Synthesis and Nuclear Magnetic Resonance Study of Neopentyl and (Trimethylsilyl)methyl Derivatives of Phosphorus

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Neopentyldiphenylphosphine and dineopentylphenylphosphine and their oxides and quaternary phosphonium salts with CH_3I, $(CH_3)_3CCH_2I$, and $(CH_3)_3SiCH_2I$ have been synthesized and their ^1H, ^{13}C, and ^{31}P NMR spectra recorded to determine the stereochemical and electronic effects of sterically hindered neopentyl and (trimethylsilyl)methyl groups. The unusually large $^2J_{PH}$ couplings (18–19 Hz) in (trimethylsilyl)methylphosphonium salts are rationalized in terms of hyperconjugative $d\pi$–$p\pi$ bonding involving d orbitals of Si and P.

Several studies describing the substituent effects on ^1H, ^{31}P, and ^{13}C chemical shifts and their coupling constants in phosphines, phosphonium salts, and phosphine oxides have been reported in the literature in recent years. For example, empirical relationships have been developed which allow fairly accurate prediction of ^{31}P chemical shifts of phosphines[2a] and phosphonium salts.[2b] Substituent effects on geminal phosphorus–proton[3,4] and directly bonded phosphorus–carbon[5,6] nuclear spin couplings have been studied in phosphonium salts and phosphine oxides, which help in understanding the nature of bonding around the phosphorus atom and, therefore, provide a useful technique for structural analysis. We have synthesized neopentylphosphines, their oxides, and neopentyl- and (trimethylsilyl)methylphosphonium salts to study the effects of these bulky groups on structure and bonding by NMR spectroscopy.

Results

The steric effects of the neopentyl groups were clearly manifested in the synthesis and the hydrolysis of phosphonium salts. For example, the yields of phosphonium salts from neopentyldiphenylphosphine and dineopentylphenylphosphine were in the following order of alkyl halides: CH_3I > $(CH_3)_3SiCH_2I$ > $(CH_3)_3CCH_2I$.

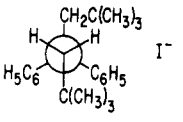
Steric hindrance reduces the rates of hydrolysis of phosphonium salts because of the sterically hindered trigonal-bipyramidal transition state.[7] Methylneopentyldiphenylphosphonium iodide (3) was hydrolyzed in alcohol/aqueous NaOH to give methylneopentylphenylphosphine oxide in 31% yield. However, methyldineopentylphenylphosphonium iodide, which is more sterically hindered than **3**, did not hydrolyze at all under these conditions.

Tables I and II list the ^1H, ^{31}P, and ^{13}C NMR data of the phosphorus compounds. The spectra were run in $CDCl_3$ unless mentioned otherwise. The spectra of (trimethylsilyl)methylphosphonium salts were run on freshly prepared compounds because they decomposed on standing to the corresponding methylphosphonium salts presumably due to hydrolysis at the Si–C bond.

$$>P^+CH_2Si(CH_3)_3\ I^- \xrightarrow{H_2O} >P^+CH_3\ I^- + (CH_3)_3SiOH$$

Discussion

The neopentyl methylene protons of dineopentylphenylphosphine (**2**), methyldineopentylphenylphosphonium iodide (**4**), and dineopentylphenylphosphine oxide (**12**) show non-equivalence. Heating to 160 °C in o-$Cl_2C_6H_4$ did not change their spectra, indicating that these compounds are locked in structures with the neopentyl groups in trans positions. Likewise, the neopentyl groups of dineopentyldiphenylphosphonium iodide (**5**) are fixed in the trans position. But



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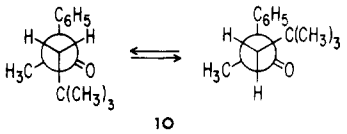
its methylene protons are in an identical magnetic environment.

In dineopentylphenylphosphine (**2**), the methylene proton gauche to the phosphorus lone pair comes at lower field and is more strongly coupled to phosphorus than the proton trans to the lone pair. Allbrand et al.[8] have shown that in phosphines $^2J_{P-C-H}$ depends on the :PCH dihedral angle (ψ); $^2J_{PH}$ is maximum for $\psi = 0°$ and $\simeq 0$ Hz when $\psi = 180°$. From their plot, the gauche coupling ($\psi = 60°$) is calculated to be 5.2 Hz. The observed coupling constants in **2**, $^2J_{PH(gauche)}$ = 5.2 Hz and $^2J_{PH(trans)} \simeq 0.8$ Hz, are in good agreement with the calculated values.

