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Reaction of Alkylidenephosphoranes with Nitrosyl Chloride and Decomposition of α-Hydroxyiminophosphonium Chlorides Formed

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The reaction of stable alkylidenephosphoranes with nitrosyl chloride in THF gave α-substituted α-hydroxyiminomethyltriphenylphosphonium chloride (A) in high yields. In the case of active alkylidenephosphoranes, "transylidation" took place simultaneously and a mixture of A and α-substituted methyltriphenylphosphonium chloride was obtained along with corresponding amounts of nitrile and triphenylphosphine oxide. By thermal decomposition, all α-hydroxyiminomethyltriphenylphosphonium chlorides (A) afforded nitriles and triphenylphosphine oxide.

Recently we have reported that the reaction of alkylidenephosphoranes with nitric oxide afforded nitriles, aldehydes and phosphine oxide.$^{1)}$ In connection with this reaction, we attempted the reaction of alkylidenephosphoranes with nitrosyl chloride.$^{2)}$

Zbiral and Fenz reported formation of nitriles from acylmethyltriphenylphosphonium salts with ethyl nitrite,$^{3)}$ but they could not obtain any intermediate.

Trippett, Walker and Hoffmann reported formation of α-substituted α-hydroxyiminomethyltriphenylphosphonium bromides by the reaction of α-bromonitroalkanes ($RCHBrNO_2$) with triphenylphosphine and also formation of nitriles by decomposition of the bromides with alkali.$^{4)}$ They could isolate the bromides only when the substituents (R) were methyl and ethyl.

We wish to report here formation of α-substituted α-hydroxyiminomethyltriphenylphosphonium chlorides (A) as intermediates and their decomposition to nitriles.

Results and Discussion

When stable α-substituted methylenetriphenylphosphoranes ($Ph_3P=CHR$; I: $R=COPh$ and II: $R=CO_2Me$) were allowed to react with nitrosyl chloride in tetrahydrofuran (THF) solution, α-substituted α-hydroxyiminomethyltriphenylphosphonium chlorides (A-I and A-II) were produced as precipitates in good yields according to reaction (3) (see Table 1).

From the filtrate, benzoyl cyanide and triphenylphosphine oxide were isolated in the case of I, and in the case of II, methyl cyanoformate was determined by g.l.c. In both cases, no α-acylmethyltriphenylphosphonium chlorides (B) were detected in spite of careful examination. This fact suggests that reaction (4) does not take place in these cases.

When α-hydroxyimino-α-benzoylmethyltriphenylphosphonium chloride (A-I) was refluxed in chloroform, benzoyl cyanide (86—98%) and triphenylphosphine oxide (82—93%) were obtained. The

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1) K. Akiba, M. Imanari and N. Inamoto, *Chem. Commun.*, **1969**, 166.

2) Preliminary report: K. Akiba, C. Eguchi and N. Inamoto, This Bulletin, **40**, 2983 (1967).

3) E. Zbiral and L. Fenz, *Monatsh. Chem.*, **96**, 1983 (1965).

4) S. Trippett, B. J. Walker and H. Hoffmann, *J. Chem. Soc.*, **1965**, 7140.

TABLE 1. FORMATION OF α-SUBSTITUTED α-HYDROXYIMINOMETHYLTRIPHENYLPHOSPHONIUM CHLORIDES (A)
$Ph_3P{=}CHR + NOCl$ (I: $R{=}COPh$ and II: $R{=}CO_2Me$)

	Temp. (°C)	$[Ph_3\overset{+}{P}C({=}NOH)R]Cl^-$ (A) Dec. point (°C)	$[Ph_3\overset{+}{P}C({=}NOH)R]Cl^-$ (A) (%)	$Ph_3P{=}O$* (%)	RCN* (%)
I	0	134—5	70	18	6
	−30—−20		72	16	18
II	−50—−40	128—9	89	5	—
	−50—−40		79	13	19

* Determined from the filtrate of A.

same products were also obtained in 73% yield by the decomposition of A-I in molten state.

