β-Substituted Organolithium Compounds. New Reagents for Synthesis

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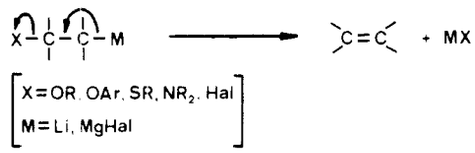
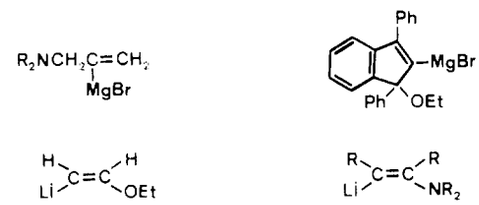
β-Substituted organolithium derivatives **3** are suitable synthons for the preparation of bifunctional compounds. The reactivity of these dianions is shown by the study of their reaction with typical electrophilic reagents which always lead to products resulting from an attack on the anionic carbon atom. In this way 1,2-diols, 1,2-amino alcohols, β-hydroxy or β-amino esters, 1,3-diols, 1,3-amino alcohols, and β-substituted silanes have been prepared by reaction of **3** with oxygen, carbon dioxide, carbonyl compounds, and trimethylchlorosilane, respectively. Some of these systems are difficult to prepare by conventional routes of synthesis.

Attempts to synthesize β-substituted organometallic compounds derived from metals of groups 1A and 2A have been reported to be unsuccessful until recently due to their tendency to undergo a β-elimination reaction to give an olefin.[1]



Nevertheless, a few more stable[2] β-substituted organomagnesium[1a] and organolithium[3,4] derivatives in which the metal was linked to a sp^2 hybridized carbon have been described.



In a previous communication,[5] we have reported the first general preparation and characterization of β-alkoxide and β-amide substituted organolithium compounds **3** with the carbon bearing the metal being sp^3 hybridized. These systems are readily available by mercury–lithium exchange at the corresponding β-hydroxy or β-amino organomercurials **2**,[6] which have previously been transformed into their lithium alkoxide or amide derivatives by treatment with phenyllithium. All reactions were carried out in THF solution at temperatures below −78 °C (see Scheme I).

Dianions **3** are greatly unstable species and decompose when the temperature is raised to over −78 °C.[5] The possibility of these high reactive chemical intermediates acting as synthons to introduce the YCC group in reactions with electrophiles prompted us to study their use in the synthesis of bifunctional compounds. In this way, the reactions of oxidation, carbonation, addition to carbonyl compounds, and silylation were initially chosen as the most characteristic.[7] Organomercurials **2** derived from repre-

Scheme I

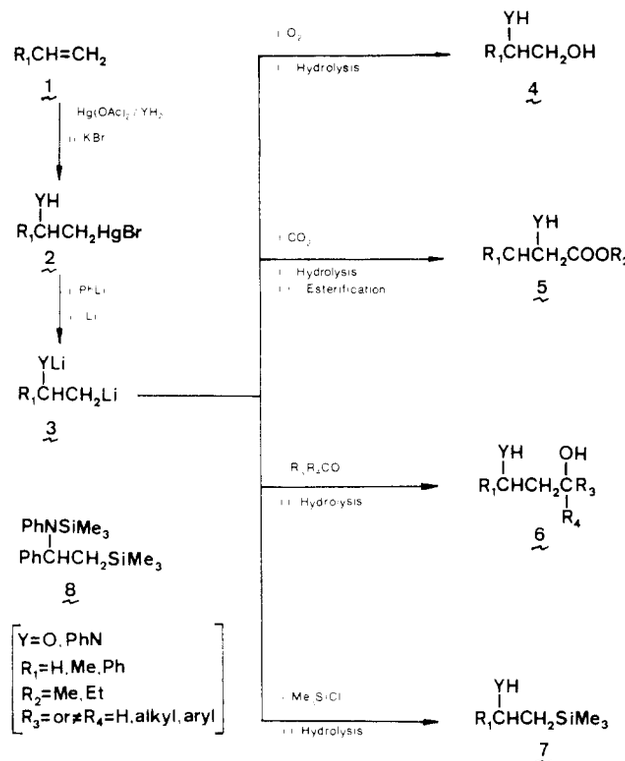


Table I. 1,2-Diols and 1,2-Amino Alcohols (4)

compd no.	Y	R_1	% yield[a]	mp, °C (solvent), or [bp, °C (mmHg)]
4a	O	Ph	72	68-69 (hexane)[b]
4b	PhN	H	79	[70-75 (0.001)][c]
4c	PhN	Me	83	[80-83 (0.001)]
4d	PhN	Ph	75	*d*

