



$\text{Ca}^+ + \text{e}^-$  with  $E^\circ_1 = 3.80 \text{ V}$ ) proceeds easier than that of the second electron ( $\text{Ca}^+ \rightarrow \text{Ca}^{2+} + \text{e}^-$  with  $E^\circ_2 = 1.94 \text{ V}$ ). In liquid ammonia at  $-50^\circ \text{C}$ ,  $E^\circ$  is  $2.39 \text{ V}$  for the process  $\text{Ca} \rightarrow \text{Ca}^{2+} + 2\text{e}^-$ .<sup>17</sup> The process  $\text{Ca}^+ \rightarrow \text{Ca}^{2+} + \text{e}^-$  can offer a higher selectivity for reducing various functional groups than the process  $\text{Ca} \rightarrow \text{Ca}^+ + \text{e}^-$  despite the fact that both are better than the process  $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$ . For example, selective reduction of benzyl ethers in the presence of a carbon-carbon triple bond or a *tert*-butyldimethylsilyl ether group is possible by proper control of the quantity of calcium metal in liquid ammonia.<sup>8</sup> Dissolving calcium metal can also selectively reduce a dithiane moiety in the presence of a weak silicon-silicon single bond.<sup>15</sup> Recently Burkard and Borschberg<sup>20</sup> have reported an efficient procedure for elimination of the 2,6-difluorobenzyl group from a complex indole derivative, hobartinol, by using dissolving calcium metal.

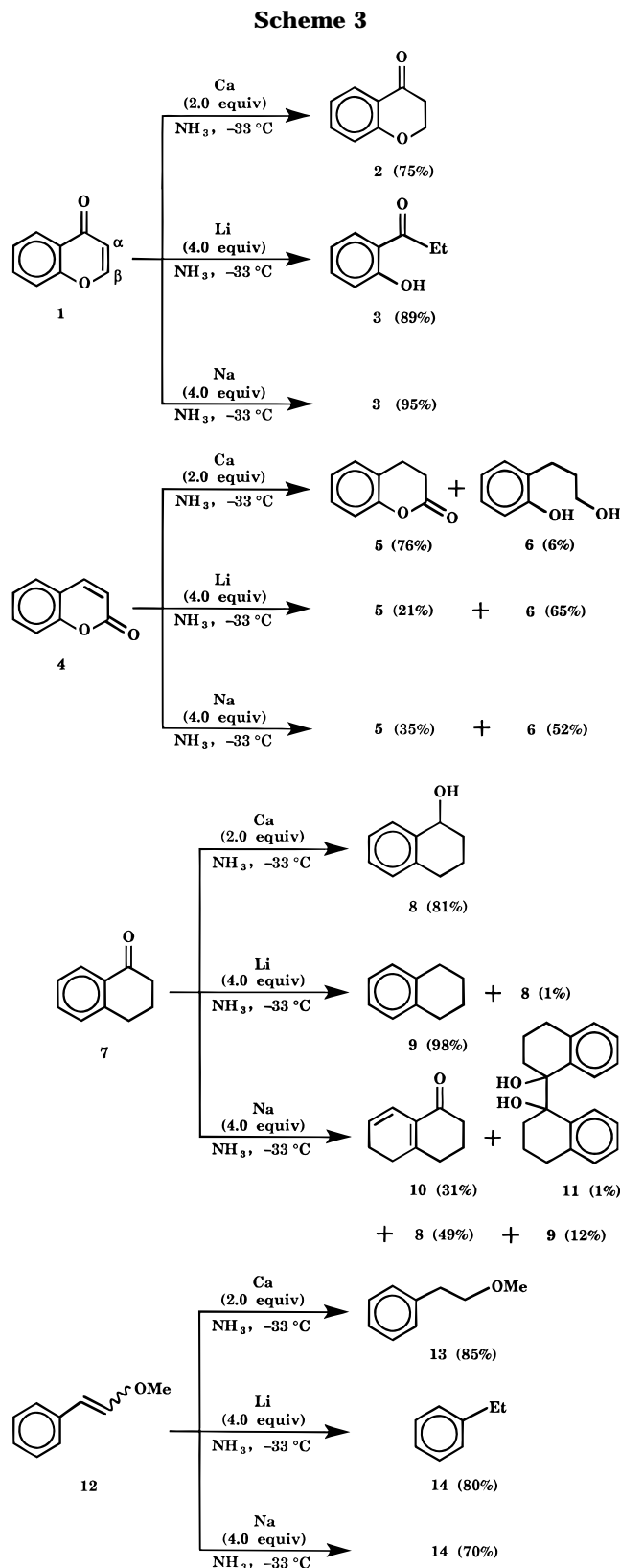
Advantages associated with the application of dissolving sodium and lithium metals include their strong reducing ability, high efficiency, low cost, and ready dissolution in liquid ammonia. Development of dissolving calcium metal with high selectivity for reduction of organic compounds would be an ideal complement to the established methods. Herein we report our results from a systematic study on similarity and diversity, especially selectivity, among sodium, lithium, and calcium metals during their applications to selective reduction of organic compounds.

## Results

We carried out a series of experiments by using dissolving metals in liquid ammonia for reduction of organic compounds containing bi- or multifunctional groups of various types. They include enal, enone, phenone, lactone, vinyl ether, pyridine *N*-oxide, indole, aromatic hydrocarbons, styrene, and cyano and benzyloxy groups. Reactions listed in Scheme 3 produced entirely different results by use of calcium to replace lithium or sodium metal. Table 1 includes reductions giving the same products by the three dissolving metals, among which calcium metal often gave the highest yields.

The standard reduction procedure involved treatment of an organic substrate in THF with calcium turnings (2.0–2.2 equiv) in liquid ammonia at  $-33^\circ \text{C}$  under an argon atmosphere for 2 h. The solution of calcium in ammonia is sufficiently acidic to bring about protonation of the metalated species.<sup>21</sup> Thus addition of other reagents as proton donor was not necessary. After the reduction was complete, it was quenched by addition of solid  $\text{NH}_4\text{Cl}$ . Normal workup followed by chromatographic purification on silica gel afforded the pure products.

