The typical procedure for β-benzenesulfenylation of enones is as follows. To a solution of triphenylphosphine (252.4 mg, 0.97 mmol) in tetrahydrofuran (4 m*l*) were added 2-cyclohexen-1-one (88.4 mg, 0.92 mmol) and TBSOTf (266.9 mg, 1.01 mmol) at 0℃. After being stirred at room temperature for 30 min, the reaction mixture was cooled to −78℃ and *n*-butyllithium (0.58 m*l*, 0.97 mmol) was added dropwise to give a black-colored solution. The reaction mixture was stirred for 30 min at −78℃ and phenyl disulfide (220.5 mg, 1.01 mmol) in tetrahydrofuran (3 m*l*) was added to the ylide solution. After being warmed to room temperature. TBAF (1.38 m*l*, 1.38 mmol) was added and the reaction mixture was stirred at room temperature for 2 h. The extractive work-up and chromatographic separation gave 3-benzenesulfenyl-2-cyclohexen-1-one (140.8 mg, 75%).

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## References

1. T. Mukaiyama, K. Inomata, and M. Muraki, *J. Am. Chem. Soc.*, **95**, 967 (1973).
2. W. R. Leonard and T. Livinghouse, *J. Org. Chem.*, **50**, 730 (1985).
3. A. Itoh, S. Ozawa, K. Oshma, and H. Nozaki, *Tetrahedron Lett.*, 361 (1980).
4. M. Suzuki, T. Kawagishi, and R. Noyori, *Tetrahedron Lett.*, 1809 (1981).
5. (a) A. P. Kozikowski and S. H. Jung, *J. Org. Chem.*, **51**, 3402 (1986); (b) A. P. Kozikowski and S. H. Jung, *Tetrahedron Lett.*, **27**, 3227 (1986); (c) H. Cristau, E. Torreilles and C. Barois-Gacherieu, *Synth. Commun.*, **18**, 185 (1988); (d) C. K. McClure and C. W. Grote, *Tetrahedron Lett.*, **32**, 5313 (1991).
6. (a) S. Kim and P. H. Lee, *Tetrahedron Lett.*, **29**, 5413 (1988); (b) S. Kim, P. H. Lee, and S. S. Kim, *Bull. Korean Chem. Soc.*, **10**, 218 (1989).
7. (a) R. E. Ireland and J. A. Marshall, *J. Org. Chem.*, **27**, 1615 (1962); (b) R. M. Coates and R. L. Sowerby, *J. Am. Chem. Soc.*, **93**, 1027 (1971); (c) T. A. Bryson, R. E. Dardis and R. B. Gammill, *Tetrahedron Lett.*, 743 (1978).
8. B. M. Trost and A. C. Lavoie, *J. Am. Chem. Soc.*, **105**, 5075 (1983).

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# Preparation of Lithium Dialkylaminoaluminum Hydrides. A New Class of Reducing Agents

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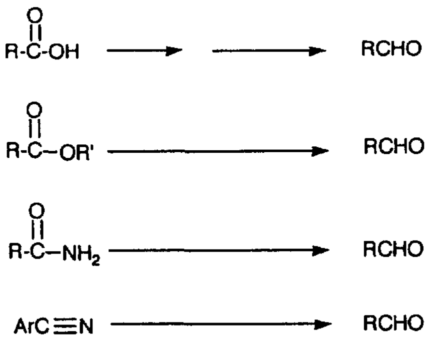
The reaction in tetrahydrofuran of lithium aluminum hydride with representative dialkylamines of varying steric requirements was examined in detail to establish the generality of this synthesis of the corresponding lithium dialkylaminoaluminum hydrides, $Li(R_2N)_nAlH_{4-n}$ ($n$=2, 3). In cases involving a less hindered dialkylamine, such as diethylamine, di-*n*-butylamine and di-*n*-hexyl amine, the reaction is very fast and gives the corresponding trisubstituted derivatives cleanly. However, a moderately hindered dialkylamine, such as diisobutylamine, reacts with lithium aluminum hydride slowly to afford the corresponding disubstituted derivative at 25℃. In this case a trisubstituted derivative can also be obtained under reflux. The reaction of more hindered dialkylamine, such as diisopropylamine and dicyclohexylamine, is sluggish even at 50℃ and gives the corresponding disubstituted derivatives cleanly. Cyclic secondary amines, such as pyrrolidine, piperidine, morpholine and N-methylpiperazine, undergo the reaction rapidly to yield the corresponding trisubstitutd derivatives even at 0℃. Finally, the reaction with diphenylamine gives the corresponding disubstituted derivative cleanly.