[a] Based on Hg^0 precipitated. [b] Lit.[3] mp, 68-9 °C. [c] Lit.[3] bp 286 °C (760 mmHg). [d] Oil.

Table II. β-Hydroxy and β-Amino Esters (5)

compd no.	Y	R_1	R_2	% yield[a]	mp, °C (solvent), or [bp, °C (mmHg)]
5a	O	Ph	Me	70	[140-143 (12)]
5b	O	*n*-C_5H_{11}	Me	44	[50-55 (0.001)]
5c	PhN	H	Et	67	[73-77 (0.001)]
5d	PhN	Me	Et	56	[78-80 (0.001)]
5e	PhN	Ph	Et	68	72-73 (hexane-$HCCl_3$)

[a] Based on Hg^0 precipitated.

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(4) L. Duhamel and J. M. Poirier, *J. Am. Chem. Soc.*, **99**, 8356 (1977).
(5) J. Barluenga, F. J. Fañanás, M. Yus, and G. Asensio, *Tetrahedron Lett.*, 2015 (1978).
(6) For a review on the preparation of organomercurials see: Houben Weyl, "Metallorganische Verbindungen Hg", Band 13/2b G. Thieme Verlag, Stuttgart, 1974, pp 130-188.

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Table III. 1,3-Diols and 1,3-Amino Alcohols 6

compd no.	Y	R_1	R_2	R_3	% yield[a]	mp, °C (solvent), or [bp °C (mmHg)]
6a	O	Ph	H	Et	62	[98-103 (0.001)]
6b	O	Ph	H	Ph	67	112-114 (hexane-ether)
6c	O	Ph	H	4-MeC_6H_4	57	[111-115 (0.01)]
6d	PhN	H	H	*i*-Pr	70	60-62 (hexane)
6e	PhN	H	Me	Ph	61	89-91 (hexane-$HCCl_3$)
6f	PhN	H	Ph	Ph	66	122-124 (hexane-$HCCl_3$)
6g	PhN	Ph	H	*i*-Pr	81	143-145 (hexane-$HCCl_3$)
6h	PhN	Ph	H	Ph	76	124-127 (hexane-$HCCl_3$)
6i	PhN	Ph	Me	Me	52	*b*
6j	PhN	Ph	Ph	Ph	61	127-129 (hexane-$HCCl_3$)

[a] Based on Hg^0 precipitated. [b] Oil.

sentative olefins (ethylene, propylene, and styrene) 1 were selected for the transmetalation process.

Results and Discussion

The treatment of 3 at −78 °C with a precooled current of dry oxygen at the same temperature followed by aqueous hydrochloric acid hydrolysis afforded 1,2-diols (Y = O) or 1,2-amino alcohols (Y = PhN) 4 (see Scheme I). The obtained results are collected in Table I.[8,9]

When β-substituted organolithium compounds 3 were allowed to react with solid carbon dioxide at −78 °C, and then the reaction mixture was hydrolyzed with aqueous hydrochloric acid, β-hydroxy or β-amino acids were obtained. Since the direct isolation and identification of these products was tedious, they were purified by previous esterification of the acid group by treatment with diazomethane[10] in the case of β-hydroxy acids or anhydrous ethanol–hydrogen chloride[11] in the case of β-amino acids to give β-hydroxy esters (Y = O) and β-amino esters (Y = PhN) 5, respectively (see Scheme I and Table II).

1,3-Diols (Y = O) and 1,3-amino alcohols (Y = PhN) 6 (Scheme I) were obtained in good yields by reaction of 3 with aliphatic or aromatic aldehydes and ketones at −78 °C, followed by acid hydrolysis. We should remark that in the reactions with carbonyl compounds, side reactions induced by the amide or the alkoxide groups, such as condensation processes, were never observed.[12] The obtained results are collected in Table III.

