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Reactions of $P(MeNCH_2CH_2)_3N$ with Primary, Secondary, and Tertiary Alkyl Halides: Evidence for a Solvent-Enhanced Dehydrohalogenation

T. Mohan, S. Arumugam, T. Wang, R. A. Jacobson, and J. G. Verkade*

Department of Chemistry and Ames Laboratory, Iowa State University, Ames, IA 50011

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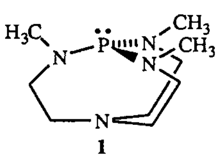
ABSTRACT

The reactions of $P(MeNCH_2CH_2)_3N$, **1**, *with MeI, EtI, EtBr, n-PrBr, n-BuI, i-PrBr,* $PhCH_2CHBrCH_3$, $MeCHBr(CH_2)_4Me$, *s-BuBr, and t-BuBr were studied. The reactions of the primary alkyl halides produced the corresponding phosphonium cationic compounds, whereas the secondary and tertiary halides underwent elimination to form the corresponding olefins and the protonated form of 1. Based on* ^1H *and* ^{13}C *NMR studies, it appears that elimination is exclusively trans, favoring the Saytzeff product. It was also observed that this reaction is enhanced by the solvent* CH_3CN. *The X-ray crystal structure of [Me(1)] I is also reported, featuring a transannular distance of 2.773 Å (2) facilitated by a rather wide average equatorial MeN–P–NMe bond angle of 113.1 (2)°.* © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In our earlier publications [1–5], we reported the unusually high basicity of the proazaphosphatrane, **1**, due to the enhanced electron density at the phosphorus atom resulting from the transannular interaction of the axial nitrogen atom. Because of the flexibility of this transannular bond, **1** also acts as an efficient catalyst in the quantitative trimerization of isocyanates to isocyanurates [6,7]. Prompted by these results, we became curious to determine whether alkyl halides would form phosphonium salts with **1** or produce salts such as **2a** plus the corresponding olefin. Also of interest was whether the phosphorus in an alkyl salt of **1** would be tetra or pentacoordinate. Here we report that the primary alkyl halides MeI, EtBr (I), *n*-PrBr, and *n*-BuI form the corresponding phosphonium salts **3–7** whereas *i*-PrBr, $PhCH_2CHBrMe$, *s*-BuBr, *t*-BuBr, and 2-bromoheptane give **2a** plus the corresponding olefins 1-propene, trans-*β*-methyl styrene, *trans*-2-butene, 2-methyl-1-butene, and *trans*-2-heptene, respectively. We also show that the phosphorus in **3** is quasi–five-coordinate.



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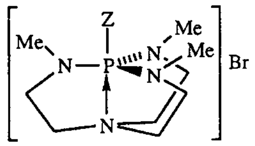

	Z
2a	H
2b	D

Dedicated to Prof. Louis D. Quin on the occasion of his retirement from the University of Massachusetts at Amherst.

*To whom correspondence should be addressed.

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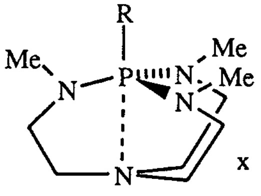


	R	X
3	Me	I
4	Et	Br
5	Et	I
6	*n*-Pr	Br
7	*n*-Bu	I

EXPERIMENTAL

General Procedures

All the solvents employed in this study were dried and distilled before use by standard procedures [8]. Proazaphosphatrane 1 was synthesized by our reported procedure [1]. MeI (Fischer), EtBr (Aldrich), EtI (Aldrich), *n*-PrBr (Baker), *n*-BuI (Aldrich), *i*-PrBr (Aldrich), $PhCH_2CHBrMe$ (Aldrich), 2-bromoheptane (Aldrich), *s*-BuBr (Aldrich), and *t*-BuBr (Eastman) were used as received. The reactions were carried out under a nitrogen atmosphere.

^1H NMR spectra were recorded on either a Nicolet NT-300 or Varian VXR-300 spectrometer. ^{13}C NMR spectra were obtained on a Varian VXR-300 spectrometer operating at 75.43 MHz. $^{31}P(^1H)$ spectra were obtained on a VXR-300 spectrometer operating at 121.43 MHz. ^{31}P MAS NMR spectra were obtained on a Bruker MSL-300 machine operating at 121.43 MHz. Mass spectra were obtained on a Finnigan TSQ 700 spectrometer under EI conditions.