Trisubstituted aluminohydrides, such as lithium trimethoxy-, triethoxy- and tri-*t*-butoxyaluminohydrides, have evolved as attractive selective reducing agents in organic synthesis.[1] They have been synthesized by treatment of 1 equiv of lithium aluminum hydride solution with 3 equiv of the corresponding alcohols.[1d, 2]

Recently we synthesized some dialkylamino-substituted derivatives of lithium aluminum hydride and applied them to the selective reduction of organic functionalities. They have proven to be useful selective reducing agents, especially in the conversion of carboxylic acid derivatives into the corresponding aldehydes.[3] These unique characteristics have been of great interest. Accordingly, we undertook a study to develop a general procedure for the synthesis of lithium dialkylaminoaluminum hydrides in tetrahydrofuran with various dialkylamines of different steric environments.



$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH \longrightarrow \quad \longrightarrow RCHO$$

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OR' \longrightarrow RCHO$$

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 \longrightarrow RCHO$$

$$ArC{\equiv}N \longrightarrow RCHO$$

## Results and Discussion

A representative series of dialkylamines with various steric and electronic environments were selected for the present study and their reaction with lithium aluminum hydride studied. The stability of the resulting lithium dialkylaminoaluminum hydrides was also examined by $^{27}$Al-NMR spectra and measuring the number of moles of $H_2$ evolved by hydrolysis of aliquots of the reagent solution at appropriate time intervals. The reagent were characterized by IR and $^{27}$Al-NMR spectroscopy.

The approximate rates and stoichiometry of the reaction

**Table 1.** Reaction of Lithium Aluminum Hydride with Excess Secondary Amines in Tetrahydrofuran

| Amine | Reaction Temp.(℃) | Reaction time (h)[b] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 0.5 | 1.0 | 3.0 | 6.0 | 12.0 | 24.0 | 48.0 | 72.0 |
| Diethylamine | 0 | 2.51 | 2.88 | 3.01 | 3.01 | | | | |
| | 25 | 2.72 | 2.94 | 3.02 | 3.02 | | | | |
| Diisopropylamine | 0 | 0.00 | 0.00 | 0.00 | | | | | |
| | 50 | 0.06 | 0.12 | 0.35 | 0.67 | 1.15 | 1.70 | 2.02 | 2.02 |
| Di-*n*-butylamine | 0 | 2.40 | 2.73 | 2.92 | 3.01 | 3.01 | | | |
| | 25 | 2.65 | 2.96 | 3.02 | 3.02 | | | | |
| Diisobutylamine | 0 | 0.30 | 0.60 | 1.25 | 1.75 | 2.01 | 2.01 | | |
| | 25 | 1.40 | 1.90 | 2.00 | 2.02 | 2.02 | – | | |
| | Reflux | 2.81 | 2.98 | 3.02 | – | – | – | 3.02 | |
| Di-*n*-hexylamine | 0 | 1.92 | 2.15 | 2.64 | 3.01 | | | | |
| | 25 | 2.43 | 2.87 | 3.02 | | | | | |
| | 50 | 2.92 | 3.01 | | | | | | |
| Dicyclohexylamine | 0 | 0.00 | 0.00 | 0.00 | | | | | |
| | 50 | 0.30 | 0.50 | 0.95 | 1.35 | 1.79 | 2.01 | 2.02 | 2.02 |
| Pyrrolidine | 0 | 2.70 | 3.02 | 3.02 | | | | | |
| | 25 | 2.72 | 3.02 | 3.08 | 3.21[c] | 3.42 | 3.70 | 3.97 | 4.02[c] |
| Piperidine | 0 | 2.64 | 2.96 | 3.01 | 3.01 | | | | |
| | 25 | 2.78 | 3.01 | 3.01 | | | | | |
| Morpholine | 0 | 3.01 | 3.01 | | | | | | |
| | 25 | 3.02 | 3.02 | | | | | | |
| N-Methylpiperazine | 0 | 2.05 | 2.87 | 3.02 | 3.02 | | | | |
| | 25 | 2.72 | 3.01 | 3.01 | | | | | |
| Diphenylamine | 0 | 0.90 | 1.20 | 1.70 | 1.93 | 2.02 | | | |
| | 25 | 1.80 | 2.02 | 2.02 | | | | | |