The reaction of trimethylchlorosilane with 3 at −78 °C in reaction times shorter than 10 min led, after acid hydrolysis, to C-silylation products 7, except in the case of lithium *N*-(2-lithium-1-phenylethyl)phenylamide which, under the same conditions, led to mixtures of C- (**7d**) and C- and N- (8) silylation products. With longer reaction times (1 h), 8 was obtained as the only product, but by using reaction times shorter than 1 min the C-silylation product **7d** was exclusively obtained (see Scheme I and Table IV).

Conclusions

β-Substituted organolithium compounds, which can be directly obtained by mercuration–transmetalation of alkenes, are highly versatile synthetic intermediates for the synthesis of bifunctional compounds from olefins. From a synthetic point of view, the preparation of 1,2-amino alcohols, 1,3-diols, 1,3-amino alcohols, and β-substituted silanes has special significance since these compounds are of difficult accessibility by conventional methods. The obtention of bifunctional compounds from olefins described herein constitutes a regioselective process.

Table IV. β-Substituted Silanes 7 and 8

compd no.	Y	R_1	% yield[a]	mp, °C, or [bp °C (mmHg)]
7a	O	Ph	61	[61-64 (0.001)]
7b	PhN	H	58	[47-50 (0.001)]
7c	PhN	Me	71	[50-52 (0.001)]
7d	PhN	Ph	65	51-54[b]
8			≈60	*c*

[a] Based on Hg^0 precipitated. [b] Could not be recrystallized. [c] Oil.

Experimental Section

General. Melting points were determined with a Büchi melting point apparatus and are uncorrected. Infrared spectra (IR) were run on a Pye-Unicam SP-1000 spectrometer. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Varian EM-390 spectrometer. The purity of volatile distilled products was determined in a GLC Varian Aerograph 2800 instrument equipped with a OV-101 Chromosorb column. Elemental analyses were carried out with a Perkin-Elmer 240 elemental analyzer.

The chemical shifts are in δ relative to Me_4Si, and coupling constants (*J* values) are in hertz. Assignments were made by double resonance experiments. The broad singlets assigned to OH and NH groups disappeared on addition of a drop of deuterium oxide to the NMR sample.

Starting mercurials 2 were prepared according to literature methods.[6,13] The lithium powder used in the transmetalation process was commercially available. The reactants were of the best commercial grade available and were used without further purification. THF was dried by reflux with potassium metal and stored under argon. All reactions were run under argon and all glassware was dried before use.

Oxidation of β-Substituted Organolithium Compounds 3. General Procedure. To a previously evacuated 250-mL two-necked flask containing dry THF (75 mL), mercurial 2 (25 mmol) was added under argon atmosphere. The solution was cooled at −78 °C, an ether solution of phenyllithium[14] (25 mmol) was dropwise added in 10 min, then lithium powder (150 mmol) was added, and the mixture was mechanically stirred for 8 h. Dry oxygen (purity >99%) precooled at −78 °C was bubbled over a 2-h period through the resulting gray suspension, and then the reaction mixture was hydrolyzed with water and neutralized with aqueous hydrochloric acid. Elemental mercury was filtered off

(7) For a review see: Houben Weyl, "Metallorganische Verbindungen Li, Na, K, Rb, Cs, Cu, Ag, Au", Band 13/1, G. Thieme Verlag, Stuttgart, 1970, pp 171–196.
(8) *Beilsteins*, 6, 887.
(9) *Beilsteins*, 12, 106.
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and weighed. The reaction mixture was extracted with ether, and the ether layer was washed with water and dried over anhydrous sodium sulfate. Solvents were removed under reduced pressure (15 mmHg), and the residue was distilled or recrystallized (see Table I).

1-Phenyl-1,2-ethanediol (4a):[8] Hg^0 precipitated 80%; IR (Nujol) 3400 (OH), 3080, 3040, 1600, 1500, 750, 700 (Ph) cm^{-1}; NMR ($CDCl_3$) δ 2.3–2.8 [br s, 2, $(COH)_2$], 3.4–3.65 (m, 2, CH_2), 4.5–4.7 (m, 1, CH), 7.0–7.2 (m, 5, Ph).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.55; H, 7.30. Found: C, 69.18; H, 7.44.

