'Reversed' Regioselectivity in the Reduction of Epoxides with Lithium 9,9-Di-n-butyl-9-borabicyclo[3.3.1]nonanate

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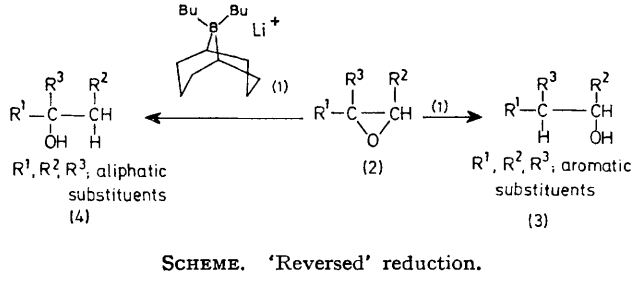
Summary Lithium 9,9-di-n-butyl-9-borabicyclo[3.3.1]nonanate reduces aromatic epoxides at the most sterically hindered position, while aliphatic epoxides are reduced at the least hindered position.

WE recently reported that the title compound (**1**) selectively reduces tertiary alkyl, benzyl, and allyl halides to the corresponding hydrocarbons without concomitant attack on secondary and primary derivatives,[1] and also permits highly stereo- and regio-selective reductions of carbonyl groups.[2] From both theoretical and practical angles, it appeared desirable to clarify the behaviour of (**1**) toward epoxides. We report that aromatic epoxides are reduced at the most substituted carbon atom whereas aliphatic



SCHEME. 'Reversed' reduction.

TABLE. Reduction of aromatic and aliphatic epoxides with (**1**)[a].

Entry	Epoxide (**2**)[b] R^1	R^2	R^3	Conversion/% (Time/h)	Product/% (**3**)	(**4**)
1	Ph	H	H	*ca.* 100 (3)	>99	trace
2	Ph	H	Me	86 (3)	98	2
3	Ph	H	Ph	94 (3)[c]	83	17
4	Oct^n	H	H	49 (3)	8	92
5	Oct^n	H	H	*ca.* 100 (20)	7	93
6	Pen^n	Me	H	trace (3)	—	—
7	Pen^n	Me	H	56 (16)	40	60
8	$-[CH_2]_4-$		H	44 (20)	—	—
9	$-[CH_2]_4-$		Me	3 (20)	>99	—

[a] When the reduction was complete (entries 1 and 5) the bicyclic ring of (**1**) was converted into bicyclo[3.3.0]octan-1-ol, but it was converted into cyclo-octanone when the epoxide was not reduced (entry 6). [b] Oct^n = n-octyl; Pen^n = n-pentyl. [c] A benzene solution of the epoxide was added to a light petroleum solution of (**1**).

derivatives are reduced at the least substituted carbon (Scheme).

A solution in light petroleum at room temperature of (**1**) and the epoxide (2 mmol each) was stirred (usually for 3 h), water was added, oxidation was accomplished with O_2, and the resulting mixture was analysed by g.l.c. The results are summarized in the Table.

Aromatic epoxides undergo anti-Markovnikov reductive ring opening (entries 1—3), while aliphatic epoxides exhibit Markovnikov opening (entries 4, 5, and 9) as usually observed in reductions with $LiAlH_4$. Moreover, the reduction occurs more readily with aromatic epoxides than with aliphatic derivatives (entries 1—3 and 4—9). The ease of reduction decreases along the series mono- (100%) > di- (44%) > tri- (3%) substituted epoxides (entries 5, 8, and 9). The 1,2-disubstituted epoxide exhibits low regioselectivity as would be expected (entry 7).

Reduction with complex metal hydrides such as $LiAlH_4$[3] and $LiEt_3BH$[4] involves attack of hydride at the least substituted carbon atom (Markovnikov ring opening), whereas mixed hydrides such as $LiAlH_4$–$4AlCl_3$[3] and BH_3–BF_3[5] attack at the most highly substituted carbon atom (anti-Markovnikov type).† Therefore, the pattern of regioselectivity in reductions with (**1**) is different from other known reductions of epoxides.

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† For the metal reduction of epoxides, see H. C. Brown, S. Ikegami, and J. H. Kawakami, *J. Org. Chem.*, 1970, **35**, 3243; E. M. Kaiser, C. G. Edmonds, S. D. Grubb, J. W. Smith, and D. Tramp, *ibid.*, 1971, **36**, 330. Under the present reaction conditions, no isomerization of the epoxides into carbonyl derivatives was detected.

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