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GEMINAL SYSTEMS.

COMMUNICATION 20.* STRUCTURE AND PROPERTIES OF AMINOMETHYLPHOSPHONIUM SALTS

R. G. Kostyanovskii, Yu. I. Él'natanov, Sh. M. Shikhaliev, S. M. Ignatov, I. I. Chervin, Sh. S. Nasibov, A. B. Zolotoi, O. A. D'yachenko, and L. O. Atovmyan

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The phosphonium form of the phosphorus has greatest configurational stability [2]. Thus, for example, the PMR spectra of salts $[i\text{-Pr}(PhCH_2)\overset{\oplus}{P}MeH]\,I^{\ominus}$ [1] and $[i\text{-Pr}_2(PhCH_2)\overset{\oplus}{P}Me]Br^{\ominus}$ (I) show nonequivalence of the methyl group protons of the isopropyl substituent (eight signals instead of four).

The properties of aminomethylphosphonium salts (AMPS) were attributed in our previous work to an anomalous reduction in the configurational stability of the phosphorus atom for the following reasons [3, 4]. First, the PMR spectra of all prepared AMPS do not display the expected nonequivalence of the geminal protons and substituent groups at the phosphorus atom [1]. For example, Fig. 1 shows the equivalence of all three indicator groups (*i*-Pr, $CH_2N<$, and CH_2Ph). Second, this spectrum lacks the additional multiplicity of the morpholine ring CH_2N signal which arises in the spectrum of the original aminomethylphosphine [1] due to asymmetric indication of the chiral phosphorus atom. These effects are retained in different solvents such as $CDCl_3$ (see Fig. 1) taken instead of CD_3OD, in which a low value is found for $\Delta\nu$ of the methyl groups in $Me_2\overset{\oplus}{P}(Ph)CH(Ph)Me\ \overset{\ominus}{Br}$ [5]. In the PMR spectrum of $[i\text{-Pr}_2(Me)\overset{\oplus}{P}CH_2N\text{-}(CH_2CH_2)_2O]\,I^{\ominus}$ (II) in Freon-21, the signals of the indicator groups are not split even upon cooling to −100°C, and the ^{13}C NMR spectrum shows equivalence of the methyl carbons and isopropyl groups in contrast to model phosphonium salt (III) (Table 1). The loss of the configurational stability of the phosphorus atom in AMPS may be attributed to the formation of a covalent P—anion bond and pseudorotation in the phosphorane formed. Since the question of the existence of iodophosphoranes is still not clear [6], we varied the $X^{\ominus}$ anions from those capable of forming a P—X bond to those to which formation of a covalent bond is very unlikely

$$i\text{-Pr}_2(Me)\overset{\oplus}{P}CH_2N(CH_2CH_2)_2O\ \overset{AgNO_3}{\underset{D_2O}{\longleftarrow}}\ (II)\ \xrightarrow[D_2O]{AgClO_4}\ i\text{-Pr}_2(Me)\overset{\oplus}{P}CH_2N(CH_2CH_2)_2O$$
$$NO_3^{\ominus}\ (V) \qquad\qquad ClO_4^{\ominus}\ (IV)$$

$$i\text{-Pr}_2(Me)\overset{\oplus}{P}CH_2NMe_2\ \xleftarrow{Me_2NCH_2F}\ i\text{-Pr}_2PMe\ \xrightarrow{O_2(CH_2CH_2)N^{\oplus}=CH_2,\ Br^{\ominus}}\ i\text{-Pr}_2(Me)\overset{\oplus}{P}CH_2N(CH_2CH_2)_2O$$
$$F^{\ominus}\ (VII) \qquad\qquad Br^{\ominus}\ (VI)$$

*For Communication 19, see our previous work [1].

