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ISOLATION AND CHARACTERIZATION OF STABLE ALKYLIDENEPHOSPHINES

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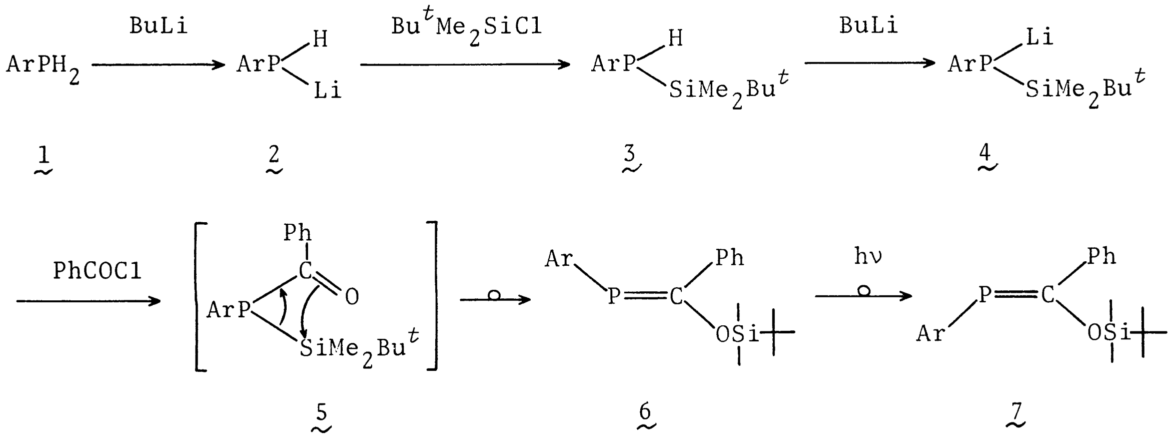
E and Z-*P*-α-(t-Butyldimethylsilyloxy)benzylidene(2,4,6-tri-t-butylphenyl)phosphines were isolated as stable compounds.

Primary phosphines are quite toxic and evil-smelling compounds. Generally they are very easily oxidized and, particularly, those containing the lower aliphatic moieties ignite spontaneously in air.[1] Recently, we[2] and others[3] reported the preparation of a primary phosphine, 2,4,6-tri-t-butylphenylphosphine (1), which is quite stable to air and odorless. The phosphine 1 has turned out to be a useful starting material for another sterically protected phosphorus-containing unusual species.[2-5] Phosphorus(III)-containing p_π-p_π double bond compounds have been of current interest, since some of those with -P=C<[6-8] -P=N-,[9] and -P=P-[10] were reported to be isolable materials if protected sterically.

We now report the preparation and characterization of alkylidenephosphines (6 and 7) starting from 1 via a silylphosphine 3 through a 1,3-silyl migration of an acylsilylphosphine intermediate 5 as shown below.



(Ar = 2,4,6-$\mathrm{Bu}^t_3\mathrm{C}_6\mathrm{H}_2$)

