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Registry No. 1, 103150-46-5; 6, 103150-45-4; DIMBOA, 69884-05-5; PG, 1075-06-5; PGH, 103150-44-3; MBOA, 532-91-2; $PhN(OH)C(O)CHCl_2$, 34282-44-5; PhNHOH, 100-65-2; $CHCl_2C(O)Cl$, 79-36-7.

Alkylsilyl Cyanides as Silylating Agents[1]

Khuong Mai* and Ghanshyam Patil

Section of Medicinal/Organic Chemistry, American Critical Care, McGaw Park, Illinois 60085

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In recent years, the alkylsilyl groups have been widely used for the protection and analysis of alcohols and carbonyl compounds.[2] In many reported methods, the reaction was carried out in either acidic or basic media. In some cases, the preparation of the reagents was required and the reaction proceeded only under forcing conditions. Furthermore, GC analysis results are ambiguous due to the possibility of peak overlapping of the byproduct and the derivatized compounds.

In the course of our study on α-amino nitrile synthesis,[3] we have "found" that trimethylsilyl cyanide (Me_3SiCN) reacts violently with methanol to generate hydrogen cyanide and methoxytrimethylsilane. To our surprise, this expected reaction has not been well documented in the literature. Only in two instances has this reaction been reported.[4,5] Stork et al. briefly described the simultaneous protection of a ketone and an alcohol on a prostaglandin chain using Me_3SiCN. However, experimental details were not given.[4] Me_3SiCN was also employed for the preparation of *N*-(trimethylsilyl)diethylamine; however, prolonged heating was required.[5] Since the exploitation of silyl cyanides for alcohol protection is so limited, we therefore investigated the reaction of Me_3SiCN with a wide variety of proton changeable compounds such as alcohols, phenols, carboxylic acids, amines and thiols. Indeed, the reaction proceeded so fast that, within a few minutes, the products were readily isolated either by distillation or recrystallization (Table I). The silylation took place very smoothly

$$RAH + Me_3SiCN \xrightarrow{\text{neat}} RASiMe_3 + HCN \qquad (1)$$

$$A = O, N, S, \text{ or } COO$$

at ambient temperature when Me_3SiCN was added to the hydroxylic compounds (in a 1.2:1.0 molar ratio). Yields are generally high, and the method provides an extremely mild and simple way of trimethylsilylation under neutral conditions. In addition, the reaction is applicable to sterically hindered alcohol as in the case of 2,6-diphenylphenol (entry 8, Table I). The silylation of amines and thiols proceeded somewhat slower, and heat was applied to accelerate the reactions. In most cases, the reactions were carried out by mixing the substrates with neat Me_3SiCN, with the exception of sugars where a small amount of DMF was used to solubilize the substrates. We also found that Me_3SiCN is very unreactive toward amide, imide, urea, and carbamate even at elevated temperature. Therefore, this might provide an access to selective silylation.

For comparative purposes, we carried out an experiment on the reactivity of various silylating reagents toward 2,6-diphenylphenol. We chose this compound due to its relative resistance to silylation. The reactions were performed according to the literature methods and were monitored by TLC. The relative reactivities of several silylating agents toward 2,6-diphenylphenol were recorded as follows: bis(trimethylsilyl)acetamide[6] > Me_3SiCN > trimethylsilyl triflate[7] ≥ bis(trimethylsilyl)sulfamide[8] > $(Me_3Si)_2NH$[9] > (trimethylsilyl)-2-oxazolidinone[10] > $(Me_3SiCl/Li_2S$[11] > Me_3SiCl/base[12]

To extend the scope of the above methodology, it was decided to prepare other silyl cyanides and to employ them in silylation.