[a] Reacted with 4 equiv of dialkylamine, [b] Mmol of hydrogen evolved per mmol of $LiAlH_4$.

**Table 2.** Reaction of Lithium Aluminum Hydride with Diisobutylamine in Tetrahydrofuran

| Amine reagent | Reaction Temp.(℃) | Reaction time (h)[a] | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0.5 | 1.0 | 3.0 | 6.0 | 12.0 | 24.0 |
| 2 : 1 | 0 | 0.22 | 0.39 | 1.05 | 1.33 | 1.75 | 2.01 |
| | 25 | 1.37 | 1.58 | 1.66 | 2.02 | | |
| 3 : 1 | 25 | 1.39 | 1.75 | 2.01 | 2.01 | | |
| | Reflux | 2.61 | 2.81 | 2.98 | 3.02 | | |
| 4 : 1 | 0 | 0.30 | 0.60 | 1.25 | 1.75 | 2.01 | |
| | 25 | 1.40 | 1.90 | 2.02 | 2.02 | | |
| | Reflux | 2.81 | 2.98 | 3.02 | 3.02 | | |

[a] Mmol of hydrogen evolved per mmol of $LiAlH_4$.

of lithium aluminum hydride with 4 equiv of dialkylamines at various reaction temperature were examined in order to establish the generality of this synthesis of lithium dialkylaminoaluminum hydrides. The course of the reaction was monitored by calculating the moles of hydrogen evolved. These results are summarized in Table 1. The reactivity of dialkylamines with lithium aluminum hydride and the stoichiometry of the reaction varied markedly with the steric requirements of the dialkylamines. Thus, in those cases where the alkyl group was a less hindered straight chain such as diethylamine, di-*n*-butylamine, or di-*n*-hexylamine the reaction evolved 3 equiv of hydrogen readily within 6 h at 0℃ or 25℃ and no further hydrogen evolution even in the presence of excess dialkylamines was apparent. However, in case where the alkyl group was a moderately hindered dialkylamine such as diisobutylamine, the reaction was slow and stopped at the stage conresponding to a disubstituted compound at 0℃ or 25℃. In this case a trisubstituted derivative can also be obtained when the reaction is carried out with three equivalent or excess diisobutylamine under reflux (Table 2). The reaction of more hindered dialkylamines, such as diisopropylamine and dicyclohexylamine, did not take place at 0℃, but evolved hydrogen slowly to reach the disubstituted stage in 48 h at 50℃. Cyclic secondary amines, such as pyrrolidine, piperidine, morpholine and N-methylpiperazine, reacted with lithium aluminum hydride rapidly to evolve only 3 equiv of hydrogen to indicate the formation of the corresponding trisubstituted derivatives both at 0℃ and 25℃, except for the case of pyrrolidine at room temperature. The reaction with excess pyrrolidine at 25℃ proceeded to the tetrasubstituted stage with concurrent formation of a white precipitate. It is worthwhile to note that the reaction with morpholine formed a white precipitate after the evolution of 3 equiv of hydrogen. Finally, the reaction with diphenylamine evolved 2 equiv of hydrogen to form the corresponding disubstituted derivative at 0℃ or 25℃.