**Diversity in the Dissolving Metal Reductions (Scheme 3).** We found that calcium reduction of chromone (**1**) produced  $\alpha,\beta$ -saturated product **2** as the exclusive product in 75% yield. The starting material **1** was recovered in 24% yield. In contrast, use of stronger reducing agents including lithium and sodium unambiguously led **1** to hydroxyphenone **3** in 89–95% yields



through saturation of the  $\text{C}_\alpha\text{--C}_\beta$  double bond followed by cleavage of the  $\text{C}_\beta\text{--O}$  bond. The mild reducing ability of calcium was also reflected during its application to the reduction of coumarin (**4**), which contains an  $\alpha,\beta$ -unsaturated lactone moiety. Treatment of **4** with calcium metal resulted in preferential reduction at the carbon-carbon double bond. Dihydrocoumarin (**5**) and the over-reduced product **6** were obtained in 76% and 6% yields, respectively. Use of lithium or sodium metal, however,

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**Table 1. Reduction of Organic Compounds Containing Various Functional Groups with Metal in Liquid Ammonia at -33 °C**

substr	metal	equiv	product	yield (%)
15	Ca	2.0	16	80
15	Li	4.0	16	32
15	Na	4.0	16	40
17	Ca	2.0	18	90
17	Li	4.0	18	75
17	Na	4.0	18	70
19	Ca	2.0	20	90
19	Li	4.0	20	72
19	Na	4.0	20	67
21	Ca	1.2	22	95
21	Li	2.4	22	96
21	Na	2.4	22	91
23	Ca	2.2	24	95
23	Li	4.4	24	96
23	Na	4.4	24	83
25	Ca	2.0	26	95
25	Li	4.0	26	93
25	Na	4.0	26	92
27	Ca	2.0	28	~8
27	Li	4.0	28	~8
27	Na	4.0	28	~8

provided diol **6** as the major product in 52–65% yields along with byproduct **5** in 21–35% yields.

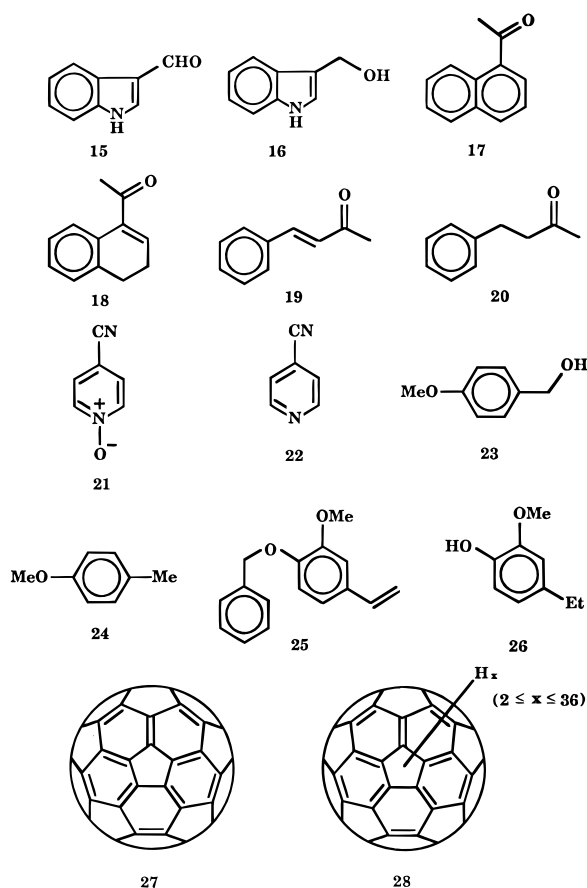
In the reduction of  $\alpha$ -tetralone (**7**), the results were extremely diverse among calcium, lithium, and sodium. Treatment of **7** with calcium afforded tetrahydronaphthol **8** exclusively in 81% yield. Marcinow and Rabideau<sup>22</sup> reported that use of lithium gave further reduced product, tetrahydronaphthalene **9**, in excellent yield (98%) through deoxygenation. Reduction by sodium produced a complex mixture including **8** (49%), **9** (12%), enone **10** (31%), and dimer **11** (1%).<sup>22</sup>

Furthermore, we found that dissolving calcium metal selectively reduced the carbon–carbon double bond in  $\beta$ -methoxystyrene (**12**) to give methyl phenethyl ether (**13**) in 85% yield. The intact starting material **12** was recovered in 12% yield. Application of lithium or sodium metal produced over-reduced product ethylbenzene (**14**, 70–80% yields); demethoxylation taking place in situ indicates the strong reducing conditions.

**Similarity in Dissolving Metal Reductions (Table 1).** Remers et al.<sup>23</sup> reported that lithium in ammonia can reduce the indole nucleus to give a mixture of dihydro- and tetrahydroindoles. We found that reduction of indole-3-carboxaldehyde (**15**) (Chart 1) by calcium gave the corresponding alcohol **16** as the major product in 80% yield. Application of lithium or sodium to the reduction of **15** afforded a complex mixture, from which we were able to isolate **16** in 32–40% yields only.

Reduction of naphthalenes depends upon the nature of substituents in the ring.<sup>24</sup> We reduced 1-acetylnaphthalene (**17**) with dissolving metals to give 1-acetyldihydronaphthalene **18** as the major product. The yields were higher by use of calcium (90%) than by lithium (75%) and sodium (70%).<sup>24</sup> Furthermore, we obtained similar results during the reduction of enone **19** to ketone **20**. Use of calcium provided **20** in excellent yield (90%), which was higher than those by lithium (72%) and sodium (67%).