Reaction of 1 *with MeI*

To a stirred solution of 1 (0.22 g, 1.0 mmol) in CH_3CN (5 mL) in an ice bath was added MeI (0.14 g, 1.0 mmol) through a syringe. A colorless solid precipitated immediately. After having been stirred for 1 hour, the reaction mixture was filtered giving a solid that was washed with 2 × 1 mL of THF and dried under vacuum. The solid was identified as 3 (0.34 g, 95%). ^1H NMR ($CDCl_3$): 2.87 (m, 6 H), 2.75 (m, 6 H), 2.74 (d, 9 H, $^3J_{PH}$ = 10.8 Hz), 1.78 (d, 3 H, $^2J_{PH}$ = 13.2 Hz). ^{13}C NMR ($CDCl_3$): 49.55, 49.24 (d, $^2J_{PC}$ = 3.6 Hz), 35.72 (d, $^2J_{PC}$ = 4.7 Hz), 12.63 (d, J_{PC} = 132.5 Hz). ^{31}P NMR ($CDCl_3$): 48.29. ^{31}P (MAS): 49.65. Elemental Anal. calcd (found): C, 33.52 (33.20); H, 6.70 (6.55); N, 15.64 (15.38); P, 8.66 (8.41).

Reaction of 1 *with EtBr*

To a stirred solution of 1 (0.26 g, 1.2 mmol) in CH_3CN (5 mL) in an ice bath was added EtBr (0.13 g, 1.2 mmol) through a syringe. After the reaction mixture had been stirred for 2 hours, the precipitated solid was filtered off, washed with 2 × 1 mL of THF, and vacuum dried. The ^1H, ^{13}C, and ^{31}P NMR spectral characteristics of the product (4, 0.35 g, 90% yield) were identical to that of product 5 obtained from the next reaction.

Reaction of 1 *with EtI*

Ethyl iodide (0.13 g, 0.83 mmol) was added via syringe to a stirred solution of 1 (0.18 g, 0.83 mmol) in CH_3CN (5 mL) in an ice bath. After the mixture had been stirred for 1 hour, the precipitated white solid was filtered off, washed with THF (2 × 1 mL), dried under vacuum, and identified as 5 (0.28 g, 93%). ^1H NMR ($CDCl_3$): 2.90 (m, 6 H), 2.79 (d, 9 H, $^3J_{PH}$ = 10.2 Hz), 2.78 (m, 6 H), 2.34 (dq, 2 H, $^2J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 7.8 Hz), 1.26 (dt, 3 H, $^3J_{PH}$ = 18.6 Hz, $^3J_{HH}$ = 7.8 Hz). ^{13}C NMR ($CDCl_3$): 50.81, 49.39 (d, $^2J_{PC}$ = 1.2 Hz), 34.50 (d, $^2J_{PC}$ = 4.3 Hz), 20.92 (d, $^1J_{PC}$ = 121.4 Hz), 8.47 (d, $^2J_{PC}$ = 5.87 Hz). ^{31}P NMR (CD_3CN): 53.63, ^{31}P (MAS) δ: 56.09. MS (*m*/*e*): 245 for the cation 5.

Reaction of 1 *with n-PrBr*

n-Propyl bromide (0.15 g, 1.2 mmol) was added via syringe to a stirred solution of 1 (0.22 g, 1.0 mmol) in CH_3CN (5 mL) in an ice bath. A white solid slowly precipitated. After having been stirred for 12 hours, the reaction mixture was filtered, the precipitate washed with 2 × 1 mL of THF, and vacuum dried. The precipitate from the reaction (0.26 g, 90%) was identified as 6 as follows. ^1H NMR ($CDCl_3$): 2.92 (m, 6 H), 2.80 (d, 9 H, $^3J_{PH}$ = 10.2 Hz), 2.79 (m, 6 H), 2.22 (m, 2 H), 1.70 (m, 2 H), 1.04 (dt, 3 H, $^4J_{PH}$ = 2.7 Hz, $^3J_{HH}$ = 7.2 Hz). ^{13}C NMR ($CDCl_3$): 50.96, 49.49 (d, $^2J_{PC}$ = 2.7 Hz), 35.40 (d, $^2J_{PC}$ = 3.7 Hz), 30.16 (d, $^1J_{PC}$ = 119.33 Hz), 17.91 ($^2J_{PC}$ = 4.9 Hz), 15.93 ($^3J_{PC}$ = 18.2 Hz). ^{31}P NMR (CD_3CN): 53.14. ^{31}P (MAS) δ: 55.94. MS (*m*/*z*): 259 for cation 6.