In general, silyl cyanides have been prepared from the corresponding silyl halides and silver cyanide. Satisfactory yields are usually obtained from iodide and bromide but not from the chloride. Anhydrous lithium cyanide has been reported to be an effective reagent for preparing Me_3SiCN from Me_3SiCl.[13] We also found that lithium cyanide reacts readily with *tert*-butyldimethylsilyl chloride, triethylsilyl chloride, dimethylphenylsilyl chloride, dimethylsilyl dichloride, diethylsilyl chloride, and diphenylsilyl dichloride to give fairly good yields of the corresponding cyanides (Table II); whereas potassium cyanide, sodium cyanide, and silver cyanide gave very poor yield. The greater reactivity of lithium cyanide is not surprising in view of its solubility in many organic solvents and the high charge density of the lithium ion. The subsequent silylations were carried out under conditions similar to those employed in the trimethylsilylation. Reacting the above silyl cyanides with alcohols, phenols, and carboxylic acids many silylated compounds were prepared in good yields (Table III). The *tert*-butyldimethylsilylation of tertiary alcohol was, however, very sluggish. In fact, there is a preference of primary over secondary alcohol (entries 32, 33, Table III). Another aspect of the method is that the reaction is carried out under essentially neutral conditions and thus can serve as an ideal procedure for the preparation of silyl ethers of acid-and/or base-sensitive compounds.

The preparation of C-silylated compounds by the reaction of Me_3SiCN with an organometallic compound was carried out in an aprotic solvent (eq 2). As compared to

$$RMet + Me_3SiCN \rightarrow RSiMe_3 + MetCN \qquad (2)$$

classical methods where an equivalent of Me_3SiCl was used to react with an alkylmetal over a prolonged period,[14] this

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[1] Presented in part at the National Meeting of the American Chemical Society, Miami Beach, FL, April 28–May 3, 1985.

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Table I. Preparation of O-, N-, and S-Trimethylsilylated Compounds

entry	product	reacn conditions	yield[a] %	bp, °C (torr) [mp, °C] found	bp, °C (torr) [mp, °C] reported
1	n-$C_4HgOSiMe_3$	neat, 5 min at 25 °C	97	122–125 (760)	125 (740)[b]
2	n-$C_8H_{17}OSiMe_3$	neat, 5 min at 25 °C	94	210–215 (760)	212 (749)[b]
3	*sec*-$C_6H_{13}OSiMe_3$	neat, 5 min at 25 °C	98	153–155 (760)	155 (741)[b]
4	*tert*-$C_5H_{11}OSiMe_3$	neat, 5 min at 25 °C	96	130–132 (760)	130 (744)[b]
5	$C_6H_5CH_2OSiMe_3$	neat, 5 min at 25 °C	93	55–60 (1.0)	65 (4.5)[c]
6	$Me_3SiOCH_2CH_2OSiMe_3$	neat, 5 min at 25 °C	91	168–170 (760)	166 (760)[d]
7	$C_6H_5OSiMe_3$	neat, 5 min at 25 °C	92	50–54 (2.1)	65 (10)[c]
8	2,6-$(C_6H_5)_2C_6H_3OSiMe_3$	neat, 30 min at 100 °C	97	[107–108][h]	[108][e]
9	n-$C_4H_9NSiMe_3$	neat, 15 min at 70 °C	88	134–136 (760)	135 (754)[b]
10	$(C_2H_5)_2NSiMe_3$	neat, 15 min at 70 °C	92	127–129 (760)	127 (738)[b]
11	n-$C_4H_9SSiMe_3$	neat, 30 min at 100 °C	80	170–174 (760)	172 (740)[b]
12	$C_6H_5CH_2SSiMe_3$	neat, 30 min at 100 °C	87	80–85 (0.5)	113 (2.5)[c]
13	$C_6H_5SSiMe_3$	neat, 30 min at 100 °C	92	75–80 (1.0)	95 (3.5)[c]
14	$CH_3CH_2COOSiMe_3$	neat, 5 min at 25 °C	96	120–122 (760)	122 (760)[f]
15	$C_6H_5COOSiMe_3$	neat, 5 min at 25 °C	90	220–224 (760)	222 (760)[f]
16	$C_6H_5CH(COOSiMe_3)_2$	neat, 5 min at 25 °C	91	83–88 (0.2)	94 (0.3)[f]
17	methyl tetrakis(trimethylsilyl)-α-glucopyranoside	DMF, 5 min at 100 °C	100[g]		
18	methyl tetrakis(trimethylsilyl)-α-mannopyranoside	DMF, 5 min at 100 °C	100[g]		

[a] Yield of distilled or recrystallized products. [b] See ref 17. [c] See ref 7. [d] See ref 18. [e] See ref 6. [f] See ref 10. [g] By GC. [h] Recrystallized from hexane.