However, in a similar decomposition of α-hydroxyimino-α-methoxycarbonylmethyltriphenylphosphonium chloride (A-II), complicated results were obtained. When chloroform solution of A-II was allowed to stand at room temperature for 4 days, only methyl cyanoformate and hydrochloride of triphenylphosphine oxide were formed quantitatively (Fig. 1). These yields were determined by NMR (Fig. 1) and also by g.l.c. The signals in Fig. 1 were assigned in comparison with those of authentic samples. On further standing, it was found from Fig. 1 that methyl cyanoformate decomposed into methyl chloride, hydrogen cyanide and carbon dioxide. To realise this fact, stability of methyl cyanoformate was checked under several conditions by NMR.

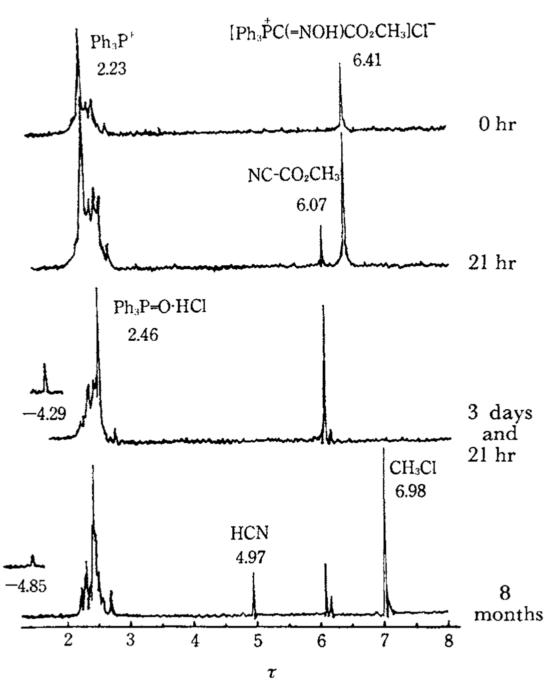
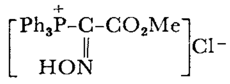


Fig. 1. Decomposition of $[Ph_3\overset{+}{P}C({=}NOH)CO_2CH_3]Cl^-$ in $CDCl_3$ at room temperature.

In chloroform solution, methyl cyanoformate was stable in the presence of triphenylphosphine oxide at room temperature for 4 days but slowly trimerized (in 40% yield after one year) in the presence of hydrogen chloride without decomposition. But when the solution was heated at 40°C for 20 hr in the presence of both triphenylphosphine oxide and hydrogen chloride, the ester was decomposed into methyl chloride, hydrogen cyanide and carbon dioxide. The last result is explicable by reaction (1).



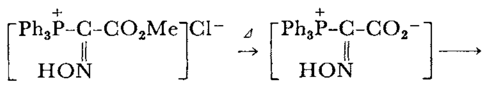
$$\left[\mathrm{Ph_3\overset{+}{P}{-}\underset{\underset{\displaystyle HON}{\|}}{C}{-}CO_2Me}\right]Cl^-$$

A-II

$$\begin{aligned}&\longrightarrow Ph_3P{=}O\cdot HCl + NC{-}CO_2Me\\&\longrightarrow Ph_3P{=}O + MeCl + [NC{-}CO_2H]\\&\longrightarrow HCN + CO_2 \qquad (1)\end{aligned}$$

This decomposition of the ester is analogous to the fission of alkyl groups of esters and ethers by triphenylphosphine hydrobromide.[5]

The thermal decomposition of A-II in molten state gave a small amount (9%) of methyl cyanoformate and large amounts of methyl chloride, hydrogen cyanide and carbon dioxide. In this case, a direct decomposition as shown in reaction (2) cannot be ruled out.[6]



$$\left[\mathrm{Ph_3\overset{+}{P}{-}\underset{\underset{\displaystyle HON}{\|}}{C}{-}CO_2Me}\right]Cl^- \xrightarrow{\Delta} \left[\mathrm{Ph_3\overset{+}{P}{-}\underset{\underset{\displaystyle HON}{\|}}{C}{-}CO_2^-}\right] \longrightarrow$$

$$Ph_3P{=}O + HCN + CO_2 \qquad (2)$$

When active α-substituted methylenetriphenylphosphoranes (III: R=Ph and IV: R=*n*-Pr) were allowed to react with nitrosyl chloride in THF, a mixture of α-substituted α-hydroxyiminomethyltriphenylphosphonium chloride (A) and α-substituted methyltriphenylphosphonium chloride (B) precipitated immediately, and the resulting nitrile (RCN-1 in Table 2) and triphenylphosphine oxide were determined from the filtrate. Formation of

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[5] H. J. Bestmann, L. Mott and J. Lienert, *Ann. Chem.*, **709**, 105 (1967).

