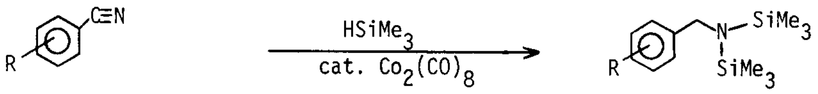
Tetrahedron Letters,Vol.26,No.42,pp 5145-5148,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

COBALT CARBONYL CATALYZED REDUCTION OF AROMATIC NITRILES WITH A HYDROSILANE LEADING TO N,N-DISILYLAMINES

Toshiaki MURAI,* Takehiko SAKANE, and Shinzi KATO
Department of Chemistry, Faculty of Engineering,
Gifu University, Yanagido, Gifu 501-11, Japan

Summary: Cobalt carbonyl catalyzed reaction of $HSiMe_3$ with aromatic nitriles having various functional groups provided a novel route to N,N-disilylamines.

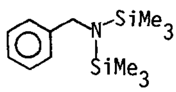
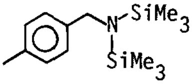
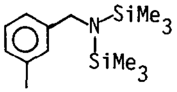
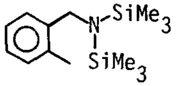
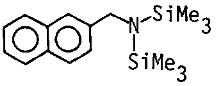
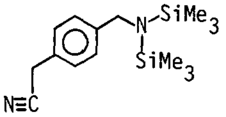
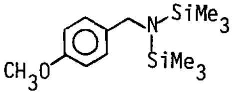
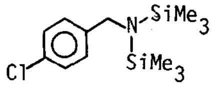
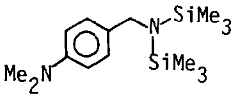
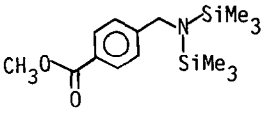
The hydrosilylation of alkynes using transition metal catalyst has been an important and well-known process not only as a method of reduction but also as a convenient route to silicon containing compounds.[1] On the other hand little attention has been paid to the addition of hydrosilanes to nitriles,[2,3] despite the potential utility of N-silylated compounds.[4] For example, the addition of $HSiMe_2Cl$ to methacryronitrile has been reported, but the product yield was very low.[3] Nevertheless the selective reduction of aromatic nitriles having various functional groups is an important route to primary amines, although few studies has been carried out.[5] We now wish to report a novel and effective method for the reduction of aromatic nitriles using cobalt carbonyl catalyzed addition of two molecules of $HSiMe_3$ (eq 1).[6]



(1)

To a solution of $CH_3C_6H_5$ (10 mL) containing $Co_2(CO)_8$ (0.0684 g, 0.2 mmol) was added $HSiMe_3$ (2.83 mL, 25 mmol) with stirring at -20°C under CO atmosphere.

Table 1. Cobalt Carbonyl Catalyzed Addition of $HSiMe_3$ to Aromatic Nitriles.[a]
Products, Yields, and Boiling points.

entry	product	yield,%[b]	bp, °C/mmHg
1	 [d]	61	130/20
2		91	150/20
3		57(68)	150/19
4[e]		11(22)	150/10
5		64(67)	150/0.5
6[e]		(36)	150/0.5
7		(88)	160/10
8[e,f]		(53)	150/5
9		(73)	120/0.5
10[e,f]		(46)[g]	150/0.7

a) All reactions were carried out on a scale as described in the text unless otherwise noted. b) GLC yields in parenthesis. c) Oven Temperature of bulb to bulb distillation apparatus. d) ref. 7. e) $Co_2(CO)_8$ (0.625 mmol) was used. f) For 48 hrs. g) Partially hydrolyzed product, i.e., a monosilylated amine , was also obtained in 19 % yield.

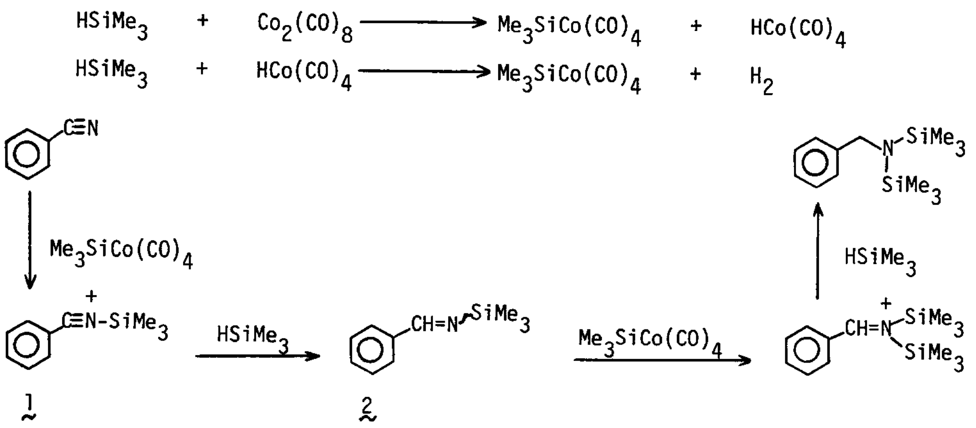
After about 5 minutes, to this solution was added p-tolunitrile (0.3 mL, 2.5 mmol) at -20°C. The reaction mixture was stirred at 60°C for 20 hrs. The solvent was removed by rotary evaporator and the residue was distilled by bulb to bulb distillation to give 0.606 g (91 % yield) of N,N-bis(trimethylsilyl)-p-methylbenzylamine as a colorless liquid. The reaction can also be effected by using a nitrogen atmosphere, although the yield being slightly decreased. The N,N-bis(silyl)amine was quantitatively converted to p-methylbenzylamine by treating with KF in methanol.

