrightarrow XIIa$$
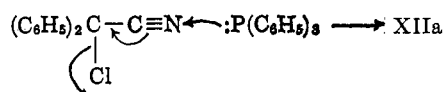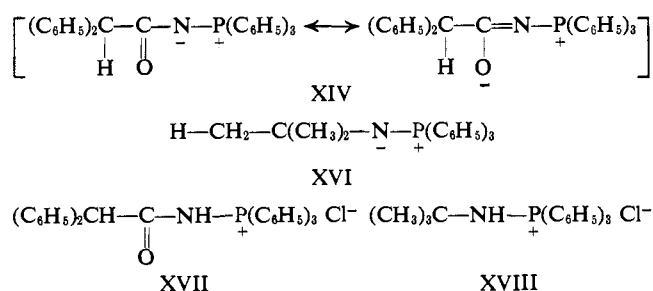
benzene solution was required. In the presence of only 1 equiv. of methanol the reaction still yielded

primarily XIV. The recombination of ion pair XI to XII is therefore extremely rapid. A "cage effect" may be operative. Since the conversion of XII to XIV had originally been accomplished with only 1 equiv. of methanol, it was necessary to ascertain the effect of 50% methanol–benzene on XII. The initial reaction mixture of triphenylphosphine and chlorodiphenylacetonitrile in benzene was evaporated after 15 min. and the residual glassy material was treated with 50% methanol–benzene. There was indeed obtained a 57% yield of XIV. The amber glass left by evaporation of the initial reaction material exhibited strong infrared absorption at 4.12, 6.29, and 9.02 μ. It is uncertain whether the benzene-soluble material exists as XIIa or b or a mixture of the two.

The infrared spectrum of XIV exhibited three strong bands, at 6.35, 7.56, and 9.06 μ. This absorption pattern is typical of acylphosphoranes. Benzoylmethylenetriphenylphosphorane, XV, exhibits peaks at 6.53, 7.19, and 9.04 μ.[13] The n.m.r. spectrum of XIV

$$C_6H_5-\underset{\underset{O}{\|}}{C}-CH=P(C_6H_5)_3$$
XV
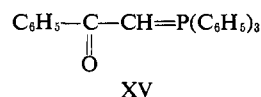
showed a multiplet at about τ 2.7 and a doublet at 4.77. The ratio of the peak areas was 25:0.85 (the theoretical value is 25:1). The splitting of the benzhydryl proton ($J_{P^{31}-H} = 3.2$ c.p.s.) is probably due to spin–spin coupling with phosphorus. A PNCCH interaction has been observed[14] in N-*t*-butyltriphenylphosphinimine (XVI); $J_{P^{31}-H} = 1.21$ c.p.s. The slightly larger splitting constant for XIV may be due to partial double bond character of the C–N bond as a result of resonance interaction with the carbonyl group. Addition of hydrogen chloride to XIV to yield salt XVII resulted in the disappearance of coupling. Similarly, when hydrogen chloride was added to XVI to yield XVIII, the coupling constant was reduced to 0.58 c.p.s. The change in coupling constants in the salts has been ascribed to either alteration of electron density or variation of bond angles.[14]

$$\begin{bmatrix} (C_6H_5)_2\underset{\underset{H}{\overset{|}{}}}{C}-\underset{\underset{O}{\overset{\|}{}}}{\overset{-}{C}}-N-\overset{+}{P}(C_6H_5)_3 \longleftrightarrow (C_6H_5)_2\underset{\underset{H}{\overset{|}{}}}{C}-\underset{\underset{O}{\overset{-}{}}}{C}=N-\overset{+}{P}(C_6H_5)_3 \end{bmatrix}$$
XIV

$$H-CH_2-C(CH_3)_2-\overset{-}{N}-\overset{+}{P}(C_6H_5)_3$$
XVI

$(C_6H_5)_2CH-\underset{O}{\overset{\|}{C}}-NH-\overset{+}{P}(C_6H_5)_3\ Cl^-$ $(CH_3)_3C-NH-\overset{+}{P}(C_6H_5)_3\ Cl^-$
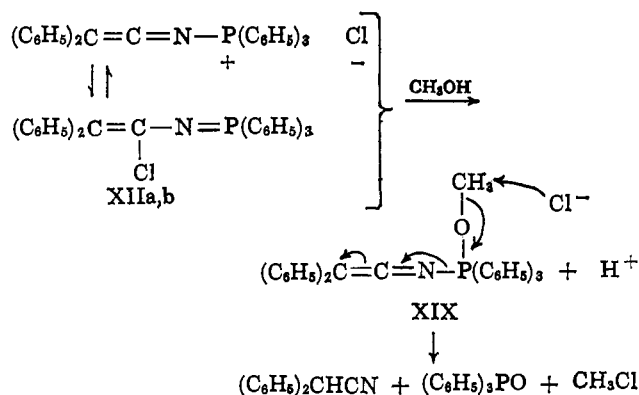
      XVII   XVIII