In the phosphine oxides, however, the methylene proton which is trans to P=O appears downfield partially due to P=O double-bond anisotropy and is more strongly coupled with phosphorus than the gauche proton. For example, in dineopentylphenylphosphine oxide (**12**), $^2J_{PCH(trans)}$ = 12.8 Hz and $^2J_{PCH(gauche)}$ = 7.8 Hz. The neopentyl methylene protons in methylneopentylphenylphosphine oxide (**10**) are



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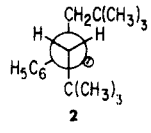
also nonequivalent and appear as two doublets (10.0 and 11.5 Hz). But at 60 °C (o-$Cl_2C_6H_4$) they converge to a single doublet. From the coalescence temperature, the energy barrier around the P–C bond has been calculated to be approximately 16 kcal/mol.

The difference in trans vs. gauche $^2J_{PH}$ in **10** is much smaller than the difference in the corresponding coupling constants in **12**, suggesting an averaging effect on the coupling constants in **10**, which is probably due to partial rotation around the P–C bond.

The methylene protons of neopentyldiphenylphosphine (**1**) and neopentyldiphenylphosphine oxide (**11**) are magnetically



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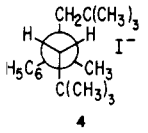

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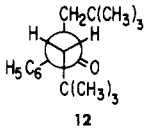

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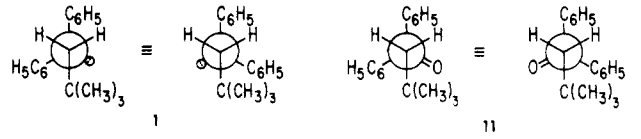

1 **11**

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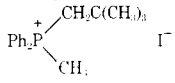
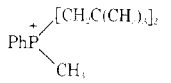
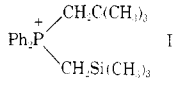
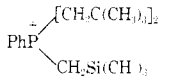
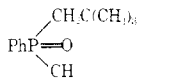
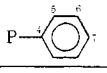
Table I. ^{1}H and ^{31}P NMR Data

no.	compd	δ_{CH_2},[a] ppm	δ_{CH_3},[a] ppm	$^{2}J_{PH}$, Hz	$^{2}J_{HH}$,[b] Hz	$^{4}J_{PH}$, Hz	$\delta_{C_6H_5}$,[a] ppm	$\delta_{^{31}P}$,[c] ppm
1	$Ph_2PCH_2C(CH_3)_3$	2.15	1.00	3.8		0.6	7.13–7.62	23.3[d]
2	$PhP[CH_2C(CH_3)_2]_2$	1.60, 1.84	0.93	0.8,[e] 5.2[f]	14.3	0.5	7.10–7.73	42.0[d]
3		3.53	1.12 2.96	13.7 13.4		0.6	7.50–8.40	19.6
4		3.03, 3.17	1.01 2.80	14.0,[e] 13.2[f] 13.5	15.3	0.8	7.66–8.32	21.79
5	$Ph_2P^+[CH_2C(CH_3)_3]_2\ I^-$	3.47	0.92	12.8		0.7	7.67–8.37	20.3
6	$Ph_3P^+CH_2C(CH_3)_3\ I^-$	3.81[g]	1.03[g]	12.8[g]		0.76[g]	7.58–8.25[g]	19.1
7	$Ph_3P^+CH_2Si(CH_3)_3\ I^-$	3.19[g]	0.07[g]	18.4[g]			7.58–8.25[g]	23.9
8		3.40 2.93	1.05 0.00	13.0 18.0		0.5	7.63–8.42	23.1
9		2.64, 3.32 2.44	1.02 0.34	13.0,[e] 14.0[f] 19.0	16.0	0.8	7.64–8.52	24.2
10		1.94, 2.00	1.06 1.67	10.0,[e] 11.5[f] 12.8	15.2		7.41–7.82	34.6
11	$Ph_2P(=O)CH_2C(CH_3)_3$	2.33	1.08	10.8		0.6	7.33–7.93	27.9
12	$PhP(=O)[CH_2C(CH_3)_3]_2$	1.73, 1.93	1.00	7.8,[e] 12.8[f]	15.2	0.6	7.33–7.93	34.8