2-(Phenylamino)ethanol (4b):[9] Hg^0 precipitated 81%; IR (film) 3400 (OH, NH), 3060, 3020, 1610, 1510, 760, 700 (Ph) cm^{-1}; NMR (CCl_4) δ 2.95 (t, 2, J = 6 Hz, CH_2N), 3.5 (t, 2, J = 6 Hz, CH_2O), 4.0 (br s, 2, NH and OH), 6.3–7.2 (m, 5, Ph).

Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 69.91; H, 8.13; N, 10.16.

2-(Phenylamino)-1-propanol (4c): Hg^0 precipitated 80%; IR (film) 3400 (OH, NH), 3060, 3010, 1600, 1500, 760, 700 (Ph) cm^{-1}; NMR (CCl_4) δ 1.0 (d, 3, J = 6 Hz, CH_3), 3.2–3.6 (m, 3, CH_2 and CH), 3.8 (br s, 2, NH and OH), 6.3–7.2 (m, 5, Ph).

Anal. Calcd for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.52; H, 8.60; N, 9.40.

2-Phenyl-2-(phenylamino)ethanol (4d): Hg^0 precipitated 82%; IR (film) 3400 (OH, NH), 3070, 3040, 1600, 1500, 760, 710 (Ph) cm^{-1}; NMR ($CDCl_3$) δ 3.6–4.0 (m, 4, CH_2, OH and NH), 4.3–4.6 (m, 1, CH), 6.4–7.5 (m, 10, aromatic H).

Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.41; H, 6.92; N, 6.62.

Carbonation and Further Esterification of the β-Substituted Organolithium Compounds 3. General Procedure. To a previously evacuated 250-mL two-necked flask containing dry THF (150 mL), mercurial **2** (50 mmol) was added under an argon atmosphere. The solution was cooled at −78 °C, an ether solution of phenyllithium[14] (50 mmol) was dropwise added in 15 min, then lithium powder (300 mmol) was added, and the mixture was mechanically stirred for 8 h. An excess of anhydrous solid carbon dioxide was added to the resulting gray suspension, and the temperature was allowed to raise to 20 °C in 12 h. The reaction mixture was hydrolyzed with water and then acidified with aqueous hydrochloric acid until neutral pH. Elemental mercury was filtered off and weighed. The resulting mixture was extracted with ether, and the ether layer was washed with water and dried over anhydrous sodium sulfate. Solvents were removed under reduced pressure (15 mmHg), and the residue was esterificated by the following two methods.

A. β-Hydroxy Esters.[10] An ether solution of diazomethane was added to the corresponding β-hydroxy acid until there was no further evolution of nitrogen and the appearance of a yellow color was observed. The solvent was removed under reduced pressure (15 mmHg), and the resulting β-hydroxy ester was distilled (see Table II).

B. β-Amino Esters.[11] β-Amino acids were dissolved in anhydrous ethanol previously saturated with anhydrous hydrogen chloride, and the reaction mixture was refluxed for 24 h, poured into water, neutralized with sodium carbonate, and extracted with ether. The organic layer was washed with water and dried over anhydrous sodium sulfate. Solvents were removed under reduced pressure (15 mmHg), and the resulting β-amino ester was distilled or recrystallized (see Table II).

Methyl 3-hydroxy-3-phenylpropanoate (5a): Hg^0 precipitated 80%; IR (film) 3400 (OH), 3080, 3060, 3030, 1600, 1490, 760, 700 (Ph), 1730 (C=O), 1270 (CO) cm^{-1}; NMR (CCl_4) δ 2.5–2.7 (m, 2, CH_2), 3.5 (s, 3, CH_3), 3.7–3.9 (br s, 1, OH), 4.85–5.1 (m, 1, CH), 7.1–7.35 (m, 5, Ph).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.72; H, 6.83.

Methyl 3-hydroxyoctanoate (5b): Hg^0 precipitated 91%; IR (film) 3460 (OH), 1740 (C=O), 1210 (CO) cm^{-1}; NMR (CCl_4) δ 0.9 (t, 3, J = 6 Hz, CH_3C), 1.1–1.6 [m, 8, $(CH_2)_4$], 2.35 (d, 2, J = 6 Hz, CH_2CO), 3.35 (br s, 1, OH), 3.55 (s, 3, CH_3O), 3.75–4.1 (m, 1, CH).