Reaction of 1 *with n-BuI*

n-Butyl iodide (0.184 g, 1 mmol) was added via syringe to a stirred solution of 1 (0.22 g, 1 mmol) in CH_3CN (5 mL) in an ice bath. After the mixture had been stirred for 12 hours, the white precipitate that had formed in the reaction was filtered off, washed with 2 × 1 mL of THF, and vacuum dried. The solid (0.36 g, 90%) was identified as 7. ^1H NMR (CD_3CN): 2.85 (m, 6 H), 2.73 (m, 6 H), 2.68 (d, 9 H, $^3J_{PH}$ = 10.8 Hz), 2.23 (m, 2 H), 1.66 (m, 2 H), 1.41 (sx, 2 H, $^3J_{HH}$ = 6.6 Hz), 0.93 (t, 3 H, $^3J_{HH}$ = 6.6 Hz), ^{13}C NMR (CD_3CN): 51.40, 49.96 (d, $^2J_{PC}$ = 2.26 Hz), 35.26 (d, $^2J_{PC}$ = 4.52 Hz), 27.79 (d, $^1J_{PC}$ = 119.18 Hz), 26.52 (d, $^2J_{PC}$ = 5.28 Hz), 24.82 (d, $^3J_{PC}$ = 18.85 Hz), 13.66 (d, $^4J_{PC}$ = 1.5 Hz). ^{31}P NMR (CD_3CN): 56.47. ^{31}P (MAS) δ 58.26. MS (*m*/*z*): 273 for cation 7.

Reaction of 1 *with i-PrBr*

Method A. To a stirred solution of **1** (0.31 g, 1.4 mmol) in CH_3CN (10 mL) in an ice bath was added *i*-PrBr (0.17 g, 1.4 mmol) through a syringe. A colorless solid began to precipitate after 6 hours. After 48 hours, the reaction mixture was filtered, and the solid was washed with 2 × 1 mL of THF and dried under vacuum. The precipitate was shown to contain the cation in **2a** (0.35 g, 90%) identified according to its known NMR spectral properties [2]. No other product was isolated from the filtrate upon evaporation.

Method B. A 5 mm NMR tube was charged with **1** (0.11 g, 0.51 mmol) in CD_3CN (0.5 mL). To this tube was added *i*-PrBr (0.63 g, 0.51 mmol), and the reaction was followed by ^{31}P NMR spectroscopy (see Results and Discussion).

Reaction of 1 *with 2-Bromo-1-phenylpropane*

To a stirred solution of **1** (0.2 g, 1 mmol) in CH_3CN (5 mL) in an ice bath was added 2-bromo-1-phenylpropane (0.2 g, 1 mmol) through a syringe in 1 mL of CH_3CN. After the mixture had been stirred for 12 hours, the solvent CH_3CN was removed under vacuum. The residue obtained was extracted with 2 × 25 mL portions of hexane. Removal of hexane gave *trans*-β-methyl styrene (0.1 g, 90%). ^1H NMR (CD_3CN): 7.28 (m, 4 H), 7.18 (m, 1 H), 6.40 (d, 1 H, $^3J_{HH}$ = 15.84 Hz), 6.26 (dq, 1 H, $^3J_{HH}$ = 15.84 and 6.35 Hz), 1.86 (d, 3 H, $^3J_{HH}$ = 6.6 Hz), ^{13}C NMR (CD_3CN): 138.74, 131.60, 129.37, 127.63, 127.51, 126.58, 126.55.

Reaction of 1 *with 2-Bromoheptane*

To a stirred solution of **1** (0.22 g, 1.0 mmol) in CH_3CN (5 mL) in an ice bath was added 2-bromoheptane (0.18 g, 1.0 mmol) through a syringe. After 12 hours, CH_3CN was removed under vacuum, and the residue was extracted with hexane (2 × 25 mL). Removal of hexane gave 0.091 g (91%) of *trans*-2-heptene. ^1H NMR (CD_3CN): 5.42 (m, 2 H), 1.98 (m, 2 H), 1.62 (d, 3 H, $^3J_{HH}$ = 6.3 Hz), 1.32 (m, 4 H), 0.88 (t, 3 H, $^3J_{HH}$ = 6.3 Hz). ^{13}C NMR (CH_3CN): 131.66, 124.61, 32.15, 31.76, 22.12, 17.36, 13.49.

