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Reaction of Silylynamines with Active Triple Bonds

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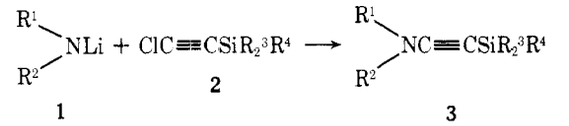
N,N-Disubstituted (triorganosilylethynyl)amines (silylynamines, **3**) reacted with dimethyl acetylenedicarboxylate (**6**), methyl propiolate (**7**), and benzyne (**18**) to give the 1:1 addition products **8**, **9**, and **20**. It appears that these adducts were formed as a result of 1,3-anionic rearrangement of the triorganosilyl group from carbon to carbon in the dipolar intermediates **16** and **19**.

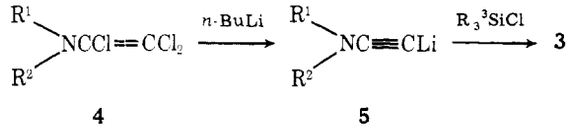
The addition reaction of ynamines with active multibonds provides a versatile tool in the syntheses of amine derivatives.[1] *N,N*-Dialkyl (alkyl or phenylethynyl) amine reacts with dimethyl acetylenedicarboxylate[2] or benzyne[3] in 1:2 mole ratio to give an aniline derivative or a mixture of phenanthrene and anthracene derivatives. These 1:2 addition products may be formed via dipolar intermediates reactive enough to add to another mole of the active triple bond (Scheme I). In this paper, we report the 1:1 addition reaction of N,N-disubstituted (triorganosilylethynyl)amines (silylynamines) with acetylenecarboxylates or benzyne.

Silylynamines **3a–j** were prepared by reaction of lithium diorganoamides **1** with triorganosilylethynyl chlorides **2** (method A[4]) or from *N*-methyl-*N*-(1,2,2-trichlorovinyl)aniline (**4**) via lithium aminoacetylide (**5**) (method B[5]). Method A gave good yields in the preparation of *N*-(triorganosilylethynyl)dialkylamines **3a–f**, and method B was adequate for *N*-(triorganosilylethynyl)arylamines **3g–j**. The results are summarized in Table I.

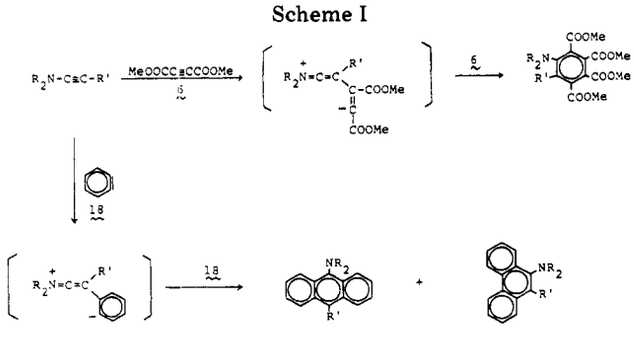
Method A



Method B

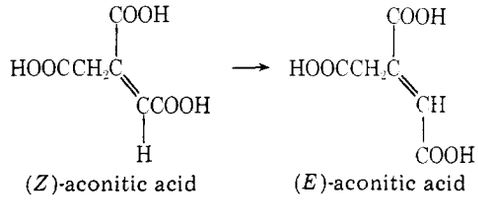


Scheme I



When *N,N*-diethyl(trimethylsilylethynyl)amine (**3a**) was mixed with an equimolar amount of dimethyl acetylenedicarboxylate (**6**) in ether, an exothermic reaction occurred immediately at room temperature to give the sole product **8a**. The elemental, NMR, and mass spectral analyses of **8a** indicated this product to be a 1:1 adduct, $C_{15}H_{25}NO_4Si$, and the IR spectrum showed a band at 2180 cm^{-1} indicating the presence of a triple bond. Thus, the structure of **8a** was assumed as (*E*)-*N,N*-diethyl[3,4-bis(methoxycarbonyl)-4-trimethylsilyl-3-buten-1-ynyl]amine (Scheme II).