Both the cyano group<sup>14</sup> and the *N*-oxide moiety<sup>25</sup> in 4-cyanopyridine *N*-oxide (**21**) could be reduced by dis-

**Chart 1**

solving metals. We found that reduction of **21** with calcium (1.2 equiv), lithium, or sodium (2.4 equiv) gave the same deoxygenation product **22** in comparable yields (91–96%), whereas the cyano group remained intact. Treatment of 4-methoxybenzyl alcohol (**23**) with these dissolving metals also afforded the identical product **24** (83–96% yields) through deoxygenation. In the reduction of 4-(benzyloxy)-3-methoxystyrene (**25**), both debenzyla-tion and saturation of the carbon–carbon double bond<sup>4</sup> took place to give ethylanisole derivative **26** exclusively in 92–95% yields. None of calcium, lithium, and sodium exhibited chemoselectivity. Reduction of buckminsterfullerene C<sub>60</sub> with calcium (2.0 equiv), lithium, or sodium (4.0 equiv) gave unanimously a mixture of polyhydrofullerenes<sup>26,27</sup> containing C<sub>60</sub>H<sub>2</sub> through C<sub>60</sub>H<sub>36</sub> with C<sub>60</sub>H<sub>18</sub> as the major component in ~8% overall yields. The intact C<sub>60</sub> starting material was recovered in >90% yield. Use of a large quantity of calcium (30 equiv), lithium, and sodium (60 equiv) provided the same products in 80–85% yields.

Our attempts to reduce selectively one functional group in the presence of the other in bifunctional molecules as listed below did not meet with synthetically valuable outcome by use of dissolving calcium metal. Often a complex mixture was produced. Those groups include

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allyl chloride versus vinyl chloride in 3,4-dichlorobicyclo-[3.2.1]oct-2-ene, benzyl chloride versus phenyl chloride in 6-chloropiperonyl chloride, hydrazine versus phenyl chloride in (4-chlorophenyl)hydrazine, ester versus alkyl chloride in 4-chlorobutyl acetate, nitrobenzene versus chlorobenzene in 4-chloro-3-nitroanisole, ketone group versus cyano group in 2-(2-cyanoethyl)hexanone, cyclopropyl ketone versus thiophene in cyclopropyl 2-thienyl ketone, and epoxide versus sulfone in 3,4-epoxytetrahydrothiophene 1,1-dioxide. Furthermore, selective reduction was not observed in favor of a particular moiety in  $\alpha,\beta$ -unsaturated nitroalkene, quinoline, or isoquinoline by use of dissolving calcium.

### Discussion

Our results shown in Scheme 1 indicate that dissolving calcium offers better chemoselectivity than lithium and sodium in the reduction of some organic compounds bearing more than one reducible site. Application of 2.0–2.2 equiv of calcium metal with the concentration of 0.030–0.080 M in liquid ammonia (e.g., 0.10–0.50 g of Ca in 100 mL of  $\text{NH}_3$ ) often gives the best selectivity. Their applications to reduction of  $\alpha,\beta$ -unsaturated ketones and esters resulted in saturation of the carbon–carbon double bond preferentially, as indicated in the conversions of **1**  $\rightarrow$  **2**, **4**  $\rightarrow$  **5** + **6** (13:1), and **19**  $\rightarrow$  **20**.

In combination with the information reported<sup>1–3,6,8,11,12,15,20</sup> and described herein, we list in Table 2 the functional groups in approximate order of decreasing ease of reduction by dissolving calcium metal. We divide those functional groups in three levels—the lower the level, the easier to be reduced. It is possible to reduce the functional groups in level 1 selectively in the presence of those in level 3 by utilization of the process  $\text{Ca}^+ \rightarrow \text{Ca}^{2+} + \text{e}^-$ . The order of some functional groups in Table 2 is on the basis of a literature survey of lithium–ammonia reductions reported by Sinclair and Jorgensen.<sup>28</sup>

### Conclusions

Acting as a weaker reducing agent than lithium and sodium, calcium metal in liquid ammonia offers better selectivity in the reduction of organic compounds bearing di- or multifunctional groups. Results from systematic studies indicate that dissolving calcium metal can selectively reduce the former group in the presence of the latter listed as follows:  $\alpha,\beta$ -unsaturated ketone versus vinyl ether,  $\alpha,\beta$ -unsaturated ketone versus phenyl group, styrene versus vinyl ether, styrene versus anisole, benzyl alcohol versus anisole, benzyl ether versus anisole, aldehyde versus indole nucleus, naphthalene activated by carbonyl group versus carbonyl group of phenone, and *N*-oxide versus cyano group. Furthermore, Table 2 is established for dissolving calcium metal toward various functional groups in approximate order of decreasing ease of reduction.

### Experimental Section

**General Procedure.** Ethyl acetate and hexanes, purchased from Mallinckrodt Chemical Co., were dried and distilled from  $\text{CaH}_2$ . 1-Acetylnaphthalene, 4-(benzyloxy)-3-methoxystyrene, calcium turnings, chromone, coumarin, 4-cyanopyridine *N*-oxide, indole-3-carboxaldehyde, lithium wire,

**Table 2. Relative Reactivity of Functional Groups toward Reduction by Use of Calcium Metal in Liquid Ammonia. It Is Possible To Reduce the Functional Groups in Level 1 Selectively in the Presence of Those in Levels 3**

level	functional group	product	basis
1		+ HOR	ref 20
	$\text{PhCH}_2\text{OR}$	$\text{PhCH}_3$ + HOR	ref 8
	$\text{PhSR}$	$\text{PhSH}$ + HR	ref 8
	$\text{PhSO}_2\text{R}$	$\text{PhH}$	ref 8
		$\text{RCH}_3$ + HS-CH <sub>2</sub> -CH <sub>2</sub> -SH	ref 15
		$\text{R}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{SH}$	ref 15
			Table 1
			Table 1
			Table 1
			Scheme 3
			Table 1
	$\text{R}-\text{CH}=\text{CH}-\text{OR}'$	$\text{R}-\text{CH}=\text{CH}-\text{Me}$ + HOR'	ref 11
			ref 12
			ref 6
2			Scheme 3
	$\text{Ph}-\text{CH}_2-\text{OH}$	$\text{PhCH}_3$	Table 1
	$\text{R}-\text{CH}=\text{CH}-\text{OR}'$	$\text{R}-\text{CH}=\text{CH}-\text{H}$ + HOR'	Scheme 3
	$\text{R}-\text{C}\equiv\text{C}-\text{R}'$		ref 8
	$\text{R}-\text{C}(=\text{O})-\text{OR}'$	$\text{R}-\text{CH}_2-\text{OH}$ + HOR'	ref 13
		+ HOR	ref 8
		+ HOR	ref 8
		+	ref 8
		+	ref 23
	$\text{R}_3\text{Si}-\text{SiR}'_3$	$\text{R}_3\text{SiH}$ + $\text{HSiR}'_3$	ref 15
3	$\text{R}_3\text{Si}-\text{OR}'$	$\text{R}_3\text{SiOH}$ + HR	ref 8
			ref 8