Reaction of 1 *with t-BuBr*

Method A. To a stirred solution of **1** (0.18 g, 0.83 mmol) in CH_3CN (5 mL) in an ice bath was added *t*-BuBr (0.13 g, 0.83 mmol) through a syringe. The reaction mixture became turbid after about 3 hours, precipitating a colorless solid. The reaction mixture was filtered after 2 days, and the precipitate was washed with 2 × 1 mL of THF. The product (0.22 g, 90%) was shown to contain the cation in **2a** by comparing its NMR spectral characteristics with those of an authentic sample [2].

Method B. A 5 mm NMR tube was charged with **1** (0.14 g, 0.65 mmol) and *t*-BuBr (0.11 g, 0.65 mmol) in CD_3CN (0.5 mL). ^{31}P NMR spectra were recorded at various time intervals to monitor the reaction (see Results and Discussion).

Reaction of 1 *with s-BuBr*

A 5 mm NMR tube was charged with **1** (0.14 g, 0.65 mmol) and *s*-BuBr (0.11 g, 0.65 mmol) in CD_3CN (0.5 mL). The reaction was monitored by ^{31}C NMR spectroscopy (see Results and Discussion).

X-ray Structural Determination of 3

Crystals of **3** were obtained from a solution of **3** in CH_3CN/THF (1:1 mixture) upon cooling at −10°C for 2 days. A crystal was selected for mounting in a glass capillary. All measurements were made on a Rigaku AFC6R diffractometer with graphite-monochromated MoKα radiation (λ = 0.70930 Å) and a 12 kW rotating anode generator. The data were collected at a temperature of 23 ± 1°C using the ω-2θ scan technique to a maximum 2θ value of 60.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.36° with a take-off angle of 6.0°. Scans of $(1.73 + 0.30 \tan \theta)°$ were made at a speed of 16.0°/min (in omega). The weak reflections [$I < 10.0\sigma(I)$] were rescanned (maximum of two rescans), and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm, and the crystal-to-detector distance was 400.0 mm. Of the 2686 reflections that were collected, 969 were unique (R_{int} = 0.02); equivalent reflections were merged. The intensities of three representative reflections that were measured after every 150 reflections remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied).

The linear absorption coefficient for MoKα is 22.2 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied, which resulted in transmission factors ranging from 0.96 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods [9]. The nonhydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 652 observed reflections [$I > 3.00\sigma(I)$] and 48 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of

$$R = \Sigma \| F_0| - |F_c\| / \Sigma |F_0| = 0.033$$

$$R_w = [(\Sigma\omega(|F_0| - |F_c|)^2 / \Sigma\omega F_0^2)]^{1/2} = 0.044$$

The standard deviation of an observation of unit weight [10] was 1.26. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\Sigma\omega(|F_0| - |F_c|)^2$ vs. $|F_0|$, reflection order in data collection, $\sin \theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.61 and -0.25 $e^-/\text{Å}^3$, respectively. Neutral atom scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in F_{calc} [11]; the values for Δf and $\Delta f'$ were those of Cromer [10]. All calculations were performed using the TEXSAN [12] crystallographic software package of Molecular Structure Corporation. Pertinent crystal data are listed in Tables 1 and 2.

RESULTS AND DISCUSSION

The reaction of the proazaphosphatrane **1** with MeI, EtBr, EtI, *n*-PrBr, and *n*-BuI produced the corresponding phosphonium cations **3–7**, respectively. As reported earlier [13], the reaction of **1** with MeI to produce **3** was quantitative. The compounds provided ^{1}H, ^{13}C, and ^{31}P NMR spectra consistent with their given formulations. The MS peak for the cations of **4** and **5** were also observed. Conclusive proof in the case of **3** was obtained by the X-ray diffraction studies discussed later.