[6] N. A. Nesmeyanov, Ya. S. Vasyak, V. A. Kalyavin and O. A. Reutov, *Zh. Org. Khim.*, **4**, 385 (1968); *Chem. Abstr.*, **68**, 104379a (1968).

TABLE 2. REACTION OF ALKYLIDENEPHOSPHORANES WITH NITROSYL CHLORIDE*
$Ph_3P{=}CHR + NOCl$ (III: R=Ph and IV: R=*n*-Pr)

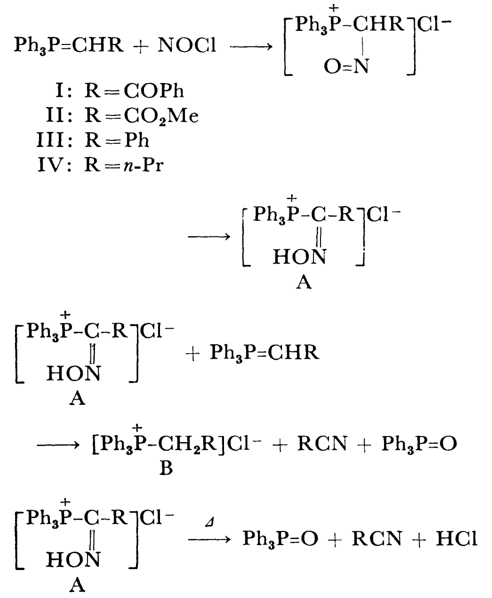
	Temp. (°C)	$[Ph_3\overset{+}{P}CH_2R]Cl^-$ B (%)	$Ph_3P{=}O$ (%)	RCN-1 (%)	RCN-2 (%)
III	−40—−30	23	21	28	17
	−40—−30	30	29	36	18
IV	−40—−30	32	27	38	15
	−40—−30	23	43	52	

* Yields are based on the initial phosphonium bromide.

these products are ascribable to reaction (4), and this is supported by the fact that B and RCN-1 were obtained in about equal amount.

In order to decompose A in the precipitates (A+B), the precipitates were refluxed in THF or in chloroform. From the filtrate, nitrile (RCN-2 in Table 2) was determined by g.l.c. and B was obtained by usual work up. Unfortunately, isolation of A-III and A-IV from the precipitates was not successful, but their existence is shown by the formation of RCN-2.

These results can be explained by the following scheme.



$$Ph_3P{=}CHR + NOCl \longrightarrow \left[\begin{array}{c} Ph_3\overset{+}{P}\text{-}CHR \\ | \\ O{=}N \end{array}\right]Cl^-$$

I: R=COPh
II: R=CO_2Me
III: R=Ph
IV: R=*n*-Pr

$$\longrightarrow \underset{A}{\left[\begin{array}{c} Ph_3\overset{+}{P}\text{-}C\text{-}R \\ \| \\ HON \end{array}\right]Cl^-} \qquad (3)$$

$$\underset{A}{\left[\begin{array}{c} Ph_3\overset{+}{P}\text{-}C\text{-}R \\ \| \\ HON \end{array}\right]Cl^-} + Ph_3P{=}CHR$$

$$\longrightarrow \underset{B}{[Ph_3\overset{+}{P}\text{-}CH_2R]Cl^-} + RCN + Ph_3P{=}O \qquad (4)$$

$$\underset{A}{\left[\begin{array}{c} Ph_3\overset{+}{P}\text{-}C\text{-}R \\ \| \\ HON \end{array}\right]Cl^-} \xrightarrow{\Delta} Ph_3P{=}O + RCN + HCl \qquad (5)$$

In the cases of stable alkylidenephosphoranes (I and II), reaction (4) was not observed because of their low basicities.[7] On the other hand, in the cases of active alkylidenephosphoranes (III and IV), reaction (4) seems to compete with reaction (3), and a mixture of A and B was obtained as precipitates. The ratio of A-III to B-III was 17 : 23 and that of A-IV to B-IV was 15 : 32, assuming that the amount of RCN-2 correspond to the amount of A.