4-methoxybenzyl alcohol,  $\beta$ -methoxystyrene, *trans*-4-phenyl-3-buten-2-one, sodium, and  $\alpha$ -tetralone were purchased from Aldrich Chemical Co. Analytical thin layer chromatography (TLC) was performed on precoated plates (silica gel 60 F-254), purchased from Merck Inc. Mixtures of ethyl acetate and hexanes were used as eluants. Purification by gravity column chromatography was carried out by use of Merck Reagent silica gel 60 (particle size 0.063–0.200 nm, 70–230 mesh ASTM). Gas chromatographic analyses were performed on a Hewlett-Packard 5890 Series II instrument equipped with a 25-m cross-linked methyl silicone gum capillary column (0.32 mm i.d.). Nitrogen gas was used as a carrier gas, and the flow rate was kept constant at 14.0 mL/min. The retention time  $t_R$  was measured under the following conditions: injector temperature 260 °C, the initial temperature for column 70 °C, duration 2.00 min, increment rate 10 °C/min, and the final temperature for column 250 °C.

#### Standard Procedure for Dissolving Metal Reduction.

Metal (Ca, Li, or Na) was dissolved in liquid ammonia at –78 °C under an argon atmosphere in a three-necked flask equipped with a dry ice–acetone cooled Dewar condenser. To this blue solution was added a solution of substrate in THF. The cooling bath was removed, and the deep blue solution was kept at reflux at –33 °C for 2 h. Solid NH<sub>4</sub>Cl was added cautiously to the reaction flask, followed by the addition of ether (50 mL). Ammonia in the solution was then allowed to evaporate overnight. Saturated aqueous NH<sub>4</sub>Cl was added to the residue, and the aqueous phase was extracted with three portions of ether. The combined ether solutions were washed with saturated aqueous NH<sub>4</sub>Cl, 10% aqueous NaHCO<sub>3</sub>, and brine, dried over MgSO<sub>4</sub>(s), filtered through Celite, and concentrated. The residue was analyzed by GC; an example is shown in the conversion of **19** → **20**. It was then purified by chromatography on silica gel (1.5 cm × 16 cm column) to provide the desired product.

**Note:** Dissolving calcium reductions in ammonia, similar to Birch and Benkeser reductions, should be performed carefully in hood. Our laboratory has carried out calcium reductions on different substrates more than 200 times on the scale from 30 mg to 10 g and, fortunately, has not experienced any danger.

**4-Chromanone (2).** The standard procedure was followed by use of chromone (**1**, 212.3 mg, 1.453 mmol, 1.0 equiv), calcium turning (116.4 mg, 2.951 mmol, 2.0 equiv), THF (10 mL), and liquid ammonia (40 mL). After the reaction mixture was stirred for 2 h, it was worked up and the residue was purified by chromatography on silica gel (10% EtOAc in hexanes as eluant) to give pure **2** (161.4 mg, 1.089 mmol) as a colorless oil in 75% yield: GC  $t_R$  10.95 min; TLC  $R_f$  0.29 (10% EtOAc in hexanes); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  2.81 (t,  $J$  = 6.4 Hz, 2 H), 4.53 (t,  $J$  = 6.4 Hz, 2 H), 6.95–7.91 (m, 4 H); IR (neat) 3065 (w, ArH), 2927 (m, C–H), 1691 (s, C=O), 1605 (s, Ar), 1468 (s, Ar), 1313 (s), 1252 (m), 1041 (m), 868 (w), 788 (w) cm<sup>–1</sup>; MS  $m/z$  (relative intensity) 148 (M<sup>+</sup>, 66), 121 (9), 120 (100), 93 (4), 92 (61), 91 (3), 65 (5), 64 (15), 63 (15), 53 (2). Its physical properties and spectroscopic characteristics are consistent with those of an authentic sample.<sup>29</sup>

**1-(2-Hydroxyphenyl)propan-1-one (3).** **Method 1.** The standard procedure was followed by use of chromone (**1**, 207.1 mg, 1.485 mmol, 1.0 equiv), lithium wire (41.3 mg, 5.94 mmol, 4.0 equiv), THF (10 mL), and liquid ammonia (40 mL). After the reaction mixture was stirred for 2 h, it was worked up and the residue was purified by chromatography on silica gel (5% EtOAc in hexanes as eluant) to give pure **3** (198.4 mg, 1.322 mmol) as a colorless oil in 89% yield: GC  $t_R$  9.94 min; TLC  $R_f$  0.65 (10% EtOAc in hexanes); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  1.24 (t,  $J$  = 7.3 Hz, 3H), 3.04 (q,  $J$  = 7.3 Hz, 2 H), 6.87–7.78 (m, 4 H); IR (neat) 2969 (s, C–H), 1631 (s, C=O), 1487 (m), 1363 (m), 1276 (s), 1205 (s, C–O), 1105 (w), 1018 (w), 954 (m), 756(s) cm<sup>–1</sup>; MS  $m/z$  (relative intensity) 150 (M<sup>+</sup>, 29), 122 (8), 121 (100), 93 (13), 77 (2), 65 (13), 64 (2), 63 (3), 53 (2), 51 (2). Its physical properties and spectroscopic characteristics are consistent with those of an authentic sample.<sup>29</sup>

**Method 2.** The standard procedure was followed by use of chromone (**1**, 206.4 mg, 1.412 mmol, 1.0 equiv), sodium (254.4 mg, 5.648 mmol, 4.0 equiv), THF (10 mL), and liquid ammonia (40 mL) to give pure **3** (201.4 mg, 1.341 mmol) as a colorless oil in 95% yield.

