The Structure of Amidinophosphonium Salts[1]

By T. WINKLER and W. VON PHILIPSBORN*
(*Organisch-chemisches Institut der Universität Zürich,* 8001 *Zürich, Switzerland*)

and J. STROH, W. SILHAN, and E. ZBIRAL
(*Organisch-chemisches Institut der Universität Wien, A*-1090 *Wien, Austria*)

Summary The synthesis of amidinotriphenylphosphonium salts from the very reactive and novel imide bromides $R^1N{=}C(Br)R^2$ and iminophosphoranes $Ph_3P{=}NR$ is reported, and variable-temperature n.m.r. spectra prove a fluxional structure for the amidinophosphonium salts.

WE reported[2] that reaction of acyl derivatives RCOX ($X = CN, N_3$) with iminophosphoranes $Ph_3P{=}NR$ leads to elimination of Ph_3PO, yielding imino-nitriles and imino-azides or tetrazoles. Further reactions with various acid halides, particularly acid bromides, pointed towards a general synthetic method for imide halides which hitherto have been difficult to prepare.[3] The very reactive imide bromides $R^1N = C(Br)R^2$ attack a second molecule of iminophosphorane as follows:

The ^1H n.m.r. spectra of the alkyl groups R^1 and R^3 exhibit a marked temperature dependence. To study this phenomenon we have chosen the model compounds (1) and (2).

The spectrum of the amidinophosphonium bromide (1) (100 MHz, $CDCl_3$) at 60° shows only one methyl signal which is split into a doublet by coupling with the phosphorus nucleus, J_{PH} 5·5 Hz (Figure, a). At −63° however, two methyl signals with different chemical shifts are observed as expected (Figure, b). The methyl group at lower field (2·94 p.p.m.) is split into a doublet with J_{PH} 11 Hz while the high-field methyl signal (Me·N : C) appears as a singlet at 2·63 p.p.m. At 27° the system is in the range of coalescence (Figure, c).

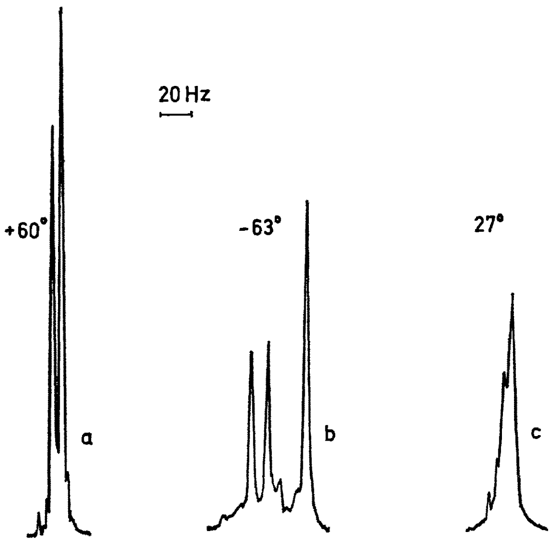
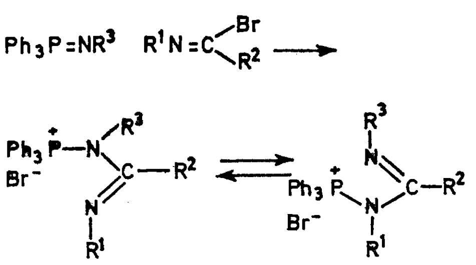


FIGURE. *Methyl resonance of the amidinophosphonium bromide* (1) *in* $CDCl_3$ *at different temperatures.*



(1) $R^1 = R^3 = Me$; $R^2 = Ph$
(2) $R^1 = R^3 = Pr^i$; $R^2 = Ph$

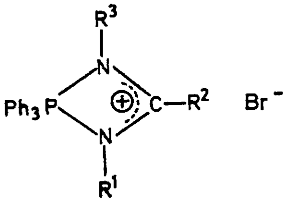
The temperature-dependence of the chemical shifts and the fact that J_{PH} at high temperature constitutes the average of the two low-temperature values (11 and *ca.*0 Hz) shows the presence of a fluxional amidinophosphonium salt in which one of the nitrogen atoms acts as internal nucleophile.