Some indication for the formation of XIII has been observed. The addition of methanol to the cooled reaction mixture of triphenylphosphine and chlorodiphenylacetonitrile in benzene caused formation of a precipitate, probably the salt XIII. When the mixture was warmed, methyl chloride (identified by n.m.r.) was evolved and the precipitate disappeared. About 33% triphenylphosphine oxide and a small amount of diphenylacetonitrile were also isolated from the reaction. These products were probably formed by
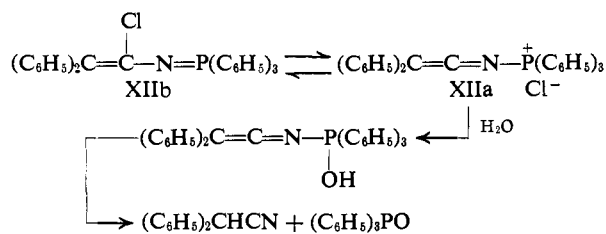
(13) A. J. Speziale and K. W. Ratts, *J. Org. Chem.*, **28**, 465 (1963).
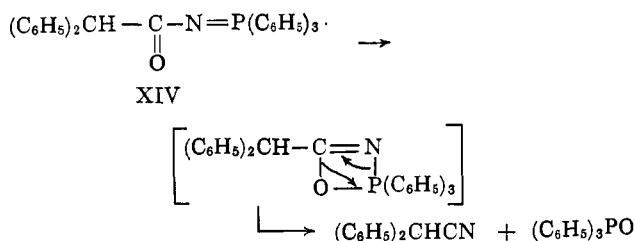(14) F. Kaplan, G. Singh, and H. Zimmer, *J. Phys. Chem.*, **67**, 2560 (1963).

attack of methanol at phosphorus followed by collapse of the intermediate XIX to final products. Treatment

$$(C_6H_5)_2C=C=N-P(C_6H_5)_3 \quad Cl^-$$
$$+$$
$$\updownarrow$$
$$(C_6H_5)_2C=C-N=P(C_6H_5)_3$$
$$|$$
$$Cl$$
$$XIIa,b$$

$\xrightarrow{CH_3OH}$

$$CH_3 \quad Cl^-$$
$$|$$
$$O$$
$$|$$
$$(C_6H_5)_2C=C=N-P(C_6H_5)_3 + H^+$$
$$XIX$$

$$\downarrow$$

$$(C_6H_5)_2CHCN + (C_6H_5)_3PO + CH_3Cl$$

of XII with aqueous acetone yielded diphenylacetonitrile (72%) and triphenylphosphine oxide (59%). There was obtained only 1% of phosphinimine XIV. Treatment of XII with water converts it to diphenylacetonitrile and triphenylphosphine oxide, while treatment with methanol yields predominantly phosphinimine XIV. A possible explanation for the difference in behavior is that in the more polar solvent, aqueous acetone, an appreciable amount of XIIa exists, favoring nucleophilic attack at phosphorus.

$$Cl$$
$$|$$
$$(C_6H_5)_2C=C-N=P(C_6H_5)_3 \rightleftharpoons (C_6H_5)_2C=C=N-\overset{+}{P}(C_6H_5)_3$$
$$XIIb \qquad\qquad XIIa \quad Cl^-$$

$$\left[\!\!-\!\!-(C_6H_5)_2C=C=N-P(C_6H_5)_3 \xleftarrow{H_2O}\right.$$
$$|$$
$$OH$$

$$\left.\!\!\longrightarrow (C_6H_5)_2CHCN + (C_6H_5)_3PO\right.$$

Pyrolysis of phosphinimine XIV affords quantitative yields of diphenylacetonitrile and triphenylphosphine oxide. Staudinger[15] has carried out similar pyrolyses on other acylphosphinimines.

$$(C_6H_5)_2CH - C - N = P(C_6H_5)_3 \cdot \qquad \longrightarrow$$
$$\|$$
$$O$$
$$XIV$$

$$\left[\begin{array}{c} (C_6H_5)_2CH - C = N \\ | \quad | \\ O \cdots P(C_6H_5)_3 \end{array}\right]$$
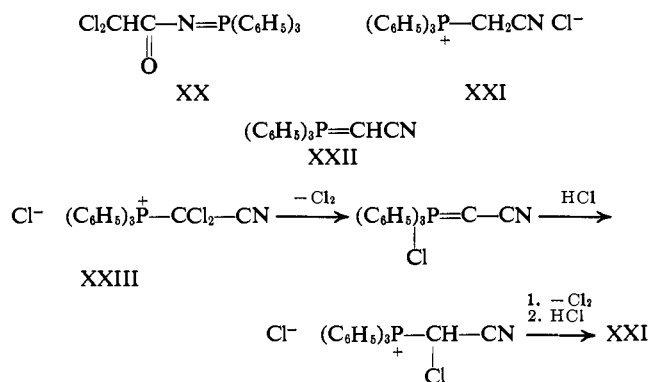
$$\longrightarrow (C_6H_5)_2CHCN + (C_6H_5)_3PO$$

Reactions of other nucleophiles with XII are being studied and will be disclosed in a subsequent paper.
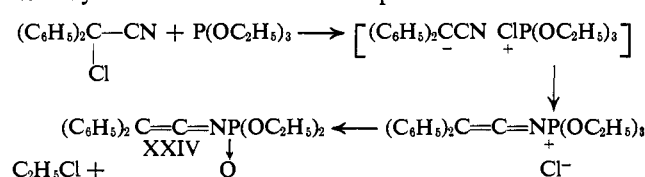
The reaction of trichloroacetonitrile with triphenylphosphine in benzene followed by methanol treatment, yielded the expected acylphosphinimine XX in poor yield. There was also obtained a small amount of phosphonium salt XXI, identified by its elemental analysis and conversion to the phosphorane XXII upon treatment with base. Formation of XXI may occur via C-phosphonium salt XXIII followed by repeated elimination of chlorine and addition of hydrogen chloride.