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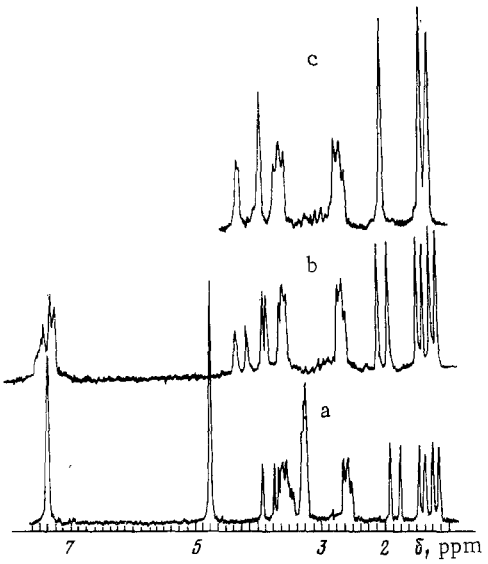


Fig. 1

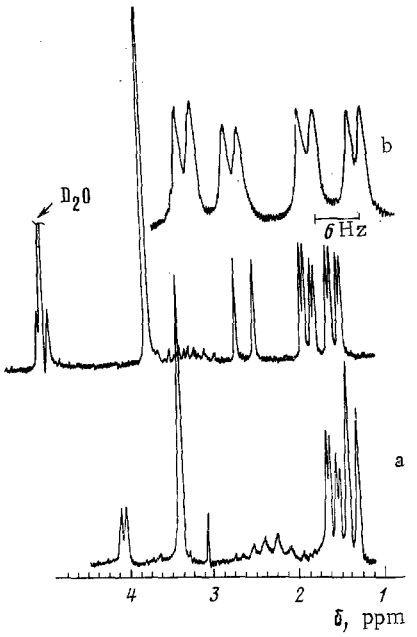
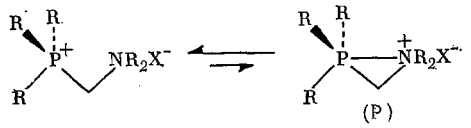


Fig. 2

Fig. 1. PMR spectrum of $[i\text{-Pr}(PhCH_2)Me\overset{\oplus}{P}CH_2N(CH_2CH_2)_2O]I^{\ominus}$; equivalence is observed for the protons of the three indicator groups (CH_2N, CH_2Ph, and i-PrP): a) in CD_3OD; b) in $CDCl_3$; c) $\{^{31}P\}$ in $CDCl_3$.

Fig. 2. PMR spectra: a) $[i\text{-}Pr_2PCH_2\overset{\oplus}{N}Me_3]FSO_3^{\ominus}$ in D_2O; b) $[i\text{-}Pr_2(Me)\overset{\oplus}{P}CH_2\overset{\oplus}{N}Me_3]I^{\ominus}FSO_3^{\ominus}$ [1] in D_2O; upon blocking the unshared electron pair of the nitrogen, the methyl groups of the isopropyl substituent becomes nonequivalent.

However, in all cases, the same spectral behavior was found with equivalence of the indicator groups. In addition, the ^{31}P NMR chemical shifts of the AMPS correspond to phosphonium salts and not to phosphoranes [1]. The loss of configurational stability of the phosphorus atom in AMPS due to reverse dissociation $R_3\overset{\oplus}{P}CH_2NR_2X^{\ominus} \rightleftharpoons R_3P + CH_2{=}\overset{\oplus}{N}R_2X^{\ominus}$ is excluded since the PMR spectra show coupling of the protons of all the substituents with the ^{31}P nucleus [1] (see, for example, Fig. 1). Even if this equilibrium were realized, we would expect nonequivalence of the geminal protons and substituent groups at the phosphorus atom since phosphorus quaternization occurs with retention of configuration [2]. The PMR spectra indicate that the configurational stability of the phosphorus atom is restored in going from AMPS to bis-quaternary ammonium–phosphonium salts [1] (Fig. 2, Table 1), i.e., upon blocking the unshared electron pair of the α-heteroatom. Thus, the cause for the loss of the configurational stability of the phosphorus atom in AMPS due to pseudorotation in the phosphorane form (P) of the aminomethylphosphonium–phosphoranemethylenimmonium equilibrium may be related specifically to the presence of this electron pair [3, 4].



The monomolecular nature of the process is supported by the invariance of the PMR spectra of AMPS upon very high dilution. The formation of structure P is apparently possible only due to the proximity of the donor and acceptor sites (N and $P^{\oplus}$) with a minimal number of degrees of freedom of the system since additives such as pyridine to the bis-quaternary salts do not lead to the loss of the configurational stability of the phosphonium phosphorus atom. The similarity of the ^{31}P chemical shifts of AMPS with those of phosphonium salts and not with phosphoranes is attributed to the small contribution of structure P to the equilibrium.