Although this method is not generally adequate for the synthesis of usual nitriles, it would be useful for preparation of special types of nitriles, because *p*-toluenesulfonyl cyanide[8] was prepared only by this method.

$$RSO_2\text{-}CH{=}PPh_3 + NOCl \xrightarrow{\text{pyridine}} RSO_2\text{-}CN + Ph_3P{=}O$$

Experimental

Materials. Phosphonium salts were prepared from organic halides and triphenylphosphine: phenacyltriphenylphosphonium bromide,[9a,b] mp 268.5—271.0°C; methoxycarbonylmethyltriphenylphosphonium chloride, mp 151—152°C; benzyltriphenylphosphonium bromide,[10] mp 269.0—271.0°C; benzyltriphenylphosphonium chloride,[11] mp 299.5—301.2°C; *n*-butyltriphenylphosphonium bromide,[11,12] mp 232—233°C; and *n*-butyltriphenylphosphonium chloride, mp 217—218.5°C.

Benzoylmethylenetriphenylphosphorane,[9a] mp 180.0—180.5°C, and methoxycarbonylmethylenetriphenylphosphorane,[13] mp 168.0—168.5°C, were prepared by the method described in literature.

Benzylidene- and *n*-butylidenetriphenylphosphoranes were prepared from the corresponding phosphonium bromides and sodium amide prepared *in situ* in liquid ammonia.[14] Evaporation of ammonia, extraction with anhydrous THF and filtration afforded the salt-free solution of the phosphoranes.

Nitrosyl chloride was prepared by Coleman's method[15] and distilled three times before use.

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7) K. Issleib and R. Lindner, *Ann. Chem.*, **707**, 120 (1967).

8) A. M. van Leusen, A. J. W. Iedema and J. Strating, *Chem. Commun.*, **1968**, 440.

9) a) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957). b) I. J. Borowitz and R. Virkhaus, *J. Amer. Chem. Soc.*, **85**, 2183 (1963).

10) M. Grayson and P. T. Keough, *J. Amer. Chem. Soc.*, **82**, 3919 (1950).

11) K. Friedrich and H. G. Henning, *Chem. Ber.*, **92**, 2756 (1959).

12) R. Mechoulam and F. Sondheimer, *J. Amer. Chem. Soc.*, **80**, 4386 (1958).

13) O. Isler, H. Gutmann, M. Montavon, R. Rüegg, G. Ryser and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1957).

14) H. J. Bestmann, *Angew. Chem.*, **77**, 609 (1965); H. J. Bestmann, *Chem. Ber.*, **95**, 58 (1962).

15) G. H. Coleman, G. A. Lillis and G. E. Gokeen, "Inorganic Syntheses," Vol. 1, p. 55 (1939).

Methyl cyanoformate as an authentic sample was prepared by dehydration of methyl oxamate with phosphorus pentoxide,[16] bp 99—100°C.

Synthesis of α-Benzoyl- and α-Methoxycarbonyl-α-hydroxyiminomethyltriphenylphosphonium Chlorides. A typical procedure is described below.

a) α-Hydroxyimino-α-benzoylmethyltriphenylphosphonium Chloride (A-I). A solution of 3.40 g (0.052 mol) of nitrosyl chloride in 170 m*l* of anhydrous THF was added dropwise to a solution of 19.0 g (0.050 mol) of benzoylmethylenetriphenylphosphorane in 400 m*l* of anhydrous THF over 50 min at -30—-20°C with stirring. As soon as the solution of nitrosyl chloride was added, white precipitates appeared and the solution showed a light blue color, which disappeared after addition of about half the nitrosyl chloride solution. After the addition, the mixture was stirred for additional 15 min at room temperature. The white precipitates (A-I) were filtered, and washed with anhydrous THF and acetone. Yield 16 g (0.036 mol, 72%), dec. point 134—135°C. IR (in C_4Cl_6): 2500 (ν_{OH}) (shifted to 2600 cm^{-1} in chloroform), 1645 (ν_{CO}), 1275, and 1050 cm^{-1}. $\lambda_{max}^{CHCl_3}$: 266 ($\varepsilon=1.49\times10^4$), 271 ($1.53\times10^4$), and 277.5 m$\mu$ (1.34×10^4).