Acid hydrolysis of **8a** afforded a mixture of two desilylated amides (**10a**) which were assigned to stereoisomers of *E* and *Z* types based on the NMR. Catalytic hydrogenation of the



(*Z*)-aconitic acid (*E*)-aconitic acid

mixture gave a 90% yield of *N,N*-diethyl-3,4-bis(methoxycarbonyl)butanamide (**13**) as a single product. Attempted separation of the stereomers by silica gel column chromatography failed, because both isomers convert to each other at room temperature. In the presence of water, isomerization of (*Z*)-aconitic acid occurs at ambient temperature.[6]

Similar 1:1 addition reactions of silylynamines with **6** were observed in the cases of *N,N*-diethyl(dimethylethylsilylethynyl)amine (**3b**), *N*-(trimethylsilylethynyl)morpholine (**3e**), and *N*-methyl-*N*-(trimethylsilylethylnyl)aniline (**3g**). *N*-Methyl-*N*-(triphenylsilylethynyl)aniline (**3h**) did not react in ether, but did in acetonitrile (see Table II). Acid hydrolysis

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Table I. N,N-Disubstituted (Triorganosilylethynyl)amines 3

Compd[a] 3	Registry no.	R^1	R^2	R^3	R^4	Yield, % Method A	Yield, % Method B	Bp (mmHg) [mp], °C	IR, cm^{-1} (C≡C)
a	33567-68-9	Et	Et	Me	Me	63[b]	44[c]	73–75 (23)	2160
b	64024-61-9	Et	Et	Me	Et	74		68–70 (7)	2140
c	57694-91-4	Et	Et	Ph	Ph	60	0	[42–43]	2140
d	64024-62-0	$-(CH_2)_4-$		Me	Me	49		95–98 (19)	2160
e	64024-63-1	$-(CH_2)_2O(CH_2)_2-$		Me	Me	55		88–90 (9)	2160
f	64024-64-2	$-(CH_2)_2O(CH_2)_2-$		Ph	Ph	80		[120–122]	2140
g	33567-67-8	Me	Ph	Me	Me	9	81[d]	87–90 (1)	2160
h	57694-92-5	Me	Ph	Ph	Ph	0	36	[115–117]	2160
i	64044-70-8	Et	Ph	Me	Me		83	78–79 (0.2)	2160
j	33567-66-7	Ph	Ph	Me	Me	0	78[e]	123–128 (0.5)	2160

[a] Satisfactory analytical data (±0.4% for C, H, and N) were reported for all new compounds listed in the table. [b] Lit. 54%, ref 4. [c] Lit. 65%, ref 5. [d] Lit. 85%, ref 5. [e] Lit. 70%, ref 5.

Table II. Reaction of N,N-Disubstituted (Triorganosilylethynyl)amines (3) with Dimethyl Acetylenedicarboxylate (6) or Methyl Propiolate (7)