TABLE 1. NMR Spectra of Phosphonium and Aminomethylphosphonium Salts

Compound	Solvent	δ, ppm						J, Hz						
		Me_A	Me_B	Me—P	CH_2P	CH—P	other	Me_ACH	Me_BCH	Me_AP	Me_BP	CH_2P	Me—P	other
$i\text{-}Pr_2\overset{\oplus}{P}(Me)\,CH_2PhBr^{\ominus}$ (I)	CD_3OD	1,25	1,25	1,75	3,74	2,57	7,34 (Ph)	7,0	7,0	17,0	17,0	–	12,5	14,5 (PCH_2Ph)
$i\text{-}Pr_2\overset{\oplus}{P}(Me)CH_2N(CH_2CH_2)_2O\overset{\ominus}{I}$ (II)	$CDCl_3$ [a]	1,39	1,39	1,99[b]	3,79	3,00	2,72 (NCH_2) 3,79 (OCH_2)	7,5	7,5	16,5	16,5	5,0	12,5	–
	CH_2Cl_2	1,35	1,35	1,94[b]	3,74	2,93	2,69 (NCH_2) 3,60 (OCH_2)	7,2	7,2	16,5	16,5	4,9	12,6	–
	Freon-21	1,43	1,43	1,98	3,82	3,05	2,75 (NCH_2) 3,68 (OCH_2)	7,0	7,0	16,5	16,5	4,8	12,5	–
	CD_3OD	1,30	1,30	1,82[b]	3,50	2,75	2,63 (NCH_2) 3,60 (OCH_2)	7,0	7,0	16,5	16,5	5,0	13,0	–
	CD_3OD[c]	1,378	1,38	1,848	3,513	2,753	2,681 (NCH_2) 3,692 (OCH_2)	7,20	7,20	16,65	17,38	5,04	12,81	2,58 (PCH)
	D_2O[d]	1,78	1,78	2,25	3,98	3,20	3,15 (NCH_2) 4,18 (OCH_2)	6,9	6,9	17,2	17,2	4,8	12,3	–
	DMSO-D_6	1,15	1,15	1,74	3,43	2,58	2,50 (NCH_2) 3,40 (OCH_2)	6,9	6,9	15,8	15,8	4,8	12,8	–
	C_5D_5N	1,34	1,24	2,10	3,90	2,98	2,69 (NCH_2) 3,56 (OCH_2)	7,0	7,0	16,5	16,5	4,9	12,9	–
$i\text{-}Pr_2\overset{\oplus}{P}(H)Me\overset{\ominus}{I}$ (III)[e]	$CDCl_3$	1,36	1,44	1,94	–	2,99	2,96 (HP)	7,0	7,0	19,0	19,0	–	13,5	206,0 (HP) 5,5 (MeH)
$i\text{-}Pr_2\overset{\oplus}{P}MeCH_2N(CH_2CH_2)_2O\overset{\ominus}{B}r$ (VI)[f]	$CDCl_3$	1,33	1,40	1,95	3,80	2,95	2,68 (NCH_2) 3,53 (OCH_2)	6,8	6,8	15,8	15,8	4,5	12,8	–
$i\text{-}Pr_2\overset{\oplus}{P}(Me)CH_2NMe_2\overset{\ominus}{F}$ (VII)[g]	$CDCl_3$	1,25	1,34	1,80	3,45	2,65	–	7,0	7,0	16,8	16,8	4,9	12,8	–
$\overset{\oplus}{i}\text{-}Pr_2\overset{\oplus}{P}(Me)CH_2O\overset{\ominus}{H}I$ (VIII)	$CDCl_3$	1,24	1,24	1,86	4,64	2,76	–	7,0	7,0	16,0	16,0	4,8	12,0	–
$i\text{-}Pr_2\overset{\oplus}{P}(Me)CH_2OMe\overset{\ominus}{C}l$ (IX)	$CHCl_3$	1,17	1,17	1,81	4,42		3,29 (MeO)	7,0	7,0	17,0	17,0	5,0	13,2	–
$i\text{-}Pr_2\overset{\oplus}{P}(Me)CH_2SEt\overset{\ominus}{C}l$ (X)	$CDCl_3$	1,33	1,33	1,80	2,77	2,70	1,26 ($\underline{Me}CH_2$) 3,50 ($\underline{CH_2}Me$)	7,0	7,0	17,0	17,0	–	13,0	7,0 ($MeCH_2$) 10,5 (PCH_2Me)
$i\text{-}Pr_2\overset{\oplus}{P}(Me)C_6H_4OMe\text{-}o\overset{\ominus}{I}$ (XI)	$CDCl_3$	1,20	1,30	2,23	–	3,25	4,03 (MeO) 7,50 (Ph)	7,2	6,8	17,3	15,8	–	12,0	–

