Phase-transfer Catalysis in Reduction by Lithium Aluminium Hydride

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Ketones, alkyl and aryl halides, nitriles, and amides undergo reduction with lithium aluminium hydride in the solid $LiAlH_4$–hydrocarbon two-phase system in the presence of typical phase-transfer catalysts (crown ethers and quaternary ammonium salts), the reaction being characterized by good yields; solubilization of lithium aluminium hydride in non-polar solvents is demonstrated.

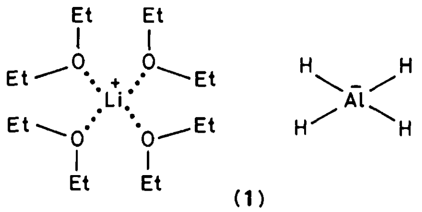
Heterogeneous reduction of various classes of compounds by lithium aluminium hydride, which facilitates the separation of reaction products, has recently been reported. The reactions include the reduction of aryl halides in hexane with silica-supported $LiAlH_4$[1] and the reduction of halogeno, alkoxy, and amino derivatives of group 4B elements in hydrocarbon solvents upon ultrasonic irradiation.[2]

We are unaware of any literature data describing reduction by lithium aluminium hydride under phase-transfer catalysis conditions.

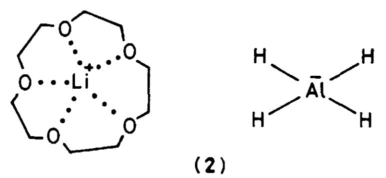
Table 1. Reduction of various organic compounds in the solid $LiAlH_4$–hydrocarbon–catalyst system (0.1 M solution, 5 mol % of catalyst with respect to the substrate, substrate: $LiAlH_4$ 1:2).

Substrate	Product	Catalyst	Solvent	T/°C	Time/h	Yield[a]
$CH_2[CH_2]_4CO$	$CH_2[CH_2]_4CHOH$[b]	—	Benzene	25	6	3
				80	1	16
$CH_2[CH_2]_4CO$	$CH_2[CH_2]_4CHOH$	15-crown-5	Benzene	25	3	15
					6	>95
				80	1	>95
$CH_2[CH_2]_4CO$	$CH_2[CH_2]_4CHOH$	18-crown-6	Benzene	25	3	>95
				80	1	>95
$CH_2[CH_2]_4CO$	$CH_2[CH_2]_4CHOH$	$Et_3(PhCH_2)NCl$	Benzene	25	3	47
				80	1	84
					6	>95
$CH_2[CH_2]_4CO$	$CH_2[CH_2]_4CHOH$	$(C_8H_{17})_4NBr$	Benzene	25	3	7
					6	12
				80	1	82
$C_6H_{13}Br$	C_6H_{14}	—	Benzene	80	6	traces
$C_6H_{13}Br$	C_6H_{14}	15-crown-5	Benzene	80	3	22
					6	83
$C_6H_{13}Br$	C_6H_{14}	$Et_3(PhCH_2)NCl$	Benzene	80	3	41
					6	92
PhBr	PhH	—	Toluene	80	6	—
PhBr	PhH	15-crown-5	Toluene	80	3	23
					6	47
PhBr	PhH	$Et_3(PhCH_2)NCl$	Toluene	80	3	27
					6	62
PhCN	$PhCH_2NH_2$	—	Benzene	80	1	16
PhCN	$PhCH_2NH_2$	15-crown-5	Benzene	80	1	>95
PhCN	$PhCH_2NH_2$	$Et_3(PhCH_2)NCl$	Benzene	80	1	86
$MeCONEt_2$	NEt_3	—	Xylene	80	1	12
$MeCONEt_2$	NEt_3	15-crown-5	Xylene	80	1	78
$MeCONEt_2$	NEt_3	$Et_3(PhCH_2)NCl$	Xylene	80	1	86

[a] As determined by g.l.c. [b] After hydrolysis.



(1)



(2)

It is generally believed that the use of $LiAlH_4$ in a two-phase catalytic system is in principle not possible,[3] since the addition of [2.1.1]-cryptand, an effective complexing agent for the Li^+ cation, during the reduction of carbonyl compounds considerably retards or completely stops the reaction.[4,5]

However, free Li^+ cations are also absent from a diethyl ether solution of $LiAlH_4$ which exists as the solvate (**1**).[6,7]

A similar situation is observed in the case of crown ethers. The Li^+–crown ether solvate formed, unlike the three-dimensional cryptate, has a planar structure,[8] hence its participation in reduction reactions in a similar way to (**1**) can be postulated.

A benzene solution of (**2**) can be obtained by adding an equimolar amount of 15-crown-5 to a $LiAlH_4$ suspension in benzene at room temperature. The i.r. spectrum of the benzene solution of (**2**) shows a band at ν(Al–H) 1685 cm^{-1} [ν(Al–H) 1740 cm^{-1} for (**1**)],[6] as well as bands at 1625 and 520 cm^{-1}. Atomic absorption analysis shows that the amount of aluminium and lithium in the solution corresponds to the initial quantity of $LiAlH_4$ used. Addition of cyclohexanone to (**2**) results in its reduction to cyclohexanol in high yield (>95%, determined by g.l.c.).

Further experiments showed that bromohexane, bromobenzene, benzonitrile, and diethylacetamide can also be reduced in the solid $LiAlH_4$–hydrocarbon–15-crown-5 (18-crown-6) two-phase catalytic system to give in high yields hexane, benzene, benzylamine, and triethylamine, respectively (see Table 1).

In addition, these compounds are also readily reduced when quaternary ammonium salts are used as the catalyst (Table 1). Therefore it can be concluded that during the reduction of ketones, alkyl and aryl halides, nitriles, and amides under phase-transfer catalysis conditions the role of the Li^+ cation can also be fulfilled by the quaternary ammonium cation R_4N^+.

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References

1 Y. Kamitori, M. Hojo, R. Masuda, T. Izumi, and T. Inoue, *Synthesis*, 1983, 387.
2 E. Lukevics, V. Gevorgyan, and Y. Goldberg, *Tetrahedron Lett.*, 1984, 1415.
3 P. Cocaque, J. Elguero, and R. Gallo, *Heterocycles*, 1983, 1379.
4 J.-L. Pierre and H. Handel, *Tetrahedron Lett.*, 1974, 2317.
5 A. Loupy, J. Seyden-Penne, and B. Tchoubar, *Tetrahedron Lett.*, 1976, 1677.
6 A. Shirk and D. F. Shriver, *J. Am. Chem. Soc.*, 1973, **95**, 5904.
7 H. Nöth, *Z. Naturforsch., Teil B*, 1980, **35**, 119.
8 C. J. Pedersen and H. K. Frensdorf, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 16.

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