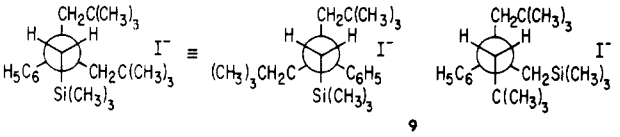
[a] Downfield from internal Me_4Si. [b] Nonequivalent methylene protons. [c] Downfield from external reference of 85% H_3PO_4. [d] Upfield from external 85% H_3PO_4. [e] Upfield proton. [f] Downfield proton. [g] From D. Seyferth and G. Singh, *J. Am. Chem. Soc.*, **87**, 4156 (1965).

Table II. ^{13}C NMR Data

	P–C_1–C_2–C_3													
	δ, ppm[b]			J, Hz			δ, ppm[b]				J, Hz			
compd[a] no.	C_1	C_2	C_3	PC_1	PC_2	PC_3	C_4	C_5	C_6	C_7	PC_4	PC_5	PC_6	PC_7
1	44.4	*c*	31.1	17	*c*	8	140.3	132.8	(128.1–128.3)		16	21		
2	47.0	*c*	30.9	15	*c*	8	143.1	133.1	(128.0–128.4)		13	20		
3	35.1 10.1	31.9	30.6	47 54	5	8	119.5	131.2	129.1	133.5	84	11	12	2
4	37.4 8.3	32.0	31.0	47 50	6	7	120.1	131.6	129.4	133.7	77	11	12	2
5	36.4	32.1	30.7	43	6	7	118.5	133.2	129.4	134.0	78	10	12	3
6	34.0	32.0	30.8	45	5	7	118.5	132.8	129.6	134.0	84	10	14	4
7	10.1		0.7	44		3	120.9	133.3	130.3	134.8	87	10	13	3
8	37.8 11.3	33.0	31.7 0.4	46 41	5	7 3	121.4	133.3	130.3	134.6	84	10	12	3
9	36.8 9.4	32.0	31.3 1.0	46 39	5	6 4	120.6	132.6	129.0	133.5	77	11	12	3
10	45.0 19.0	*c*	31.2	68 70	*c*	7	135.6	129.7	128.3	131.0	95	9	12	2
11	42.5	32.0	31.4	71	5	8	135.3	130.4	128.3	131.0	98	10	12	4
12	45.1	31.9	31.3	68	5	6	136.7	130.5	128.1	~130.7[3]	90	9	11	~2[d]

[a] From Table I. [b] Downfield form internal Me_4Si. [c] Partially under the absorption of the methyl carbons. [d] Ortho and para carbons partially overlapped.

equivalent presumably due to partial free rotation around the P–C bond. Likewise, the methylene protons of $(CH_3)_3SiCH_2$ in [(trimethylsilyl)methyl]dineopentylphenylphosphonium iodide (**9**) are equivalent, but the methylene protons of the



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$(CH_3)_3CCH_2$ groups are nonequivalent because the neopentyl groups are fixed in trans configuration.

$^{2}J_{PH}$ Coupling in (Trimethylsilyl)methylphosphonium Salts. In the (trimethylsilyl)methylphosphonium salts (**7–9**), $^{2}J_{PH}$ for the (trimethylsilyl)methyl group is 5–6 Hz larger than that for the neopentyl group, which strongly suggests unique bonding between $(CH_3)_3SiCH_2$ and P. The possibility of σ–π conjugation, $>P^+CH_2Si(CH_3)_3 \leftrightarrow >P \cdots CH_2 \cdots {}^+Si(CH_3)_3$, is excluded on the basis that phosphorus in the (trimethylsilyl)methylphosphonium salts is more deshielded than in the corresponding neopentylphosphonium salts. Had the σ–π conjugation been the deciding factor, the phosphorus in the (trimethylsilyl)methylphosphonium salts would have been more shielded because of the incipient phosphorane structure.[9]

