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Preparation and Reaction of *N*-Imidoyliminotriphenylphosphoranes

Hiroshi YOSHIDA,* Tsuyoshi OGATA, and Saburo INOKAWA

Department of Synthetic Chemistry, Faculty of Engineering, Shizuoka University, Johoku, Hamamatsu 432

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Synopsis. *N*-Imidoyliminotriphenylphosphoranes **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 paper[1] the reaction of imidoyltriphenylphosphonium methylides **1** with carbon disulfide was reported. The products were a result of the attack on either the ylide carbon atom or the imidoyl nitrogen atom.

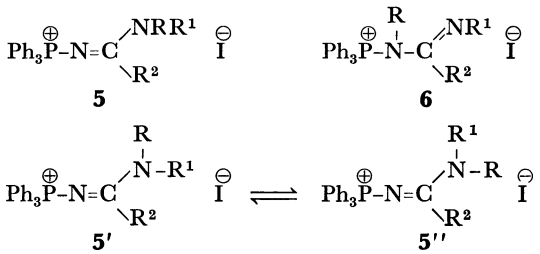
Iminophosphoranes show similar chemical properties to those of phosphonium methylides.[2] In this paper the reaction of *N*-imidoyliminotriphenylphosphoranes **2** with carbon disulfide and halides will be reported.

Iminophosphoranes **2** have been prepared by the reaction of *N*-(1-chloro-2,2-diphenylvinyl)iminophosphorane, prepared from chlorodiphenylacetonitrile and triphenylphosphine, with aromatic amines[3] 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=aryl, R^2=$CHPh_2$), prepared by the reaction of **2** with hydrochloric acid, have been found to be **3**(R^1=aryl, R^2=$CHPh_2$)[3] [protonation on imidoyl nitrogen] not **4** [protonation on the nitrogen atom of iminophosphorane].

The structure of **3** has been elucidated by NMR analysis of the N–C=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*-$Me_2NC_6H_4$, R^2=$CHPh_2$) and **3** (R^1=*p*-$NO_2C_6H_4$, R^2=$CHPh_2$) 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 ($^5J_{PNCNCH}$=2 Hz). The NMe protons of the hydrochloride of **2h** in $CDCl_3$ appear at δ 3.36 as a doublet (J=5 Hz). The addition of D_2O to the solution disappeared the splitting indicating that the splitting is due to HNCH interaction not PNCNCH.

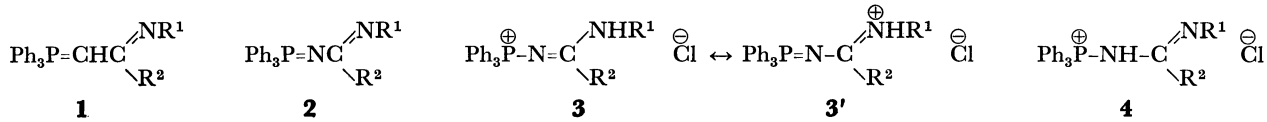
The reaction of **2** with methyl iodide was conducted at room temperature to give **5** (R=Me). The structures of the products were elucidated on the basis of the NMR results (Table 3). The NMe protons of



5 show no coupling with phosphorus, indicating that methylation of the nitrogen atom in the imidoyl group occurs, since $^3J_{PNCH}$=10—12 Hz[5] has been reported for compounds of the type $Ph_3\overset{\oplus}{P}NCH_3$.

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**



1 **2** **3** **3′** **4**

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

	R^1	R^2	Yield (%)	Mp (°C)	NMR (δ in $CDCl_3$)	IR (KBr) cm^{-1} $\nu_{C=N}$	IR (KBr) cm^{-1} $\nu_{P=N}$	M^+	Found (Calcd) (%) C	Found (Calcd) (%) H	Found (Calcd) (%) N	Reaction with CS_2 Temp (°C)	Time (d)	Products (%)
2a	*p*-MeC_6H_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^1NCS(85)
2b	Ph	*p*-MeC_6H_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^1NCS(81)
2c	*m*-MeC_6H_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^1NCS(79)
2d	Ph	*m*-MeC_6H_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^1NCS(88)
2e	*o*-MeC_6H_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^1NCS(64)
2f	Ph	*o*-MeC_6H_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^1NCS(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^1NCS(83)
2h	Me	Ph	30	172—175	3.23(d, J=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^1NCS(95)
2i	Et	Ph	25	160—161	1.84(t, J=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)			