When chlorodiphenylacetonitrile is treated with triethyl phosphite in benzene, in the absence of methanol, an interesting modification of the Perkow reaction occurs. The product is the ketene imine XXIV.
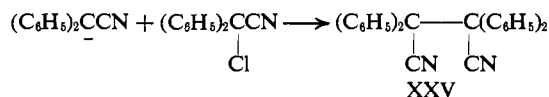
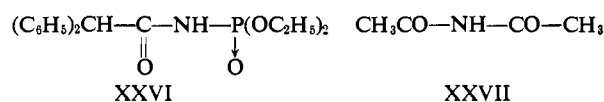(15) H. Staudinger and E. Hauser, *Helv. Chim. Acta*, 4, 861 (1921).

$$Cl_2CHC-N=P(C_6H_5)_3 \qquad (C_6H_5)_3\overset{+}{P}-CH_2CN \; Cl^-$$
$$\|$$
$$O$$
$$XX \qquad\qquad\qquad XXI$$

$$(C_6H_5)_3P=CHCN$$
$$XXII$$

$$Cl^- \; (C_6H_5)_3\overset{+}{P}-CCl_2-CN \xrightarrow{-Cl_2} (C_6H_5)_3P=C-CN \xrightarrow{HCl}$$
$$| $$
$$Cl$$
$$XXIII$$

$$Cl^- \; (C_6H_5)_3\overset{+}{P}-CH-CN \xrightarrow[2. \; HCl]{1. \; -Cl_2} XXI$$
$$|$$
$$Cl$$

Ethyl chloride evolved during the reaction was identified by n.m.r. The infrared spectrum of XXIV exhibited strong absorption at

$$(C_6H_5)_2C-CN + P(OC_2H_5)_3 \longrightarrow \left[(C_6H_5)_2\underset{-}{C}CN \; Cl\overset{+}{P}(OC_2H_5)_3\right]$$
$$|$$
$$Cl$$

$$\downarrow$$

$$(C_6H_5)_2C=C=NP(OC_2H_5)_2 \longleftarrow (C_6H_5)_2C=C=N\overset{+}{P}(OC_2H_5)_3$$
$$XXIV \downarrow \qquad\qquad\qquad\qquad\qquad Cl^-$$
$$C_2H_5Cl + \qquad O$$

hibited strong absorption at 4.95 μ, typical of ketene imines.[16] N.m.r. analysis showed a singlet at τ 2.76, a multiplet at 6.03, and a multiplet at 8.85; the peak areas were in the ratio 10:3.8:5.8 (theory 10:4:6). There was also obtained from the reaction a small amount of tetraphenylsuccinonitrile (XXV). This supports the halogen attack mechanism since the material probably arises via attack of diphenyl cyanomethyl carbanion on chlorodiphenylacetonitrile.

$$(C_6H_5)_2CCN + (C_6H_5)_2CCN \longrightarrow (C_6H_5)_2C\!-\!\!-\!\!C(C_6H_5)_2$$
$$| \qquad\qquad\qquad\qquad\qquad | \quad |$$
$$Cl \qquad\qquad\qquad\qquad\qquad CN \; CN$$
$$\qquad\qquad\qquad\qquad\qquad\qquad XXV$$

Ketenimine XXIV was hydrolyzed with dilute hydrochloric acid to amide phosphate XXVI, which exhibits carbonyl absorption in the infrared at 5.85 μ. The carbonyl absorption for diacetylamine, XXVII, has been reported[17] at 5.85 μ.

$$(C_6H_5)_2CH-C-NH-P(OC_2H_5)_2 \qquad CH_3CO-NH-CO-CH_3$$
$$\| \qquad\qquad \downarrow$$
$$O \qquad\qquad O$$
$$XXVI \qquad\qquad\qquad\qquad XXVII$$

Experimental Section[18]

Enol Phosphonium Salt IIa. A solution of 15.2 g. (0.0497 mole) of chlorodiphenylacetophenone, m.p. 78–81°, prepared by the procedure of Stevens and Tazuma,[19] and 13.0 g. (0.0497 mole) of triphenylphosphine in 70 ml. of xylene was refluxed for 45 min. The mixture was filtered in a dry atmosphere and residual solvent was removed in a vacuum desiccator to give a 19 g. (68%) yield of IIa. The infrared absorption spectrum of this material was as follows (purified CHCl₃): 3.40 (s), 4.16 (w), 5.92 (w), 6.30 (m), 6.74 (m), 6.96 (s), 8.58 (s), 8.94 (s), 9.63 (s), 9.86

(16) C. L. Stevens and J. C. French, *J. Am. Chem. Soc.*, 75, 657 (1953).

(17) S. F. D. Orr, P. Sims, and D. Manson, *J. Chem. Soc.*, 1337 (1956).

(18) 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. N.m.r. spectra were determined on a Varian A-60 spectrophotometer. The chloroform for the infrared spectra of salts II was purified by shaking with concentrated sulfuric acid, washing with water, and drying with magnesium sulfate.

(19) C. L. Stevens and J. Tazuma, *J. Am. Chem. Soc.*, 76, 715 (1954).

(s), 10.05 (s), and 10.34 (s) μ. Proton magnetic resonance analysis disclosed a multiplet centered at about τ 2.6. The phosphorus-31 magnetic resonance spectrum exhibited a peak at -63 p.p.m. relative to 85% phosphoric acid.

