

FRAGMENTATION OF ARYLALKOXYALANE RADICAL ANIONS: DEOXYGENATION OF ARYLALKANOLS AND FACILE
REDUCTION OF CINNAMYL ALCOHOL VIA CYCLISATION OF A CINNAMYLOXYALANE RADICAL ANION

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SUMMARY: Benzylic alcohols were reduced to hydrocarbons by radical-induced reactions with lithium aluminium hydride. Cinnamyl alcohol suffers hydrogenation to phenylpropanol via an alkoxyalane radical cyclisation reaction.

A number of radical-forming reactions from lithium aluminium hydride has previously been discovered and they have been attributed to electron-transfer processes^{1,2}. It is usually not easy to demonstrate conclusively if single-electron transfer (SET) is actually a major pathway in many of these reactions although it is quite clear that radicals have been generated. The lack of reliable redox potential data³ for most of these systems has also impeded the understanding of the mechanisms involved but in some instances alternative mechanistic schemes have been convincingly formulated⁴.

Among radical reactions involving lithium aluminium hydride, the dehalogenation of aromatic halides, which is usually slow and difficult to reproduce, has been shown to be efficiently carried out if the reaction is radical initiated⁴. From electron spin resonance studies², the slow formation of radicals from certain alkoxyaluminium hydride derivatives, where the alkoxy groups are benzylic and/or bulky groups, has been attributed to SET reactions. We have examined some simple systems where alkoxyaluminium hydrides of principally benzylic alcohols, were allowed to undergo reactions induced with t-butoxy radicals; without deliberate induction by radicals the reactions generally do not proceed except for some cases (e.g. triphenylcarbinol²) which reacted incompletely and extremely slowly over weeks probably initiated by radicals⁴ from traces of oxygen and/or diffuse light.

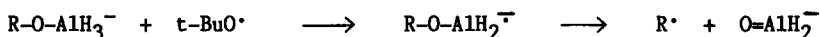
A typical reaction is described for the photochemical induced deoxygenation of benzhydrol. The alcohol (4 mmole) was reacted with 50 ml of a clear solution of 0.08 M LAH in tetrahydrofuran and 8 mmole of di-t-butyl peroxide was added. Photolysis was carried out using a 125W Hanovia medium pressure Hg lamp for 5 h under nitrogen or argon with water cooling at ambient temperature. After photolysis, 30 ml water were introduced followed by 10 ml of 10% aqueous hydrochloric acid added and the mixture extracted by 3 x 15 ml of hexane. The extract was dried (NaSO₄), rotary-evaporated to 1/4 volume and further concentrated by N₂ gas before analysis by gas chromatography and nmr spectroscopy. Typical results are shown in the Table.

Table. Radical-Induced Reactions of Arylalkoxyaluminium Hydride

Substrate	Products (Yield / %)
Triphenylcarbinol	Triphenylmethane (61)
Benzhydrol	Diphenylmethane (65)
Benzyl alcohol	Toluene (75)
1-Phenylethanol	Ethylbenzene (20)
Cinnamyl alcohol	3-Phenyl-1-propanol (81)
Cinnamyl alcohol	3-Phenyl-1-propanol-3-d ₁ * (80)

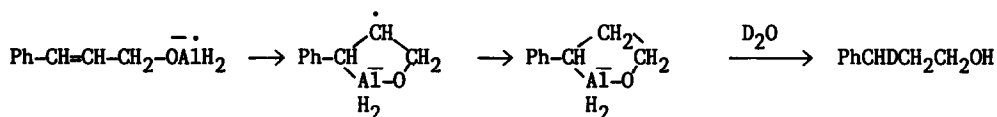
*Quenched in D₂O; 27% d₁ in C₆H₅CHDCH₂CH₂OH from HNMR and mass spectra

Best results were obtained by using 1:1 mole ratio of alcohol : LiAlH₄; generally however aliphatic alcohols, e.g. n-alkanols, sec. & tert. aliphatic alcohols, and adamantanol, do not react appreciably. The results for benzylic alcohol deoxygenation may be rationalized as a radical fragmentation reaction which is favoured for stabilized benzylic radicals, viz.



As a radical fragmentation reaction it is expected that the reaction will be facile for groups that will stabilize R or when large steric effects⁵ are present in the alkoxyalane radical. These requirements are present in the earlier observations² of slow radical formation from alkoxyalane anions.

The facile reaction of cinnamyl alcohol to give phenylpropanol with a net hydrogenation, is interesting in that it indicates that a rapid intramolecular cyclisation of the alkoxyalane radical intermediate occurs before H-atom abstraction from ROAlH₃⁻ and provides further evidence on the radical nature of the reaction.



When the reaction was quenched with heavy water it was determined by HNMR and GCMS that the product phenylpropanol contained 27% d₁ at the benzylic position. This is to be expected from the intermediates from a 5-membered ring radical-cyclisation reaction as shown above, and the low deuterium content probably arising from competing quenching by t-butanol being produced from t-butoxy radicals.

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