We interpret our data in terms of pπ–dπ hyperconjugation involving α-hydrogen and the 3d orbitals of Si and P:

$$>P^+CH_2Si(CH_3)_3\ I^- \leftrightarrow >P\text{–}\overset{H^+}{\overset{\cdot\cdot\cdot\cdot\cdot}{C}}H\text{–}Si(CH_3)_3\ I^-$$

Hyperconjugative $C_{p\pi}$–$P_{d\pi}$ bonding in phosphonium salts has been suggested to have a shielding effect on the phosphorus chemical shift.[2a] In the (trimethylsilyl)methylphosphonium salts, the 3d orbitals of Si would compete with the 3d orbitals of P for this bonding and, consequently, diminish the shielding of phosphorus.

^{31}P and ^{13}C NMR Data. The shielding of ^{31}P decreases in the order phosphines > phosphonium salts > phosphine oxides. Likewise, the shielding of C_1 (neopentyl) and C_4 (phenyl), which are directly bonded to phosphorus, decreases in the same order except that in phosphines the phosphorus lone pair has a very strong deshielding effect on the chemical shifts of C_1 and C_4.

The quaternization of phosphines to phosphonium salts changes the phosphorus hybridization from nearly p^3 to sp^3. Consequently, the s character in the phosphorus orbitals bonding to carbon increases and gives larger P–C coupling constants in phosphonium salts vs. phosphines. The P–C coupling constants in phosphine oxides are even larger than those in the phosphonium salts, which is due to the high electronegativity of oxygen which directs more s character in the phosphorus orbitals bonding to C_1 and C_4. This would also explain why C_1 and C_4 in phosphine oxides are more deshielded than in phosphonium salts.

Experimental Section

NMR Spectra. Proton spectra were run on Varian Associates T60 and HR-220 spectrometers at probe temperatures of 35 and 20 °C, respectively. The ^{31}P and ^{13}C NMR spectra were obtained on a Bruker HFX-90 spectrometer, probe temperature 28 °C, equipped with a Digilab NMR-3 Fourier transform accessory. The spectrometer was operated at 36.43 and 22.63 MHz for ^{31}P and ^{13}C spectra, respectively, with a time-shared deuterium lock on $CDCl_3$. A broad band noise decoupler was used to eliminate the ^{31}P–^{1}H and ^{13}C–^{1}H couplings.

Neopentyldiphenylphosphine (1). To an ice-cold solution of 44.1 g (0.2 mol) of chlorodiphenylphosphine in 500 mL of anhydrous ether was added dropwise during stirring and under N_2 a solution of neopentylmagnesium chloride prepared from 26.6 g (0.25 mol) of freshly distilled neopentyl chloride in 150 mL of anhydrous THF. After the Grignard addition was complete, the reaction mixture was decomposed with 300 mL of water and the organic layer was separated and dried over anhydrous Na_2SO_4. Ether was distilled to leave **1**, which distilled at 110–111 °C (0.2 mm) to give 46 g (90%) of clear liquid, n^{25}_D 1.5823. Anal. Calcd for $C_{17}H_{21}P$: C, 79.7; H, 8.2; P, 12.1. Found: C, 80.1; H, 8.1; P, 11.6.

Dineopentylphenylphosphine (2). To an ice-cold solution of 35.8 g (0.2 mol) of phenyldichlorophosphine in 800 mL of anhydrous ether was added dropwise during stirring and under N_2 a solution of neopentylmagnesium chloride prepared from 48.3 g (0.45 mol) of neopentyl chloride in 300 mL of anhydrous THF. The reaction was exothermic, and the Grignard was added slowly to ensure gentle refluxing of ether. The mixture was then decomposed with 500 mL of ice-cold water, and the organic layer was separated and dried over anhydrous Na_2SO_4. Ether was distilled, leaving **2** which distilled at 75–77 °C (0.15 mm) as colorless liquid: 46 g (92%); n^{25}_D 1.5109. Anal. Calcd for $C_{16}H_{27}P$: P, 12.4. Found: P, 12.4.