Anal. Calcd for $C_9H_{18}O_3$: C, 62.04; H, 10.41. Found: C, 61.91; H, 10.50.

Ethyl 3-(phenylamino)propanoate (5c): Hg^0 precipitated 80%; IR (film) 3400 (NH), 3060, 3040, 1600, 1510, 760, 700 (Ph), 1740 (C=O), 1230 (CO) cm^{-1}; NMR (CCl_4) δ 1.15 (t, 3, J = 6 Hz, CH_3), 2.45 (t, 2, J = 6 Hz, CH_2CO), 3.3 (t, 2, J = 6 Hz, CH_2N), 3.9 (br s, 1, NH), 4.05 (q, 2, J = 6 Hz, CH_2O), 6.3–7.2 (m, 5, Ph).

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.49; H, 7.93; N, 7.02.

Ethyl 3-(phenylamino)butanoate (5d): Hg^0 precipitated 83%; IR (film) 3400 (NH), 3100, 3060, 3030, 1600, 1500, 760, 700 (Ph), 1730 (C=O), 1200 (CO) cm^{-1}; NMR (CCl_4) δ 1.15 [d and t, 6, J = 6 Hz, $(CH_3C)_2$], 2.0–2.7 (m, 3, CH_2C and CH), 3.8 (br s, 1, NH), 4.0 (q, 2, J = 6 Hz, CH_2O), 6.3–7.2 (m, 5, Ph).

Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.73; H, 8.30; N, 6.58.

Ethyl 3-phenyl-3-(phenylamino)propanoate (5e): Hg^0 precipitated 78%; IR (Nujol) 3380 (NH), 3070, 3010, 1610, 1520, 1500, 760, 710 (Ph), 1720 (C=O), 1300 (CO) cm^{-1}; NMR ($CDCl_3$) δ 1.15 (t, 3, J = 6 Hz, CH_3), 2.75 (d, 2, J = 6 Hz, CH_2C), 4.05 (q, 2, J = 6 Hz, CH_2O), 4.5 (br s, 1, NH), 4.8 (t, 1, J = 6 Hz, CH), 6.3–7.4 (m, 10, aromatic H).

Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.76; H, 7.02; N, 5.43.

Reaction of 3 with Carbonyl Compounds. General Procedure. To a previously evacuated 250-mL two-necked flask containing dry THF (40 mL), mercurial **2** (15 mmol) was added under an argon atmosphere. The solution was cooled at −78 °C, an ether solution of phenyllithium[14] (15 mmol) was dropwise added in 10 min, then lithium powder (90 mmol) was added, and the mixture was mechanically stirred for 8 h. The reaction mixture was filtered (G-3 funnel) at −78 °C, the collected mercury weighed, and the corresponding carbonyl compound (15 mmol) added to the resulting clear solution of **3**. The temperature was allowed to rise to 20 °C in 12 h. The reaction mixture was hydrolyzed with water and neutralized with aqueous hydrochloric acid. The resulting mixture was extracted with ether, and the ether layer was washed with water and dried over anhydrous sodium sulfate. Solvents were removed under reduced pressure (15 mmHg), and the residue was distilled or recrystallized (see Table III).

1-Phenyl-1,3-pentanediol (6a): Hg^0 precipitated 76%; IR (film) 3380 (OH), 3090, 3060, 3040, 1610, 1500, 760, 700 (Ph) cm^{-1}; NMR ($CDCl_3$) δ 0.85 (t, 3, J = 6 Hz, CH_3), 1.1–1.5 (m, 2, CH_2CH_3), 1.5–1.9 (m, 2, CH_2CH), 3.5–3.9 (m, 1, $CHCH_2$), 3.9–4.7 [br s, 2 $(COH)_2$], 4.7–5.1 (m, 1, CHPh), 7.1–7.4 (m, 5, Ph).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.28; H, 8.90.