**Dihydrocoumarin (5).** The standard procedure was followed by use of coumarin (**4**, 439.5 mg, 3.007 mmol, 1.0 equiv), calcium turning (244.7 mg, 6.014 mmol, 2.0 equiv), THF (10 mL), and liquid ammonia (40 mL). After the reaction mixture was stirred for 2 h, it was worked up and the residue was purified by chromatography on silica gel (10% EtOAc in hexanes as eluant) to give pure **5** (258.4 mg, 1.744 mmol) as a yellow oil in 76% yield and **6** (27.4 mg, 0.180 mmol) as yellow oil in 6% yield. For **5**: GC  $t_R$  11.77 min; TLC  $R_f$  0.58 (25% EtOAc in hexanes); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  2.71 (t,  $J$  = 6.4 Hz, 2 H), 2.91 (t,  $J$  = 6.4 Hz, 2 H), 6.83–7.13 (m, 4 H); IR (neat) 3030 (w, ArH), 2982 (m, C–H), 1734 (s, C=O), 1602 (w, Ar), 1495 (w, Ar), 1453 (m), 1248 (s), 1154 (s), 1030 (m), 711 (s) cm<sup>–1</sup>; MS  $m/z$  (relative intensity) 148 (M<sup>+</sup>, 100), 120 (77), 119 (25), 106 (10), 92 (15), 91 (61), 78 (40), 77 (11), 63 (9), 51 (17). Its physical properties and spectroscopic characteristics are consistent with those of an authentic sample.<sup>29</sup>

**3-(2-Hydroxyphenyl)-1-propanol (6).** **Method 1.** The standard procedure was followed by use of coumarin (**4**, 440.2 mg, 3.012 mmol, 1.0 equiv), lithium wire (83.8 mg, 12.0 mmol, 4.0 equiv), THF (10 mL), and liquid ammonia (40 mL). After the reaction mixture was stirred for 2 h, it was worked up and the residue was purified by chromatography on silica gel (10% EtOAc in hexanes as eluant) to give pure **5** (120.5 mg, 0.6344 mmol) in 21% yield and **6** (297.9 mg, 1.959 mmol) as a yellow oil in 65% yield. For **6**: GC  $t_R$  13.44 min; TLC  $R_f$  0.31 (25% EtOAc in hexanes); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  1.63–2.04 (m, 2 H), 2.66 (t,  $J$  = 5.2 Hz, 2 H), 2.95–3.04 (m, 2 H), 3.18 (s, 1 H), 5.60 (s, 1 H), 6.78–7.12 (m, 4 H); IR (neat) 3456 (s, O–H), 3029 (w, ArH), 2985 (m, C–H), 1603 (m, Ar), 1487 (s), 1425 (m), 1351 (s), 1211 (s), 988 (w), 785 (m) cm<sup>–1</sup>; MS  $m/z$  (relative intensity) 152 (M<sup>+</sup>, 31), 151 (10), 113 (5), 114 (7), 111 (100), 85 (14), 84 (4), 83 (7), 69 (13), 56 (4). Its spectroscopic characteristics are consistent with those of the same compound reported.<sup>30</sup>

**Method 2.** The standard procedure was followed by use of coumarin (**4**, 441.1 mg, 3.018 mmol, 1.0 equiv), sodium (277.6 mg, 12.07 mmol, 4.0 equiv), THF (10 mL), and liquid ammonia (40 mL) to give pure **5** (156.3 mg, 1.056 mmol) in 35% yield and **6** (235.4 mg, 1.569 mmol) as a yellow oil in 52% yield.

**1,2,3,4-Tetrahydro-1-naphthol (8).** The standard procedure was followed by use of  $\alpha$ -tetralone (**7**, 177.5 mg, 1.200 mmol, 1.0 equiv), calcium turning (106.8 mg, 2.640 mmol, 2.2 equiv), THF (10 mL), and liquid ammonia (40 mL). After the reaction mixture was stirred for 2 h, it was worked up and the residue was purified by chromatography on silica gel (5% EtOAc in hexanes as eluant) to give pure **8** (142.3 mg, 0.9631 mmol) as a colorless oil in 81% yield: GC  $t_R$  11.35 min; TLC  $R_f$  0.32 (10% EtOAc in hexanes); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  1.70–1.89 (m, 2 H), 1.90–2.01 (m, 3 H), 2.70–2.86 (m, 2 H), 4.78 (br, s, 1 H), 7.09–7.45 (m, 4 H); IR (neat) 3342 (s, OH), 2916 (s, C–H), 1605 (w, Ar), 1443 (m), 1278 (w), 1200 (w), 1045 (s, C–O), 961 (w), 745 (m) cm<sup>–1</sup>; MS  $m/z$  (relative intensity) 148 (M<sup>+</sup>, 43), 147 (42), 130 (98), 129 (41), 120 (100), 119 (65), 115 (26), 104 (40), 91 (67), 77 (18). Its physical properties and spectroscopic characteristics are consistent with those of an authentic sample.<sup>29</sup>

**Methyl Phenethyl Ether (13).** The standard procedure was followed by use of  $\beta$ -methoxystyrene (**12**, 405.6 mg, 3.023 mmol, 1.0 equiv), calcium turning (254.4 mg, 6.048 mmol, 2.0 equiv), THF (10 mL), and liquid ammonia (40 mL). After the reaction mixture was stirred for 2 h, it was worked up and the residue was purified by chromatography on silica gel (5% EtOAc in hexanes as eluant) to give pure **13** (345.0 mg, 2.533 mmol) as a colorless oil in 85% yield: GC  $t_R$  9.39 min; TLC  $R_f$  0.65 (5% EtOAc in hexanes); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  2.88 (t,  $J$  = 7.1 Hz, 2 H), 3.36 (s, 3 H), 3.60 (t,  $J$  = 7.1 Hz, 2 H), 7.21–7.29 (m, 5 H); IR (neat) 3026 (s, ArH), 2835 (s, C–H),

(29) Compounds are available from Aldrich Chemical Co.