Methylneopentyldiphenylphosphonium Iodide (3). Neopentyldiphenylphosphine (12.8 g, 0.05 mol) and 40 mL of freshly distilled CH_3I were refluxed in 50 mL of dry benzene under N_2 for 2 h. After being cooled, ethyl acetate (100 mL) was added to complete the precipitation of the phosphonium salt which separated as white solid. It was collected by filtration, 19.5 g (98%). An analytical sample was prepared by recrystallization from chloroform/ethyl acetate, mp 196–197 °C dec. Anal. Calcd for $C_{18}H_{24}IP$: C, 54.3; H, 6.0; I, 31.9. Found: C, 54.4; H, 6.1; I, 32.3.

Methyldineopentylphenylphosphonium Iodide (4). A mixture of 2.5 g (0.01 mol) of **2** and 10 mL of CH_3I was refluxed for 1 h under N_2. Anhydrous ether (100 mL) was added to complete the precipitation of the phosphonium salt, 3.7 g (98%). It was recrystallized from chloroform/ethyl acetate, mp 272–273 °C dec. Anal. Calcd for $C_{17}H_{30}IP$: C, 52.0; H, 7.7. Found: C, 52.1; H, 7.7.

Dineopentyldiphenylphosphonium Iodide (5). A mixture of 12.86 g (0.04 mol) of neopentyldiphenylphosphine and 11.86 g (0.06 mol) of neopentyl iodide was refluxed during stirring for 24 h under N_2. Ethyl acetate (50 mL) was added. A white solid separated which was collected by filtration, 11.5 g. From C, H analysis and its ^{1}H NMR spectrum it appeared to be a mixture of **5** and neopentyldiphenylphosphonium iodide. From the NMR spectrum the yield of **5** was 7.2 g (40%). It was separated from the mixture by the following procedure.

To the white solid was added 25 mL of a 1 N NaOH aqueous solution and 100 mL of ethanol. The mixture was refluxed for 24 h. The volatiles were bulb-to-bulb distilled, and the remaining solid was extracted with 40 mL of $CHCl_3$. The extract was washed with 120 mL of water. The chloroform layer was separated, dried over anhydrous Na_2SO_4, and filtered. Ethyl acetate (250 mL) was added. The phosphonium salt separated as white solid and was collected by filtration, 5 g. It was recrystallized from chloroform/ethyl acetate, mp 258 °C dec. Anal. Calcd for $C_{22}H_{32}IP$: C, 58.2; H, 7.1; I, 28.0. Found: C, 57.9; H, 7.0; I, 27.9.

[(Trimethylsilyl)methyl]neopentyldiphenylphosphonium Iodide (8). A mixture of 12.8 g (0.05 mol) of neopentyldiphenylphosphine and 21.4 g (0.1 mol) of (trimethylsilyl)methyl iodide was refluxed in 200 mL of dry benzene for 24 h under N_2. The phosphonium salt separated as white solid. Ethyl acetate (200 mL) was added to complete the precipitation of the phosphonium salt. It was collected by filtration, 12.5 g (53%), and was recrystallized from chloroform/ethyl acetate, mp 215–217 °C. Anal. Calcd for $C_{21}H_{32}IPSi$: C, 53.2; H, 6.8; I, 27.0. Found: C, 53.6; H, 6.8; I, 27.5.

[(Trimethylsilyl)methyl]dineopentylphenylphosphonium Iodide (9). A mixture of 10 g (0.04 mol) of dineopentylphenylphosphine and 12.6 g (0.06 mol) of (trimethylsilyl)methyl iodide was refluxed in 20 mL of dry benzene for 24 h under N_2. The phosphonium salt separated as white solid. Ether (200 mL) was added to complete the precipitation of the phosphonium salt. It was collected by filtration, 8.0 g (43%), and was recrystallized from chloroform/ethyl acetate, mp 206–208 °C. Anal. Calcd for $C_{20}H_{38}IPSi$: C, 51.7; H, 8.2. Found: C, 51.3; H, 8.1.

