bridged to give a cavitand using CH_2BrCl/K_2CO_3.[7] The crystal structure of a hexadecol derivative was resolved and will be reported elsewhere.

The representative synthetic procedure of hexadecol 2 is as follows: Resorcinol (4.2 g, 38.1 mmol), octanal (4.5 mL, 28.8 mmol), and 4,4'-bisformylbiphenyl (1.0 g, 4.7 mmol) were dissolved in 95% EtOH (50 mL) at 80℃. Through the condenser, conc. HCl (12.5 mL) was slowly added, and then the mixture was stirred for 18 h at 80℃ under argon. After cooling to room temperature, the solution was poured into 500 mL of water with shaking. The precipitation was filtered, washed with 200 mL of water 3 times, and then dissolved in minimum amount of hot MeOH. After standing overnight, octol was filtered off and the filtrate was concentrated. The concentrate was loaded on C-18 capped reversed phase flash column (5×15 cm, 25% H_2O in acetone and then 5 to 3% H_2O in MeOH).[13] The best portions were collected and the solvent was evaporated to give precipitates. The precipitates were filtered through medium fritted glass funnel and dried under high vacuum to give 1.2 g (14.6%) of hexadecol 2.

Conclusively we observed that the hetero condensation procedure described above is an efficient method to get hexadecols which could be valuable starting vessels for multifunctional hosts only if structually rigid bridging units (dialdehyde or bisresorcinol) were applied. The back-to-back connected hexadecol 2 and 3 could be derivatized to biscavitands and biscarcerands as well as monomers leading to a new kind of polymers formed not by covalent bonds but by π-π stacking interactions.[14] Unfortunately pure hexadecols 2 and 3 are too insoluble in CH_2Cl_2 or $CHCl_3$ to be useful for guest recognition studies in nonpolar solvents. Preparation of more soluble hexadecols and their molecular recognition studies are in progress.

Acknowledgement. The financial supports from Korea Science and Engineering Foundation and Korea Institute of Science and Technology are gratefully acknowledged.

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11. 2: mp>290℃ (decompose): ^{1}H NMR (200 MHz, Acetone-d_6) 0.85-0.91 (m, 18H, CH_3×6), 1.20-1.35 (m, 60H, CH_2×30), 1.97-2.13 (m, 12H, CH_2×6), 4.30-4.34 (m, 6H, methine), 6.09 (s, 2H, methine), 6.26 (s, 4H, Ar-H), 6.38 (s, 4H, Ar-H), 7.29 (s, 4H, ArH), 7.35 (s, 4H, Ar-H), 7.40, 7.44, 7.65, 7.69 (AB quartet, 8H, biphenyl), 8.39, 8.50, 8.56, 8.63 (four s, each 4H, OH, exchange with D_2O); FAB$^+$ MS (Xenon, NOBA) m/z 1714 (M^+, 27%). 1614 (M^+ -$(CH_2)_6CH_3$+1, 100%); Anal. Calcd for $C_{110}H_{138}O_{16}+2H_2O$ (dried at 80℃ ×10^{-5}×5 hr): C, 75.40; H, 8.18. Found: C, 75.32; H, 8.03.
12. 3: mp>220℃ (decompose); ^{1}H NMR (200 MHz, Acetone-d_6) 0.80-1.00 (m, 18H, CH_3×6), 1.13-1.50 (m, 36H, CH_2×18), 1.95-2.25 (m, 30H, CH_3×6+CH_2×6), 4.36 (m, 6H, methine×6), 6.11 (s, 2H, methine×2), 7.11, 7.14 (s, 8H, Ar-H), 7.39, 7.43, 7.67, 7.71 (AB quartet, 8H, biphenyl), 7.86, 7.94, 7.98, 8.11 (four s, each 4H, OH); FAB$^+$ MS (Xenon, NOBA) m/z 1659 (M^++1, 50%), 1587 (M^+-$(CH_2)_4CH_3$, 50%); Anal. Calcd for $C_{106}H_{130}O_{16}+2H_2O$ (dried at 80℃ ×10^{-5}×5 hr): C, 75.06; H, 7.96. Found: C, 75.12; H, 7.97.
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Transformation of Primary Carboxamides to Aldehydes by Sodium Tris(dialkylamino)aluminum Hydrides

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Received June 30, 1994

A new class of reducing agents, dialkylamino-substituted derivatives of lithium aluminum hydride have appeared useful reagents for the selective transformation of organic functionalities.[1] Especially, the successful conversion of primary carboxamides to the corresponding aldehydes by lithium tris (diethylamino)aluminum hydride (LTDEA)[1a,e] and lithium tripiperidinoaluminum hydride (LTPDA)[1c] provides a new methodology in organic synthesis.