1,3-Diphenyl-1,3-propanediol (6b): Hg^0 precipitated 89%; IR (Nujol) 3400 (OH), 3100, 3060, 1610, 1500, 760, 700 (Ph) cm^{-1}; NMR ($CDCl_3$) δ 1.6 (br s, 1, OH), 2.2 (t, 2, J = 6 Hz, CH_2), 2.9 (br s, 1, OH), 4.95 (t, 2, J = 6 Hz, CH), 7.2–7.5 (m, 10, aromatic H).

Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.45; H, 6.94.

1-Phenyl-3-*p*-tolyl-1,3-propanediol (6c): Hg^0 precipitated 77%; IR (film) 3380 (OH), 3100, 3080, 3040, 1610, 1520, 1500, 830, 770, 710 (Ph) cm^{-1}; NMR ($CDCl_3$) δ 1.8–2.05 (m, 2, CH_2), 2.25 (s, 3, CH_3), 3.6–4.3 [br s, 2, $(COH)_2$], 4.6–4.9 [m, 2, $(CHC)_2$], 6.8–7.3 (m, 9, aromatic H).

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.23; H, 7.51.

4-Methyl-1-(phenylamino)-3-pentanol (6d): Hg^0 precipitated 82%; IR (Nujol) 3400 (OH), 3300 (NH), 3080, 3040, 1610, 1510, 760, 700 (Ph) cm^{-1}; NMR ($CDCl_3$) δ 0.9 [d, 6, J = 6 Hz, $(CH_3C)_2$], 1.4–1.9 (m, 3, CHC and CH_2C), 3.1 (br s, 2, OH and NH), 3.25 (t, 2, J = 6 Hz, CH_2N), 3.35–3.6 (m, 1, CHO), 6.5–7.3 (m, 5, Ph).

Anal. Calcd for $C_{12}H_{19}NO$: C, 74.57; H, 9.91; N, 7.25. Found: C, 74.30; H, 9.94; N, 7.17.

2-Phenyl-4-(phenylamino)-2-butanol (6e): Hg^0 precipitated 80%; IR (Nujol) 3380 (NH), 3360 (OH), 3080, 1610, 1510, 770, 710 (Ph) cm^{-1}; NMR ($CDCl_3$) δ 1.6 (s, 3, CH_3), 2.1 (t, 2, J = 6 Hz, CH_2C), 3.1 (t, 2, J = 6 Hz, CH_2N), 3.0–3.3 (br s, 2, OH and NH), 6.5–7.5 (m, 10, aromatic H).

Anal. Calcd for $C_{16}H_{19}NO$: C, 79.63; H, 7.94; N, 5.80. Found: C, 79.70; H, 7.91; N, 5.73.

1,1-Diphenyl-3-(phenylamino)-1-propanol (6f): Hg^0 precipitated 80%; IR (Nujol) 3400 (NH), 3380 (OH), 3040, 1610, 1510, 770, 710 (Ph) cm^{-1}; NMR ($CDCl_3$) δ 2.55 (t, 2, J = 6 Hz, CH_2C), 3.2 (t, 2, J = 6 Hz, CH_2N), 3.1–3.6 (2 br s, 2, OH and NH), 6.5–7.5 (m, 15, aromatic H).

Anal. Calcd for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62. Found: C, 83.20; H, 7.07; N, 4.68.

4-Methyl-1-phenyl-1-(phenylamino)-3-pentanol (6g): Hg^0 precipitated 81%; IR (Nujol) 3300 (OH, NH), 3090, 3060, 1610, 1500, 760, 700 (Ph) cm^{-1}; NMR ($CDCl_3$) δ 0.9 [d, 6, J = 6 Hz, $(CH_3C)_2$], 1.4–2.0 (m, 3, CHC and CH_2), 2.2–3.1 (br s, 1, NH), 3.2–3.9 (m, 2, OH and CHO), 4.45 (t, 1, J = 6 Hz, CHN), 6.3–7.4 (m, 10, aromatic H).

Anal. Calcd for $C_{18}H_{23}NO$: C, 80.26; H, 8.61; N, 5.20. Found: C, 80.07; H, 8.66; N, 5.30.