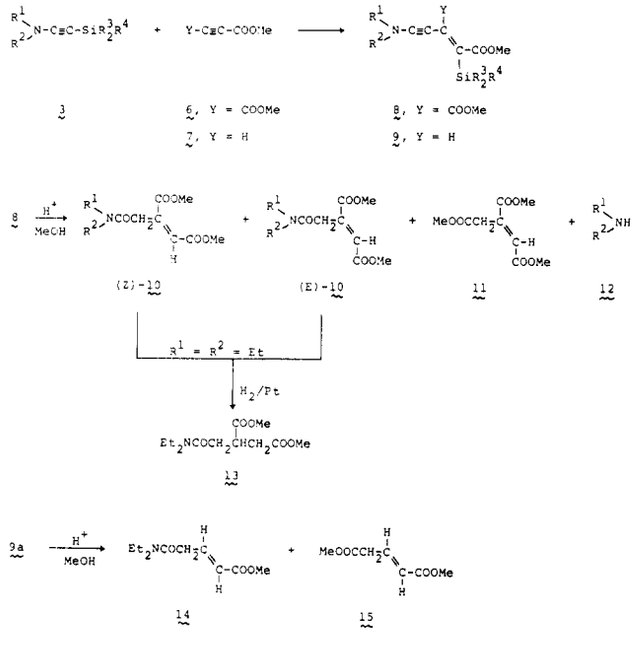
	R^1	R^2	R^3	R^4	Y	Reaction condition: Solvent[a]	Temp, °C	Time, h	Yield, %
8a	Et	Et	Me	Me	COOMe	E	20	2	82
8b	Et	Et	Me	Et	COOMe	E	Reflux	5	74
8e	$-(CH_2)_2O(CH_2)_2-$		Me	Me	COOMe	E	Reflux	2	43
8g	Me	Ph	Me	Me	COOMe	E	Reflux	10	62
8h	Me	Ph	Ph	Ph	COOMe	E	Reflux	24	0[b]
						A	80	8	40
9a	Et	Et	Me	Me	H	E	Reflux	24	0[b]
						A	80	24	24
9g	Me	Ph	Me	Me	H	E	Reflux	24	0[b]
						A	80	24	0[c]

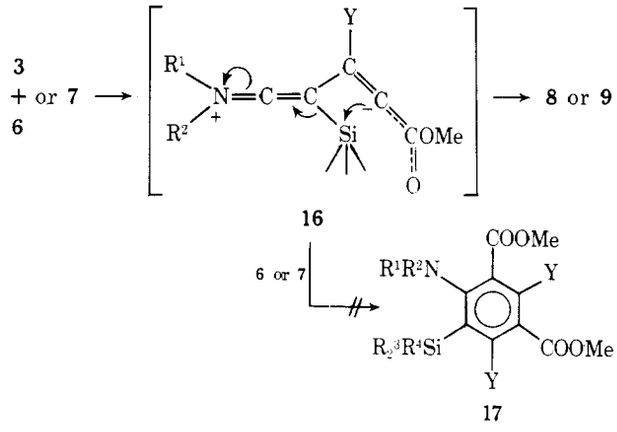
[a] E = ether, A = acetonitrile. [b] No reaction. [c] Polymerization.

of *N*-methyl-*N*-[3,4-bis(methoxycarbonyl)-4-trimethylsilyl-3-buten-1-ynyl]aniline (**8g**) gave a mixture of (*E*)-**10g** and (*Z*)-**10g** with (*E*)-aconitic acid trimethyl ester (**11**) and *N*-methylaniline (**12**).

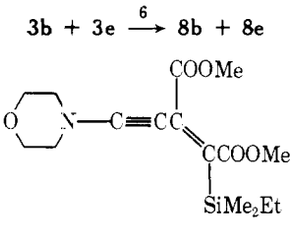
The reaction of **3a** or **3g** with methyl propiolate (**7**) did not occur in ether. However, in boiling acetonitrile a low yield of the 1:1 adduct **9a** was obtained from **3a**, but not from **3g**. Acid hydrolysis of **9a** gave (*E*)-*N*,*N*-diethyl-4-methoxycarbonyl-3-butenamide (**14**) and (*E*)-glutaconic acid dimethyl ester (**15**), which were identical with their authentic samples.

Scheme II





The reaction of silylynamines with acetylenecarboxylates, which is influenced by polarity of the solvent, may take place via a dipolar intermediate **16**, in which an anionic rearrangement of the silyl group giving **8** or **9** precedes the addition of **16** to another mole of **6** or **7** to form the aniline derivative **17**. The intramolecular nature of the silyl migration was confirmed by a crossover experiment. An equimolar amount of **3b** and **3e** was mixed and treated with **6** under the above-mentioned reaction condition. The products in the reaction

