Lithium Triethylborohydride and Monomeric Aluminium t-Butoxide as the Active Intermediates in the Reductive Opening of Tetrahydrofuran and Related Ethers by the Triethylborane Induced Reaction of Lithium Tri-t-butoxyaluminohydride

By HERBERT C. BROWN* and S. KRISHNAMURTHY
(*R. B. Wetherill Laboratory, Purdue University, Lafayette, Indiana* 47907)

Summary The remarkable reductive opening of tetrahydrofuran and related ethers by lithium tri-t-butoxyaluminohydride in the presence of triethylborane involves lithium triethylborohydride and a metastable monomeric aluminium t-butoxide formed initially in the reaction of the two reagents.

WE recently reported[1] that addition of even trace quantities of triethylborane to tetrahydrofuran (THF) solutions of lithium tri-t-butoxyaluminohydride (ltba), a very mild reducing agent,[2] resulted in the rapid reductive cleavage of THF. Surprisingly, triethylborane fails to induce a similar reductive cleavage of THF by the otherwise more powerful reducing agent, lithium trimethoxyaluminohydride (ltma).[3]

A possible explanation of these phenomena involved reaction of triethylborane with the sterically strained ltba to form $LiEt_3BH$ [equation (1)] but failure of the corresponding reaction with the less strained ltma. This explanation required that $LiEt_3BH$ be the reactive species responsible for the reductive opening of THF and related cyclic ethers.

$$Li(Bu^tO)_3AlH + Et_3B \longrightarrow LiEt_3BH + (Bu^tO)_3Al \qquad (1)$$

This hydride was readily prepared in quantitative yield from lithium hydride and triethylborane[4] in THF [equation (2)]. However, such solutions proved to be stable indefinitely and no evidence of reductive cleavage of the THF was detected.

$$LiH + Et_3B \xrightarrow[25^\circ]{THF} LiEt_3BH \qquad (2)$$

Indeed, convincing evidence was obtained that both ltba and ltma react with triethylborane to produce $LiEt_3BH$ and the corresponding aluminium alkoxide [equations (1), (3)]. The stereochemistry of the reduction of cyclic ketones, such as 2-methylcyclohexanone, varies greatly with individual reducing agents.[5] Accordingly, 2-methylcyclohexanone was treated with $LiEt_3BH$, ltba + Et_3B and ltma + Et_3B at 0° in THF for 30 min. The resulting product was analysed by g.l.p.c. for the *cis-trans* ratio in the 2-methylcyclohexanol product. The results, summar-

$$Li(MeO)_3AlH + Et_3B \longrightarrow LiEt_3BH + (MeO)_3Al \qquad (3)$$

ized in the Table, clearly support the conclusion that triethylborane reacts with both ltba and ltma to form $LiEt_3BH$.

Table

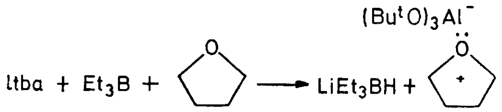
Isomer distribution in the reduction of 2-methylcyclohexanone by various complex hydrides

Reagent	*cis*-2-Methylcyclohexanol/%	*trans*-2-Methylcyclohexanol/%
ltba[5]	30	70
ltma[5]	69	31
$LiEt_3BH$	75	25
ltba + Et_3B	75	25
ltma + Et_3B	75	25

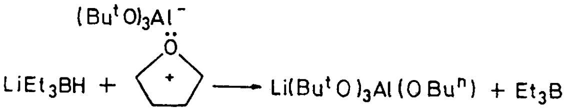
These results suggested the involvement of aluminium alkoxides in the reaction. Aluminium alkoxides are known to exist uniformly in polymeric form.[6] Aluminium methoxide is a high polymer of very low volatility and is highly insoluble in organic solvents. On the other hand, aluminium t-butoxide is a dimer, readily sublimed under reduced pressure. Possibly the difference in the behaviour of ltba and ltma in the reaction under investigation was the result of the difference in the nature of the two aluminium alkoxides produced in the reaction with triethylborane.

Addition of either aluminium methoxide or freshly sublimed aluminium t-butoxide† to a solution of $LiEt_3BH$ in THF failed to induce reductive cleavage of the THF.

Thus, it is possible that the reaction of triethylborane with ltba [equation (3)] produces aluminium t-butoxide in an exceptionally active form, possibly the hitherto unknown monomeric species capable of co-ordinating with the oxygen atom of THF and related ethers [equation (4)]. The highly active hydride reagent, $LiEt_3BH$, next reacts with the polarized carbon–oxygen bond to open the ring and to regenerate triethylborane [equation (5)].



(4)



(5)

THF and 2-methyltetrahydrofuran readily undergo this reductive cleavage, but very little cleavage was observed with 2,2-dimethyltetrahydrofuran[1] owing to hindrance towards the formation of the addition compound with monomeric aluminium t-butoxide.

Methanesulphonic acid (1 mol. equiv.) was added to ltba in THF at 25°. After 5 min, $LiEt_3BH$ (1 mol. equiv.) was added. Reductive opening of the THF ring was observed. When the ltba + $MeSO_3H$ solution was maintained for longer periods of time before the $LiEt_3BH$ was added, the amount of reductive opening of the THF ring decreased sharply. These results suggest that the THF–$Al(Bu^tO)_3$ adduct possess a limited life-time, probably converting into the inert aluminium t-butoxide dimer.

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† Aluminium t-butoxide exists as the dimer in THF, as revealed by n.m.r. examination of the solution.

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