In a similar manner a number of N,N-disilylamines were obtained from the corresponding nitriles as shown in Table 1. The products were identified by ^{1}H NMR, IR, and Mass spectra, and/or comparison with the values of the literature.[7] The reaction conditions could be tolerant of various functional groups like methoxy, chloro, dimethylamino, or methoxycarbonyl (entry 7, 8, 9, 10). Since the aliphatic nitriles did not react with $HSiMe_3$, the cyano group ajacent to benzene ring selectively reacted with $HSiMe_3$ in the case of p-(cyanomethyl)-benzonitrile (entry 6). The rate of conversion of aromatic nitriles having electron withdrawing group or sterically hindered nitriles was rather low (entry 4, 8, 10).

The plausible reaction pathway is depicted in Scheme 1. $R_3SiCo(CO)_4$, generated by the reaction of $HSiR_3$ and $Co_2(CO)_8$[9], may react with a nitrile to give N-silylnitrilium ion intermediate (**1**) and $Co(CO)_4^-$. Transfer of hydrogen from a hydrosilane to **1** might occur to form silylimine (**2**). The addition of $HSiMe_3$ to **2** in a similar manner would result in the formation of N,N-disilylamine.[11]

More works in the area concerning the addition of hydrosilanes to carbon, nitrogen multiple bond are now in progress.

Scheme 1



References and Notes

1) (a) Y. Nagai, Org. Prep. Proced. Int., 12, 13(1980). (b) E. Colvin in " Silicon in Organic Synthesis " , Butterworth and Co Ltd, 1981, P. 325.

2) Calas et al. have reported that the addition of $HSi(C_2H_5)_3$ to nitriles in the presence of $ZnCl_2$ gave N-Silylimine. (a) E. Frainnet, P. Lionch, E. Dubourdin, and R. Calas, Bull. Soc. Chim. Fr., 1172(1966). (b) R. Calas, Pure. Appl. Chem. 13, 61(1966).

3) A. J. Chalk, J. Organomet. Chem., 21, 207(1970).

4) (a) R. J. P. Corriu and J. J. E. Moreau in " Selectivity- a Goal for Synthetic Efficiency " W. Bartmann and B. M. Trost ed., Verlag Chemie, Weinheim, 1984, p. 21. (b) R. J. P. Corriu, R. Perz, and C. Reye, Tetrahedron, 39, 999(1983).

5) (a) N. Umino, T. Iwakuma, and N. Itoh, Tetrahedron Lett., 2875(1976). (b) T. Wakamatsu, H. Inaki, A. Ogawa, M. Watanabe, and Y. Ban, Heterocycles, 14, 1437(1980). (c) H. C. Brown, Y. M. Choi, and C. S. Narasimhan, Synthesis, 605(1981). (d) S. W. Heinzman and B. Ganem, J. Am. Chem. Soc., 104, 6801 (1982). (e) M. Hudlicky in " Reductions in Organic Chemistry ", Ellis Horwood Ltd., 1984, p. 173.

6) Cobalt carbonyl catalyzed reaction of $HSiR_3$ has been well documented. For example, see: (a) S. Murai and N. Sonoda, Angew. Chem. Int. Ed. Engl., 18, 837(1979). (b) N. Chatani, H. Furukawa, T. Kato, S. Murai, and N. Sonoda, J. Am. Chem. Soc., 106, 430(1984) and references cited therein, see also ref. 9.

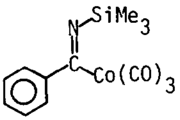
7) H. J. Bestmann and G. Wolfel, Chem. Ber., 117, 150(1984).

8) The other catalyst species: $HCo(CO)_4$ has been reported to be unreactive with a benzonitrile even at high temperature.: S. Murahashi, S. Horie, T. Jo, Nippon Kagaku Zasshi, 79, 68(1958). Chem. Abstr., 54, 5558d(1960).

9) (a) A. J. Chalk and J. F. Harrod, J. Am. Chem. Soc., 89, 1640(1967). (b) Y. L. Baay, A. G. MacDiarmid, Inorg. Chem., 8, 986(1969). (c) D. L. Morrison, A. P. Hagen, In " Inorganic Syntheses " F. A. Cotton, Ed., MacGrawHill; New York, Vol XIII, 1972, P. 5.

10) The reduction of N-alkylnitrilium ions with organosilicon hydrides has been reported.: (a) J. L. Fry, J. Chem. Soc., Chem. Commun., 45(1974). (b) J. L. Fry and R. A. Ott, J. Org. Chem., 46, 602(1981).

11) An alternative mechanism involving **i** in place of the silylimine intermediate (**1**) may exist.



i

(Received in Japan 4 July 1985)