TABLE 1 Crystallographic Data for **3**

Empirical formula	$IPN_4C_{10}H_{24}$
Formula weight	358.20
Crystal color, habit	Light yellow, irreg. shaped
Crystal dimensions (mm)	0.20 × 0.40 × 0.20
Crystal system	Trigonal (hexagonal setting)
No. reflections used for unit cell determination (2θ range)	25 (39.5–39.8°)
Lattice parameters	
a, Å	8.107 (1)
b, Å	13.1193 (8)
c, Å^3	746.7 (2)
Space group	P31c (#159)
Z	2
d_{calcd} g/cm^3	1.807
$\mu_{(\text{MoK}\alpha)}$	22.22 cm^{-1}
Diffractometer	Rigaku AFC6R
Radiation, graphite monochromated	MoKα (λ = 0.71069 Å)
Temperature	23°C
Scan type	ω-2θ
$2\theta_{\max}$	60.0°
No. of reflections measured	Total: 2686 Unique: 969 (R_{int} = 0.032)
Corrections	Lorentz-polarization absorption (trans. factors: 0.96–1.00)
No. observations [$I > 3.00\sigma(I)$]	652
No. variables	48
Residuals: *R*; R_w[a]	0.033: 0.044
Goodness-of-fit indicator[b]	1.26
Max shift/error in final cycle	0.01
Max, min difference peak ($e^-/\text{Å}^3$)	0.61, −0.25

[a] $R = \Sigma \| F_0| - |F_c\| / \Sigma |F_0|$; $R_w = [\Sigma w(|F_0| - |F_c|)^2 / \Sigma w|F_0|]^{1/2}$.
[b] Goodness of fit = $[w(|F_0| - |F_c|^2 / (n_{\text{obs}} - n_{\text{par}})]^{1/2}$.

TABLE 2 Selected Bond Angles and Bond Distances in **3**

	Bond Angles (deg)		
N(1)–P(2)–N(1)	113.2(1)	C(4)–N(1)–C(2)	116.1(3)
N(1)–P(2)–C(1)	105.4(1)	P(2)–N(1)–C(2)	119.7(3)
P(2)–N(1)–C(4)	120.7(3)	C(3)–N(2)–C(3)	118.2(1)
	Bond Distances (Å)		
P(2)–C(1)	1.810(9)	N(2)–C(3)	1.446(5)
P(2)–N(1)	1.634(3)	N(1)–C(4)	1.462(6)
N(1)–C(2)	1.474(6)	C(2)–C(3)	1.517(6)

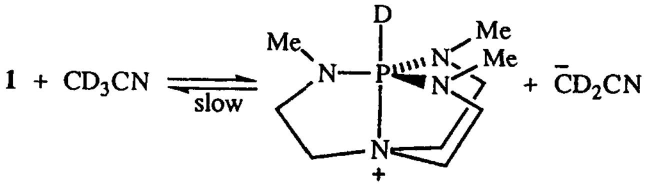
The reactions of *i*-PrBr and *t*-BuBr were very different from those of the primary alkyl halides. The former reactions were very slow, and the only isolable solid product was **2a**. While following the reaction by NMR spectroscopy, we observed that, in CD_3CN, both *i*-PrBr and *t*-BuBr reacted with **1** to produce the cation of **2b** in which deuterium is attached to phosphorus instead of a proton. Moreover, monitoring the reaction by ^{31}P NMR spectroscopy revealed that **1** reacts about three times faster with *t*-BuBr than with *i*-PrBr. It should be noted that *t*-BuBr does not react with phosphines, such as Ph_3P in MeCN [14]. The supernatant solution in the ^{31}P NMR tube was syringed out after the reaction was over and subjected to ^{13}C and ^{1}H NMR spectroscopies. The ^{13}C NMR peaks at 133.67, 115.21, and 18.61 demonstrated the presence of 1-propene [15] in the reaction of *i*-PrBr with **1**. Similarly, the ^{13}C peaks at 110.63 and 23.66 revealed the presence of 2-methyl-1-butene [15] in the analogous reaction with *t*-BuBr. These data are consistent with ^{1}H NMR spectra that showed broad multiplets for the olefinic protons. To further confirm the formation of *trans*-olefins, a preparative scale reaction of compound **1** with 2-bromo-1-phenylpropane was undertaken in order to obtain an easily isolated product for identification. The ^1H NMR spectra of the product isolated from this reaction showed a doublet and a doublet of quartets at δ 6.4 ($^3J_{HH}$ = 15.84 Hz) and 6.26 ($^3J_{HH}$ = 15.84 and 6.35 Hz), respectively, for the olefinic protons. The higher coupling constant J = 15.84 Hz confirms that the olefin is *trans*. The ^1H and ^{13}C NMR spectral values compared well with those of an authentic sample of *trans*-β-methylstyrene.