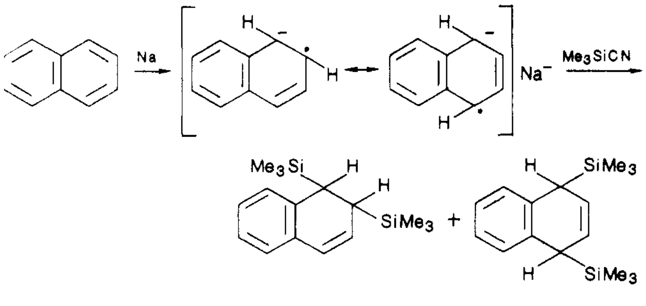
Table II. Preparation of Alkylsilyl Cyanides

entry	alkylsilyl cyanide	yield %	bp, °C (torr) [mp, °C] found	bp, °C (torr) [mp, °C] reported
19	*tert*-butyldimethylsilyl cyanide	69	163–167 (760) [82–84]	167 (760) [83][a]
20	triethylsilyl cyanide	76	180–183 (760)	181 (760)[b]
21	dimethylphenylsilyl cyanide	73	228–235 (760)	230 (760)[c]
22	dimethylsilyl dicyanide	71	166–170 (760) [82–85]	165 (760) [83][d]
23	diethylsilyl dicyanide	75	210–215 (760)	212 (760)[e]
24	diphenylsilyl dicyanide	58	110–115 (0.1) [45–47]	142 (2.0) [48][f]

[a] See ref 19. [b] See ref 20. [c] See ref 21. [d] See ref 22. [e] See ref 23. [f] See ref 24.

new method offers simpler conditions. The reactions were completed within seconds to afford good yields of silylated compounds (Table IV). In general, the reactions were performed at room temperature. However, in many cases where the reactions were very exothermic, cooling was applied to prevent the loss of volatile reagents as well as products. It has been reported that *tert*-butyllithium deprotonated Me_3SiCl to give rise to various products.[15] In our case, only one product (t-$BuMe_3Si$) was isolated; apparently the reaction rate of silylation is much greater than that of deprotonation.

When we attempted to react Me_3SiCN with sodium naphthalene radical–anion, several products were isolated. This is an expected feature and further confirms the existence of the radical at the 2- and 4-positions.[16]



The employment of silyl cyanides in silylation represents a significant improvement over earlier methods and offers a mild and simple alternative way of silylation.

Experimental Section

Melting points were determined with a Thomas-Hoover melting apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, and by the

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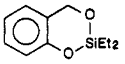
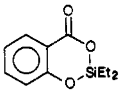
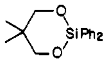
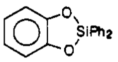
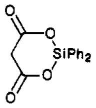
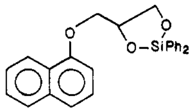
Table III. Preparation of O-Alkylsilylated Compounds