Found: C, 69.94; H, 4.62; N, 3.04%. Calcd for $C_{26}H_{21}NO_2PCl$: C, 70.04; H, 4.75; N, 3.14%.

After removal of THF from the filtrate, the residue was extracted with petroleum ether (bp 40—60°C), and the extract was distilled under reduced pressure to yield 1.25g (0.0095 mol, 18%) of benzoyl cyanide, bp 77—78°C/10 mmHg, mp 31.0—32.1°C, IR (Nujol): 2240 (ν_{CN}) and 1680 cm^{-1} (ν_{CO}).

Insoluble part in petroleum ether was washed three times with ether to afford 2.2g (0.0079 mol, 16%) of triphenylphosphine oxide, mp 153.5—155°C.

b) α-Hydroxyimino-α-methoxycarbonylmethyltriphenylphosphonium Chloride (A-II). This salt was prepared by addition of a solution of 4.00g (0.061 mol) of nitrosyl chloride in 200 m*l* of anhydrous THF to a solution of 20.0g (0.060 mol) of methoxycarbonylmethylenetriphenylphosphorane in 350 m*l* of anhydrous THF at -50—-40°C. Appearance of the reaction was similar to that of a), except that the color of the solution changed to cherry pink. Yield 19.0g (0.0476 mol, 80%), dec. point 128—129°C. IR (in C_4Cl_6): 2220 (ν_{OH}) (shifted to 2540 cm^{-1} in chloroform), 1730 (ν_{CO}), 1275, and 1070 cm^{-1}. $\lambda_{max}^{CHCl_3}$: 262.5 (shoulder), 270 ($\varepsilon=6.45\times10^3$), and 277.5 m$\mu$ (4.69×10^3).

Found: C, 62.97; H, 4.78; N, 3.40%. Calcd for $C_{21}H_{19}NO_3PCl$: C, 63.09; H, 4.79; N, 3.50%.

The filtrate was analyzed by g.l.c. (diisodecyl phthalate, 78°C; dibenzyl ether, 74°C), and found to contain 0.986g (0.0116 mol, 19%) of methyl cyanoformate and a trace of carbon dioxide. Attempt to isolate methyl cyanoformate by distillation was unsuccessful, but 2.24g (0.00805 mol, 13%) of triphenylphosphine oxide was obtained from the residue.

Decomposition of α-Benzoyl- and α-Methoxycarbonyl-α-hydroxyiminomethyltriphenylphosphonium Chlorides (A-I and A-II). *a) For A-I.* 1) In boiling chloroform. A solution of 4.0g (0.09 mol) of A-I in 200 m*l* of chloroform was refluxed for 22 hr. After generation of hydrogen chloride ceased and the chloroform was removed, the residue was treated by the procedure described in "synthesis of A-I" to afford 1.15g (0.0088 mol, 98%) of benzoyl cyanide and 2.2g (0.00785 mol, 87%) of triphenylphosphine oxide.

2) In molten state. Heating of 2.2g (0.0049 mol) of A-I at 140°C (bath temperature) for 45 min gave 0.468 g (0.0036 mol, 73%) of benzoyl cyanide and 0.985 g (0.00353 mol, 72%) of triphenylphosphine oxide.

b) For A-II. 1) In molten state. In an oil bath, 3.16g (0.0079 mol) of A-II was gradually heated and then at 200°C (bath temperature) for further 3 hr under dry nitrogen stream. The liquid collected with a dry ice-ethanol trap was analyzed by g.l.c. and found to contain methyl cyanoformate (9%), methyl chloride and hydrogen cyanide. The residue in the reaction flask was recrystallized from ethyl acetate - petroleum ether to yield 1.8g (0.0065 mol, 82%) of triphenylphosphine oxide.