Very recently, we have synthesized various dialkylamino-substituted derivatives of sodium aluminum hydride, and applied them for selective reduction of organic functionalities.[2] In the course of this study, we found that the sodium deriva-

Table 1. Yields of Aldehydes in the Reduction of Representative Primary Carboxamides with STDEA, STDBA, and STPDA in Tetrahydrofuran[a]

Amide	Temp. (℃)	Yields (%) STDEA[b]	STDBA[c]	STPDA[c]
Benzamide	25	95,93[d],86[d,e]	85[d],90	85[d,i],95[i],89
	50	88[g],80[g,e]	82[f],90[g]	88[g,i],84[g]
o-Toluamide	25	70	65	66
4-Methoxybenzamide	25	91	87	95
2-Ethoxybenzamide	25	75	70	80
2-Chlorobenzamide	25	67	64	75
2-Nitrobenzamide	25	38	41	35
Nicotinamide	25	39	42	66
Acetamide	50	47	40	48
2-Chloroacetamide	50	25	26	24
Trimethylacetamide	50	68	66	68
n-Butyramide	50	53	44	54
Isobutyramide	50	77	68	71
Caproamide	25	35[j]	34[j]	32[i,j]
	50	59,55[k],50[e,k]	48[g],50	58[i],50
Octadecanamide	50	96	82	94
Cyclohexanecarboxamide	50	82	80	81

[a] Ratio of reagent to compound is 2 : 1, unless otherwise indicated. Yields are based on the formation of 2,4-dinitrophenylhydrazone. [b] Reacted for 24 h for aromatic and 3 h for aliphatic. [c] Reacted for 72 h for aromatic and 6 h for aliphatic. [d] Reacted for 48 h. [e] Reagent : compound = 1.5 : 1. [f] Reacted for 1 h. [g] Reacted for 3 h. [i] Reagent : compound = 2.2 : 1. [j] Reacted for 72 h. [k] Reacted for 6 h.

tives effect such transformation equally well. Herein, we wish to report a simple method for conversion of primary carboxamides to the corresponding aldehydes in good yields.

Like lithium aluminum hydride,[1h] sodium aluminum hydride reacts readily with only 3 equivalents of dialkylamine with the evolution of 3 equivalents of hydrogen at 0 ℃, even in the presence of excess amines, to form stable sodium tris(dialkylamino)aluminum hydrides[3] (Eq. 1).

$$NaAlH_4 + 3\ R_2NH \xrightarrow[0\ ℃ \rightarrow 25\ ℃]{THF} Na(R_2N)_3AlH + 3\ H_2\uparrow \quad (1)$$

STDEA(R = Et)
STDBA(R = Bu)
STPDA(R_2N = N⟨ ⟩)

These sodium tris(dialkylamino)aluminum hydrides show an unique reducing characteristics.[2c] Excess reagent reduces both aliphatic and aromatic carboxamides with evolution of hydrogen slowly in an amount of less than 1 equivalent. In the case of utilizing 2 equivalents of reagent, one reagent is consumed for hydrogen evolution and the other for reduction, leading to the formation of aldehyde intermediate, as is the case of reduction with the lithium derivatives.[1j,k]

As shown in Table 1, all the sodium derivatives studied are good enough to convert aromatic primary carboxamides to the corresponding aldehydes. Benzamide is readily reduced to benzaldehyde in 24-72 h at 25 ℃ in yields of 90-95%. Derivatives containing substituents, such as alkyl, alkoxy and halogeno groups on benzene ring, are readily accommodated to yield better than 65%. However, the yield for nitrobenzamide is significantly lower, apparently due to the reduction of nitro group itself by these reagents. Nicotinamide undergoes the reaction in yields of 40-65%. The reduction of aliphatic primary carboxamides requires a higher reaction temperature (50 ℃) to afford better yields of aldehydes. The yields of aldehydes from the aliphatic series are variable with structure in the range of 25-95%. Generally, the more sterically hindered aliphatic carboxamides are, the higher yields of aldehydes are. Thus, the yields of aldehydes from acetamide, *n*-butyramide and caproamide are only around 50%, whereas the yields from trimethylacetamide, isobutyramide, octadecanamide and cyclohexanecarboxamide are 70-95%.

The following procedure for the reduction of 4-methoxybenzamide with STDEA is illustrative. An oven-dried, 50-mL flask, fitted with a side arm and a bent adapter connected to a mercury bubbler, was charged with 0.454 g of 4-methoxybenzamide (3.0 mmol) and 1.7 mL of THF. To this solution was added 4.0 mL of 1.5 M STDEA (6.0 mmol) solution in THF at 25 ℃. The reaction mixture was stirred for 24 h at that temperature. Analysis of the reaction mixture with 2,4-dinitrophenylhydrazine yielded 91% of the corresponding aldehyde: mp of the hydrazone 252-254 ℃ (lit.[4] mp. 253-254 ℃).

The use of sodium aluminum hydride rather than lithium aluminum hydride[5,6] for reduction of organic functionalities and preparation of other reducing agents would be desirable because of lower cost of production and its relative mildness. Therefore, sodium tris(dialkylamino)aluminum hydrides would be used more widely in organic synthesis.

Acknowledgment. The support of this work by the Organic Chemistry Research Center-KOSEF is gratefully acknowledged. The senior author thanks Ethyl Corporation for the generous supply of sodium aluminum hydride.