a) ^{13}C NMR in $CDCl_3$ from TMS: MeP (δ 2.71 ppm, J_{CP} = 47.9 Hz), MeCH (18.2 ppm, 3.1 Hz), CHP (22.3 ppm, 43.4 Hz), PCH_2 (49.3 ppm, 62.2 Hz), NCH_2 (56.5 ppm, 6.4 Hz), OCH_2 (67.3 ppm, 0 Hz). For the J_{CP} values, see lit. ref. [8]. b) The equivalence of the methyl groups of the isopropyl substituent remains after the addition of C_6F_6. c) The PMR spectrum of a 1% solution was measured from TMS on a Nicolet NT-360-WB spectrometer at 360 MHz. d) Values for δ from external HMDS. e) ^{13}C NMR spectrum in $CDCl_3$ from TMS: MeP (δ −1.3 ppm, J_{CP} = 48.9 Hz), $\underline{Me}^1CH$ (15.9 ppm, 1.7 Hz), $\underline{Me}^2CH$ (17.2 ppm, 0.9 Hz), CHP (19.23 ppm, 44.8 Hz). f) ^{13}C NMR spectrum in $CDCl_3$ from TMS: MeP (δ 3.5 ppm, J_{CP} = 49.6 Hz), MeCH (20.4 ppm, 0 Hz), CHP (42.3 ppm, 44.1 Hz), CH_2P (52.0 ppm, 63.6 Hz), CH_2N (59.7 ppm, 6.8 Hz), CH_2O (70.8 ppm, 0 Hz). g) δ NMe 2.34 ppm.

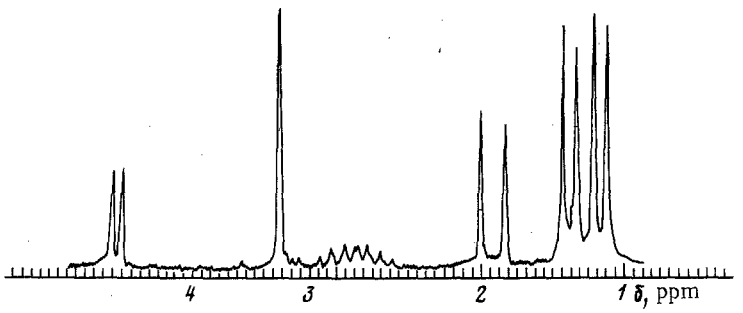


Fig. 3. PMR spectrum of (IX) in $CHCl_3$; the equivalence of the methyl groups of the isopropyl substituent is retained in various solvents and from +30 to −80°C in CD_3OD.

Since the formation of a P structure may be provided by the unshared electron pairs of the oxygen and sulfur atoms, we obtained hydroxymethylphosphonium (VIII), methoxymethylphosphonium (IX), and ethylthiomethylphosphonium (X) salts

$$i\text{-}Pr_2PCH_2OH \xrightarrow[Et_2O]{MeI} i\text{-}Pr_2(Me)\overset{\oplus}{P}CH_2OH\ I^{\ominus} \quad \text{(VIII)}$$

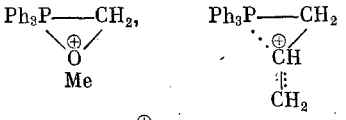
$$i\text{-}Pr_2(Me)\overset{\oplus}{P}CH_2SEt\ Cl^{\ominus} \xleftarrow[100^\circ]{EtSCH_2Cl} i\text{-}Pr_2PMe \xrightarrow[Et_2O]{MeOCH_2Cl} i\text{-}Pr_2(Me)\overset{\oplus}{P}CH_2OMe\ Cl^{\ominus}$$

