(2-Cyanoallyl)trimethylsilane and (2-Cyanoethyl)trimethylsilane.
Unique σπ Captodative Systems[1]

Hideki SAKURAI,* Soichiro KYUSHIN, and Yasuhiro NAKADAIRA[†]
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

Addition reactions of (2-cyanoallyl)trimethylsilane as well as hydrogen abstraction reactions of (2-cyanoethyl)trimethylsilane were examined. These compounds exhibit high reactivities in free-radical reactions, demonstrating existence of the σπ capto-dative effect.

The captodative effect, which is related to the synergetic stabilization of free radicals having both electron-withdrawing (captor) and electron-donating (donor) substituents, has been widely recognized as a factor of controlling the free-radical reactivities.[2,3] However, all the donors so far investigated are n- or π-donors. The σπ captodative effect is thus unknown. Actually, almost nothing has been reported on the captodative effect for organosilicon compounds, except for some examples of silyl enol ethers.[2]

The electron-donating effect of the trimethylsilylmethyl (Me_3SiCH_2-) and related organosilicon groups has been well documented.[4] Both methoxy and trimethylsilylmethyl groups have σ^+ constants of approximately the same magnitude.[4] Since the degree of electron-donating abilities may be measured by the magnitudes of σ^+ constants, one can expect that the trimethylsilylmethyl group can also participate as a donor in captodative systems. We thought that exploration of the effect for organosilicon compounds would give an opportunity to access theoretically and synthetically interesting systems. This is the objective of the present investigation.

(2-Cyanoallyl)trimethylsilane (1) was prepared from (2-bromoallyl)trimethylsilane[5] and cuprous cyanide in 17% yield.[6,7]
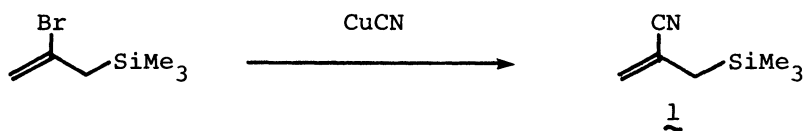

As a substituted acrylonitrile, 1 is very unreactive toward nucleophilic addition as evidenced by the fact that no reaction occurred when 1 was refluxed with pyrrolidine in ether or in THF. Under the conditions, however, acrylonitrile gave the addition product in quantitative yield. As an allylsilane,[8] 1 also show the very much reduced reactivity towards electrophiles. Thus no reaction took

---

[†] Present address: University of Electro-Communications, Chofu, Tokyo.

place with benzaldehyde in the presence of a Lewis acid such as BF_3 etherate.[9, 10]

Although acrylonitrile and α-methacrylonitrile are known to polymerize readily in the presence of a free-radical initiator such as azobisisobutyronitrile, no polymerization of 1 occurred under the conditions and following products were obtained instead.
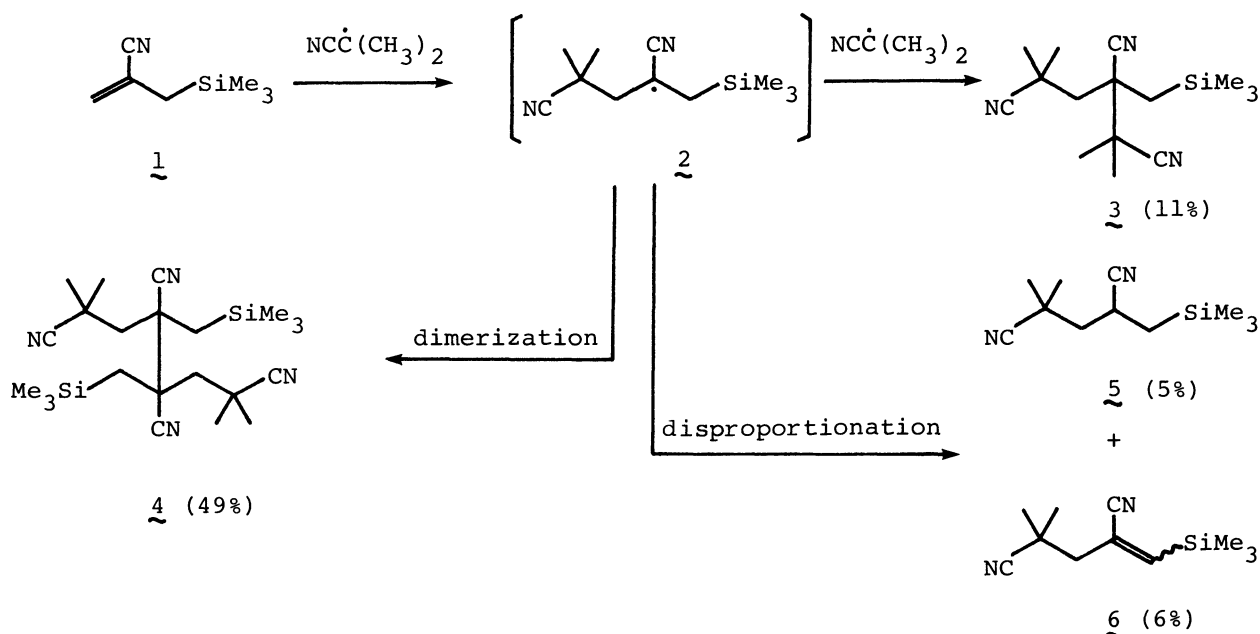