In another NMR experiment, the ^{13}C NMR spectrum of a reaction mixture of *s*-BuBr and **1** in CD_3CN showed, after 5 days, only two peaks (in addition to those for **2**) at 126.01 and 17.60, confirming the presence of only *trans*-2-butene [15].

Reactions of 2-bromo-1-phenylpropane and 2-bromoheptane were also carried out on a preparative scale, giving a 90% yield of *trans*-β-methylstyrene and a 91% yield of *trans*-2-heptene, respectively, which were identified by ^1H and ^{13}C NMR spectroscopies. Our observations show that these elimination reactions with **1** in acetonitrile are highly stereospecific. The formation of *trans*-2-butene and the complete absence of 1-butene in the NMR tube experiment involving *s*-BuBr is in accord with Saytzeff's rule, and the isolation of high yields of *trans*-β-methyl styrene and *trans*-2-heptene in the preparative scale experiments confirm this conclusion. To our knowledge, the only literature report on such an elimination reaction with a phosphorus compound [namely, $P(OMe)_3$] involves an intermediate in the synthesis of provitamin D_3 [16]. Since that reaction took place on a six-membered ring in the intermediate, the stereochemical course of the dehydrohalogenation was predetermined. Thus, our results are the first to demonstrate the usefulness of proazaphosphatrane **1** in achieving efficient stereospecific dehydrohalogenations of secondary and tertiary alkyl halides.

It is of interest to speculate on a possible dehydrohalogenation pathway for secondary and tertiary halides in the presence of **1** in acetonitrile. Since we have already reported [7] that **1** abstracts a proton from CH_3CN, and, since **2a** was isolated as the only phosphorus-containing compound in the reactions of **1** with *i*-PrBr and *t*-BuBr in CH_3CN, these reactions in CD_3CN may well take place according to Scheme 1. Furthermore, in the ^1H-decoupled ^{13}C NMR spectrum of the reaction mixture of 2-bromoheptane with **1** in CD_3CN, a quintet at δ 0.84 indicative of the presence of two deuterium substituents in HCD_2CN lends further credence to the pathway shown in Scheme 1. Because the $t\text{-Bu}^+$ ion is more stable than the $i\text{-Pr}^+$ ion under the S_N1 conditions favored in a polar solvent such as acetonitrile, our observation of a faster reaction of *t*-BuBr with **1** than of *i*-PrBr with **1** (by a factor of ~3; discussed previously) is rationalized. This observation is also consistent with the strong E2 component expected in these dehydrohalogenations. It should be noted that the reaction of *t*-BuBr with **1** was about three times slower in THF, further suggesting that CH_3CN participates in this reaction.

The computer drawing of the cation of **3** shown in Figure 1 reveals that the phosphorus resides in a distorted tbp geometry with a mean equatorial NPN angle of 113.2 (1)°. The axial $P\text{–}N_2$ distance is 2.773 (2) Å, which is significantly (ca. 20%) less than the sum of the van der Waals radii. The average equatorial P–N bond distance [1.634 (3) Å] is significantly shorter than that expected for a single bond distance