(X) (IX)

The PMR spectra of these compounds such as (IX) (Fig. 3), similar to the AMPS spectra, show equivalence of the indicator groups (see Table 1), which indicates an equilibrium with contribution of phosphoranemethylenoxonium and **phosphoranemethylensulfonium structures.**

The most serious doubts concerning the configurational lability of hydromethylphosphonium salts is raised by the separation of chiral triarylphosphines into antipodes through hydroxymethylphosphonium salts, although there are indications that this method is unsuitable for trialkyl- and alkylarylphosphines [7]. The remaining literature data are in accord with our interpretation.

1. The anomalies in the NMR spectra for $R_3\overset{\oplus}{P}CH_2X\ Y^{\ominus}$ systems are attributed to the formation of P structures



and compounds with distant donor groups ($Ph_3\overset{\oplus}{P}CH_2CH_2OMeY^{\ominus}$) have normal properties [8].

2. a) The phosphonium—phosphorane equilibrium has been reported [9] and the extreme forms of this equilibrium may sometimes be isolated [10]. b) The phosphite—phosphorane equilibrium has been reported due to intramolecular N → P coordination [11]. c) The phosphate—phosphorane equilibrium has been demonstrated [12].

3. The formation of a P—N bond occurs in some reactions when these atoms lie close to one another [13].

4. The anomalously high rate of quaternization of o-anisylphosphines is attributed to the anchimeric effect of the MeO group and the NMR spectral anomalies of o-anisylphosphonium salts have been attributed to a O → P interaction. These effects are **diminished upon removal** of the donor site (introduction of the $MeOCH_2$ group instead of MeO). The formation of a P structure is confirmed by x-ray **structural** analysis of the salt $[o\text{-}MeOC_6H_4\overset{\oplus}{P}(Ph_2)CH_2Ph]Br^{\ominus}$, in which the O···P distance is 2.878 Å, which is less than the sum of the van der Waals radii (3.3 Å) [14]. In this case, we would expect a decrease in the configurational stability of the phosphorus atom. Thus, we obtained o-anisylphosphonium salt (XI) containing suitable indicator groups

$$o\text{-}MeOC_6H_4Br \xrightarrow[Et_2O]{Mg} o\text{-}MeOC_6H_4MgBr \xrightarrow{i\text{-}Pr_2PCl} o\text{-}MeOC_6H_4PPr_2\text{-}i \xrightarrow[Et_2O]{MeI}$$

$$\rightarrow o\text{-}MeOC_6H_4\overset{\oplus}{P}(Me)Pr_2\text{-}i\ I^{\ominus} \quad \text{(XI)}$$

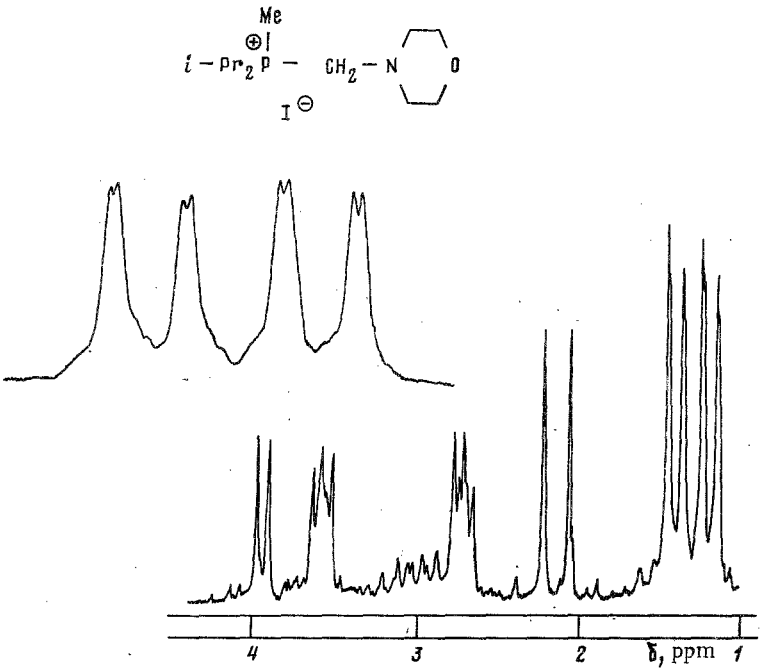


Fig. 4. PMR spectrum of (II) in C_5D_5N: the methyl groups of the isopropyl substituent are nonequivalent.