On the basis of results in Table 1 and 2, we utilized a

**Table 3.** Reaction Conditions for the Synthesis of Lithium Dialkylaminoaluminum Hydrides in Tetrahydrofuran[a]

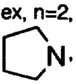
| Entry | Dialkylaminoaluminum hydride | Amine reagent | Reaction Temp. (℃) | Reaction time (h) |
|---|---|---|---|---|
| 1 | tris(diethylamino)aluminum hydride | 3 : 1 | 25 | 6 |
| 2 | tris(di-*n*-butylamino)-aluminum hydride | 3 : 1 | 25 | 6 |
| 3 | tris(di-*n*-hexylamino)-aluminum hydride | 3 : 1 | 25 | 6 |
| 4 | bis(diisopropylamino)-aluminum hydride | 2 : 1 | 50 | 72 |
| 5 | bis(diisobutylamino)-aluminum hydride | 2 : 1 | 25 | 6 |
| 6 | tris(diisobutylamino)-aluminum hydride | 3 : 1 | Reflux | 6 |
| 7 | bis(dicyclohexylamino)-aluminum hydride | 2 : 1 | 50 | 48 |
| 8 | tripyrrolidinoaluminum hydride | 3 : 1 | 0 | 3 |
| 9 | tripiperidinoaluminum hydride | 3 : 1 | 25 | 3 |
| 10 | trimorpholinoaluminum hydride[b] | 3 : 1 | 25 | 1 |
| 11 | tris(N-methylpiperazino)-aluminum hydride | 3 : 1 | 25 | 3 |
| 12 | bis(diphenylamino)aluminum hydride | 2 : 1 | 25 | 3 |

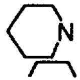
[a] 5% Excess dialkylamine utilized, [b] White precipitate formed.

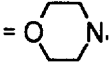
slight excess over the stoichiometric amount of dialkylamines (5% excess) in the reaction with lithium aluminum hydride under the practical condition. The reaction conditions for this synthesis are summarized in Table 3.

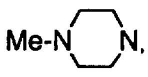
$Li(R_2N)_nAlH_{4-n}$

1, R = Et, n=3, LTDEA
2, R = *n*-Bu, n=3, LTDBA
3, R = *n*-Hex, n=3, LTDHA
4, R = *i*-Pr, n=2, LBDIPA
5, R = *i*-Bu, n=2, LBDIBA
6, R = *i*-Bu, n=3, LTDIBA
7, R = c-Hex, n=2, LBDCHA


8, $R_2N$ = N, n=3, LTPRA


9, $R_2N$ = N, n=3, LTPDA


10, $R_2N$ = O N, n=3, LTMPA


11, $R_2N$ = Me-N N, n=3, LTMPPA

12, R = ph, n=2, LBDPA

The dialkylaminoaluminum hydrides thus prepared in THF were characterized by IR and $^{27}$Al-NMR spectroscopy and the results are summarized in Table 4. Solution of the lithium dialkylaminoaluminum hydrides in THF display typical absorption in the IR: a strong absorption around 1650 cm$^{-1}$, attributed to the Al-H stretching vibration. The $^{27}$Al-NMR spectra of the THF solutions of lithium dialkylaminoaluminum hydride exhibit broad singlet peaks around δ 120-130 downfield region relative to $[Al(H_2O)_6]^{3+}$ as a reference. Among the derivatives examined, only one exception was noted. Thus, lithium trimorpholinoaluminum hydride precipitates from the reaction mixture. The white solid melts at 312℃. All the lithium dialkylaminoaluminum hydrides examined were stable to disproportionation for an extended period of time provided the THF solutions of the aluminum hydride reagents were maintained under a positive pressure of nitrogen at 0℃. During the period, moreover, no significant change in the hydride concentration was observed.