Anal. Calcd. for $C_{38}H_{30}ClOP$: C, 80.28; H, 5.28; Cl, 6.16; ionic Cl, 6.16; P, 5.46. Found: C, 80.05; H, 5.49; Cl, 6.18; ionic Cl, 6.16; P, 5.48.

Enol Phosphonium Salt IIb. Triphenylphosphine, 5 g. (0.019 mole), and 5 g. (0.019 mole) of dichlorophenyl-acetophenone, m.p. 58–60°, prepared by the procedure of Zinin,[20] were refluxed in 30 ml. of benzene for 15 min. The enol phosphonium salt was collected in a dry atmosphere, washed with benzene and ether, and residual solvent was removed in a vacuum desiccator. The yield was 6.2 g. (62%). The infrared absorption spectrum was as follows (purified CHCl₃): 3.43 (s), 4.08 (w), 5.91 (w), 6.31 (m), 6.76 (w), 6.97 (s), 8.92 (s), 9.59 (m), 9.83 (m), 10.03 (m), and 10.36 (m) μ.

Anal. Calcd. for $C_{32}H_{25}Cl_2OP$: C, 72.87; H, 4.78; Cl, 13.44; ionic Cl, 6.72; P, 5.87. Found: C, 72.67; H, 4.94; Cl, 13.41; ionic Cl, 6.62; P, 6.04.

Enol Phosphonium Salt IIc. To a solution of 6.1 g. (0.023 mole) of triphenylphosphine in 40 ml. of benzene was slowly added 5 g. (0.023 mole) of trichloro-acetophenone, b.p. 97° (0.3 mm.), prepared according to the procedure of Cohen,[21] in 10 ml. of benzene. The mixture was stirred at room temperature for 30 min. The salt was collected in a dry atmosphere, washed with benzene and ether, and residual solvent was removed in a vacuum desiccator. The yield was 8.7 g. (78%). The infrared absorption spectrum was as follows (purified CHCl₃): 3.48 (s), 4.11 (w), 5.91 (w), 6.36 (m), 6.81 (m), 7.0 (s), 8.99 (s), 9.50 (s), 9.80 (m), 10.08 (m), 10.21 (s), and 11.21 (m) μ.

Anal. Calcd. for $C_{26}H_{20}Cl_3OP$: C, 64.28; H, 4.15; Cl, 21.90; ionic Cl, 7.30; P, 6.38. Found: C, 64.05; H, 4.20; Cl, 21.80; ionic Cl, 7.07; P, 6.16.

Phosphonium Salts IIIa, b. α-Benzoylbenzylidene triphenylphosphorane, m.p. 188–191°, was prepared by the method of Trippett.[22] Conversion to IIIa was accomplished by adding 210 mg. of the phosphorane to 15 ml. of chloroform, saturated with chlorine. The mixture was evaporated immediately to an oil, crude salt IIIa, infrared absorption (capillary film): 3.50 (s), 4.10 (w), 6.02 (s), 6.32 (m), 6.80 (m), 7.00 (s), 8.1 (s), 8.48 (m), 9.16 (s), 9.86 (m), and 10.05 (m) μ.

The above oil was dissolved in 10 ml. of methanol and 1 ml. of 70% perchloric acid was added. The solution was warmed and water was added. When the solution cooled, there was obtained 250 mg. of IIIb, m.p. 230–232°. Infrared absorption was as follows (CHCl₃): 2.88 (w), 3.38 (m), 6.02 (s), 6.32 (s), 6.79 (m), 7.00 (s), 7.63 (m), 9.25 (s), 9.88 (m), and 10.03 (s) μ.

Anal. Calcd. for $C_{32}H_{25}Cl_2O_5P$: C, 64.98; H, 4.26; Cl, 11.99; P, 5.24. Found: C, 64.63; H, 4.12; Cl, 11.92; P, 5.37.

Solvolysis of IIa. A solution of 5 g. of IIa in about 75 ml. of aqueous methanol was warmed for 0.5 hr. and then diluted with water and extracted with ether and then chloroform. The combined extracts were dried and evaporated to give 4.7 g. of a pale yellow solid. Chromatography on 125 g. of silica gel gave 1.6 g. (67%) diphenylacetophenone, m.p. 132–136°. Recrystallization from benzene–hexane raised the melting point to 134–136°, undepressed upon admixture of authentic diphenylacetophenone, m.p. 135–136°. There was also obtained 2.3 g. (76%) of crude triphenylphosphine oxide. Recrystallization from benzene–hexane yielded 1.2 g. (50%) of triphenylphosphine oxide, m.p. 154–157°, mixture melting point with authentic material 155–158°.

Authentic Diphenylacetophenone. Diphenylaceto-phenone, m.p. 135–136°, was prepared by treatment of desylchloride[23] with benzene in the presence of alumi-num chloride, by the method of Anschütz and Förster.[24]

Solvolysis of IIb. To a solution of 9.0 g. (0.017 mole) of enol phosphonium salt IIb in 30 ml. of meth-anol was added 5 ml. of water. The mixture was stirred for 10 min. and then diluted with water and extracted with chloroform. The chloroform solution was washed, dried, and evaporated, and the residual oil was chromatographed on silica gel. There was obtained 3.1 g. (81%) of desyl chloride, m.p. 60–63°, undepressed (61–64°) upon admixture of authentic material (m.p. 65–66°). Further elution gave 3.7 g. (80%) of triphenylphosphine oxide, m.p. 150–155°, undepressed (153–157°) upon admixture of authentic material (m.p. 156–157°).