However, the PMR spectrum of (XI) showed nonequivalence of the isopropyl group methyl protons which is retained upon heating to 190°C (see Table 1).

This finding casts doubt on the reliability of the results discussed above. The cause for the observed equivalence of the indicator groups in AMPS may be a small value for $\Delta\nu$. Indeed, nonequivalence is found in the PMR spectrum of (II) in CD_3OD for the isopropyl group methyl protons at 360 MHz and is only 0.72 Hz (see Table 1); it can be observed at 80 MHz only in C_5D_5N ($\Delta\nu \sim 0.85$ Hz) (Fig. 4). Thus, we may conclude that the configurational stability of the phosphorus atom in AMPS is retained and the considerations given above are incorrect.

This is supported by the x-ray structural analysis of salt (II) (Fig. 5, Table 2) which indicates tetrahedral configuration of the phosphorus atom. The N···P distance is 2.69 Å, which is less than the sum of the van der Waals radii (3.48 Å) but significantly greater than the sum of the covalent radii (1.84 Å), i.e., there is no direct interaction beteen the nitrogen and phosphorus atoms. Of the structural features of (II), we should note the marked deviation of the bond angles at the phosphorus atom from the normal tetrahedral angles and lengthening of the P—C_8 bond to 1.91(2) Å, which may be attributed to an $n \rightarrow \sigma^*$ interaction of the unshared electron pair of nitrogen with the antibonding orbital of the C—P bond (the dihedral angle of the unshared electron pair (N)—N—C_8—P is about 30°). The other structural parameters are in accord with mean values for ordinary phosphonium salts (∠CPC = 109.5°, P—C(sp^3) bond length = 1.84 Å [15]).

We found that AMPS have aminomethylating action relative to nucleophiles

$$(II) \xrightarrow[2)\ MeI]{1)\ MeONa/MeOH} \underset{(XII)}{i\text{-}Pr_2\overset{\oplus}{P}Me_2\ \overset{\ominus}{I}} + O_2(CH_2CH_2)NCH_2OMe$$

This may be attributed to the formationof bis(aminomethyl)phosphonium salts in the iodoalkylation of aminomethylphosphines reported in our previous work [1]. Aminomethylphosphines do not undergo phosphinomethylation even under vigorous conditions [16]. This reaction could not be carried out for the phosphinomethylammonium salts $[i\text{-}Pr_2PCH_2\overset{\oplus}{N}(Me)_2CH_2Ph]\ Br^{\ominus}$ and $[PhCH_2(t\text{-}Bu)PCH_2\overset{\oplus}{N}Me_3]\ I^{\ominus}$, which are unchanged upon heating for 18 h in methanol with MeONa in MeOH at reflux.

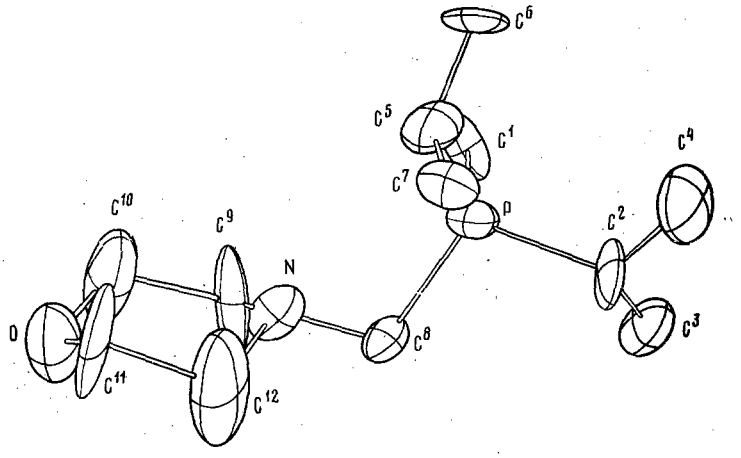


Fig. 5. Molecular structure of (II). Major bond lengths: P–C^1 1.83(3) Å, P–C^2 1.87(3) Å, P–C^5 1.82(4) Å, P–C^8 1.91(2) Å; the bond angles at the phosphorus atom: C^1PC^2 110(1)°, C^1PC^5 110(1)°, C^1PC^8 112(1), C^2PC^5 115(1)°, C^2PC^8 101(1),, C^5PC^8 108(1)°.