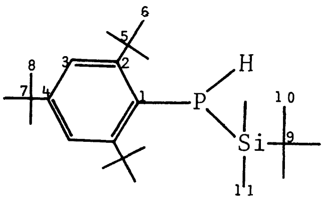
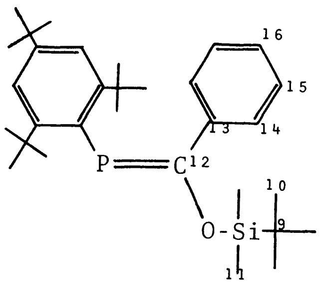
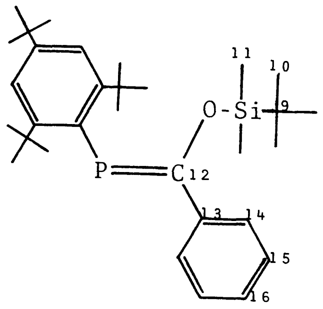
The phosphine 1 was metallated with butyllithium in tetrahydrofuran (THF) at room temperature under argon and the resulting phosphide 2 was quenched with t-butylchlorodimethylsilane to give t-butyldimethylsilyl(2,4,6-tri-t-butylphenyl)-phosphine (3) almost quantitatively after removal of THF, addition of pentane, and filtration of insoluble material. 3: oil; ^{1}H NMR (CDCl$_3$) δ=7.21 (2H, d, $^4J_{PH}$=2.4 Hz, arom.), 4.30 (1H, d, $^1J_{PH}$=211.1 Hz, P$\underline{H}$), 1.52 (18H, s, o-Bu^t), 1.27 (9H, s, p-Bu^t), 0.89 (9H, s, Si-Bu^t), and -0.24 (6H, d, $^3J_{PH}$=8.8 Hz, Si-Me); IR (KBr) 2375 cm^{-1} (P-H); MS m/e 392 (M$^+$). The silylphosphine 3 was repeatedly lithiated with butyllithium in THF at room temperature under argon to give the corresponding phosphide 4 and allowed to react with benzoyl chloride to give E-*P*-α-(t-butyldimethylsilyloxy)benzylidene(2,4,6-tri-t-butylphenyl)phosphine (6) in 63% yield from 1 after purification by column chromatography (SiO$_2$). 6: mp 121 - 124 °C; ^{1}H NMR (CDCl$_3$) δ=7.38 (2H, d, $^4J_{PH}$=1.5 Hz, arom.), 7.0-6.4 (5H, m, Ph), 1.49 (18H, d, $^5J_{PH}$=0.7 Hz, o-Bu^t), 1.38 (9H, s, p-Bu^t), 1.07 (9H, s, Si-Bu^t), and 0.39 (6H, d, $^3J_{PH}$=1.8 Hz, Si-Me); IR (KBr) 840 cm^{-1} (P=C); MS m/e 496 (M$^+$); UV (CH$_2$Cl$_2$) 247 (ε 14700) and 321 nm (10000). The E-isomer 6 was irradiated with a medium pressure mercury lamp for 2 h in benzene at 0 °C under argon to give the corresponding Z-isomer 7 almost quantitatively. 7: mp 102 - 104 °C; ^{1}H NMR (CDCl$_3$) δ=7.5 - 7.3 (5H, m, Ph), 7.25 (2H, d, $^4J_{PH}$=0.9 Hz, arom.), 1.55 (18H, s, o-Bu^t), 1.33 (9H, s, p-Bu^t), 0.56 (9H, s, Si-Bu^t), and -0.36 (6H, s, Si-Me); IR (KBr) 830 cm^{-1} (P=C); MS (field desorption ionization) m/e 496; UV (CH$_2$Cl$_2$) 244 (ε 15800) and 306 nm (10600). Table 1 shows ^{31}P NMR parameters of some phosphorus compounds obtained during the course of this work. Table 2 shows ^{13}C{^{1}H} NMR data of 3, 6, and 7. It should be noted that the alkyls on the silicon atom in 6 interact more strongly with the phosphorus atom than those in 7[8] in terms of spin-spin coupling constants J_{PC}.

The reaction might proceed via the benzoylsilylphosphine 5 first formed as an intermediate and the silyl group migrates in a 1,3-fashion to give the E-isomer 6. By considering the Dreiding models of 6 and 7, the E-isomer 6 is more crowded than the Z-isomer 7, therefore photoisomerization of E to Z is reasonably explained, however, 6 did not isomerize to 7 in refluxing benzene for several hours. A preliminary measurement of spin-lattice relaxation times (T_1) by an inversion recovery FT method in ^{31}P NMR (in CDCl$_3$ at 30 °C) indicated that the more crowded E-isomer 6 has a shorter T_1 (5.6 s) than that for the Z-isomer 7 (8.3 s), which is also consistent with this assignment of configurations.[11] It should also be noted