Hydrolysis of Methylneopentyldiphenylphosphonium Iodide (3). To a solution of 3.98 g (0.01 mol) of **3** in 20 mL of ethanol was added 1 N aqueous NaOH (20 mL). The mixture was refluxed for 17 h. The volatiles were distilled in vacuo, and the remaining solid was extracted with 20 mL of chloroform. The chloroform extract was dried over anhydrous Na_2SO_4. The chloroform was distilled, and the residue was extracted with 30 mL of boiling cyclohexane. The remaining solid (1.0 g) was identified as the starting phosphonium salt by its NMR spectrum. Cyclohexane was distilled from the extract in vacuo, leaving 0.65 g (31%) of methylneopentylphenylphosphine oxide (**10**), mp 76 °C. Anal. Calcd for $C_{12}H_{19}OP$: C, 68.6; H, 9.0. Found: C, 68.1; H, 9.1.

Neopentyldiphenylphosphine Oxide (11). To an ice-cold solution of 2.56 g (0.01 mol) of neopentyldiphenylphosphine in 10 mL of glacial acetic acid was added dropwise during stirring 2 mL of 30% aqueous H_2O_2. The reaction mixture was poured into 200 mL of water. **11** precipitated as white solid and was collected by filtration, 2.5 g (92%). An analytical sample was prepared by recrysatllization from cyclohexane, mp 165 °C. Anal. Calcd for $C_{17}H_{21}OP$: C, 75.0; H, 7.7; P, 11.4. Found: C, 75.2; H, 8.1; P, 11.5.

Dineopentylphenylphosphine Oxide (12). To a solution of 2.5 g (0.01 mol) of dineopentylphenylphosphine in 10 mL of glacial acetic acid was added dropwise and during stirring 2 mL of 30% aqueous H_2O_2. After the addition of H_2O_2 was complete, 100 mL of water was added to the reaction mixture. **12** separated as white solid. It was collected by filtration and thoroughly washed with water. It was recrystallized from EtOH/H_2O, mp 136 °C. Anal. Calcd for $C_{16}H_{27}OP$: C, 72.2; H, 10.2; P, 11.7. Found: C, 72.4; H, 9.7; P, 12.4.

Registry No.—**1**, 7660-85-7; **2**, 57620-68-5; **3** (charged form), 68890-52-8; **3** (uncharged form), 68890-53-9; **4** (charged form), 68890-54-0; **4** (uncharged form), 68890-55-1; **5** (charged form), 68890-56-2; **5** (uncharged form), 68890-57-3; **6** (charged form), 3740-00-9; **6** (uncharged form), 68914-57-8; **7** (charged form), 3739-98-8; **7** (uncharged form), 68890-64-2; **8** (charged form), 68890-58-4; **8** (uncharged form), 68890-59-5; **9** (charged form), 68890-60-8; **9** (uncharged form), 68890-61-9; **10**, 68890-62-0; **11**, 3740-04-3; **12**, 68890-63-1; chlorodiphenylphosphine, 1079-66-9; neopentylmagnesium chloride, 13132-23-5; phenyldichlorophosphine, 644-97-3; neopentyl iodide, 15501-33-4; (trimethylsilyl)methyl iodide, 4206-67-1.

References and Notes

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Synthesis and Thermolysis of Poly(2,2-dimethyltrimethylene phenylphosphinate)

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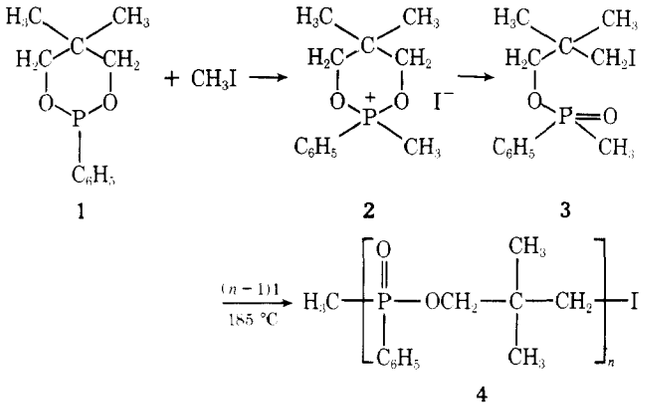
Poly(2,2-dimethyltrimethylene phenylphosphinate) has been synthesized through the ring-opening polymerization of 2,2-dimethyltrimethylene phenylphosphonite using CH_3I as an initiator. The structure of the polymer has been established by NMR spectroscopy, and its thermal and other properties are reported. Its thermolysis at 300 °C gave cyclic 2,2-dimethyltrimethylene phenylphosphinate, whose conformational analysis has been conducted from ^1H NMR spectral data.