entry	product	reacn conditions	yield, %	bp, °C (torr) [mp] found	bp, °C (torr) [mp] reported	^{1}H NMR ($CDCl_3$), δ[a]
25	*tert*-butyldimethylsilyl 1-adamantanecarboxylate	80 °C, 5 min	92	[70–72]		1.9 (m, 15 H), 1.0 (s, 9 H), 0.3 (s, 6 H)
26	*trans-p*-$AcOC_6H_4CH{=}CHCOOSiMe_2$-*t*-Bu	80 °C, 5 min	88	[52–54]		6.2–7.8 (m, 6 H), 2.3 (s, 3 H), 1.0 (s, 9 H), 0.3 (s, 6 H)
27	*p*-$O_2NC_6H_4COOSiMe_2$-*t*-Bu	80 °C, 5 min	83	[130–132]		8.3 (s, 4 H), 1.1 (s, 9 H), 0.4 (s, 6 H)
28	*p*-$AcNHC_6H_4COOSiMe_2$-*t*-Bu	80 °C, 5 min	93	[133–137]		7.5–8.1 (q, 4 H), 2.2 (s, 3 H), 1.0 (s, 9 H), 0.4 (s, 6 H)
29	*p*-$AcNHC_6H_4OSiMe_2$-*t*-Bu	80 °C, 5 min	95	[100–102]		6.7–7.5 (q, 4 H), 2.1 (s, 3 H), 1.0 (s, 9 H), 0.2 (s, 6 H)
30	$C_6H_5CH_2OSiMe_2$-*t*-Bu	80 °C, 5 min	89	56–61 (0.2)	60 (0.2)[b]	
31	*c*-$C_6H_{11}OSiMe_2$-*t*-Bu	80 °C, 5 min	94	50–52 (0.2)	58 (0.4)[b]	
32	1-naphthyl-$OCH_2CH(OH)CH_2OSiMe_2$-*t*-Bu	80 °C, 5 min	88[c]			6.7–8.5 (m, 7 H), 3.7–4.7 (m, 5 H), 1.0 (s, 9 H), 0.2 (s, 6 H)
33	$C_6H_5CH(OH)CH_2OSiMe_2$-*t*-Bu	80 °C, 5 min	92[c]			7.1–7.5 (m, 5 H), 4.7 (m 1 H), 3.6 (m, 2 H), 1.0 (s, 9 H), 0.2 (s, 6 H)
34	*p*-2-$PrC_6H_4OSi(Et)_3$	80 °C, 5 min	94	162–166 (0.1)	165 (0.1)[d]	
35	*c*-$C_6H_{11}OSi(Et)_3$	80 °C, 5 min	89	233–238 (760)	237 (756)[e]	
36	$C_6H_5CH_2OSi(Et)_3$	80 °C, 5 min	91	262–265 (760)	263 (756)[e]	
37	$C_6H_5COOSi(Et)_3$	80 °C, 5 min	88	73–78 (0.1)	133 (8.0)[e]	
38	*t*-$C_4H_9COOSi(Et)_3$	80 °C, 5 min	94	202–207 (760)	205 (760)[e]	
39	*n*-$C_4H_9OSIMe_2Ph$	80 °C, 5 min	93	215–220 (760)	103 (11)[e]	
40	*m*-$AcOC_6H_4COOSiMe_2Ph$	80 °C, 5 min	80	140–148 (0.1)		6.9–7.9 (m, 9 H), 2.3 (s, 3 H), 0.3 (s, 6 H)
41	$(C_6H_5CH_2O)_2SiMe_2$	25 °C, 5 min	91	120–127 (0.1)	160 (3.0)[f]	
42	$(C_6H_5O)_2SiMe_2$	25 °C, 5 min	93	58–63 (0.1)	90 (3.0)[f]	
43		80 °C, 5 min	90	114–121 (0.1)		6.9–7.9 (m, 4 H), 0.4–1.3 (m, 10 H)
44		25 °C, 5 min	88	102–108 (0.1)		6.9–7.5 (m, 4 H), 4.6 (s, 2 H), 0.4–1.3 (m, 10 H)
45	*n*-$(C_4H_9O)_2SiPh_2$	25 °C, 5 min	85	145–152 (0.1)	201 (16)[g]	
46	*i*-$(C_3H_7O)_2SiPh_2$	25 °C, 5 min	82	113–118 (0.1)	170 (16)[g]	
47		25 °C, 5 min	94	107–113 (0.1)		7.1–7.9 (m, 10 H), 3.9 (s, 4 H), 1.2 (s, 6 H)
48		80 °C, 5 min	92	136–143 (0.1)		6.8–7.9 (m)
49		80 °C, 5 min	87	105–110 (0.1)		7.1–7.9 (m, 10 H), 3.4 (s, 2 H)
50		80 °C, 5 min	90[c]			6.7–8.4 (m, 17 H), 3.7–4.6 (m, 5 H)

[a] For new compounds only, with Me_4Si as internal standard. [b] See ref 25. [c] Purified by column chromatography. [d] See ref 26. [e] See ref 27. [f] See ref 28. [g] See ref 29.