Solvolysis of IIc. To a solution of 8.7 g. (0.018 mole) of IIc in 30 ml. of methanol was added 5 ml. of water. The solution was stirred for 10 min., diluted with water, and extracted with chloroform. The chloroform solution was washed, dried, and evaporated, and the residual oil was chromatographed on silica gel. There was obtained 2.7 g. (79%) of dichloro-acetophenone; infrared and n.m.r. spectra were superimposable on those of the authentic compound prepared by the method of Aston.[25] Further elution afforded 3.6 g. (76%) triphenylphosphine oxide, m.p. 154–158°; upon admixture of authentic material the melting point was 153–158°.

Pyrolysis of IIa. The phosphonium salt IIa (5 g.) was heated in a sublimation apparatus at 0.2 mm. to 195°, whereupon the solid melted. The temperature was reduced to about 150° and the melt was sublimed. A white solid (4.8 g.) was collected. Trituration with pentane left 2.3 g. (92%) of crude triphenylphosphine oxide. Recrystallization from benzene–hexane yielded 1.5 g. (61%) of triphenylphosphine oxide, m.p. 157–158°, infrared spectrum superimposable upon that of authentic material.

The pentane solution from trituration was evaporated to yield 2.5 g. (97%) of crude chlorotriphenylethylene. Recrystallization from methanol gave 1.5 g. (59%) of

(20) N. Zinin, *Ann.*, 119, 177 (1861).
(21) S. G. Cohen, H. T. Wolosinski, and P. J. Scheur, *J. Am. Chem. Soc.*, 72, 3952 (1950).
(22) S. Trippett and D. M. Walker, *J. Chem. Soc.*, 3874 (1959).
(23) A. M. Ward, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 159.
(24) R. Anschütz and P. Förster, *Ann.*, 368, 89 (1909).
(25) J. E. Aston, J. D. Newkirk, D. M. Jenkins, and J. Dorsky, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 538.

chlorotriphenylethylene, m.p. 116–118°, undepressed upon admixture of authentic material, prepared by the procedure of van de Kamp.[26]

Pyrolysis of IIb. The enol phosphonium salt IIb, 6.2 g. (0.012 mole), was heated at 200° until a melt resulted (about 10 min.) and then kept at 200° for 5 min. more. A small amount of the mixture was dissolved in benzene and subjected to vapor phase chromatographic analysis (v.p.c.) (12-ft. Apiezon L column at 220°). V.p.c. showed that the dichlorostilbene obtained was 73% *cis* and 27% *trans*. V.p.c. of authentic *cis*- and *trans*-dichlorostilbene showed that isomerization was not occurring on the column. V.p.c. of the reaction mixture plus the authentic olefins showed no new peaks.

Alumina chromatography of the pyrolysis mixture afforded 2.4 g. (72%) of triphenylphosphine oxide (infrared absorption identical with that of authentic material) and 1.5 g. (50%) of a mixture of *cis*- and *trans*-dichlorostilbene. The olefin mixture was washed with cold ethanol, leaving 200 mg. of *trans*-dichlorostilbene, m.p. 138–141°. The melting point was undepressed (139–143°) upon admixture of authentic *trans*-dichlorostilbene (m.p. 140–143°) and the infrared spectra were superimposable.

Evaporation of the ethanol gave 1.0 g. of crude *cis*-dichlorostilbene, m.p. 46–60°. Two recrystallizations from aqueous ethanol afforded material with m.p. 55–60°. The mixture melting point with authentic *cis*-dichlorostilbene (m.p. 53–56°) was 53–58°; infrared spectra were superimposable.

Pyrolysis of IIb in the Presence of Excess trans-Dichlorostilbene. A mixture of 6.6 g. of IIb and 1.0 g. of *trans*-dichlorostilbene was heated at 200°. Five minutes after a melt resulted, a small amount was removed, dissolved in benzene, and subjected to v.p.c. analysis. V.p.c. showed the olefin mixture was 60% *trans*. After an additional 30 min., another sample was removed from the pyrolysis mixture. V.p.c. analysis of this sample showed the olefin composition to be 57% *trans*-dichlorostilbene.

Authentic cis- and trans-Dichlorostilbene. The procedure of Johnson[27] was followed to convert benzotrichloride to tolane tetrachloride, m.p. 160–162.5°. The tolane tetrachloride was treated with zinc according to a modified procedure of Blank.[28] To a boiling mixture of 25 g. (0.078 mole) of tolane tetrachloride and 250 ml. of ethanol was added slowly (in portions) 10 g. (0.153 g.-atom) of zinc dust. The mixture was refluxed for 30 min., filtered to remove excess zinc, diluted with water, and extracted with chloroform. The chloroform solution was washed with water, dried, and evaporated. The residue was leached with cold ethanol to leave 6.4 g. of crude *trans*-dichlorostilbene,[29,30] m.p. 136–141°. Recrystallization from ethanol yielded white plates, m.p. 139–142°.

The ethanol solution was diluted with water and extracted with ether. The ethereal solution was dried

(26) J. van de Kamp and M. Stetzinger, *J. Am. Chem. Soc.*, **63**, 1879 (1941).
(27) L. V. Johnson, F. Smith, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 4710 (1952).
(28) A. Blank, *Ann.*, **248**, 1 (1888).
(29) The geometry of the two isomers of dichlorostilbene was established by Bergman, *J. Chem. Soc.*, 402 (1936).
(30) J. H. Billman and P. H. Hides, *J. Am. Chem. Soc.*, **65**, 760 (1943).

and evaporated to yield 15 g. of crude *cis*-dichlorostilbene, m.p. 45–56°. Sublimation raised the melting point to 51–56°.

