

Preparation and Reaction of *N*-Imidoilyminotriphenylphosphoranes

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Synopsis. *N*-Imidoilyminotriphenylphosphoranes **2** have been prepared by the reaction of triphenylphosphine with *N*-chloroamidines followed by treatment with base. **2** can react readily with hydrochloric acid or methyl iodide to give the corresponding salts. Treatment of **2** with carbon disulfide gave *N*-(thioacyl)iminotriphenylphosphoranes together with isothiocyanates.

In a previous paper¹⁾ the reaction of imidoilytriphenylphosphonium methylides **1** with carbon disulfide was reported. The products were a result of the attack on either the ylide carbon atom or the imidoily nitrogen atom.

Iminophosphoranes show similar chemical properties to those of phosphonium methylides.²⁾ In this paper the reaction of *N*-imidoilyminotriphenylphosphoranes **2** with carbon disulfide and halides will be reported.

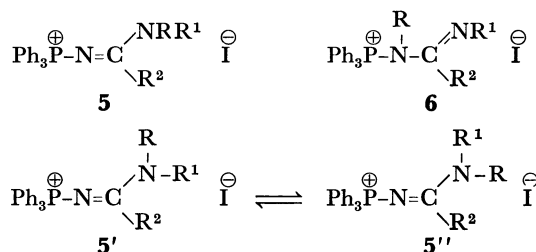
Iminophosphoranes **2** have been prepared by the reaction of *N*-(1-chloro-2,2-diphenylvinyl)iminophosphorane, prepared from chlorodiphenylacetonitrile and triphenylphosphine, with aromatic amines³⁾ or the reaction of *N*-chlorobenzamidines with triphenylphosphine followed by treatment with base.⁴⁾ In the reports however, no information of the nature of the compounds **2** was reported. Based on the second route, several iminophosphoranes **2** have been synthesized to give moderate yields, the results of which are given in Table 1. The hydrochloric acid salts of **2** ($R^1 = \text{aryl}$, $R^2 = \text{CHPh}_2$), prepared by the reaction of **2** with hydrochloric acid, have been found to be **3** ($R^1 = \text{aryl}$, $R^2 = \text{CHPh}_2$)³⁾ [protonation on imidoily nitrogen] not **4** [protonation on the nitrogen atom of iminophosphorane].

The structure of **3** has been elucidated by NMR analysis of the $\text{N}-\text{C}=\text{NH}$ proton,³⁾ which shows a down field shift due to the electron withdrawing group R^1 .³⁾ The NH protons in **3** ($R^1 = p\text{-Me}_2\text{NC}_6\text{H}_4$, $R^2 = \text{CHPh}_2$) and **3** ($R^1 = p\text{-NO}_2\text{C}_6\text{H}_4$, $R^2 = \text{CHPh}_2$) appear

at δ 11.4 and 12.8 in CDCl_3 , respectively.

Elucidation of the structure of the hydrochloric acid salts of **2a—i** posed difficulties. The salt of **2h**, however, was confirmed as **3h** and not **4h** on the basis of the NMR studies. The NMe protons of **2h** appear at δ 3.23 as a doublet due to coupling with phosphorous ($^5J_{\text{PNCNH}} = 2 \text{ Hz}$). The NMe protons of the hydrochloride of **2h** in CDCl_3 appear at δ 3.36 as a doublet ($J = 5 \text{ Hz}$). The addition of D_2O to the solution disappeared the splitting indicating that the splitting is due to HNCH interaction not PNCNH.