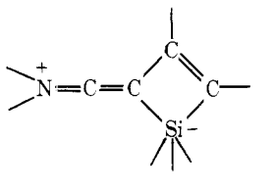


8k

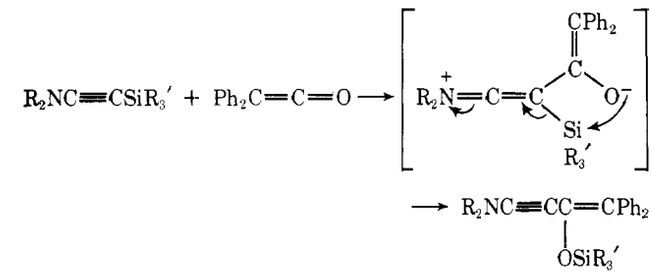
mixture were **8b** and **8e** only, and no crossover products (**8a** and **8k**) were detected.

The reaction of **3a** or **3g** with benzyne (**18**), generated from *o*-fluorobromobenzene and magnesium, also gave the 1:1 addition product **20a** or **20g** and no 1:2 adduct. *N,N*-Diethyl(*o*-trimethylsilylphenylethynyl)amine (**20a**) was hydrolyzed to amide **21**. Then **21** was reduced by lithium aluminum hydride to *N,N*-diethyl-2-(*o*-trimethylsilylphenyl)-ethylamine (**22**), which was identified by spectral comparison with an authentic sample prepared from *N,N*-diethyl-2-(*o*-bromophenyl)ethylamine (**23**) via a lithiated intermediate **24** (Scheme III).

The benzyne reaction of silylynamines seems to proceed via a similar dipolar intermediate **19** to that of acetylenecarboxylates. The rapid 1,3 rearrangement of the silyl group from carbon to carbon in **16** and **19** may be accelerated by the participation of a pentacoordinated intermediate.



Recently, Himbert reported a 1,3-silyl rearrangement from carbon to oxygen in the reaction of silylynamine with diphenylketene.[7]



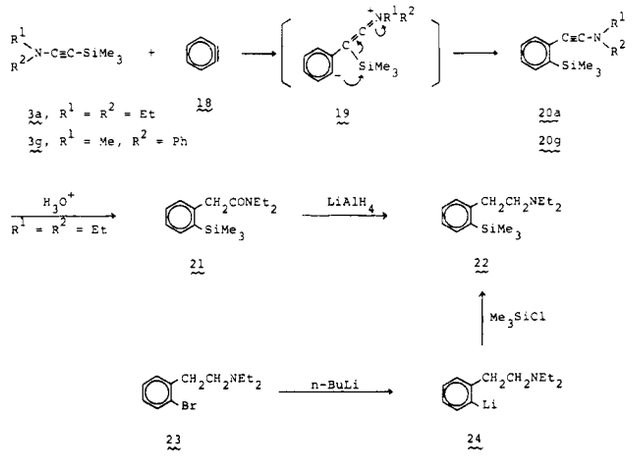
Experimental Section

^{1}H NMR spectra were recorded using a JEOL Model JNM-NH-100 spectrometer employing Me_4Si as internal standard. IR spectra were taken on a JASCO Model IRA-2 spectrometer. Mass spectra were recorded on a Hitachi Model M-52 spectrometer. GLC analyses were performed on a JEOL Model JGC-1100 chromatograph using stainless-steel columns with a nitrogen flow rate of 50 mL/min. Quantitative analysis of the reaction mixtures was carried out by the internal standard method. Fractional distillation was accomplished by a Büchi Model GKR-50 Kugelrohr distillation apparatus. All boiling and melting points are uncorrected. All reactions were carried out under nitrogen atmosphere. Ether and THF were dried by distillation from $LiAlH_4$ just prior to use.

N,N-Disubstituted (Triorganosilylethynyl)amines (3). Method A.[4] A solution of 220 mmol of phenyllithium in ether (150 mL) was added to a solution of 220 mmol of *sec*-amine in ether (150 mL) at 0–10 °C, and stirring was continued for 0.5 h. Then to the reaction mixture was added a solution of 200 mmol of triorganosilylethynyl chloride (**2**) in ether (50 mL) at the same temperature. After 2 h of stirring at room temperature, the reaction mixture was hydrolyzed with saturated aqueous potassium bicarbonate and extracted with ether. The ethereal extract was dried, concentrated, and distilled or recrystallized from hexane, giving **3a–g**.