Table IV. Preparation of C-Trimethylsilylated Compounds

entry	starting material	product	reacn[a] conditions	yield,[b] %	bp °C (torr) [mp, °C] found	bp °C (torr) [mp, °C] reported
51	$HC{\equiv}CNa$[c]	$HC{\equiv}CSiMe_3$	THF, 0 °C	77	52–53 (760)	52 (760)[e]
52	*n*-$BuC{\equiv}CLi$[d]	*n*-$BuC{\equiv}CSiMe_3$	THF, −20 °C	80	153–156 (760)	155 (760)[f]
53	*t*-$BuC{\equiv}CLi$[d]	*t*-$BuC{\equiv}CSiMe_3$	THF, −20 °C	79	112–116 (760)	57 (760)[g]
54	$PhC{\equiv}CLi$[d]	$PhC{\equiv}CSiMe_3$	THF, −20 °C	66	68–71 (1.0)	67 (5)[g]
55	$H_2C{=}CHMgBr$[c]	$H_2C{=}CHSiMe_3$	Et_2O, −20 °C	35	55–57 (760)	55 (739)[h]
56	(*E*)-*n*-$BuCH{=}CHLi$[i]	(*E*)-*n*-$BuCH{=}CHSiMe_3$	THF, −78 °C	37	55–60 (5.0)	80 (21)[i]
57	PhLi[c]	$PhSiMe_3$	hexane, −20 °C	62	166–170 (760)	167 (760)[j]
58	PhMgBr[c]	$PhSiMe_3$	Et_2O, −20 °C	80	166–170 (760)	167 (760)[j]
59	*n*-BuLi[c]	*n*-$BuSiMe_3$	hexane, −20 °C	51	112–116 (760)	117 (760)[k]
60	*n*-BuMgCl[c]	*n*-$BuSiMe_3$	Et_2O, −20 °C	72	112–116 (760)	117 (760)[k]
61	*t*-BuLi[c]	*t*-$BuSiMe_3$	hexane, −20 °C	54	103–106 (760)	103 (740)[l]
62	*t*-BuMgCl[c]	*t*-$BuSiMe_3$	Et_2O, −20 °C	65	103–106 (760)	103 (740)[l]
63	*n*-$BuC{\equiv}CCH_2Li$[m]	*n*-$BuC{\equiv}CCH_2SiMe_3$	Et_2O, −78 °C	72	60–65 (5.0)	69 (10)[m]
64	$(Me_3Si)_3CLi$[n]	$(Me_3Si)_4C$	THF, 25 °C	78	[>300]	[>360][n]

[a] Unoptimized after one run. [b] Purified products. [c] Purchased from Aldrich. [d] Prepared as shown in Experimental Section. [e] See ref 30. [f] See ref 31. [g] See ref 32. [h] See ref 33. [i] See ref 34. [j] See ref 35. [k] See ref 36. [l] See ref 37. [m] See ref 38. [n] See ref 39.

Analytical Chemistry Section, American Critical Care, and were within ±0.4% of theoretical values. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer and ^{1}H NMR spectra were determined on a Varian T-60A instrument. Spectral data

(IR, NMR) were consistent with the assigned structures in all cases.

General Procedure for O-, N-, and S-Trimethylsilylation (Table I). Freshly distilled Me_3SiCN (1.1 g, 0.11 mol) was added dropwise directly to the substrate (0.10 mol) under a nitrogen atmosphere. An exothermic reaction occurred immediately as HCN formed was vented and trapped in a bottle containing an aqueous solution of sodium hydroxide. The reaction was then stirred at the indicated temperature. The progress of the reaction was monitored by TLC at regular intervals. Soon after the completion of the reaction, a stream of nitrogen was allowed to pass through the mixture for 5 min. The resulting clear oil, practically pure at this stage, was distilled to afford the desired compound. Physical constants (mp, bp) and spectral properties (IR, ^1H NMR) of all products were in agreement with the reported data.