Diethyl Triphenylvinyl Phosphate (V). To a solution of 2.71 g. (0.016 mole) of triethyl phosphite in 15 ml. of xylene was added 5 g. (0.016 mole) of chlorodiphenylacetophenone. The solution was refluxed for 2 hr. and then evaporated. The yellow oil remaining was chromatographed on 100 g. of alumina. There was obtained 1.5 g. (23%) of crude V, which, on recrystallization from hexane, yielded material with melting point 69–71°. The infrared spectrum showed no carbonyl absorption and was consistent with the postulated structure.

Anal. Calcd. for $C_{24}H_{25}O_4P$: C, 70.59; H, 6.13; P, 7.60. Found: C, 70.60; H, 6.15; P, 7.60.

Chlorodiphenylacetmorpholide (IX). To a solution of 20 g. (0.076 mole) of chlorodiphenylacetyl chloride, m.p. 44–48° (prepared according to the procedure of Billman[30]), in 100 ml. of ether at 0°, was added 13.2 g. (0.16 mole) of morpholine (dropwise) in 100 ml. of ether. The temperature was kept below 0°. The final mixture was stirred for 20 min. at 0° and was then washed with water, dilute hydrochloric acid, water, dilute sodium carbonate solution, and finally with water again. The solution was dried and evaporated to give 26 g. of crude product; recrystallization from cyclohexane gave 17 g. (71%) of chlorodiphenylacetmorpholide, m.p. 113–116°. The infrared spectrum (CHCl₃) exhibited carbonyl absorption at 6.18 μ.

Anal. Calcd. for $C_{18}H_{18}ClNO_2$: C, 68.46; H, 5.71; Cl, 11.25; N, 4.44. Found: C, 68.50; H, 5.87; Cl, 11.06; N, 4.72.

Treatment of IX with Triphenylphosphine. A solution of 10 g. (0.032 mole) of IX and 8.3 g. (0.032 mole) of triphenylphosphine in 50 ml. of xylene was refluxed for 2 hr. The solution was filtered and evaporated, and the residue was chromatographed on alumina. There was obtained about 6 g. (72%) of triphenylphosphine and 6.5 g. (65%) of the starting amide. There was also obtained about 1 g. (11%) of triphenylphosphine oxide. The infrared spectra were identical with those of the authentic materials.

Treatment of Chlorodiphenylacetonitrile with Triphenylphosphine. A. In Anhydrous Benzene, Followed by Treatment with Methanol. To a solution of 5.8 g. (0.022 mole) of triphenylphosphine in 25 ml. of benzene was added 5 g. (0.022 mole) of chlorodiphenylacetonitrile (prepared by the method of Stevens[31]) in 5 ml. of benzene. The solution was stirred for 10 min. at room temperature and then cooled to about 5°. A solution of 750 mg. (0.023 mole) of methanol in 5 ml. of benzene was then added. A thick, white precipitate appeared in a few minutes. The mixture was slowly warmed. This caused the disappearance of the precipitate and the evolution of a gas, which was bubbled through deuteriochloroform. The n.m.r. spectrum of the chloroform solution exhibited a single peak at τ 7.00.[32] The reaction mixture was refluxed until no more gas was evolved, and was then evaporated. The residue was chromatographed on silica gel. There was obtained 2.0 g. (33%) of triphenylphosphine oxide

(31) C. Stevens and C. T. Lenk, *J. Org. Chem.*, **19**, 538 (1954).
(32) An authentic sample of methyl chloride was found to exhibit a single peak at τ 7.03.

(infrared spectrum superimposable on that of authentic material), and 7.5 g. of an oily solid. Trituration of the oily solid with cold ether left 5.1 g. (49%) of acylphosphinimine XIV, m.p. 149–151°. The ether solution was evaporated. Infrared analysis of the residue indicated it to be a mixture of XIV and diphenylacetonitrile. Recrystallization of the phosphinimine from benzene–hexane raised the melting point to 151–153.5°; infrared absorption (CHCl₃): 6.35 (s), 7.56 (s), and 9.06 (s) μ; n.m.r. absorption (CDCl₃): multiplet at about τ 2.7, doublet at 4.77 ($J_{P^{31}H}$ = 3.2 c.p.s.), peak areas in the ratio 25:0.85.

Anal. Calcd. for $C_{32}H_{26}NOP$: C, 81.53; H, 5.52; N, 2.97; P, 6.58. Found: C, 81.56; H, 5.78; N, 3.10; P, 6.44.

B. In Anhydrous Benzene Followed by Treatment with Water. To a solution of 5.8 g. (0.022 mole) of triphenylphosphine in 25 ml. of benzene was slowly added 5 g. (0.022 mole) of chlorodiphenylacetonitrile in 5 ml. of benzene. The solution was refluxed for 0.5 hr. and then was evaporated. The residue (infrared analysis showed absorption at 4.12 (m), 6.28 (s), and 9.02 (s) μ) was dissolved in 20 ml. of acetone and 5 ml. of water was added. The solution was refluxed for 5 min., diluted with water, and extracted with chloroform. The chloroform solution was dried and evaporated. Infrared analysis did not detect the presence of phosphinimine XIV. Chromatography on alumina and rechromatography on silica gel yielded 3.1 g. (72%) of diphenylacetonitrile, m.p. 60–71°, and 3.6 g. (59%) of triphenylphosphine oxide, m.p. 148–154°. Recrystallization from aqueous methanol raised the melting point of the nitrile to 70–73°, undepressed upon admixture of authentic material. Recrystallization of the phosphine oxide from benzene–hexane yielded material with melting point 156–158°, undepressed upon admixture of authentic material. There was also obtained 0.4 g. (6.9%) of triphenylphosphine, m.p. 75–79° (undepressed upon admixture of authentic material), and 0.1 g. (1%) of acylphosphinimine XIV, m.p. 149–152°, mixture melting point with authentic material 150–152°.