Characterizing data are summarized in Table I.

Scheme III



Method B.[5] A solution of 125 mmol of *n*-butyllithium in *n*-hexane (80 mL) was added dropwise to a solution of 50 mmol of N,N-disubstituted 1,2,2-trichlorovinylamine (**4**) in ether (100 mL) at 0–10 °C, and stirring was continued for 2 h at room temperature. Then to the reaction mixture was added a solution of 60 mmol of triorganochlorosilane in ether (100 mL) at 0–10 °C. After 2 h of stirring at room temperature, the reaction mixture was hydrolyzed with 20% ammonia water and extracted with ether. The ethereal extract was dried, concentrated, and distilled or recrystallized from hexane, giving **3a,g–j**. Characterizing data are summarized in Table I.

N,N-Disubstituted [3,4-Bis(methoxycarbonyl)-4-trialkylsilyl-3-buten-1-ynyl]amines (8a, 8b, 8e, and 8g). A solution of dimethyl acetylenedicarboxylate (**6**, 1.42 g, 10 mmol) in ether (5 mL) was added dropwise to a solution of 10 mmol of N,N-disubstituted (trialkylsilylethynyl)amine (**3a, 3b, 3e,** or **3g**) in ether (25 mL). The mixture was stirred at reflux (at room temperature in the case of **3a**) for 2–10 h. After removal of the solvent, the residue was distilled to give **8a, 8b, 8e,** or **8g**.

Characterizing data are shown in Tables II and III.

***N*-Methyl-*N*-[3,4-bis(methoxycarbonyl)-4-triphenylsilyl-3-buten-1-ynyl]aniline (8h).** A mixture of *N*-methyl-*N*-(triphenylsilylethynyl)aniline (**3h**, 1.37 g, 3.5 mmol) and **6** (0.50 g, 3.5 mmol) in 30 mL of acetonitrile was heated at 80 °C for 8 h. After removal of the solvent, the residue was recrystallized from ethyl acetate to give 0.743 g (40%) of **8h**. Data are summarized in Table III.

Mixing Experiment. A mixture of **3b** (1.47 g, 8 mmol), **3e** (1.47 g, 8 mmol), and **6** (2.27 g, 16 mmol) in 30 mL of ether was heated at reflux for 2 h. The reaction mixture was analyzed by GLC using a 3 mm × 1 m column filled with 10% silicone SE-30, programed from 150–200 °C at 6 °C/min. The chromatogram showed the presence of **8b** (76%) and **8e** (47%). No crossover products (**8a** and **8k**) were detected.

***N,N*-Diethyl(4-methoxycarbonyl-4-trimethylsilyl-3-buten-1-ynyl)amine (9a).** A mixture of **3a** (3.39 g, 20 mmol) and methyl propiolate (**7**, 1.68 g, 20 mmol) in 40 mL of acetonitrile was heated at 80 °C for 24 h. Distillation of the reaction mixture gave 1.22 g (24%) of **9a**. Characterizing data are shown in Table III.

Acid Hydrolysis of 8a. To a solution of **8a** (1.85 g, 6 mmol) in 5 mL of methanol was added 20 mL of 5% HCl–MeOH. After 5 h of stirring at room temperature, the reaction mixture was neutralized with aqueous potassium bicarbonate, and the methanol was removed under reduced pressure. The ethereal extract of the aqueous layer was dried, concentrated, and distilled giving 1.10 g (72%) of a mixture of (*Z*)- and (*E*)-*N,N*-diethyl-3,4-bis(methoxycarbonyl)-3-butenamide (**10a**): bp 110–113 °C (0.1 mm); NMR (CCl_4) δ 0.95–1.40 (m, NCH_2CH_3), 3.15–3.50 (m, NCH_2), 3.60 and 3.96 (s × 2, $COCH_2$ × 2), 3.64, 3.76, 3.78, and 3.82 (s × 4, OCH_3 × 4), 6.80 and 7.22 (s × 2, vinyl H × 2); IR (neat) 1640 and 1720 cm^{-1} (C=O).