The reaction of **2** with methyl iodide was conducted at room temperature to give **5** ($R = \text{Me}$). The structures of the products were elucidated on the basis of the NMR results (Table 3). The NMe protons of

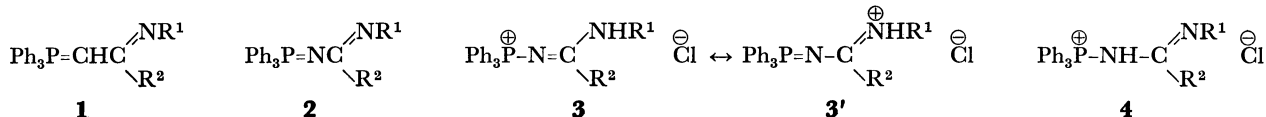


5 show no coupling with phosphorus, indicating that methylation of the nitrogen atom in the imidoily group occurs, since $^3J_{\text{PNCH}} = 10\text{—}12 \text{ Hz}$ ⁵⁾ has been reported

for compounds of the type $\text{Ph}_3\text{P}^+\text{NCH}_3$.

The NMR spectra of **5** derived from **2h** with ethyl iodide and **2i** with methyl iodide showed two groups of peaks of the same intensity (Table 3), indicating the presence of two isomers **5'** and **5''**,⁶⁾ especially in the case of sterically hindered compounds **5e**, **f**, **h**, **i**.

The reaction of *N*-alkyl or aryl iminotriphenylphosphoranes with carbon disulfide has been shown to give phosphine sulfide and isothiocyanates.²⁾ In contrast, it was found here that iminophosphorane **2**

TABLE 1. PREPARATION AND PHYSICAL PROPERTIES OF **2**

R ¹	R ²	Yield (%)	Mp (°C)	NMR (δ in CDCl ₃)	IR (KBr) cm ⁻¹		M ⁺	Found (Calcd) (%)			Reaction with CS ₂		
					ν _{C=N}	ν _{P=N}		C	H	N	Temp (°C)	Time (d)	Products (%)
2a	<i>p</i> -MeC ₆ H ₄	Ph	37	161—163	2.17(s, Me), 6.7—7.7(m, arom)	1530 1340	470	81.32 (81.68)	5.92 (5.78)	5.81 (5.95)	25	3	6a (96), R ¹ NCS (85)
2b	Ph	<i>p</i> -MeC ₆ H ₄	48	199—202	2.20(s, Me), 6.3—8.1(m, arom)	1530 1340	470	81.52 (81.68)	5.64 (5.78)	6.01 (5.95)	25	3	6b (92), R ¹ NCS (81)
2c	<i>m</i> -MeC ₆ H ₄	Ph	39	177—180	2.13(s, Me), 6.2—8.2(m, arom)	1530 1340	470	81.74 (81.68)	5.81 (5.78)	5.77 (5.95)	25	3	6a (90), R ¹ NCS (79)
2d	Ph	<i>m</i> -MeC ₆ H ₄	44	173—174	2.18(s, Me), 6.3—8.1(m, arom)	1530 1340	470	81.43 (81.68)	5.71 (5.78)	5.84 (5.95)	25	3	6c (87), R ¹ NCS (88)
2e	<i>o</i> -MeC ₆ H ₄	Ph	23	172—174	2.18(s, Me), 7.1—8.1(m, arom)	1520 1330	470	81.63 (81.68)	6.04 (5.78)	5.83 (5.95)	70	2	6a (89), R ¹ NCS (64)
2f	Ph	<i>o</i> -MeC ₆ H ₄	38	169—172	2.15(s, Me), 6.1—8.1(m, arom)	1500 1300	470	81.55 (81.68)	5.54 (5.78)	6.19 (5.95)	70	3	6d (72), R ¹ NCS (57)
2g	Ph	Ph	49	157—159	6.6—8.3(m, arom)	1520 1340	456	81.33 (81.56)	5.37 (5.52)	5.94 (6.14)	25	3	6a (94), R ¹ NCS (83)
2h	Me	Ph	30	172—175	3.23(d, <i>J</i> = 2, Me), 6.9—8.0(m, arom)	1630 1390	394	78.98 (79.19)	6.03 (5.88)	6.91 (7.10)	25	1	6a (93), R ¹ NCS (95)
2i	Et	Ph	25	160—161	1.84(t, <i>J</i> = 7, Me), 4.16(q, CH ₂) 6.5—7.7(m, arom)	1630 1390		79.73 (79.39)	6.03 (6.17)	6.41 (6.86)			