TABLE 2. Atomic Coordinates in Structure (II)

Atom	X	Y	Z
I	0,1373(1)	0,1478(1)	0*
P	−0,1578(3)	0,1403(3)	−0,0724(6)
O	0,016(1)	0,395(1)	−0,172(4)
N	−0,095(1)	0,276(1)	−0,133(2)
C^1	−0,088(2)	0,078(1)	−0,150(3)
C^2	−0,260(1)	0,101(2)	−0,086(3)
C^3	−0,275(2)	0,075(2)	−0,210(2)
C^4	−0,286(2)	0,052(3)	0,005(5)
C^5	−0,125(2)	0,156(2)	0,079(4)
C^6	−0,096(2)	0,085(2)	0,123(3)
C^7	−0,183(2)	0,202(1)	0,145(2)
C^8	−0,169(1)	0,2373(9)	−0,148(2)
C^9	−0,038(3)	0,272(2)	−0,223(4)
C^{10}	0,036(2)	0,322(2)	−0,200(4)
C^{11}	−0,041(3)	0,407(2)	−0,085(7)
C^{12}	−0,113(2)	0,350(2)	−0,106(7)

*Coordinate fixed for selection of origin.

EXPERIMENTAL

The experimental conditions and instruments used for determination of the physicochemical indices are the same as those in our previous work [1]. The ^{13}C NMR spectra were taken on a JNM-PS-100 spectrometer at 25.2 MHz with internal TMS as standard. The NMR spectra are given in Table 1.

Methyldiisopropylbenzylphosphonium Bromide (I). A sample of 0.26 g (1.5 mmole) $PhCH_2Br$ was added to a solution of 0.2 g (1.5 mmole) i-Pr_2PMe in 5 ml ether. After 2 h, the precipitate was removed and twice washed with ether. Recrystallization from methanol–ether yielded 0.35 g (76%) (I) as white crystals with mp 129–131°C. Found: C 55.1; H 8.48%. Calculated for $C_{14}H_{24}PBr$: C 55.44; H 7.92%.

N-Morpholinomethyldiisopropylmethylphosphonium Iodide (II) was obtained according to our previous procedure [1], mp 138–140°C, as transparent white parallelepiped crystals which are elongated along the c axis of the rhombic cell. The major crystallographic data: $[C_{12}H_{27}NOP]^{\oplus}I^{\ominus}$ a = 16.871(6) Å, b = 17.510(6) Å, c = 11.323(6) Å, V = 3344.94 Å^3, sp. gr. ba2, M = 359.233, Z = 8, d_{calc} = 1.434 g/cm^3, μ(Mo K_α) = 20.2 cm^{-1}. The intensities of 622 independent nonzero reflections ($I \geqslant 2(I)$) of the type kh0–hk9 were measured on an automatic equiinclined DAR-UM diffractometer by layer recording. The absorption was not taken into account. The structure was deciphered using the three-dimensional Patterson map and refined in the full-matrix aniso-

tropic approximation using the Rentgen-75 program [17] to R = 0.049. The atomic coordinates are given in Table 2.

Methyldiisopropylphosphonium Iodide (III). A solution of 1.18 g (10 mmoles) i-Pr_2PH in 10 ml ether was treated with an excess of MeI. The precipitate was removed after 2 h. Recrystallization from methanol–ether yielded 2.45 g (94%) (III) as colorless prisms with mp 150-151°C. Found: C 32.75; H 6.80; P 11.71%. Calculated for $C_7H_{18}PI$: C 32.30; H 6.92; P 11.92%.

N-Morpholinomethyldiisopropylmethylphosphonium Perchlorate (IV). An excess of $AgClO_4$ solution in D_2O was added to a solution of (II) in D_2O. The AgI precipitate was removed. A solution of (IV) was obtained with PMR spectrum identical to that of (II) in D_2O (see Table 1).