Acid Hydrolysis of 8g. A mixture of a solution of **8g** (1.35 g, 3.9 mmol) in 5 mL of methanol and 20 mL of 5% HCl–MeOH was allowed to react and treated in a similar manner as described above for **8a**. Fractional distillation gave 940 mg (36%) of *N*-methylaniline (**12**), 192 mg (23%) of (*E*)-aconitic acid trimethyl ester[8] (**11**), and 320 mg (24%) of a mixture of (*Z*)- and (*E*)-*N*-methyl-*N*-phenyl-3,4-bis(methoxycarbonyl)-3-butenamide (**10g**): bp 130–135 °C (0.015 mm); NMR (CCl_4) δ 3.22 and 3.30 (s × 2, NCH_3 × 2), 3.12 and 3.85 (s × 2, $COCH_2$ × 2), 3.63, 3.65, 3.70, and 3.76 (s × 4, OCH_3 × 4), 6.74 (s, vinyl H), and 7.10–7.55 (m, aromatic H); IR (neat) 1655 and 1720 cm^{-1} (C=O).

Table III. N,N-Disubstituted [3,4-Bis(methoxycarbonyl)- or 4-Methoxycarbonyl-4-triorganosilyl-3-buten-1-ynyl]amines 8 or 9

Compd[a]	Registry no.	Bp (mmHg) [mp], °C	IR (neat), cm^{-1} C≡C	IR (neat), cm^{-1} C=O	NMR (CCl_4), δ
8a	64024-65-3	120–122 (0.07)	2180	1710, 1725	0.26 (s, 9, $SiCH_3$), 1.23 (t, 6, NCH_2CH_3), 3.08 (q, 4, NCH_2), 3.63 (s, 3, OCH_3), and 3.70 (s, 3, OCH_3)
8b	64024-66-4	133–135 (0.2)	2180	1710, 1725	0.16 (s, 6, $SiCH_3$), 0.7–1.0 (m, 5, $SiCH_2CH_3$), 1.20 (t, 6, NCH_2CH_3), 3.14 (q, 4, NCH_2), 3.62 (s, 3, OCH_3), and 3.68 (s, 3, OCH_3)
8e	64024-67-5	158–160 (0.6)	2220	1710, 1735	0.23 (s, 9, $SiCH_3$), 3.12–3.24 (m, 4, NCH_2), 3.60–3.75 (m, 4, OCH_2), 3.64 (s, 3, OCH_3), and 3.70 (s, 3, OCH_3)
8g	64024-68-6	185–190 (0.15)	2210	1715, 1730	0.30 (s, 9, $SiCH_3$), 3.37 (s, 3, NCH_3), 3.69 (s, 3, OCH_3), 3.80 (s, 3, OCH_3), and 6.90–7.30 (m, 5, aromatic H)
8h	64024-69-7	[160–161]	2190[b]	1705, 1725	2.46 (s, 3, NCH_3), 3.30 (s, 3, OCH_3), 3.89 (s, 3, OCH_3), and 6.75–7.90 (m, 20, aromatic H)
9a	64024-70-0	121–123 (3)	2180	1690	0.22 (s, 9, $SiCH_3$), 1.25 (t, 6, NCH_2CH_3), 3.12 (q, 4, NCH_2), 3.67 (s, 3, OCH_3), and 7.44 (s, 1, vinyl H)

[a] Satisfactory analytical data (±0.4% for C, H, and N) were reported for all new compounds listed in the table. [b] KBr disk.