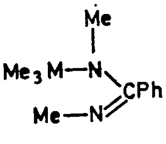
$\Delta\nu$ (Hz)	T_c (K)	E_a (kcal./mole)	$\Delta G^{\ddagger}_{77}$ [a] (kcal./mole)	$\Delta H^{\ddagger}$ (kcal./mole)	$\Delta S^{\ddagger}$ (cal. deg.$^{-1}$ mole^{-1})
60·5	350 ± 2	14·9 ± 0·7	17·2 ± 0·9	14·2 ± 0·7	−8 ± 2

[a] Obtained from total line-shape analysis as well as from the coalescence point.

As expected the spectrum of (2) (100 MHz, 1,1,2,2-tetrachloroethane) exhibits the signals of two different isopropyl groups whose methyl doublets coalesce at +77°. The temperature-dependence of the methyl signals has been studied between +37° and +140°† using the total line shape method of Rabinovitz and Pines.[4] The activation parameters listed in the Table have been obtained.

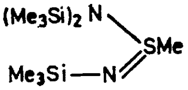
(3)



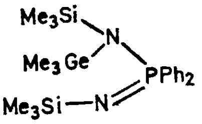


M = Si, Sn

(4)

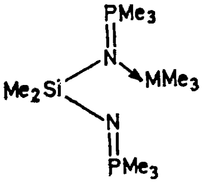


(5)



(6)

(7)



M = Ga, Al

The negative activation entropy for the process is noteworthy. This indicates that the conformation of the transition state for the valence isomerisation does not correspond to the preferred conformation of (2), in which the steric interaction of the bulky triphenylphosphonium group and the alkylimino-group is relieved.

As an intermediate of the rearrangement, structure (3) with a quinquelignant phosphorus could also be discussed. If the stationary concentration of (3) is high enough such a structure might be detected by phosphorus n.m.r. spectroscopy because of the higher shielding of quinquelignant phosphorus as compared to onium-phosphorus. Recently very similar rearrangements have been reported by Scherer *et al.*[5] in compounds (4) and (5) and by Schmidbaur *et al.*[6] in compound (6).

Furthermore, compounds of structure (7) undergo exchange of the MMe_3 group and activation energies of

---

† The compound starts to decompose above 120°.

12·8 kcal./mole (M=Ga) and 13·4 kcal./mole (M=Al) have been reported.

E.Z. is indebted to J. R. Geigy A.G., Basel, and the Zürich authors acknowledge support of this work by the Schweizerischer Nationalfonds.

(*Received, September* 28*th*, 1970; *Com.* 1659.)

---

[1] For previous paper in the series, see E. Zbiral, E. Bauer, and J. Stroh, *Monatsh.*, 1970, in the press.

[2] E. Zbiral and J. Stroh, *Annalen*, 1969, **725**, 29.

[3] To be published. See also: G. Fodor, J. J. Ryan, and F. Letourneau, *J. Amer. Chem. Soc.*, 1969, **91**, 7768.

[4] M. Rabinovitz and A. Pines, *J. Amer. Chem. Soc.*, 1969, **91**, 1585.

[5] O. J. Scherer, *Angew. Chem.*, 1969, **81**, 885; O. J. Scherer and R. Schmitt, *J. Organometallic Chem.*, 1969, **16**, P11; O. J. Scherer and P. Hornig, *Chem. Ber.*, 1968, **101**, 2533.

[6] H. Schmidbaur and W. Wolfsberger, *Angew. Chem.*, 1967, **79**, 411; H. Schmidbaur, *Fortschr. chem. Forsch.*, 1969, **13**, 217.