(30) Billman, J. H.; Tonniss, J. A. *J. Pharm. Sci.* **1971**, *60*, 1188.

1605 (w, Ar), 1491 (w), 1450 (m), 1400 (m), 1270 (s), 1085 (s, C—O), 770 (s)  $\text{cm}^{-1}$ ; MS  $m/z$  (relative intensity) 136 ( $\text{M}^+$ , 91), 105 (11), 104 (27), 103 (11), 92 (8), 91 (100), 78 (7), 77 (15), 65 (19), 51 (10). Its spectroscopic characteristics are consistent with those of the same compound reported.<sup>31</sup>

**Ethylbenzene (14). Method 1.** The standard procedure was followed by use of  $\beta$ -methoxystyrene (**12**, 402.8 mg, 3.002 mmol, 1.0 equiv), lithium wire (87.5 mg, 12.0 mmol, 4.0 equiv), THF (10 mL), and liquid ammonia (40 mL). After the reaction mixture was stirred for 2 h, it was worked up and the residue was purified by chromatography on silica gel (5% EtOAc in hexanes as eluant) to give pure **14** (254.7 mg, 2.402 mmol) as a colorless oil in 80% yield: GC  $t_R$  3.56 min; TLC  $R_f$  0.92 (5% EtOAc in hexanes);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  1.25 (t,  $J$  = 7.6 Hz, 3 H), 2.66 (t,  $J$  = 7.6 Hz, 2 H), 7.16–7.30 (m, 5 H); IR (neat) 3025 (w, ArH), 2981 (m, C—H), 1608 (w, Ar), 1452 (m), 1407 (s), 1025 (m), 891 (w), 743 (m), 675 (s)  $\text{cm}^{-1}$ ; MS  $m/z$  (relative intensity) 106 ( $\text{M}^+$ , 30), 103 (3), 92 (8), 91 (100), 79 (4), 78 (7), 77 (8), 65 (8), 63 (4), 51 (9). Its physical properties and spectroscopic characteristics are consistent with those of an authentic sample.<sup>29</sup>

**Method 2.** The standard procedure was followed by use of  $\beta$ -methoxystyrene (**12**, 425.2 mg, 2.853 mmol, 1.0 equiv), sodium (275.5 mg, 11.98 mmol, 4.0 equiv), THF (10 mL), and liquid ammonia (40 mL) to give pure **14** (211.7 mg, 1.997 mmol) as a colorless oil in 70% yield.

**3-Indolemethanol (16). Method 1.** The standard procedure was followed by use of indole-3-carboxaldehyde (**15**, 213.3 mg, 1.452 mmol, 1.0 equiv), calcium turning (116.7 mg, 2.851 mmol, 2.0 equiv), THF (10 mL), and liquid ammonia (40 mL). After the reaction mixture was stirred for 2 h, it was worked up and the residue was purified by chromatography on silica gel (10% EtOAc in hexanes as eluant) to give pure **16** (167.7 mg, 1.140 mmol) as an orange oil in 80% yield: TLC  $R_f$  0.49 (50% EtOAc in hexanes);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  4.87 (s, 2 H), 7.12–7.73 (m, 5 H), 8.24 (br, s, 1 H); IR (neat) 3382 (s, O—H), 3054 (w, ArH), 2974 (s, C—H), 2868 (s, C—H), 1645 (m, Ar), 1455 (s, Ar), 1382 (w), 1350 (w), 1114 (s, C—O), 742 (m); MS  $m/z$  (relative intensity) 147 ( $\text{M}^+$ , 10), 145 (80), 108 (62), 144 (100), 130 (5), 117 (5), 116 (25), 89 (20), 63 (7), 62 (4). Its physical properties and spectroscopic characteristics are consistent with those of an authentic sample.<sup>29</sup>

**Method 2.** The standard procedure was followed by use of indole-3-carboxaldehyde (**15**, 210.5 mg, 1.407 mmol, 1.0 equiv), lithium wire (39.4 mg, 5.63 mmol, 4.0 equiv), THF (10 mL), and liquid ammonia (40 mL) to give pure **16** (66.3 mg, 0.451 mmol) as an orange oil in 32% yield.

**Method 3.** The standard procedure was followed by use of indole-3-carboxaldehyde (**15**, 207.5 mg, 1.429 mmol, 1.0 equiv), sodium (131.4 mg, 5.716 mmol, 4.0 equiv), THF (10 mL), and liquid ammonia (40 mL) to give pure **16** (82.9 mg, 0.571 mmol) as an orange oil in 40% yield.

**1-Acetyl-3,4-dihydronaphthalene (18).** The standard procedure was followed by use of 1-acetylnaphthalene (**17**, 351.4 mg, 2.023 mmol, 1.0 equiv), calcium turning (170.3 mg, 4.408 mmol, 2.0 equiv), THF (10 mL), and liquid ammonia (40 mL). After the reaction mixture was stirred for 2 h, it was worked up and the residue was purified by chromatography on silica gel (10% EtOAc in hexanes as eluant) to give pure **18** (313.5 mg, 1.821 mmol) as a colorless oil in 90% yield: GC  $t_R$  14.19 min; TLC  $R_f$  0.47 (10% EtOAc in hexanes);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.40–2.45 (m, 2 H), 2.46 (s, 3 H), 2.75 (t,  $J$  = 7.7 Hz, 2 H), 7.01 (t,  $J$  = 4.9 Hz, 1 H), 7.16–7.70 (m, 4 H); IR (neat) 3043 (w, ArH), 2940 (m, C—H), 1674 (s, C=O), 1435 (m), 1365 (w), 1257 (m), 1166 (w), 1020 (w), 832 (w), 768 (m)  $\text{cm}^{-1}$ ; MS  $m/z$  (relative intensity) 172 ( $\text{M}^+$ , 58), 157 (20), 130 (14), 129 (100), 128 (57), 127 (24), 102 (7), 77 (8), 63 (8), 51 (9). Its spectroscopic characteristics are consistent with those of the same compound reported.<sup>24</sup>

