Formation of α-Hydroxyiminophosphonium Chlorides by Reaction of Phosphine-alkylenes with Nitrosyl Chloride and Their Decompositions

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Recently, Zbiral and Fenz reported the formation of nitriles by the reaction of acylmethyltriphenylphosphonium salts with ethyl nitrite.[1] We wish to report the reaction of phosphine-alkylenes with nitrosyl chloride to give α-substituted α-hydroxyiminomethyltriphenylphosphonium chloride (A) and the decomposition of the chloride to yield the corresponding nitriles.

When benzoylmethylenetriphenylphosphorane (I) was allowed to react with nitrosyl chloride in tetrahydrofuran (THF) solution at −20——30°C, α-hydroxyiminophosphonium chloride (A-I) precipitated immediately in 72% yield. Similar results were obtained performing the reaction of II with nitrosyl chloride (Table 1).

$$\mathrm{Ph_3P{=}CHCOR + NOCl \rightarrow \left[\begin{array}{c} Ph_3P\text{-}C\text{-}COR \\ \| \\ NOH \end{array}\right]^{+}Cl^{-}}$$

I R=Ph
II R=OMe
A (1)

$$\mathrm{\left[\begin{array}{c} Ph_3P\text{-}C\text{-}COR \\ \| \\ NOH \end{array}\right]^{+}Cl^{-} \xrightarrow{\Delta} NC\text{-}COR + Ph_3P{=}O}$$

A B C (2)
+HCl

The IR spectra support the α-hydroxyimino structure[2]: A-I (in $CHCl_3$) ν_{OH} 2600 cm^{-1} (broad), $\nu_{C=O}$ 1650 cm^{-1}; A-II (in $CHCl_3$) ν_{OH} 2530 cm^{-1} (broad), $\nu_{C=O}$ 1730 cm^{-1}.

When A-I was refluxed in chloroform for 20—30 hr, B-I (86—98%) and C (82—89%) were obtained, and also B-I (73%) and C (72%) were obtained in the decomposition of A-I in molten state. In similar decomposition of A-II, B-II (*ca.* 37%, determined by G. L. C. and NMR) and C (70%) were also obtained. As other volatile products, methyl chloride, hydrogen cyanide and carbon dioxide were observed by mass spectrometry.

Phosphine-alkylenes III and IV were prepared in salt free state and treated in THF solutions analogously.

In those cases, elimination of hydrogen chloride from A-III and A-IV by III and IV occurred subsequently to (1), giving immediately triphenylphosphine oxide and the corresponding nitriles as shown in (3).

$$\mathrm{Ph_3P{=}CHR + \left[\begin{array}{c} Ph_3P\text{-}C\text{-}R \\ \| \\ NOH \end{array}\right]^{+}Cl^{-} \rightarrow}$$

III R=Ph
IV R=*n*-Pr
(A)

$$\mathrm{[Ph_3PCH_2R]^{+}Cl^{-} + \left[\begin{array}{c} Ph_3\overset{+}{P}\text{-}C\text{-}R \\ \| \\ {}^{-}O\text{-}N \end{array}\right]} \quad (3)$$

(D)

$$\mathrm{Ph_3P{=}O + R\text{-}CN} \longleftarrow$$

The resultant precipitate was a mixture of D and the remaining A, and the filtrate contained triphenylphosphine oxide (C) and nitrile (B).

TABLE 1. α-HYDROXYIMINOPHOSPHONIUM CHLORIDE (A)

	Reaction temperature(°C)	Yield of products A	B	C(%)	Mp (dec) of A (°C)		Elemental analyses of A C	H	N
I	0.2	70	6*	18*	133.5	calcd	70.04	4.75	3.14
	−20——30	72	18*	16*	—135.0	found	69.94	4.62	3.04
II	−40——50	77	0	13*	125	calcd	63.09	4.79	3.50
	−40——50	89	0	5*	—130	found	62.97	4.78	3.40

* Resulted from the filtrate of A

From the mixture of D and A, A was not isolated in a pure form, but the content of A was estimated from the yield of the nitrile obtained by refluxing the mixture in chloroform or in THF for 15—25 hr. The results are shown in Table 2.

TABLE 2. REACTION PRODUCTS OF III AND IV WITH NOCl

	Products from (3) (%) B	C	D	RCN from (2) B (%)	Recovery of R (%)
III	36	29	30	17	83
IV	38	28	32	15	85

1) E. Zbiral and L. Fenz, *Monatsh. Chem.*, **96**, 1983 (1965).
2) S. Trippett, B. J. Walker and H. Hoffmann, *J. Chem. Soc.*, **1965**, 7140.