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LETTERS

Lithium Azidohydridodiisobutylaluminate in THF as An Efficient Azide Donor

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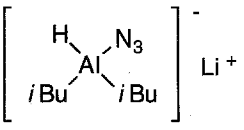
Abstract: Lithium azidohydridodiisobutylaluminate (**1**), prepared as a solution in THF from DIBAH and lithium azide at rt, transfers the azide rather than the hydride to the unsymmetrical epoxides regioselectively to produce *vic*-azidoalcohols in high yields.

Diisobutylaluminum hydride (DIBAH) and its ate complexes have the powerful ability to reduce a variety of functional groups[1]. We have recently shown that lithium *B*-azido-*B*-hydrido-9-BBN (**2**) transfers an azido group to the epoxides regioselectively to produce *vic*-azidoalcohols, even if **2** possesses a potential hydride functionality[2]. In connection with these unprecedented results, we have also prepared a structurally related aluminum reagent, lithium azidohydridodiisobutylaluminate (**1**), and examined its reactivities.



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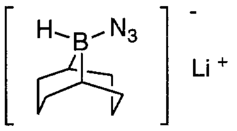

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Treatment of a suspension of lithium azide in dry THF with an equimolar amount of DIBAH at rt gave rise to a clear solution of **1** in a few minutes. Sodium azide, potassium azide, or cesium azide, however, afforded a salt-like mixture under the same condition. Treatment of potassium azide or cesium azide with DIBAH in dichloromethane also provided an emulsified solution[3]. Since lithium azide and DIBAH in THF gave a clear solution, we chose this ate complex and studied its reactivities.When benzaldehyde was added to this solution, no reduction took place even after 24 hr. Treatment of benzoyl chloride with this solution, however, afforded benzoyl azide in 95 % yield within 30 min at rt[4,5]. These results clearly indicate that **1** serves as an azide donor rather than a reductant even though it has a potential hydride functionality.

Since we found **1** transferred the azide rather than the hydride, we have further examined the ring opening reaction of various epoxides with this reagent . A typical reaction procedure is as follows: DIBAH (5.5 mmol, 5.5 ml of 1M solution in THF) was added to a stirred suspension of dry lithium azide (0.27 g, 5.5 mmol) in dry THF (10 ml) under argon atmosphere at rt, and the mixture was stirred for 30 min. To the resulting clear solution was added a solution of an unsymmetrical epoxide (5 mmol) in THF (5 ml) and the solution was stirred for 2 hr at rt. Treatment with aqueous sodium bicarbonate, usual work-up and silica gel column chromatography produced *vic*-azidoalcohols in high yields. The results are summarized in the Table.

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As shown in the Table, the azide attacked the less hindered carbon of the unsymmetrical epoxides. This implies that the regioselectivity is governed mainly by the steric factor rather than the electronic one. In the case of styrene oxide, however, the electronic factor dominated and 2-azido-2-phenylethanol was obtained in 72 % yield.

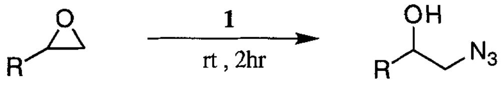

Table. Reaction of Epoxides with Lithium Azidohydridodiisobutylaluminate (**1**)

Entry	Description	Isolated Yield, %
1	R=CH_2CH_3	70
2	R=*n*-Hexyl	78
3	R=*N*-CH_2-Phthalimide	76
4	R=CH_2OPh	75
5	R=$(CH_2)_2CH=CH_2$	78

In conclution, it is demonstrated that lithium azidohydridodiisobutylaluminate (**1**), which can be so easily prepared as a solution in THF, has the ability to transfer the azide regardless of its potential hydride functionality and may thus be employed as one of the azide transferring reagents[6].This is, to our knowledge, the first example of the ate complex that is derived from DIBAH but does not transfer the hydride.

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2. Lee, H. W.; Kim, Y. J.; Chung, B. Y. *Bull. Korean Chem. Soc.* **1997**, *18*, 1144-1145.
3. Lithium azide or sodium azide did not form the ate complex with DIBAH in dichloromethane. Reaction of benzoyl chloride with the excess amounts of the resulting suspension produced benzyl alcohol only.
4. Sodium azide, potassium azide, or cesium azide with DIBAH in THF, and potassium azide or cesium azide with DIBAH in dichloromethane also reacted with benzoyl chloride to afford benzoyl azide.
5. Other acid chlorides such as phenacetyl chloride, cinnamoyl chloride, and *p*-chlorobenzoyl chloride also gave the corresponding acid azide in 93, 90, and 90 % yield, respectively.
6. (a) Previous references are cited in ref. 2. (b) Saito, A.; Saito, K.; Tanaka, A.; Oritani, T. *Tetrahedron Lett.* **1997**, *38*, 3955-3958.