**4-Phenyl-2-butanone (20). Method 1.** The standard procedure was followed by use of *trans*-4-phenyl-3-buten-2-one (**19**, 180.7 mg, 1.221 mmol, 1.0 equiv), calcium turning (101.2 mg, 2.513 mmol, 2.0 equiv), THF (10 mL), and liquid

ammonia (40 mL). After the reaction mixture was stirred for 2 h, it was worked up to give a crude mixture. Analysis by GC indicated that **20** and 4-phenyl-2-butanol were obtained in a ratio of 29.3:1. The mixture was then purified by chromatography on silica gel (10% EtOAc in hexanes as eluant) to give pure **20** (165.1 mg, 1.111 mmol) as a colorless oil in 90% yield: GC  $t_R$  9.39 min; TLC  $R_f$  0.51 (10% EtOAc in hexanes);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.14 (s, 3 H), 2.76 (t,  $J$  = 7.1 Hz, 2 H), 2.89 (t,  $J$  = 7.1 Hz, 2 H), 7.17–7.31 (m, 5 H); IR (neat) 3032 (w, ArH), 1714 (s, C=O), 1602 (w, Ar), 1459 (m), 1452 (m), 1361 (w), 1160 (m), 749 (m), 699 (s)  $\text{cm}^{-1}$ ; MS  $m/z$  (relative intensity) 148 ( $\text{M}^+$ , 100), 133 (18), 115 (5), 105 (97), 92 (6), 91 (64), 79 (13), 77 (19), 65 (10), 51 (11), 76 (38). Its physical properties and spectroscopic characteristics are consistent with those of an authentic sample.<sup>29</sup>

**Method 2.** The standard procedure was followed by use of *trans*-4-phenyl-3-buten-2-one (**19**, 186.5 mg, 1.263 mmol, 1.0 equiv), lithium wire (35.4 mg, 5.05 mmol, 4.0 equiv), THF (10 mL), and liquid ammonia (40 mL) to give pure **20** (134.6 mg, 0.909 mmol) as a colorless oil in 72% yield. On the other hand, analysis of the crude reaction products by GC indicated that **20** and 4-phenyl-2-butanol were obtained in a ratio of 3.78:1.

**Method 3.** The standard procedure was followed by use of *trans*-4-phenyl-3-buten-2-one (**19**, 220.7 mg, 1.509 mmol, 1.0 equiv), sodium (138.9 mg, 6.036 mmol, 4.0 equiv), THF (10 mL), and liquid ammonia (40 mL) to give pure **20** (149.6 mg, 1.011 mmol) as a colorless oil in 67% yield. On the other hand, analysis of the crude reaction products by GC indicated that **20** and 4-phenyl-2-butanol were obtained in a ratio of 3.07:1.

**4-Cyanopyridine (22). Method 1.** The standard procedure was followed by use of 4-cyanopyridine *N*-oxide (**21**, 222.2 mg, 1.850 mmol, 1.0 equiv), calcium turning (88.9 mg, 2.22 mmol, 1.2 equiv), THF (10 mL), and liquid ammonia (40 mL). After the reaction mixture was stirred for 2 h, it was worked up and the residue was purified by chromatography on silica gel (10% EtOAc in hexanes as eluant) to give pure **22** (182.8 mg, 2.109 mmol) as a colorless oil in 95% yield: GC  $t_R$  4.86 min; TLC  $R_f$  0.22 (10% EtOAc in hexanes);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.54 (d,  $J$  = 6.0 Hz, 2 H), 8.82 (d,  $J$  = 6.0 Hz, 2 H); IR (neat) 3082 (w, ArH), 3027 (w, ArH), 2214 (m, C $\equiv$ N), 1592 (s, Ar), 1544 (s, Ar), 1414 (s), 1200 (m), 1084 (w), 910 (m), 827 (s), 732 (m)  $\text{cm}^{-1}$ ; MS  $m/z$  (relative intensity) 104 ( $\text{M}^+$ , 100), 78 (3), 77 (52), 76 (19), 75 (6), 74 (2), 64 (11), 59 (3), 52 (5), 51 (12). Its physical properties and spectroscopic characteristics are consistent with those of an authentic sample.<sup>29</sup>

**Method 2.** The standard procedure was followed by use of 4-cyanopyridine *N*-oxide (**21**, 250.9 mg, 2.005 mmol, 1.0 equiv), lithium wire (33.6 mg, 4.81 mmol, 2.4 equiv), THF (10 mL), and liquid ammonia (40 mL) to give pure **22** (198.1 mg, 4.617 mmol) as a colorless oil in 96% yield.

**Method 3.** The standard procedure was followed by use of 4-cyanopyridine *N*-oxide (**21**, 252.5 mg, 2.018 mmol, 1.0 equiv), sodium (111.4 mg, 4.843 mmol, 2.4 equiv), THF (10 mL), and liquid ammonia (40 mL) to give pure **22** (199.4 mg, 4.407 mmol) as a colorless oil in 91% yield.