Acid Hydrolysis of 9a. In a similar manner as described for above **8a, 9a** (1.15 g, 4.5 mmol) was hydrolyzed and distilled to give 117 mg (17%) of (*E*)-glutaconic acid dimethyl ester[9] (**15**) and 215 mg (26%) of (*E*)-*N,N*-diethyl-4-methoxycarbonyl-3-butenamide (**14**): bp 133–135 °C (20 mm); NMR (CCl_4) δ 0.95–1.35 (m, 6, NCH_2CH_3), 3.10–3.50 (m, 6, NCH_2 × 2 and $COCH_2$), 5.82 (d, 1, *J* = 16 Hz, =CHCO—), and 6.93 (dt, 1, *J* = 16 and 7 Hz, CH_2CH=); IR (neat) 1640 and 1725 cm^{-1} (C=O).

Anal. Calcd for $C_{10}H_{17}NO_3$: C, 60.28; H, 8.60; N, 7.03. Found: C, 60.17; H, 8.66; N, 7.20.

***N,N*-Diethyl-3,4-bis(methoxycarbonyl)butanamide (13).** A mixture of 100 mg of platinum oxide and the (*Z*)- and (*E*)-**10a** mixture (1.5 g, 5.8 mmol) in 50 mL of methanol was stirred with 100 atm of hydrogen at room temperature for 3 h in an autoclave. After removal of the catalyst, the filtrate was concentrated and distilled, giving 1.35 g (89%) of **13:** bp 128–131 °C (2 mm); NMR (CCl_4) δ 1.00–1.35 (m, 6, NCH_2CH_3), 2.35–2.84 (m, 4, $COCH_2$), 3.00–3.50 (m, 5, NCH_2 × 2 and >CH–), 3.64 (s, 3, OCH_3), 3.66 (s, 3, OCH_3); IR (neat) 1640 and 1735 cm^{-1} (C=O); mass spectrum *m/e* 259 (M^+).

Anal. Calcd for $C_{12}H_{21}NO_5$: C, 55.58; H, 8.16; N, 5.40. Found: C, 55.37; H, 8.15; N, 5.22.

***N,N*-Diethyl(*o*-trimethylsilylphenylethynyl)amine (20a).** A solution of *o*-fluorobromobenzene (1.58 g, 9 mmol) in ether (5 mL) was added to a boiling mixture of **3a** (1.19 g, 7 mmol) and magnesium turnings (0.22 g, 9 mg-atom). After 1 h of stirring at reflux, the reaction mixture was hydrolyzed with saturated aqueous NH_4Cl and extracted with ether. The ethereal extract was dried, concentrated, and distilled, giving 0.36 g (21%) of **20a:** bp 87–90 °C (0.9 mm); NMR (CCl_4) δ 0.32 (s, 9, $SiCH_3$), 1.26 (t, 6, NCH_2CH_3), 3.00 (q, 4, NCH_2), 6.90–7.40 (m, 4, aromatic H); IR (neat) 2210 cm^{-1} (C≡C).

Anal. Calcd for $C_{15}H_{23}NSi$: C, 73.40; H, 9.45; N, 5.71. Found: C, 73.11; H, 9.43; N, 5.45.

***N*-Methyl-*N*-(*o*-trimethylsilylphenylethynyl)aniline (20g).** A solution of *o*-fluorobromobenzene (1.76 g, 10 mmol) in THF (10 mL) was added at reflux to a mixture of **3g** (1.02 g, 5 mmol) and magnesium turnings (0.25 g, 10 mg-atom) in THF (20 mL). After 15 h of stirring at the same temperature, the mixture was hydrolyzed with saturated aqueous NH_4Cl and extracted with ether. Distillation of the ethereal extract gave 0.22 g (16%) of **20g:** bp 131–133 °C (0.1 mm); NMR (CCl_4) δ 0.38 (s, 9, $SiCH_3$), 3.35 (s, 3, NCH_3), 6.80–7.44 (m, 9, aromatic H); IR (neat) 2220 cm^{-1} (C≡C).

Anal. Calcd for $C_{18}H_{21}NSi$: C, 75.23; H, 8.29; N, 5.48. Found: C, 75.56; H, 8.18; N, 5.40.