$$RBr \rightleftharpoons R^+ + Br^-$$

$$^-CD_2CN + R^+ \longrightarrow HCD_2CN + \text{olefin}$$

SCHEME 1

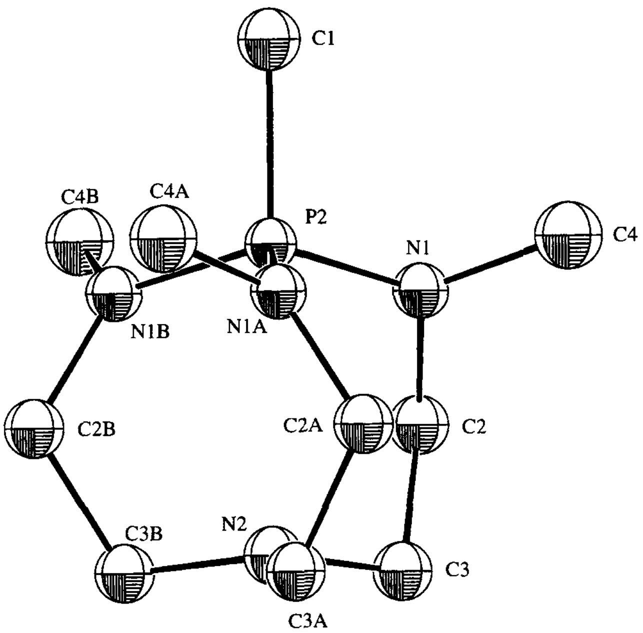


FIGURE 1 Computer drawing of **3** showing the cation $CH_3P(MeNCH_2CH_2)_3N^+$ with thermal ellipsoids at the 50% probability level.

(1.78 Å) [17]. We reported earlier [3] on the variation of the axial P–N bond distances with the equatorial NPN angle in azaphosphatranes. The average value of this angle and the transannular bond distance for **3** predicted by this study (Figure 2) very closely match the corresponding values reported here. It might be conjectured that the wide equatorial NPN angles and the shorter-than-expected transannular PN distance in **3** is associated with some degree of PN (2) interaction. If this is so, an upfield ^{31}P chemical shift is expected, as is the case in **2a** (−10 ppm [1]). Compared with δ^{31}P for $[MeP(NMe_2)_3]I$ (58.5 ppm [18]), **3** does display somewhat of an upfield shift (48.3 ppm). The upfield shift from $[n\text{-}BuP(NMe_2)_3]Br$ (62 ppm [18]) to its cage analog **7** (58.3 ppm) is less pronounced, perhaps owing to lessened transannular N → P interaction stemming from the greater electron induction effect of the *n*-Bu group and/or its larger size. Not unexpectedly, δ^{31}P values for the ethyl (**4**,**5**: 53.6 ppm) and *n*-propyl (**6**: 53.1 ppm) derivatives lie between the values observed for **3** and **7**. It may be noted that the δ^{31}P values for **3**–**5** are quite constant from the solution to the solid state, suggesting that the solution and solid-state structures are nearly the same. Interestingly, the coordinates for **3** and $MeS(S)CP(MeNCH_2CH_2)_3N$ in Figure 2 are very similar, even though the bridgehead substituent in the latter compound is considerably larger than in **3**.

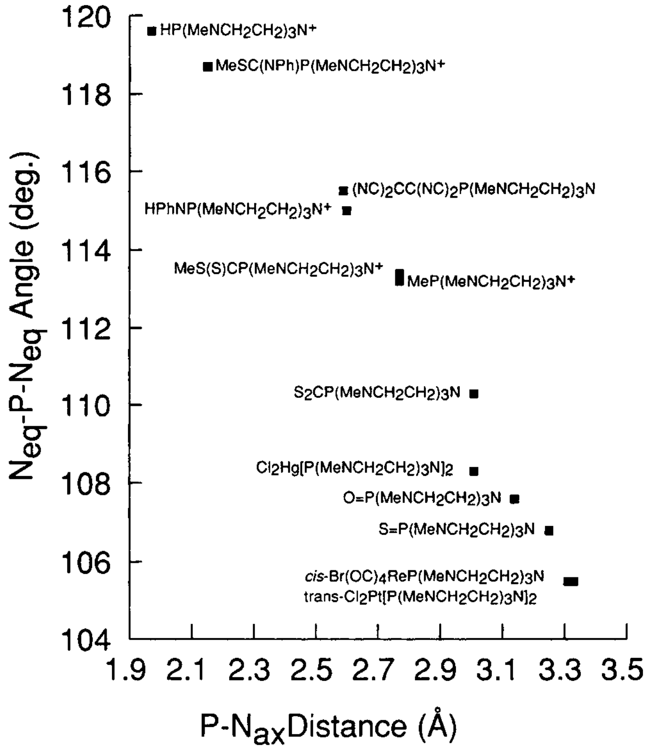


FIGURE 2 Plot of P–N$_{ax}$ distance (Å) against N_{eq}–P–N$_{eq}$ angle (°) in $Z\text{–}P(MeNCH_2CH_2)_3N$ systems.

ACKNOWLEDGMENTS

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SUPPLEMENTARY MATERIAL AVAILABLE

Tables of atomic coordinates, bond lengths, bond angles, and thermal parameters for **3** can be obtained by a written request to the senior author or to the Editor-in-Chief.

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