**4-Methylanisole (24). Method 1.** The standard procedure was followed by use of 4-methoxybenzyl alcohol (**23**, 286.4 mg, 2.031 mmol, 1.0 equiv), calcium turning (179.1 mg, 4.468 mmol, 2.2 equiv), THF (10 mL), and liquid ammonia (40 mL). After the reaction mixture was stirred for 2 h, it was worked up and the residue was purified by chromatography on silica gel (10% EtOAc in hexanes as eluant) to give pure **24** (233.7 mg, 1.915 mmol) as a colorless oil in 95% yield: GC  $t_R$  6.07 min; TLC  $R_f$  0.78 (10% EtOAc in hexanes);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  2.27 (s, 3 H), 3.76 (s, 3 H), 6.78–7.08 (m, 4 H); IR (neat) 3044 (w, ArH), 2935 (s, C—H), 1621 (m, Ar), 1511 (s, Ar), 1459 (m), 1294 (m), 1244 (s, C—O), 1177 (w), 1037 (s), 814 (s), 719 (w)  $\text{cm}^{-1}$ ; MS  $m/z$  (relative intensity) 122 ( $\text{M}^+$ , 45), 112 (21), 108 (62), 107 (23), 91 (18), 81 (40), 79 (100), 77 (39), 52 (30), 51 (21). Its physical properties and spectroscopic characteristics are consistent with those of an authentic sample.<sup>29</sup>

**Method 2.** The standard procedure was followed by use of 4-methoxybenzyl alcohol (**23**, 288.7 mg, 2.089 mmol, 1.0 equiv), lithium wire (64.3 mg, 9.19 mmol, 4.4 equiv), THF (10 mL),

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and liquid ammonia (40 mL) to give pure **24** (245.0 mg, 2.005 mmol) as a colorless oil in 96% yield.

**Method 3.** The standard procedure was followed by use of 4-methoxybenzyl alcohol (**23**, 286.4 mg, 2.073 mmol, 1.0 equiv), sodium (200.2 mg, 8.701 mmol, 4.4 equiv), THF (10 mL), and liquid ammonia (40 mL) to give pure **24** (210.2 mg, 1.721 mmol) as a colorless oil in 83% yield.

**2-Methoxyphenethyl Alcohol (26). Method 1.** The standard procedure was followed by use of 4-(benzyloxy)-3-methoxystyrene (**25**, 377.3 mg, 1.523 mmol, 1.0 equiv), calcium turning (124.2 mg, 3.046 mmol, 2.0 equiv), THF (10 mL), and liquid ammonia (40 mL). After the reaction mixture was stirred for 2 h, it was worked up and the residue was purified by chromatography on silica gel (5% EtOAc in hexanes as eluant) to give pure **26** (219.9 mg, 1.447 mmol) as a colorless oil in 95% yield: GC  $t_R$  10.15 min; TLC  $R_f$  0.83 (10% EtOAc in hexanes); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  1.21 (t,  $J$  = 7.6 Hz, 3 H), 2.58 (q,  $J$  = 7.6 Hz, 2 H), 3.88 (s, 3 H), 5.48 (br, s, 1 H), 6.68–6.85 (m, 3 H); IR (neat) 3450 (s, OH), 2945 (s, C–H), 1606 (m, Ar), 1514 (m, Ar), 1449 (s), 1239 (s), 1033 (m, C–O), 806 (w) cm<sup>-1</sup>; MS  $m/z$  (relative intensity) 152 (M<sup>+</sup>, 36), 122 (8), 138 (9), 137 (100), 122 (11), 109 (5), 107 (4), 94 (7), 91 (9), 79 (6), 77 (8), 53 (5). Its physical properties and spectroscopic characteristics are consistent with those of an authentic sample.<sup>29</sup>

**Method 2.** The standard procedure was followed by use of 4-(benzyloxy)-3-methoxystyrene (**25**, 372.9 mg, 1.552 mmol, 1.0 equiv), lithium wire (43.5 mg, 6.21 mmol, 4.0 equiv), THF (10 mL), and liquid ammonia (40 mL) to give pure **26** (219.3 mg, 1.443 mmol) as a colorless oil in 93% yield.

**Method 3.** The standard procedure was followed by use of 4-(benzyloxy)-3-methoxystyrene (**25**, 364.8 mg, 1.518 mmol, 1.0 equiv), sodium (139.6 mg, 6.072 mmol, 4.0 equiv), THF (10 mL), and liquid ammonia (40 mL) to give pure **26** (212.3 mg, 1.396 mmol) as a colorless oil in 92% yield.

### Polyhydrofullerenes C<sub>60</sub>H<sub>2</sub>–C<sub>60</sub>H<sub>36</sub> (**27**). Method 1.

The standard procedure was followed by use of buckminsterfullerene C<sub>60</sub> (**27**, 34.5 mg, 0.050 mmol), calcium turning (57.8 mg, 1.44 mmol, 30.0 equiv), THF (10 mL), and liquid ammonia (40 mL). After the reaction mixture was stirred for 2 h, it was worked up to give the mixture of C<sub>60</sub>H<sub>*x*</sub> (**28**, 2 ≤ *x* ≤ 36, 29.3 mg) as a pale-yellow solid in ~85% yield. The intact C<sub>60</sub> (3.5 mg) was recovered in <10% yield. FAB/MS: MS  $m/z$  (relative intensity) 756 (M<sup>+</sup>, 12), 754 (24), 744 (16), 742 (23), 740 (44), 739 (74), 738 (100), 730 (21), 728 (23), 724 (25), 722 (24).

**Method 2.** The standard procedure as described as above was followed by use of lithium wire (20.2 mg, 2.88 mmol, 60.0 equiv) or sodium (66.5 mg, 2.89 mmol, 60.0 equiv) to give the same the mixture **28** in ~80% yield. The intact C<sub>60</sub> (3.5 mg) was recovered in <10% yield.

**Method 3.** The standard procedure was followed by use of buckminsterfullerene C<sub>60</sub> (**27**, 207.4 mg, 0.2881 mmol), calcium turning (23.1 mg, 0.571 mmol, 2.0 equiv), THF (10 mL), and liquid ammonia (40 mL). After the reaction mixture was stirred for 2 h, it was worked up to give the mixture of C<sub>60</sub>H<sub>*x*</sub> (**28**, 2 ≤ *x* ≤ 36, 16.6 mg) as a pale-yellow solid in ~8% yield. The intact C<sub>60</sub> (186.6 mg) was recovered in >90% yield.

**Method 4.** The standard procedure as described above was followed by use of lithium wire (7.9 mg, 1.2 mmol, 4.0 equiv) or sodium (21.1 mg, 0.922 mmol, 4.0 equiv) to give the same the mixture **28** in ~8% yield. The intact C<sub>60</sub> (186.8 mg) was recovered in >90% yield.

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