Table 2. The HCl salts of 2

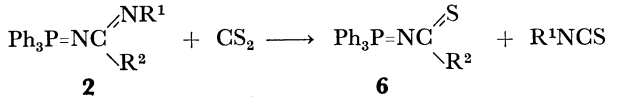
	Mp (°C)	NMR (δ in $CDCl_3$)	IR(KBr) cm^{-1}
3a	262—264	2.27(s, Me), 6.8—8.4(m, arom), 12.57(broad s, NH)	1530
3b	232—334	2.22(s, Me), 6.7—8.4(m, arom), 12.73(broad d, J=6, NH)	1530
3c	192—195	2.31(s, Me), 6.8—7.9(m, arom), 12.92(broad s, NH)	1530
3d	205—210	1.96(s, Me), 6.8—8.1(m, arom), 12.28(broad d, J=5, NH)	1530
3e	251—253	2.36(s, Me), 6.5—8.0(m, arom), 12.66(broad d, J=7, NH)	1580, 1500
3f	167—169	1.92(s, Me), 6.6—8.2(m, arom), 12.53(broad d, J=6, NH)	1530
3g	240—242	6.6—8.2(m, arom), 12.61(broad s, NH)	1530
3h	257—262	3.36(d, J=5, NMe), 6.8—8.0(m, arom), 10.28(broad s, NH)	1640, 1590
3i	146—148	1.47(t, J=7, Me), 3.87(q, CH_2), 6.8—8.0(m, arom), 10.32(broad s, NH)	1640, 1600

Table 3. Alkylation of 2 with alkyl iodide in chloroform

5	Mp (°C)	RI	NMR (δ in $CDCl_3$)
5a	Resinous	MeI	2.15(s, Me), 4.04(s, NMe), 6.6—7.9(m, arom)
5b	142—144	MeI	2.10(s, Me), 3.98(s, NMe), 6.4—7.9(m, arom)
5c	Resinous	MeI	2.21(s, Me), 4.00(s, NMe), 7.0—7.9(m, arom)
5d	Resinous	MeI	1.84(s, Me), 4.03(s, NMe), 6.4—8.0(m, arom)
5e	203—206	MeI	1.39 and 1.46(s, 44 : 56, Me), 3.39 and 4.02 (s, 56 : 44, NMe), 6.7—8.0(m, arom)
5f	255—256	MeI	1.65 and 1.88(s, 56 : 44, Me), 3.27 and 4.07 (s, 44 : 56, NMe), 6.5—7.8(m, arom)
5g	Resinous	MeI	3.92 (s, NMe), 6.5—8.0(m, arom)
5h	230—232	MeI	3.09 and 3.75(s, NMe), 6.8—7.8(m, arom)
	214—216[a] + 230—232	EtI	1.18 and 1.59(t, J=7, 59 : 41, Me), 3.07 and 3.74(s, 41 : 59, NMe), 3.44 and 3.80(q, J=7, 59 : 41, CH_2), 6.8—8.0(m, arom)
5i	216—218[a] + 230—232	MeI	1.18 and 1.59(t, J=7, 63 : 37, Me), 3.07 and 3.74(s, 37 : 63, NMe), 3.44 and 3.80(q, J=7, 63 : 37, CH_2), 6.8—8.0(m, arom)

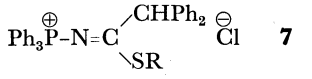
a) A mixture of two crystalline compounds.

readily reacted with carbon disulfide to give *N*-(thioacyl)iminophosphorane **6** and isothiocyanate:



2 **6**

Iminophosphoranes **6** have been considered as intermediates in the reaction of thiobenzoyl azide (phenyl thiatriazole) with triphenylphosphine,[7] giving benzonitrile and phosphine sulfide. In the thermolysis of the phosphonium salts **7** (R=Me, *t*-Bu), the isolation of **6** have not been successful.[3,7] The structure of **6** has been confirmed on the basis of NMR, IR, and MS.[8]



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Experimental

Preparation of **2**. As a typical experiment the preparation of **2a** will be given. *N*-Phenyl-*N'*-chlorobenzamidine was prepared according to the literature[9] and used without purification. To a stirred solution of *N*-phenyl-*N'*-chlorobenzamidine(0.01 mol) in dry benzene(30 ml) was added a solution of triphenylphosphine(0.01 mol) in dry ether(20 ml), the temperature being kept below 10 °C. After 2 h the oily precipitate was separated and dissolved in EtOH (20 ml). To the solution was added in one step a solution of KOH (0.03 mol) in EtOH(10 ml) and the solution stirred vigorously. After 3 min the mixture was quenched with water (60 ml) and extracted with $CHCl_3$(50 ml). The extract was dried over Na_2CO_3 and concentrated *in vacuo* to give a crystalline material. Crystallization from $CHCl_3$–petroleum ether gave **2a** in 37% yield, the results of which are shown in Table 1.

Preparation of the Hydrochloric Acid Salts of **2**. To a solution of **2a**(5 mmol) in $CHCl_3$(20 ml) was added concd HCl(1 ml) in one portion. The mixture was stirred and the organic layer separated. Concentration of the solution *in vacuo* gave white crystalline substance **3a** quantitatively (Table 2).

Alkylation of **2** *with Alkyl Iodide*. To a solution of **2a** (5 mmol) in $CHCl_3$(20 ml) was added MeI(0.5 ml) in one portion. The mixture was left at room temperature for 24 h. Concentration of the solution *in vacuo* gave a white resin **5a**(R=Me)quantitatively.

The Reaction of **2** *with Carbon Disulfide*. A solution of **2a** (10 mmol) and CS_2(100 mmol) in $CHCl_3$(30 ml) was left to stand for 3 days at room temperature. The mixture was dried *in vacuo* and extracted with petroleum ether. On crystallization from AcOEt the extracts gave **6a** in 96% yield. The mother liqour was found to be *p*-tolyl isothiocyanate by comparison of the IR spectrum with that of authentic sample. The yield was determined by VPC (Silicone Grease 20% on celite) using mesitylene as an internal standard.

6a(R^2=Ph): mp 158—160 °C. NMR($CDCl_3$) δ=6.6—8.2(m, arom). M^+ 397. IR(KBr) 1340 cm^{-1}(P=N). Found: C, 75.23; H, 4.98; N, 3.61%. Calcd for $C_{25}H_{20}NSP$: C, 75.55; H, 5.07; N, 3.53%.

6b(R^2=*p*-MeC_6H_4): mp 159—160 °C. NMR($CDCl_3$) δ =2.31(s, Me), 6.9—8.1(m, arom). M^+ 411. IR(KBr) 1350 cm^{-1}(P=N). Found: C, 75.96; H, 5.43; N, 3.21%. Calcd for $C_{26}H_{22}NSP$: C, 75.89; H, 5.39; N, 3.40%.

6c(R^2=*m*-MeC_6H_4): mp 144—145 °C. NMR($CDCl_3$) δ= 2.38(s, Me), 6.9—8.2(m, arom). M^+ 411. IR(KBr) 1350 cm^{-1}(P=N). Found: C, 75.64; H, 5.14; N, 3.26%. Calcd for $C_{26}H_{22}NSP$: C, 75.89; H, 5.39; 3.40%.

6d(R^2=*o*-MeC_6H_4): mp 143—145 °C. NMR($CDCl_3$) δ= 2.54(s, Me), 6.9—8.1(m, arom). M^+ 411. IR(KBr) 1350 cm^{-1}(P=N). Found: C, 75.81; H, 5.26; N, 3.49%. Calcd for $C_{26}H_{22}NSP$: C, 75.89; H, 5.39; N, 3.40%.

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