General Procedure for the Preparation of Alkylsilyl Cyanide (Table II). *n*-Butyllithium (Aldrich, 1.6 M in hexane, 200 mL, 0.32 mol) was transferred under nitrogen pressure into a 1-l round-bottomed flask containing 300 mL of dry toluene. The mixture was stirred and cooled to 0 °C as Me_3SiCN (36 g, 0.36 mol) was added dropwise over a period of 10 min. There was immediate precipitation of LiCN as a white solid. After the addition was complete, the reaction mixture was stirred for an additional 15 min. The chloroalkylsilane (0.30 equiv) was added to the LiCN slurry in one lot. The reaction mixture was heated to reflux overnight under nitrogen and then filtered by a course fritted disk under nitrogen pressure. The solid was washed with two small portions of cyclohexane. The filtrate was concentrated under reduced pressure to a small volume. Distillation yielded the desired alkylsilyl cyanide, of which the physical constants and spectral properties are the same as those of the known compounds.

General Procedure for O-Alkylsilylation (Table III). Alkylsilyl cyanide (0.1 equiv) was added to the hydroxylic compound (0.1 equiv) under a nitrogen atmosphere. The neat mixture was stirred at the indicated conditions. Soon after the completion of the reaction, the product was purified either by recrystallization from hexane or by distillation. spectral properties and combustion analyses of all new compounds were consistent with the assigned structure.

General Procedure for C-Trimethylsilylation (Table IV). Preparation of 1-Hexynyltrimethylsilane. *n*-Butyllithium in hexane (1.6 M, 62.5 mL, 0.1 mol) was added dropwise to a solution of 1-hexyne (8.2 g, 0.1 mol) in hexane (100 mL) at room temperature. An exothermic reaction was observed. Me_3SiCN (10 g, 0.1 mol) was then added to the reaction mixture. After being stirred for 5 min, the slurry mixture was filtered, and the solid was washed with a small portion of hexane. The filtrate was concentrated and distilled at amospheric pressure to yield 9.6 g (60%) of the title compound, bp 153–155 °C (lit.[31] bp 155 °C).

Reaction of Me_3SiCN with Naphthalene–Sodium. To a cold solution (0–5 °C) of naphthalene (12.8 g, 0.1 mol) in 100 mL of dry THF was added metallic sodium (2.5 g, 0.11 mol). The solution was stirred at 5 °C for 4 h as sodium was being consumed. Me_3SiCN (25 g, 0.25 mol) was then added to the dark green solution. There was immediate precipitation of sodium cyanide. Solvent was removed under reduced pressure, and the residue was taken up in cyclohexane, washed with water, dried over $MgSO_4$, and evaporated to a semisolid. This was distilled under reduced pressure [135–150 °C (0.1 mmHg)] to a semisolid which consisted of unreacted naphthalene, 1,2-bis(trimethylsilyl)-1,2-dihydronaphthalene and 1,4-bis(trimethylsilyl)-1,4-dihydronaphthalene. ^1H NMR spectrum ($CDCl_3$, Me_4Si) of the distilled mixture exhibits the following characteristic peaks: δ 7.0 (m), 6.2 (t), 5.8 (d), 5.7 (s), 3.1 (br s), 2.3 (s), 2.0 (d).