C. In Benzene Containing 1.4 Equiv. of Methanol. A solution of 5 g. (0.022 mole) of chlorodiphenylacetonitrile in 5 ml. of benzene was slowly added to a solution of 5.8 g. (0.022 mole) of triphenylphosphine in 30 ml. of benzene containing 1 g. (0.031 mole) of methanol. The mixture was refluxed for 5 min. and then evaporated. Infrared analysis of the residue indicated that XIV was still the major product. The mixture was not worked up further.

D. In 50% Methanol–Benzene. To 5.8 (0.022 mole) of triphenylphosphine in 35 ml. of 50% methanol–benzene was added 5 g. (0.022 mole) of chlorodiphenylacetonitrile in 10 ml. of 50% methanol–benzene. The mixture was refluxed for 5 min. and evaporated. Infrared analysis of the residue showed the major products to be diphenylacetonitrile and triphenylphosphine oxide. The residue was chromatographed on alumina and then silica gel. There was obtained 3.2 g. (74%) of diphenylacetonitrile, m.p. 68–72°, undepressed upon admixture of authentic material; 3.4 g. (56%) of triphenylphosphine oxide, m.p. 154–157° (from benzene–hexane), undepressed upon admixture of authentic material; and 0.5 g. (5%) of XIV, m.p. 145–150°.

Recrystallization from benzene–hexane raised the melting point to 152–154°, undepressed upon admixture of authentic material. There was also obtained 0.7 g. (10%) of methyltriphenylphosphonium chloride, m.p. 219–221°, identified by its conversion with perchloric acid to the corresponding perchlorate, m.p. 162–165°, undepressed upon admixture of authentic material (m.p. 162–165°) obtained by treatment of methyltriphenylphosphonium bromide[33] with perchloric acid.

E. In Anhydrous Benzene Followed by Treatment with 50% Methanol–Benzene. A solution of 5 g. (0.022 mole) of chlorodiphenylacetonitrile in 5 ml. of benzene was added slowly to a solution of 5.8 g. (0.022 mole) of triphenylphosphine in 25 ml. of benzene. The mixture was stirred for 15 min. and evaporated, and 30 ml. of 50% methanol–benzene was added to the residue. The solution was refluxed until gas evolution ceased and then evaporated to an oily solid. Infrared analysis showed phosphinimine XIV to be the major product. Chromatography on silica gel yielded (57%) of phosphinimine XIV, m.p. 146–149°. Recrystallization from benzene–hexane raised the melting point to 148–151°, undepressed (m.p. 149–151°) upon admixture of material from run A, above.

Phosphonium Salt XVII. Anhydrous hydrogen chloride was bubbled through a solution of 50 mg. of XIV in 5 ml. of benzene and 1 ml. of chloroform. Evaporation left a white solid, m.p. 184–186°. Recrystallization from acetonitrile gave white prisms, m.p. 185–186°. Infrared absorption spectrum showed the following (CHCl₃): 3.39 (m), 3.80 (m), 3.95 (m), 5.89 (m), 6.96 (s), and 8.96 (s) μ. N.m.r. absorption showed (CDCl₃): broad peak at τ −3.3, multiplet at about 2.6, and a singlet at 3.28; areas in the ratio 0.9:25:1.1.

Anal. Calcd. for $C_{32}H_{27}ClNOP$: C, 75.65; H, 5.36; Cl, 6.98; N, 2.76; P, 6.10. Found: C, 75.34; H, 5.45; Cl, 7.04; N, 2.78; P, 6.03.

Pyrolysis of XIV. Phosphinimine XIV, 2.0 g. (4.25 moles) was heated in an oil bath at 200° for 5 hr. The resulting oil was chromatographed on silica gel. There was obtained 0.8 g. (100%) of diphenylacetonitrile, m.p. 68–71°, undepressed upon admixture of authentic material; and 1.2 g. (100%) of triphenylphosphine oxide, m.p. 154–157°, undepressed upon admixture of authentic material.

Acylphosphinimine XX. To a solution of 5 g. (0.035 mole) of trichloroacetonitrile in 20 ml. of benzene at 5° was added slowly 9 g. (0.035 mole) of triphenylphosphine in 15 ml. of benzene. The temperature was kept below 10°. After addition was complete 1.1 g. (0.035 mole) of methanol was added. The mixture was then refluxed until gas evolution ceased. (The gas was identified as methyl chloride by n.m.r. analysis.) The mixture was filtered; 2.0 g. of cyanomethyltriphenylphosphonium chloride (XXI), m.p. 271–274°, was collected.

Anal. Calcd. for $C_{20}H_{17}ClNP$: C, 71.10; H, 5.07; Cl, 10.50; N, 4.15; P, 9.17. Found: C, 70.72; H, 5.25; Cl, 10.54; N, 4.19; P, 8.94.