The formation of the products can be explained by the intermediacy of the radical 2. The radical 2 is not reactive enough to add to 1 and undergoes only dimerization and disproportionation.

When 1 was heated in a sealed tube at 200 °C, a dimer (7) was obtained as a sole product. No cyclobutane derivative (8) was detected. In the case of acrylonitrile the cyclobutane formation is the main fate of the intermediate radical in addition to polymerization.[11] The difference of the behaviors of cyclobutanes may be attributed to the weak C-C bond of 8 which undergoes homolysis very easily under the conditions. These facts strongly suggest that intermediate radicals 2 and 9 derived from 1 are really stabilized in some extent by στ captodative effect similar to nπ and ππ captodative systems.
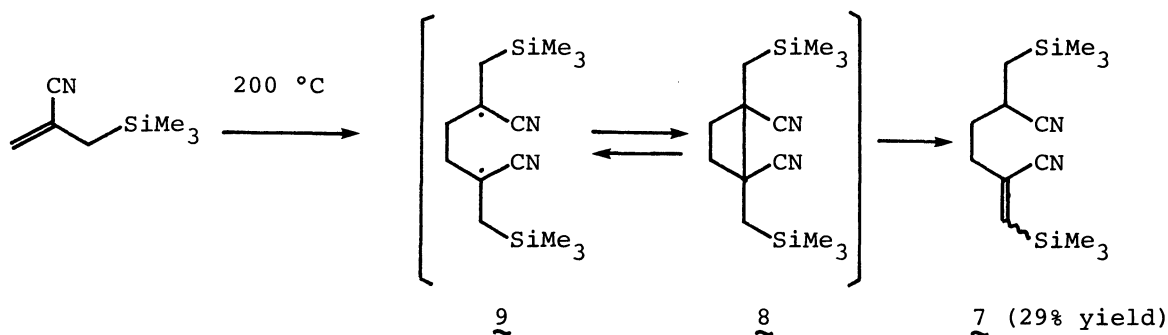

In order to get more insight into the nature of the effect, we have examined next hydrogen abstraction reactions of (2-cyanoethyl)trimethylsilane (10).[12]