Registry No. $n\text{-}C_4H_9OSiMe_3$, 1825-65-6; $n\text{-}C_8H_{17}OSiMe_3$, 14246-16-3; $sec\text{-}C_6H_{13}OSiMe_3$, 17888-63-0; $C_5H_{11}OSiMe_3$, 6689-16-3; $C_6H_5CH_2OSiMe_3$, 14642-79-6; $Me_3SiOCH_2CH_2OSiMe_3$, 7381-30-8; $C_6H_5OSiMe_3$, 1529-17-5; $2,6\text{-}(C_6H_5)_2C_6H_3OSiMe_3$, 10416-72-5; $(C_2H_5)_2NSiMe_3$, 996-50-9; $n\text{-}C_4H_9SSiMe_3$, 3553-78-4; $C_6H_5CH_2SSiMe_3$, 14629-67-5; $C_6H_5SSiMe_3$, 4551-15-9; $CH_3CH_2COOSiMe_3$, 16844-98-7; $C_6H_5COOSiMe_3$, 2078-12-8; $C_6H_5CH(COOSiMe_3)_2$, 80372-12-9; *trans*-*p*-$AcOC_6H_4CH{=}CHCOOSiMe_2\text{-}t\text{-}Bu$, 103202-02-4; $p\text{-}O_2NC_6H_4COOSiMe_2\text{-}t\text{-}Bu$, 96185-30-7; $p\text{-}AcNHC_6H_4COOSiMe_2\text{-}t\text{-}Bu$, 103202-03-5; $p\text{-}AcNHC_6H_4OSiMe_2\text{-}t\text{-}Bu$, 103202-04-6; $C_6H_5CH_2OSiMe_2\text{-}t\text{-}Bu$, 53172-91-1; $c\text{-}C_6H_{11}OSiMe_2\text{-}t\text{-}Bu$, 67124-67-8; 1-adamantanecarboxylate $SiMe_2\text{-}t\text{-}Bu$, 103202-01-3; 1-naphthyl-$OCH_2CH(OH)CH_2OSiMe_2\text{-}t\text{-}Bu$, 103202-05-7; $C_6H_5CH(OH)CH_2OSiMe_2\text{-}t\text{-}Bu$, 71009-09-1; $p\text{-}2\text{-}PrC_6H_4OSi(OEt)_3$, 66967-06-4; $c\text{-}C_6H_{11}OSi(Et)_3$, 4419-18-5; $C_6H_5CH_2OSi(Et)_3$, 13959-92-7; $C_6H_5COOSi(Et)_3$, 1018-20-8; $t\text{-}C_4H_9COOSi(Et)_3$, 18002-65-8; $n\text{-}C_4H_9OSiMe_2Ph$, 18052-58-9; $m\text{-}AcOC_6H_4COOSiMe_2Ph$, 103202-06-8; $(C_6H_5CH_2O)_2SiMe_2$, 50870-64-9; $(C_6H_5O)_2SiMe_2$, 3440-02-6; $n\text{-}(C_4H_9O)_2SiPh_2$, 13320-38-2; $i\text{-}(C_3H_7O)_2SiPh_2$, 18056-95-6; $HC{\equiv}CSiMe_3$, 1066-54-2; $n\text{-}BuC{\equiv}CSiMe_3$, 3844-94-8; $t\text{-}BuC{\equiv}CSiMe_3$, 14630-42-3; $PhC{\equiv}CSiMe_3$, 2170-06-1; $H_2C{=}CHSiMe_3$, 754-05-2; $(E)\text{-}n\text{-}BuCH{=}CHSiMe_3$, 54731-58-7; $PhSiMe_3$, 768-32-1; $n\text{-}BuSiMe_3$, 1000-49-3; $t\text{-}BuSiMe_3$, 5037-65-0; $n\text{-}BuC{\equiv}CCH_2SiMe_3$, 84140-28-3; $(Me_3Si)_4C$, 1066-64-4; $n\text{-}C_4H_9OH$, 71-36-3; $n\text{-}C_8H_{17}OH$, 111-87-5; $sec\text{-}C_6H_{13}OH$, 626-93-7; $C_5H_{11}OH$, 75-84-3; $C_6H_5CH_2OH$, 100-51-6; $HOCH_2CH_2OH$, 107-21-1; C_6H_5OH, 108-95-2; $2,6\text{-}(C_6H_5)_2C_6H_3OH$, 2432-11-3; $(C_2H_5)_2NH$, 109-89-7; $n\text{-}C_4H_9SH$, 109-79-5; $C_6H_5CH_2SH$, 100-53-8; C_6H_5SH, 108-98-5; CH_3CH_2COOH, 79-09-4; C_6H_5COOH, 65-85-0; $C_6H_5CH(CO_2H)_2$, 2613-89-0; Me_3SiCN, 7677-24-9; LiCN, 2408-36-8; *trans*-*p*-$AcC_6H_4CH{=}CHCOOH$, 27542-85-4; $p\text{-}O_2NC_6H_4COOH$, 62-23-7; $p\text{-}AcHC_6H_4COOH$, 556-08-1; $p\text{-}AcNHC_6H_4OH$, 103-90-2; $o\text{-}HOC_6H_4CH_2OH$, 90-01-7; $c\text{-}C_6H_{11}OH$, 108-93-0; 