N-Morpholinomethyldiisopropylmethylphosphonium Nitrate (V). A solution of (V) was obtained analogously from a solution of (II) and $AgNO_3$ in D_2O. The PMR spectrum of (V) was identical to that of (II) in D_2O (see Table 1).

Hydroxymethyldiisopropylmethylphosphonium Iodide (VIII). A solution of 0.3 g (2.0 mmoles) MeI in 5 ml ether was added to a solution of 0.3 g (2.0 mmoles) i-Pr_2PCH_2OH in 10 ml ether. The precipitate was removed after 12 h and washed with ether. Recrystallization from methanol–ether yielded 0.4 g (69%) (VIII) as white crystals with mp 175°C. Found: C 34.1; H 6.91%. Calculated for $C_8H_{20}OPI$; C 33.1; H 6.89%.

Methoxymethyldiisopropylmethylphosphonium Chloride (IX). A sample of (IX) was obtained analogously from 1 g (7.6 mmoles) i-Pr_2PMe and 0.62 g (7.6 mmoles) $MeOCH_2Cl$ in 40 ml ether. Recrystallization from methanol–ether yielded 1.17 g (55%) (IX) as white, very hygroscopic crystals. Found: C 50.55; H 10.29; P 14.25%. Calculated for $C_9H_{22}OPCl$: C 59.85; H 10.35; P 14.58%.

Ethylthiomethyldiisopropylmethylphosphonium Chloride (X). A mixture of 1.06 g (8 mmoles) i-Pr_2PMe and 1.16 g (10.4 mmoles) $EtSCH_2Cl$ was heated for 2 h at 100°C and left overnight. Excess $EtSCH_2Cl$ was removed from the dark mixture and the residue was recrystallized from methanol–ether to yield 0.97 g (50%) (X) as slightly yellowish, extremely hygroscopic crystals. Found: C 49.35; H 10.13; P 12.47%. Calculated for $C_{10}H_{24}PClS$: C 49.58; H 9.92; P 12.81%.

o-Anisyldiisopropylmethylphosphonium Iodide (XI). A solution of 10 g (66 mmoles) i-Pr_2PCl was added to the Grignard reagent obtained from 2.4 g (100 mmoles) Mg and 18.7 g (100 mmoles) o-bromoanisole in 100 ml ether at –15°C over 15 min, heated at reflux for 30 min, and then cooled to 0°C. The excess Grignard reagent was decomposed with concentrated aq. NH_4Cl (~75 ml). The ethereal layer was separated and dried over $MgSO_4$. After removal of ether, the residue was distilled in vacuum to yield 9.8 g (70%) o-anisyldiisopropylphosphine as a colorless liquid with bp 87-88°C (1 mm). PMR spectrum ($CDCl_3$, δ, ppm, J_9 Hz): 0.88 (Me_A, J_{HH} = 6.8, J_{HP} = 13.5) 1.04, (Me_B, J_{HH} = 6.8, J_{HP} = 12.0), 2.18 (HCP), 3.75 (MeO), 7.10 (Ph).

b) The action of excess MeI in ether on o-anisyldiisopropylphosphine yielded (XI) as white crystals with mp 121°C. Found: C 45.79; H 6.64; P 8.9%. Calculated for $C_{14}H_{24}POI$: C 45.90; H 6.56; P 8.47%.

CONCLUSIONS

1. The arguments for the phosphonium–phosphorane equilibrium involving the formation of a tricyclic phosphorane previously proposed for phosphonium salt cations $R_3\overset{+}{P}CH_2X$ (X = R_2N, RO, HO, RS) were examined. This proposal was rejected in light of a) the observed nonequivalence of the isopropyl group methyl protons of $[i\text{-}Pr_2(Me)\overset{+}{P}CH_2N(CH_2CH_2)_2O]\,I^-$ in its PMR spectrum in C_5D_5N solution, b) x-ray structural analysis of this salt (N···P distance 2.69(2) Å), and c) the configurational stability of $[o\text{-}MeOC_6H_4\overset{\oplus}{P}(Me)Pr_2\text{-}i]\,I^{\ominus}$ up to 190°C.

2. Aminomethylphosphonium salts have aminomethylating action relative to $MeO^{\ominus}$, while phosphineomethylammonium salts do not react with Me.

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