2) A solution of A-II (*ca.* 2%) was allowed to stand at room temperature for 4 days and the resulting methyl cyanoformate was determined simultaneously both by NMR (91%) and by g.l.c. (95%).

A solution of 1.09g (0.00274 mol) of A-II in 65 m*l* of chloroform was refluxed for 25 hr. The formation of methyl cyanoformate (15%), methyl chloride, and hydrogen cyanide was observed by g.l.c.

Reaction of Benzylidenetriphenylphosphorane with Nitrosyl Chloride. To a solution of 3.30g (0.0505 mol) of nitrosyl chloride in 250 m*l* of anhydrous ether was added dropwise a solution of salt-free benzylidenetriphenylphosphorane (0.050 mol) in 150 m*l* of anhydrous THF under nitrogen at -40—-30°C with stirring. After the addition, the reaction mixture was stirred for a further 10 min at room temperature. White precipitates (C) thus formed were filtered, washed with anhydrous THF and anhydrous ether, and dried over phosphorus pentoxide *in vacuo*. Yield 12.1g. The filtrate was analyzed by g.l.c. (Apiezon grease M, 197°C) to contain 1.85g (0.018 mol, 36%) of benzonitrile, the isolation of which was unsuccessful. The residue was recrystallized from ether to yield 3.9g (0.014 mol, 29%) of triphenylphosphine oxide.

A suspension of C (3.5g) in 50 m*l* of anhydrous THF was refluxed for 35 hr and 0.269g (0.0026 mol) of benzonitrile was determined by g.l.c. The precipitates insoluble in anhydrous THF were recrystallized twice from chloroform - ethyl acetate to yield 1.7g (0.0048 mol) of benzyltriphenylphosphonium chloride, mp 295.5—297.0°C. A mixed mp with authentic benzyltriphenylphosphonium chloride (mp 299.5—301.2°C) was 299.0 301.0°C and that with benzyltriphenylphosphonium bromide (mp 269.0—271.0°C) was 277.5—281.0°C. From this result, the precipitates C were found to consist of α-hydroxyiminobenzyltriphenylphosphonium chloride (A-III) and benzyltriphenylphosphonium chloride (B-III). The yields were 18 and 30% on the basis of the initial benzyltriphenylphosphonium bromide, respectively.

Reaction of *n*-Butylidenetriphenylphosphorane with Nitrosyl Chloride. The procedure and the reaction scale were the same as those of benzylidenetriphenylphosphorane. The white precipitates (D) thus obtained were very hygroscopic. Yield 10.9g. The filtrate was analyzed by g.l.c. (Polyethylene glycol, 120°C), and found to contain 1.32g (0.019 mol, 38%) of *n*-butyronitrile, the isolation of which was unsuccessful. Chromatography of the residue of distillation on silica gel with benzene gave 3.82g (0.0137 mol, 27%) of tri-

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[16] A. Weddige, *J. Prakt. Chem.*, **10**, 197 (1874).

phenylphosphine oxide.

A solution of D (2.3g) in 79 m*l* of chloroform was refluxed for 20 hr and the reaction mixture was analyzed by g.l.c., and found to contain 0.109g (0.0016 mol) of *n*-butyronitrile. From the solution chloroform was removed, and the residue was recrystallized three times from chloroform - ethyl acetate to afford 1.20g (0.0034 mol) of *n*-butyltriphenylphosphonium chloride, mp 218.0—219.0°C (Found: Cl, 9.85%). A mixed mp with authentic sample (mp 217.0—218.5°C) was 217.5—218.5°C and that with *n*-butyltriphenylphosphonium bromide (mp 232.0—233.0°C) was 222.5—224.5°C.

From this result, the precipitates (D) were found to consist of α-hydroxyimino-*n*-butyltriphenylphosphonium chloride (A-IV) and *n*-butyltriphenylphosphonium chloride (B-IV). The yields were 15 and 32% on the basis of the initial *n*-butyltriphenylphosphonium bromide, respectively.