TABLE 1. ^{31}P NMR Parameters of Some Phosphorus Compounds

Compound		Solvent	δ_P/ppm	$^1J_{PH}$/Hz
$ArPH_2$	(1)	$CDCl_3$	-129.9	210.6
ArP(H)Li	(2)	THF	-108.8	170.9
$ArP(H)SiMe_3$		THF	-130.1	212.4
$ArP(SiMe_3)Li$		THF	-151.2	-----
$ArP(H)SiMe_2Bu^t$	(3)	$CDCl_3$	-136.2	210.0
$ArP(SiMe_2Bu^t)Li$	(4)	THF	-156.0	-----
E-$ArP{=}C(OSiMe_2Bu^t)Ph$	(6)	$CDCl_3$	160.3	-----
Z-$ArP{=}C(OSiMe_2Bu^t)Ph$	(7)	$CDCl_3$	141.3	-----

TABLE 2. $^{13}C\{^1H\}$ NMR Data of Compounds 3, 6, and 7 in $CDCl_3$

Compound	δ_C/ppm (assignment, multiplicity, J_{PC})	
 3	154.4 (C^2, d, ^2J=6.1 Hz)	38.3 (C^5, s)
	146.9 (C^4, d, ^4J=1.2 Hz)	34.5 (C^7, s)
	128.3 (C^1, d, ^1J=32.4 Hz)	33.7 (C^6, d, ^4J=6.7 Hz)
	121.0 (C^3, d, ^3J=3.7 Hz)	31.4 (C^8, s)
		27.4 (C^{10}, d, ^3J=2.4 Hz)
		19.6 (C^9, d, ^2J=9.8 Hz)
		-3.0 (C^{11}, d, ^2J=5.5 Hz)
 6	192.1 (C^{12}, d, ^1J=42.7 Hz)	38.2 (C^5, s)
	154.9 (C^2, d, ^2J=2.4 Hz)	35.0 (C^7, s)
	150.6 (C^4, s)	32.6 (C^6, d, ^4J=6.7 Hz)
	140.6 (C^{13}, d, ^2J=14.0 Hz)	31.5 (C^8, s)
	132.8 (C^1, d, ^1J=56.2 Hz)	26.0 (C^{10}, d, ^5J=1.2 Hz)
	127.3 (C^{16}, d, ^5J=4.3 Hz)	18.5 (C^9, s)
	126.9 (C^{14}, d, ^3J=5.5 Hz)	-4.9 (C^{11}, d, ^4J=8.6 Hz)
	126.7 (C^{15}, d, ^4J=8.5 Hz)	
	122.2 (C^3, s)	
 7	188.5 (C^{12}, d, ^1J=51.9 Hz)	38.1 (C^5, s)
	154.6 (C^2, d, ^2J=2.4 Hz)	34.9 (C^7, s)
	149.0 (C^4, s)	32.9 (C^6, d, ^4J=6.7 Hz)
	142.6 (C^{13}, d, ^2J=32.3 Hz)	31.5 (C^8, s)
	133.2 (C^1, d, ^1J=53.7 Hz)	25.7 (C^{10}, s)
	128.6 (C^{16}, d, ^5J=3.1 Hz)	18.2 (C^9, s)
	128.0 (C^{14}, d, ^3J=10.4 Hz)	-3.1 (C^{11}, s)
	127.5 (C^{15}, d, ^4J=14.0 Hz)	
	121.6 (C^3, d, ^3J=1.2 Hz)	

that both **6** and **7** are stable for a long period of time in the pure state and neither isomerize nor polymerize.

Further studies on the reactions of **6** and **7** are in progress.12) We thank Mr. Hiroaki Shiraishi at the National Institute for Environmental Research, Japan, for obtaining FD-MS of **7** and Shin-Etsu Chemical Co., Ltd. for donation of the silyl halides used in this work. This work was also supported in part by the Scientific Research Grant-in-Aid (Nos. 543008, 57540276, and 58840023) from the Ministry of Education, Science and Culture of Japan.

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12) Attempts to use chlorotrimethylsilane instead of t-butylchlorodimethylsilane have been unsuccessful because the silylphosphine obtained was unstable and the further lithiation was not efficient enough to give exclusively the corresponding phosphide (δ_P -151.2 ppm in THF) and addition of butyllithium in excess amount cleaved the silyl group to give the starting **2** (see Table 1).

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