1,3-Diphenyl-3-(phenylamino)-1-propanol (6h): Hg^0 precipitated 91%; IR (Nujol) 3320 (OH), 3300 (NH), 3070, 3040, 3010, 1600, 1500, 750, 690 (Ph) cm^{-1}; NMR ($CDCl_3$) δ 1.6 (br s, 1, NH), 2.0–2.4 (m, 2, CH_2), 2.5–3.3 (br s, 1, OH), 4.5–4.7 (m, 1, CHN), 4.75–4.95 (m, 1, CHO), 6.4–7.4 (m, 15, aromatic H).

Anal. Calcd for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62. Found: C, 83.45; H, 6.86; N, 4.60.

2-Methyl-4-phenyl-4-(phenylamino)-2-butanol (6i): Hg^0 precipitated 76%; IR (film) 3400 (OH, NH), 3080, 3060, 1610, 1500, 760, 710 (Ph) cm^{-1}; NMR ($CDCl_3$) δ 1.25, 1.35 [2 s, 2, $(CH_3C)_2$], 1.75–1.95 (m, 2, CH_2), 3.5–4.2 (br s, 2, OH and NH), 4.45–4.65 (m, 1, CH), 6.4–7.4 (m, 10, aromatic H).

Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 79.80; H, 8.12; N, 5.37.

1,1,3-Triphenyl-3-(phenylamino)-1-propanol (6j): Hg^0 precipitated 77%; IR (Nujol) 3290 (OH, NH), 3040, 3010, 1600, 1520, 1500, 750, 700 (Ph) cm^{-1}; NMR ($CDCl_3$) δ 2.6–2.8 (m, 2, CH_2), 4.3–4.5 (m, 1, CH), 4.75 (br s, 2, NH and OH), 6.3–7.7 (m, 20, aromatic H).

Anal. Calcd for $C_{27}H_{25}NO$: C, 85.45; H, 6.64; N, 3.69. Found: C, 85.26; H, 6.60; N, 3.73.

Reaction of 3 with Trimethylchlorosilane. General Procedure. To a previously evacuated 250-mL two-necked flask containing dry THF (75 mL), mercurial **2** (25 mmol) was added under an argon atmosphere. The solution was cooled at −78 °C, an ether solution of phenyllithium[14] (25 mmol) was dropwise added in 10 min, then lithium powder (150 mmol) was added, and the mixture was mechanically stirred for 8 h. The reaction mixture was filtered (G-3 funnel) at −78 °C, the collected mercury weighed, and trimethylchlorosilane (25 mmol for **7**; 50 mmol for **8**) added to the resulting clear solution of **3**. The silylation reaction took place in times from 1 to 60 min, as remarked in the Results and Discussion section, depending on the product to be obtained. The reaction mixture was hydrolyzed with water and neutralized with aqueous hydrochloric acid. The resulting mixture was extracted with ether, and the ether layer was washed with water and dried over anhydrous sodium sulfate. Solvents were removed under reduced pressure (15 mmHg), and the residue was distilled (see Table IV).

2-(Trimethylsilyl)-1-phenylethanol (7a): Hg^0 precipitated 71%; IR (film) 3380 (OH), 3060, 3020, 1600, 1580, 1500, 760, 710 (Ph), 870 (CSi) cm^{-1}; NMR (CCl_4) δ 0.05 [s, 9, $(CH_3Si)_3$], 1.15–1.3 (m, 2, CH_2), 3.55 (br s, 1, OH), 4.7–5.0 (m, 1, CH), 7.3–7.6 (m, 5, Ph).

Anal. Calcd for $C_{11}H_{18}OSi$: C, 67.98; H, 9.34. Found: C, 68.04; H, 9.46.

***N*-[2-(Trimethylsilyl)ethyl]aniline (7b)**: Hg^0 precipitated 75%; IR (film) 3400 (NH), 3040, 3010, 1600, 1500, 750, 690 (Ph), 850 (CSi) cm^{-1}; NMR (CCl_4) δ 0.05 [s, 9, $(CH_3Si)_3$], 0.7 (t, 2, J = 7 Hz, CH_2Si), 3.0 (t, 2, J = 7 Hz, CH_2N), 3.2 (br s, 1, NH), 6.3–7.2 (m, 5, Ph).

Anal. Calcd for $C_{11}H_{19}NSi$: C, 68.33; H, 9.90; N, 7.24. Found: C, 68.02; H, 9.79; N, 7.31.