***N,N*-Diethyl-*o*-trimethylsilylphenylacetamide (21).** A solution of **20a** (1.00 g, 4.1 mmol) in ether (10 mL) was vigorously stirred with 10 mL of 10% HCl at room temperature for 1 h. The ether layer was separated, dried, and distilled, giving 0.90 g (83%) of **21:** bp 103–105 °C (0.09 mm); NMR (CCl_4) δ 0.32 (s, 9, $SiCH_3$), 1.00–1.25 (m, 6, NCH_2CH_3), 3.04–3.48 (m, 4, NCH_2), 3.70 (s, 2, $COCH_2$), 6.98–7.50 (m, 4, aromatic H); IR (neat) 1645 cm^{-1} (NCO).

Anal. Calcd for $C_{15}H_{25}NOSi$: C, 68.39; H, 9.56; N, 5.32. Found: C, 68.67; H, 9.58; N, 5.43.

***N,N*-Diethyl-2-(*o*-trimethylsilylphenyl)ethylamine (22). A.** A mixture of **21** (0.30 g, 1.1 mmol) and $LiAlH_4$ (0.05 g, 1.3 mmol) in THF (20 mL) was heated at reflux for 8 h. After the reaction mixture was hydrolyzed with saturated aqueous NH_4Cl, the THF layer was separated, and the aqueous layer was extracted with ether. The combined organic layer was dried, concentrated, and distilled, giving 0.26 g (80%) of **22:** bp 117–122 °C (9 mm); NMR (CCl_4) δ 0.34 (s, 9, $SiCH_3$), 1.05 (t, 6, NCH_2CH_3), 2.60 (q, 4, NCH_2), 2.65–2.90 (m, 4, CH_2CH_2), 6.98–7.45 (m, 4, aromatic H); mass spectrum *m/e* 249 (M^+).

Anal. Calcd for $C_{15}H_{27}NSi$: C, 72.22; H, 10.91; N, 5.61. Found: C, 72.40; H, 11.02; N, 5.50.

B. To a solution of *N,N*-diethyl-2-(*o*-bromophenyl)ethylamine (**23,** 1.38 g, 5.4 mmol) in ether (20 mL) was added 15% *n*-butyllithium in *n*-hexane (4.5 mL, 7 mmol). After 3 h of stirring, trimethylchlorosilane (7.6 g, 7 mmol) was added to the reaction mixture and stirring was continued at room temperature for 2 h. Then the mixture was hydrolyzed with saturated aqueous NH_4Cl and extracted with ether. The ethereal extract was dried, concentrated, and distilled, giving 1.07 g (80%) of **22.**

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Registry No.—**1**(R_1, R_2 = Et), 816-43-3; **1**(R_1, R_2 = $-(CH_2)_4-$), 4439-90-1; **1**(R_1, R_2 = $-(CH_2)_2O(CH_2)_2-$), 37828-58-3; **1**(R_1 = Me, R_2 = Ph), 35954-01-9; **2**(R_3, R_4 = Me), 7652-06-4; **2**(R_3 = Me, R_4 = Et), 64024-71-1; **2**(R_3, R_4 = Ph), 18676-70-5; **4**(R_1, R_2 = Et), 686-10-2; **4**(R_1 = Me, R_2 = Ph), 708-88-3; **4**(R_1 = Et, R_2 = Ph), 38488-67-4; **4**(R_1, R_2 = Ph), 727-65-1; **6**, 762-42-5; **7**, 922-67-8; (*E*)-**10a**, 64024-72-2; (*Z*)-**10a**, 64024-73-3; (*E*)-**10g**, 64024-74-4; (*Z*)-**10g**, 64024-75-5; **13**, 64024-76-6; **14**, 64024-77-7; **20a**, 64024-78-8; **20g**, 64024-79-9; **21**, 64024-80-2; **22**, 64024-81-3; **23**, 64024-82-4; Me_3SiCl, 75-77-4; Ph_3SiCl, 76-86-8; *o*-fluorobromobenzene, 1072-85-1.

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