When a mixture of $\underset{\sim}{10}$ and di-t-butyl peroxide was heated in a sealed tube at 135 °C for 10 h, two dehydrodimers $\underset{\sim}{11}$ and $\underset{\sim}{12}$ were formed as main products in 71% yield,[13] along with a trace amount of dehydrotrimers $\underset{\sim}{13}$ (detected by GC-MS).
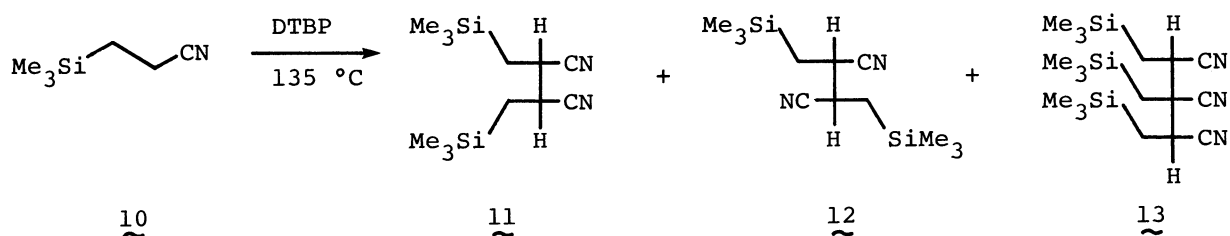
Bromination of $\underset{\sim}{10}$ with N-bromosuccinimide (NBS) in the presence of benzoyl peroxide also took place smoothly to give (2-bromo-2-cyanoethyl)trimethylsilane ($\underset{\sim}{14}$) and (2,2-dibromo-2-cyanoethyl)trimethylsilane ($\underset{\sim}{15}$) in 65 and 16% yield, respectively. Trialkylsilylmethyl groups alone can stabilize the radical only weakly[14] and indeed 1,3-bis(trimethylsilyl)propane did not react with NBS under the same conditions.
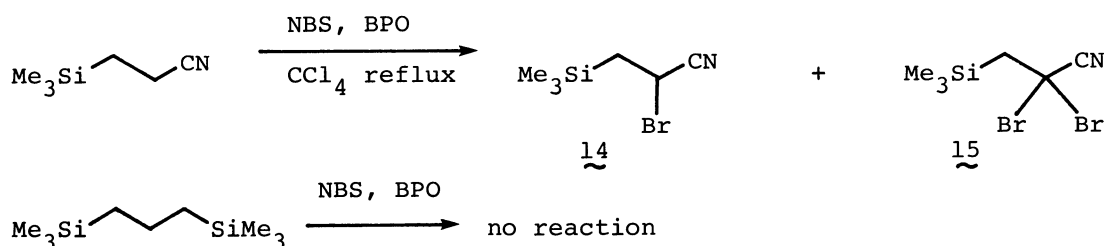
Therefore, it is now clear that the combination of the trimethylsilylmethyl and cyano groups can stabilize the intermediate radicals. Then we have carried out competitive bromination reactions with NBS for several substrates including $\underset{\sim}{10}$, cyanoethane ($\underset{\sim}{16}$), 2-cyanopropane ($\underset{\sim}{17}$), and benzyl cyanide ($\underset{\sim}{18}$) to evaluate the relative reactivities. The reactions were carried out with carbon tetrachloride (3.0 ml) solutions of an appropriate combination of two samples (2.00 mmol) and NBS (1.70-2.00 mmol) at 78$\pm$0.5 °C. The relative reactivities of one hydrogen are listed below.

$NCC\underline{H}_2CH_2SiMe_3$ $\underset{\sim}{10}$ (1.0) $NCC\underline{H}_2CH_3$ $\underset{\sim}{16}$ (0.05) $NCC\underline{H}(CH_3)_2$ $\underset{\sim}{17}$ (1.2) $NCC\underline{H}_2Ph$ $\underset{\sim}{18}$ (3.9)

The reactivity of $\underset{\sim}{10}$ is almost the same with that of $\underset{\sim}{17}$ and is far larger than $\underset{\sim}{16}$. The radical formed after hydrogen abstraction from $\underset{\sim}{17}$ is the same one derived from azobisisobutyronitrile (AIBN). However, the effect of the trimethylsilylmethyl group is much smaller than the most prominent dative substituent such as the methylthio group. Thus the similar competitive bromination with $\underset{\sim}{10}$, cyanomethyl methyl sulfide ($\underset{\sim}{19}$), cyanomethyl methyl ether ($\underset{\sim}{20}$), and acetoxymethyl cyanide ($\underset{\sim}{21}$) resulted in the following relative reactivities at 78$\pm$0.5 °C.