Ring-opening polymerization of cyclic phosphonites to polyphosphinates has been reported in literature. For example, Petrov[2] and Mukaiyama[3] and their co-workers prepared poly(trimethylene phenylphosphinate) from the corresponding cyclic phosphonite at 120–200 °C using CH_3I as an initiator. However, only low molecular weight polymer ($\leq$3200) was obtained,[2] presumably due to decomposition at these temperatures. Assuming that the low molecular weight polymer resulted due to β-elimination, $>P(=O)OCH_2CH_2- \rightarrow >P(=O)OH + CH_2=CH-$, we have prepared poly(2,2-dimethyltrimethylene phenylphosphinate) in which both of the β-hydrogens are substituted by methyl groups. This paper describes the thermolysis of poly(2,2-dimethyltrimethylene phenylphosphinate) and compares it with that of poly(trimethylene phenylphosphinate).

Results and Discussion

Poly(2,2-dimethyltrimethylene phenylphosphinate) was prepared by the reaction shown in Scheme I.

Scheme I



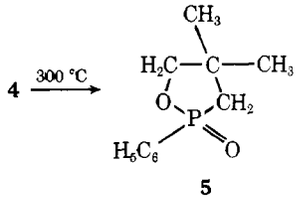
The reaction of the cyclic phosphonite **1** with CH_3I proceeds via the phosphonium salt intermediate **2**, which undergoes Arbuzov rearrangement to give phosphinate **3**. Both **2** and **3** were isolated and identified by their NMR spectra (Figure 1). The rearrangement of the phosphonium salt to the phosphinate is quite facile as it occurred even when running the NMR spectrum. The spectrum of **3** shows the OCH_2 protons to be magnetically nonequivalent. Heating to 100 °C in toluene did not change its spectrum, suggesting that the nonequivalence of the methylene protons is due to chiral phosphorus and not to restricted rotation around the P–O bond.

Phosphonite **1** is known to exist in the chair conformation,[4,5] but different configurations have been assigned at the phosphorus atom. Gagnaire et al.[4] originally assigned the phenyl substituent to the equatorial position on steric grounds. However, from NMR studies of cyclic phosphonites, Verkade and Bentrude and their co-workers[5,6] assigned the phenyl group to the axial position in **1**. Bentrude et al.[6] showed that $^3J_{POCH}$ depends on the dihedral angle POCH and the orientation of the lone pair on phosphorus. If the substituent is axial, $^3J_{PH_a} \approx 2$ Hz and $^3J_{PH_e} \approx 10$ Hz; and if the substituent is equatorial, $^3J_{PH_a} \approx 2$ Hz and $^3J_{PH_e} \approx 20$ Hz. In phosphonite **1** the $^3J_{POCH}$ couplings are 3 and 10.2 Hz for the axial and equatorial protons, respectively, which are consistent with the structure in which the phenyl group is in the axial arrangement.

The phosphonium salt intermediate **2** probably has the same stereochemistry as the cyclic phosphonite; that is, the phenyl group is in the axial position.

Poly(2,2-dimethyltrimethylene phenylphosphinate) (4). **4** is a colorless polymer. The low molecular weight polymer is a viscous liquid, but the high molecular weight polymer is usually a glassy solid. A typical polymer, $\overline{M}_n \approx 16\,000$, has $T_g = 4$ °C and $T_m = 160$ °C. Its structure has been established by its NMR spectrum (Figure 1), which shows multiplets of equal area for the CH_2 and CH_2O groups bonding to phosphorus. The polymer was shown by X-ray analysis to be mainly amorphous. The lack of crystallinity is attributed to the bulky groups on phosphorus and close proximity of the phosphorus moieties along the polymer chain.

The polymer is stable up to about 250 °C, but decomposes at higher temperatures to give cyclic 2,2-dimethyltrimethylene phenylphosphinate (**5**) in almost quantitative yield (eq 1). The



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