**Table 4.** Infrared and $^{27}$Al-NMR Spectra of Lithium Dialkylaminoaluminum Hydrided in Tetrahydrofuran

| Entry | $Li(R_2N)_nAlH_{4-n}$ | IR $\nu_{Al-H}$, cm$^{-1}$ | $^{27}$AL-NMR chemical shift[a], δ |
|---|---|---|---|
| 1 | LTDEA | 1695 | 120 |
| 2 | LTDBA | 1650 | 128 |
| 3 | LTDHA | 1635 | 130 |
| 4 | LBDIPA | 1670 | 108 |
| 5 | LBDIBA | 1640 | 127 |
| 6 | LTDIBA | 1660 | 132 |
| 7 | LBDCHA | 1675 | 124 |
| 8 | LTPRA | 1660 | 125 |
| 9 | LTPDA | 1665 | 124 |
| 10 | LTMPA[b] | – | – |
| 11 | LTMPPA | 1630 | 123 |
| 12 | LBDPA | 1690 | 137 |

[a] Chemicals shifts are relative to $[Al(H_2O)_6]^{3+}$. All spectra are broad singlets, [b] An insoluble white solid in THF; mp. 312℃.

## Conclusion

The reaction of lithium aluminum hydride with dialkylamines provides the corresponding bis- or tris(dialkylamino)-aluminum hydrides, depending upon the steric bulk of the alkyl groups of the dialkylamine. Thus, in cases involving a less hindered dialkylamine such as diethylamine, di-*n*-butylamine, di-*n*-hexylamine, pyrrolidine, piperidine, morpholine, and N-methylpiperazine, the corresponding trisubstituted derivatives are readily produced at 25℃. In cases involving a more hindered dialkylamine such as diisopropylamine, dicyclohexylamine, and diphenylamine, the reaction at 50℃ affords the corresponding disubstituted derivatives cleanly. However, in the case of a moderately hindered dialkylamine such as diisobutylamine, a disubstituted derivative is produced exclusively at 25℃, and a trisubstituted one under reflux. These dialkylaminoaluminum hydrides examined are stable to disproportionation.

As reported previously in the literature,[3] the dialkylamino-substituted derivatives of lithium aluminum hydride appear to be useful selective reducing agents, especially in the conversion of carboxylic acid derivative into aldehydes. Further-more, since every dialkylamine is expected to be an auxiliary of this class of reducing agents, this study should extend the scope of selective reduction in organic synthesis.

## Experimental Section

All glassware used was dried in an oven, assembled hot, and cooled with a stream of nitrogen. All reaction were carried out under nitrogen atmosphere. Experimental techniques used in handing air-sensitive materials are described elsewhere.[4] Tetrahydrofuran was dried over a 4-Å molecular sieve and distilled from sodium benzophenone ketyl just prior to use. Lithium aluminum hydride (LAH) was from the Aldrich Company and was standardized by measurement of the $H_2$ produced by hydrolysis prior to use. All of the dialkylamines were high grade commercial reagent (Aldrich) and distilled after drying over KOH. $^{27}$Al-NMR spectra were recorded on a Bruker WP 80 SY spectrometer and all $^{27}$Al-NMR chemical shifts were reported in $\delta$ (ppm) relative to $[Al(H_2O)_6]^{3+}$. IR spectra were recored on a Perkin-Elmer 1330 spectrometer.

**Reaction of Lithium Aluminum Hydrides with Excess Dialkylamines.** The reaction of LAH with 4 equiv of $Et_2NH$ is representative. An oven-dried, 100 m*l*, round-bottomed flask with a side arm, a condenser, and an adaptor was attached to a mercury bubbler. The flask flushed with $N_2$ and maintained under a static pressure of $N_2$. In the flask was placed 5.0 m*l* LAH-THF solution (2.0 M, 10.0 mmol) and the flask was brought to 0℃ by using an ice-bath. A total of 2.93 g (40.0 mmol) of $Et_2NH$ was added dropwise with stirring. The evolution of 3.01 equiv of hydrogen was observed in 3 h at 0℃ and no further hydrogen evolution was apparent. An aliquot of the resulting solution was hydrolyzed to evolve 1.00 equiv of hydrogen.