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J. *Org. Prep. Proced. Int.* **1994**, *26*, 000. (c) The full scope of reducing characteristics of sodium tris(dialkylamino) aluminum hydrides is under investigation.
3. The ^{27}Al NMR spectra showed a broad singlet at δ 116 for STDEA, δ 115 for STDBA, and δ 114 for STPDA, relative to $Al(H_2O)_6^{3+}$.
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Samarium(II) Iodide Promoted Intramolecular Coupling between Carbonyl Groups and Activated Olefins Under Sterically Crowded Environment

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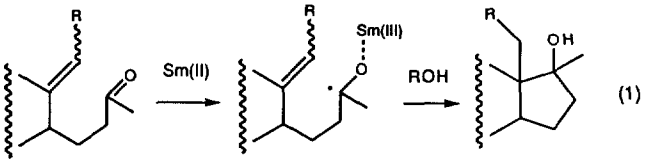
Received June 22, 1994

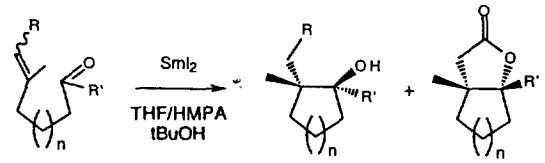
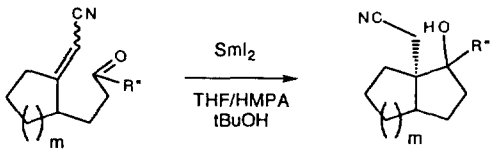
We have reported that intramolecular radical addition to properly activated olefins can be successfully employed in the construction of carbon centers under sterically crowded environment.[1] Since it is well known that the reaction of samarium(II) iodide[2] with the carbonyl group of ketones or aldehedes generate ketyl radicals, it would be interesting to investigate the addition ability of ketyl radicals to olefins under sterically crowded environment. The transformations of interest can be represented by the following equation (1).



(1)

The results of the investigation were shown in Table 1. Our study was focused only on the olefins with activating groups, that is, electron withdrawing groups such as alkoxycarbonyl (entries 1-4) or nitrile (entries 5-10) groups. The yields obtained for the corresponding five membered ring forming cases were not poor ($n=1$, entries 1 and 2). The cyclization in which six membered ring would form ($n=2$, entries 3 and 4), however, proceeded ineffectively. In particular, the coupling between the ketone group and the olefin ($R'=CH_3$) was not successful (entry 4). It has been known

Table 1. Samarium(II) iodine promoted cyclization to construct a quaternary carbon center

Entry[a,b]	Educt	Product (Yield)	
			
1	$n=1$, $R=CO_2Et$, $R'=H$	**1** (75%)	–
2	$n=1$, $R=CO_2Et$, $R'=CH_3$	**2** (68%)	–
3	$n=2$, $R=CO_2Et$, $R'=H$	–	**3** (43%)
4	$n=2$, $R=CO_2Et$, $R'=CH_3$	(0%)	–
5	$n=2$, $R=CN$, $R'=H$	**4** (45%)	–
6	$n=2$, $R=CN$, $R'=CH_3$	(0%)	–
			
7	$m=1$, $R''=H$	**5** (61%)	
8	$m=1$, $R''=CH_3$	**6** (61%)	
9	$m=2$, $R''=H$	**7** (71%)	
10	$m=2$, $R''=CH_3$	**8** (74%)	

[a]E/Z ratio of the starting materials (>9 : 1) (entries 1-6). [b]E/Z ratio of the starting materials (7 : 3 to 15 : 1) (entries 7-10).

that the rate of the free radical addition to olefins is much more increased when olefin is activated with the nitrile group than with the alkoxycarbonyl group.[3] This is what exactly observed when CO_2R was replaced with CN. From the entry 5 it can be learned that the 6-heptenyl radical type cyclization can be realized albeit in low yield. The coupling between the ketone and the olefin is, however, not yet feasible (entry 6).

The difference in the cyclization rates upon replacement of the olefin activating group from CO_2R to CN is clearly shown in the case of producing fused ring products (entries 7-10). The cyclizations were, in fact, not possible for the olefins substituted with alkoxycarbonyl groups. It could be, however, efficiently achieved even under sterically crowed environment with olefins activated with nitrile groups.

A critical point that should be addressed is the stereoselectivity of the products formed. In each case single isomer was observed exclusively. The excellent stereoselectivity has been frequently reported in the samarium(II) iodide promoted couplings, especially in the intramolecular carbonyl-olefin couplings in which the predominant formation of *trans*-products was observed.[4] The *trans* stereochemistry of the products **1** and **2** is also supported since no lactone was formed. The cyclized product **3** has, however, a *cis* stereochemistry since it was proved to be a lactone. The *trans* stereochemistry of **4** was also assumed, although the stereochemistry was nor rigorously determined in this case.

This stereochemical aspect became more fascinating, considering the products obtained in the cases shown in entries