1-naphthyl-$OCH_2CH(OH)CH_2OH$, 36112-95-5; $C_6H_5CH(OH)CH_2OH$, 93-56-1; $p\text{-}2\text{-}PrC_6H_4OH$, 99-89-8; $o\text{-}HOC_6H_4COOH$, 69-72-7; $t\text{-}C_4H_9COOH$, 75-98-9; $m\text{-}AcOC_6H_4COOH$, 6304-89-8; $i\text{-}C_3H_7OH$, 67-63-0; $HOCH_2C(CH_3)_2CH_2OH$, 126-30-7; $o\text{-}HOC_6H_4OH$, 120-80-9; $HOOCCH_2COOH$, 141-82-2; $HC{\equiv}CNa$, 1066-26-8; $t\text{-}BuC{\equiv}CH$, 917-92-0; $PhC{\equiv}CH$, 536-74-3; $H_2C{=}CHMgBr$, 1826-67-1; $(E)\text{-}n\text{-}BuCH{=}CHLi$, 62839-68-3; PhLi, 591-51-5; PhMgBr, 100-58-3; *n*-BuLi, 109-72-8; *n*-BuMgBr, 693-04-9; *t*-BuLi, 594-19-4; *t*-BuMgBr, 677-22-5; $n\text{-}BuC{\equiv}CCH_2Li$, 82511-26-0; $(Me_3Si)_3CLi$, 28830-22-0; methyl tetrakis(trimethylsilyl)-α-glucopyranoside, 2641-79-4; methyl tetrakis(trimethylsilyl)-α-mannopyranoside, 1769-06-8; *tert*-butyldimethylsilyl cyanide, 56522-24-8; triethylsilyl cyanide, 18301-88-7; dimethylphenylsilyl cyanide, 103201-99-6; dimethylsilyl dicyanide, 5158-09-8; diethylsilyl dicyanide, 103202-00-2; diphenylsilyl dicyanide, 4669-68-5; 2,2-diethyl-4*H*-1,3,2-benzodioxasilin, 103202-07-9; 2,2-diethyl-4-oxa-1,3,2-benzodioxasilin, 103202-08-0; 2,2-diethyl-4,4-dimethyl-1,3-dioxa-2-silacyclohexane, 18106-01-9; 2,2-diphenyl-1,3,2-benzodioxasilole, 14857-41-1; 4,6-dioxo-2,2-diphenyl-1,3-dioxa-2-silacyclohexane, 103202-09-1; 4-((1-naphthyloxy)methyl)-2,2-diphenyl-1,3-dioxa-2-silacyclopentane, 103202-10-4; methyl α-glucopyranoside, 97-30-3; methyl α-mannopyranoside, 617-04-9; *tert*-butylchlorodimethylsilane, 18162-48-6; chlorotriethylsilane, 994-30-9; chlorodimethylphenylsilane, 768-33-2; dichlorodimethylsilane, 75-78-5; dichlorodiethylsilane, 1719-53-5; dichlorodiphenylsilane, 80-10-4; 1-adamantanecarboxylic acid, 828-51-3; 3-((1-naphthyl)oxy)-1,2-propanediol, 36112-95-5; 1-hexyne, 693-02-7; naphthalene, 91-20-3; 1,2-bis(trimethylsilyl)-1,2-dihydronaphthalene, 1085-99-0; 1,4-bis(trimethylsilyl)-1,4-dihydronaphthalene, 1085-97-8.

Complexes between *N*-Bromosuccinimide and Quaternary Ammonium Bromides and Their Role in the Addition of Bromine to Olefins

Manuel Finkelstein, Shirley A. Hart, W. Michael Moore, and Sidney D. Ross*

Research and Development Center, Sprague Electric Company, North Adams, Massachusetts 01247

Lennart Eberson*

Division of Organic Chemistry 3, Chemical Center, University of Lund, S-221-00 Lund, Sweden

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N-Bromosuccinimide (SBr) is a reagent of remarkable versatility. It can participate in free radical chain reactions[1-4] as well as react by a variety of polar mecha-

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