**Preparation of Lithium Dialkylaminoaluminum Hydrides.** The preparation of lithium tris(diethylamino)aluminum hydride (LTDEA) is illustrative. In a 100 m*l*, round-bottomed flask was placed 50 m*l* of 2 M solution of LAH (100 mmol) in THF and the solution was kept at 25℃ by using a water bath. To this solution was added 23 g of $Et_2NH$ (315 mmol, 5% excess) dropwise with vigorous stirring. The reaction mixture was stirred for 6 h at 0℃ until the evolution of hydrogen was complete. There resulting LTDEA solution in THF was diluted with THF to be 1.0 M, and the $^{27}$Al-NMR spectrum of the solution showed a broad singlet at 120 ppm. The IR spectrum of the solution displayed a strong absorption at 1695 cm$^{-1}$, attributed to the Al-H stretching vibration.

In the case of morpholine, a white solid was precipitated from the reaction mixture after evolution of 3 equiv of hydrogen. The precipitate was filtered and washed with THF. The white solid, LTMPA, melted at 312℃. LTMPA, **11**, was also insoluble in $CH_2Cl_2$, $Et_2O$, or pentane.

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## References

1. (a) H. C. Brown and P. M. Weissman, *Israel J. Chem.*, **1**, 430 (1963); (b) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **80**, 5377 (1958); (c) P. M. Weissman and H. C. Brown, *J. Org. Chem.*, **31**, 283 (1966); (d) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **86**, 1085 (1964); (e) H. C. Brown and A. Tsukamoto, *ibid.*, **86**, 1089 (1964); (f) H. C. Brown and P. M. Weissman, *ibid.*, **87**, 5614 (1965); (g) H. C. Brown and H. R. Deck, *ibid.*, **87**, 5620 (1965).
2. (a) H. C. Brown and R. F. McFarlin, *J. Am. Chem. Soc.*, **80**, 5372 (1958); (b) H. C. Brown and C. J. Shoaf, *ibid.*, **86**, 1079 (1964).
3. (a) J. S. Cha, J. C. Lee, S. E. Lee, J. M. Kim, O. S. Kwon, H. S. Lee, and S. J. Min, *Tetrahedron Lett.*, **32**, 6903 (1991); (b) J. S. Cha, S. E. Lee, and H. S. Lee, *Bull. Korean Chem. Soc.*, **12**, 644 (1991); (c) J. S. Cha, J. C. Lee, S. E. Lee, and H. S. Lee, *ibid.*, **12**, 598 (1991); (d) J. S. Cha, J. C. Lee, S. E. Lee, and H. S. Lee, *Org. Prep. Proced. Int.*, **24**, 327 (1992); (e) J. S. Cha, S. E. Lee, and H. S. Lee, *ibid.*, **24**, 331 (1992); (f) J. S. Cha, S. J. Min, J. C. Lee, H. S. Lee, and S. E. Lee, *ibid.*, **24**, 335 (1992).
4. H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, "Organic Syntheses *via* Boranes", Wiley-Interscience, New York, 1975.

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# New Glyceroglycolipids from the Brown Alga *Sargassum thunbergii*

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The brown alga *Sargassum thunbergii* is growing on rocks in the lower littoral and sublittoral belts, and this species is the most common *Sargassum* in our coast.[1] This alga metabolites antitumor polysaccharide,[2] iodoamino acid of depressing the blood cholesterol level,[3] and particular calcium-binding substances.[4] As a part of search for new biologically active substances from marine organisms, we have examined the metabolites of the brown alga *S. thunbergii*. Here we describe the isolation and characterization of two new glyceroglycolipids (**1**, **3**).

The methanol extract of *S. thunbergii* (1.5 kg, collected at Chungmu, Kyung-nam Prefacture in August 1990) was concentrated into an aqueous residue, which was successively extracted with ethyl acetate and *n*-butanol. The ethyl acetate soluble portion was concentrated to give a brown solid (10 g). Repeated column chromatography of this residue with silica gel (Merck, Kiesel gel 60) ($CHCl_3$-MeOH$=7:1\rightarrow 3:1$), TSK gel (Toyo pearl HW-40F) (MeOH), octadecyl silica gel (Waters, μ-Bondapak $C_{18}$) (MeOH-$H_2O=5:1$), and HPLC