$\underset{\sim}{10}$ (1.0) $NCC\underline{H}_2SCH_3$ $\underset{\sim}{19}$ (150) $NCC\underline{H}_2OCH_3$ $\underset{\sim}{20}$ (6.3) $NCC\underline{H}_2OC(O)CH_3$ $\underset{\sim}{21}$ (0.04)

As a dative substituent in the captodative effect, the methylthio group is an exceptionally strong donor. On the other hand, methyl and acetoxymethyl groups are weak donors. Judging from the data above, one can classify the trimethylsilylmethyl group as a medium donor like methoxy and benzyl groups. We will report in a forthcoming paper results of spectroscopic studies such as ESR of captodative systems together with semi-quantitative evaluations of the rotational barriers of the concerning C-C bonds which should be related to the stabilization effect more quantitatively.

References

1) Chemistry of Organosilicon Compounds 226.

2) H. G. Viehe, R. Merényi, L. Stella, and Z. Janousek, Angew. Chem., Int. Ed. Engl., 18, 917 (1979).

3) H. G. Viehe, Z. Janousek, and R. Merényi, Acc. Chem. Res., 18, 148 (1985).

4) W. Hanstein, H. Berwin, and T. G. Traylor, J. Am. Chem. Soc., 92, 829, 7476 (1970); G. D. Hartman and T. G. Traylor, ibid., 97, 6147 (1975).

5) N. Furuya and T. Sukawa, J. Organomet. Chem., 96, C1 (1975).

6) Substitution of bromine at the vinylic position by cuprous cyanide was reported by R. Lapouyade, M. Daney, M. Lapenue, and H. Bouas-Laurent, Bull. Soc. Chim. Fr., 1973, 720.

7) 1: ^{1}H NMR (CDCl$_3$) δ 0.14 (9H, s), 1.77 (2H, d, J = 1.5 Hz), 5.47 (1H, dd, J = 1.5, 0.7 Hz), 5.67 (1H, d, J = 0.7 Hz); ^{13}C NMR (CDCl$_3$) δ 2.15, 25.65, 119.59, 120.37, 127.22; IR (neat, cm^{-1}) 2224, 1611; MS m/e (%) 139 (M$^+$, 7), 124 (5), 97 (15), 84 (11), 73 (100).

8) H. Sakurai, Pure Appl. Chem., 54, 1 (1982); 57, 1759 (1985) and references cited therein.

9) A. Hosomi and H. Sakurai, Tetrahedron Lett., 1976, 1295.

10) However, 1 can react with stronger electrophiles such as benzaldehyde dimethylacetal activated by trimethylsilyl triflate to afford the expected product in 60% yield. In the presence of a catalytic amount of fluoride ions, 1 also reacted with benzaldehyde at room temperature to give the expected product in quantitative yield.

11) E. C. Coyner and W. S. Hillman, J. Am. Chem. Soc., 71, 324 (1949).

12) G. A. Shvekhgeimer and A. P. Kruchkova, Zh. Obshch. Khim., 36, 1852 (1966).

13) Assignment of the stereochemistry is tentative. 11: ^{1}H NMR (CDCl$_3$) δ 0.24 (18H, s), 1.05-1.20 (4H, m), 2.64-2.95 (2H, m); ^{13}C NMR (CDCl$_3$) δ 1.50, 18.08, 33.94, 119.78; IR (KBr, cm^{-1}) 2240; MS m/e (%) 237 (M$^+$-15, 9), 138 (14), 126 (44), 73 (100). 12: ^{1}H NMR (CDCl$_3$) δ 0.24 (18H, s), 0.84-1.53 (4H, m), 2.69-2.96 (2H, m); ^{13}C NMR (CDCl$_3$) δ 1.50, 18.08, 33.81, 119.33; IR (KBr, cm^{-1}) 2238; MS m/e (%) 237 (M$^+$-15, 9), 138 (13), 126 (41), 73 (100).

14) H. Sakurai, A. Hosomi, and M. Kumada, Bull. Chem. Soc. Jpn., 44, 568 (1971).