The filtrate was evaporated and the residue was chromatographed on silica gel. There was obtained about 5.2 g. (54%) of triphenylphosphine oxide (identified by

(33) The Aldrich Chemical Co.

infrared analysis) and 2.5 g. (19%) of crude XX. This material was chromatographed on alumina, then recrystallized from acetonitrile to give colorless plates, m.p. 136–139°. Infrared absorption gave the following (CHCl₃): 6.23 (s), 7.5 (s), and 9.0 (s) μ.

Anal. Calcd. for $C_{20}H_{16}Cl_2NOP$: C, 61.87; H, 4.15; Cl, 18.26; N, 3.61. Found: C, 61.97; H, 4.33; Cl, 18.05; N, 3.65.

Salt XXI was dehydrohalogenated as follows. A solution of 500 mg. of XXI in water was treated with excess sodium carbonate. There was collected 350 mg. of phosphorane XXII, m.p. 192–195° (from ethyl acetate), undepressed upon admixture of authentic material.[34]

Ketenimine XXIV. A solution of 3.7 g. (0.022 mole) of triethyl phosphite in 10 ml. of benzene was added to 5 g. of chlorodiphenylacetonitrile in 20 ml. of benzene. The mixture was refluxed until gas evolution stopped. (The gas was collected by passing it through deuteriochloroform; n.m.r. analysis showed it to be ethyl chloride.[35]) The solution was evaporated and the residue was suspended in ether and filtered. There was collected 300 mg. of tetraphenylsuccinonitrile (XXV), m.p. 210–213°. Recrystallization raised

the melting point to 210–215°, undepressed (213–216°) upon admixture of authentic material, m.p. 211–216°, prepared by the method of Auwers.[36]

The ethereal filtrate was evaporated; 6.6 g. of yellow oil (crude XXIV) remained; infrared absorption showed (capillary film): extremely intense absorption at 4.95 μ. N.m.r. absorption showed (CDCl₃): singlet at τ 2.76, multiplet at 6.03, and multiplet at 8.85 peak areas in the ratio 10:3.8:5.8 (theory 10:4:6).

Hydrolysis of XXIV. To a solution of 2.0 g. (6.1 mmoles) of XXIV in 15 ml. of acetone was added 1 ml. of water and 3 drops of concentrated hydrochloric acid. The solution was refluxed for 1 hr. and stirred overnight at room temperature. It was then diluted with water and extracted with chloroform. The extracts were washed, dried, and evaporated to 1.6 g. of viscous oil. Chromatography on silica gel followed by recrystallization from methylcyclohexane yielded a white solid, m.p. 114–115°; infrared absorption spectrum (CHCl₃) revealed a carbonyl band at 5.85 μ.

Anal. Calcd. for $C_{18}H_{22}NO_4P$: C, 62.24; H, 6.39; N, 4.03; P, 8.92. Found: C, 62.06; H, 6.30; N, 3.97; P, 8.75.

(34) Prepared by Dr. K. W. Ratts.
(35) The spectrum obtained was identical with that reported for ethyl chloride in the NMR Spectra Catalog, Vol. 1, Varian Associates, Inc., Palo Alto, Calif, 1962.
(36) K. Auwers and V. Meyer, *Ber.*, 22, 1227 (1889).

The Preparation and Reactions of a Homologous Series of Aliphatic Polyenylic Cations

T. S. Sorensen

Contribution from the Department of Chemistry, University of Alberta, Calgary, Alberta, Canada. Received May 7, 1965

Solutions of a number of stable, aliphatic polyenylic cations have been obtained in concentrated sulfuric acid and other strong acids. The structure of the ions has been proven using n.m.r. and ultraviolet spectroscopy. The cyclization reaction of these ions was investigated, the structure of the resulting carbonium ions was deduced, and a comparison of the $T_{1/2}$ values for this reaction was made. Free-radical formation was shown for one of the higher members during its oxidative decomposition by the sulfuric acid. An attempt has been made to relate the n.m.r. proton shifts with the excess positive charge density on the carbon atoms to which the protons are bonded. The value of this proportionality constant was found to be about 13–15 p.p.m. per electron charge. A linear relationship between λ_{max} and n is found for the electronic spectra of the ions. A number of new polyenes have been synthesized in this work and characterized by all of the usual physical tools.

Introduction

The preparation of the carbonium ions I ($n = 0$ and 1) have been recently reported.[1–3] Ion I ($n =$

1) is particularly interesting because of the subsequent slow cyclization reaction which it undergoes and which

I
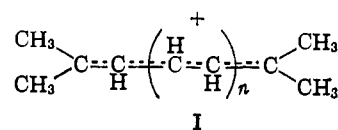
now appears to be a general reaction for dienylic cations. It thus became of interest to attempt to extend the number of double bonds in I, to study the effects of this presumed further delocalization of the positive charge by n.m.r. and ultraviolet spectroscopy, and particularily to examine any cyclization reactions in view of the multiple sites now available for this process.

Only one previous example of a stable aliphatic polyenylic cation of established structure has been reported.[2] The ion II has been prepared by dissolving the corresponding alcohol in concentrated sulfuric acid. This ion however has a rather complex n.m.r. spec-

(1) N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, 85, 2991 (1963).
(2) N. C. Deno, C. U. Pittman, Jr., and J. O. Turner, *ibid.*, 87, 2153 (1965).
(3) T. S. Sorensen, *Can. J. Chem.*, 42, 2768 (1964).