***N*-[1-Methyl-2-(trimethylsilyl)ethyl]aniline (7c)**: Hg^0 precipitated 82%; IR (film) 3440 (NH), 3100, 3060, 3030, 1600, 1500, 760, 700 (Ph), 860 (CSi) cm^{-1}; NMR (CCl_4) δ 0.05 [s, 9, $(CH_3Si)_3$], 0.75 (t, 2, J = 7 Hz, CH_2), 1.1 (d, 3, J = 7 Hz, CH_3C), 3.1 (br s, 1, NH), 3.4–3.7 (m, 1, CH), 6.3–7.2 (m, 5, Ph).

Anal. Calcd for $C_{12}H_{21}NSi$: C, 69.50; H, 10.21; N, 6.75. Found: C, 69.43; H, 10.14; N, 6.62.

***N*-[2-(Trimethylsilyl)-1-phenylethyl]aniline (7d)**: Hg^0 precipitated 78%; IR (Nujol) 3400 (NH), 3060, 3010, 1600, 1500, 770, 710 (Ph), 870 (CSi) cm^{-1}; NMR (CCl_4) δ 0.05 [s, 9, $(CH_3Si)_3$], 1.15 (d, 2, J = 7 Hz, CH_2), 3.8 (br s, 1, NH), 4.45 (t, 1, J = 7 Hz, CH), 6.4–7.5 (m, 10, aromatic H).

Anal. Calcd for $C_{17}H_{23}NSi$: C, 75.78; H, 8.60; N, 5.20. Found: C, 75.32; H, 8.33; N, 5.42.

***N*-(Trimethylsilyl)-*N*-[2-(trimethylsilyl)-1-phenylethyl]aniline (8)**: Hg^0 precipitated 76%; IR (film) 3070, 3020, 1600, 1500, 760, 700 (Ph), 860 (C–Si) cm^{-1}; NMR (CCl_4) δ 0.05 [s, 9, $(CH_3SiC)_3$], 0.15 [s, 9, $(CH_3SiN)_3$], 1.15–1.3 (m, 2, CH_2), 4.4–4.65 (m, 1, CH), 6.4–7.4 (m, 10, aromatic H).

Anal. Calcd for $C_{20}H_{31}NSi_2$: C, 70.31; H, 9.15; N, 4.10. Found: C, 70.02; H, 9.40; N, 3.97.

Registry No. 2 (Y = O; R_1 = Ph), 67931-44-6; **2** (Y = NPh; R_2 = H), 52969-23-0; **2** (Y = NPh; R_1 = Me), 52969-24-1; **2** (Y = NPh; R_1 = Ph), 55552-57-3; **2** (Y = O; R_1 = C_5H_{11}), 67931-43-5; **3** (Y = O; R_1 = Ph), 68090-83-5; **3** (Y = NPh; R_1 = H), 68110-48-5; **3** (Y = NPh; R_1 = Me), 71912-91-9; **3** (Y = NPh; R_1 = Ph), 68090-82-4; **3** (Y = O; R_1 = C_5H_{11}), 71912-92-0; **4a**, 93-56-1; **4b**, 122-98-5; **4c**, 16955-09-2; **4d**, 13891-02-6; **5a**, 7497-61-2; **5b**, 7367-87-5; **5c**, 62750-11-2; **5d**, 30448-31-8; **5e**, 6846-55-5; **6a**, 54876-95-8; **6b**, 5471-97-6; **6c**, 71912-93-1; **6d**, 22991-41-9; **6e**, 71912-94-2; **6f**, 71912-95-3; **6g**, 71912-96-4; **6h**, 4566-58-9; **6i**, 71912-97-5; **6j**, 71912-98-6; **7a**, 17993-97-4; **7b**, 23452-22-4; **7c**, 71912-99-7; **7d**, 58541-16-5; **8**, 71913-00-3; propionaldehyde, 123-38-6; benzaldehyde, 100-52-7; *p*-methylbenzaldehyde, 104-87-0; 2-methylpropionaldehyde, 78-84-2; acetophenone, 98-86-2; benzophenone, 119-61-9; acetone, 67-64-1.