Reaction of 2-Phenylallylic Alcohols with Lithium Aluminium Hydride

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Summary Hydride attack on 2-phenylallylic alcohols occurs at C-3 and is accompanied by C–O bond fission.

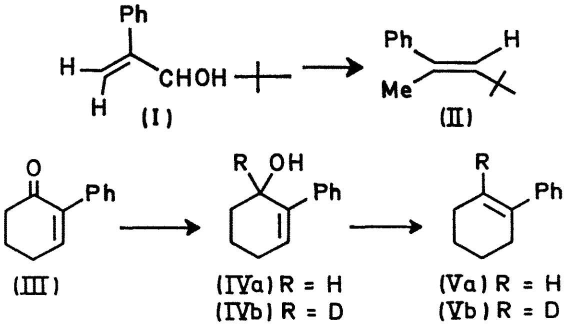
IN the reduction of *trans*-1-t-butyl-3-phenylallyl alcohol by $LiAlH_4$ the hydride was found to be delivered to the double bond intramolecularly by an aluminium bound to the proximate oxygen.[1] The presence of the phenyl at C-3 in this molecule not only activates the double bond to reduction[2] but also causes hydride donation to occur exclusively at C-2. This positional specificity is the same as that observed in the reduction of 3-alkyl substituted prop-2-ynyl alcohols in the presence of Lewis bases,[3,4] and we have suggested[1] that hydride attack proceeds by the same mechanism in both these cases. Donation has been shown to be intramolecular in a 3-phenylprop-2-ynyl substrate.[1]

The directive influence of the phenyl group in the 3-phenylallylic and prop-2-ynyl systems suggested that in a 2-phenylallylic alcohol, hydride attack might be directed to C-3. Attack at this position occurs in alkyl substituted prop-2-ynyl alcohols when reaction with $LiAlH_4$ is carried out in the presence of $AlCl_3$;[3,4] and we were interested in ascertaining whether C–O bond fission, which produces allenes in these reactions when more than trace amounts of $AlCl_3$ are employed,[4,5] would also be important in 2-phenylallylic systems.

Reaction of α-styrylmagnesium bromide with pivaldehyde produced 1-t-butyl-2-phenylallyl alcohol (**I**)† in 70% yield after purification by distillation (b.p. 63—65° at 0·2 mmHg). Reaction of (**I**) with $LiAlH_4$ in refluxing tetrahydrofuran (THF) gave a single product (>99·5% pure by g.l.c.). Its i.r. spectrum showed no OH absorption and its n.m.r. spectrum ($CDCl_3$) δ 1·21 (s, 9), 2·12 (d, 3, J 1·5 Hz), 5·72 (q, 1, J 1·5 Hz) and 7·3 (m, 5) p.p.m. was consistent with its formulation as 1-t-butyl-2-phenylpropene (**II**).‡

Similarly, 2-phenylcyclohex-2-enone (**III**)[6] was converted directly into 1-phenylcyclohexene (**Va**)[7] by reaction with $LiAlH_4$ in refluxing THF. With ether as solvent at 25° the alcohol (**IVa**) was isolated. Preparation of (**IVb**) by use of lithium aluminium deuteride followed by reaction with $LiAlH_4$ in refluxing THF gave (**Vb**) in whose n.m.r. spectrum the mulitplet near δ 6 p.p.m., present in (**Va**) and due to the vinyl proton, was absent.

The gross features of the above transformations are similar to the prop-2-ynyl alcohol → allene reactions. As in the latter, the hydrogen introduced at C-3 comes from hydride as shown by incorporation of deuterium in (**II**) at this position when the reaction with (**I**) was carried out with $LiAlD_4$. However, the similarity may be only superficial, for although difficulty in intramolecular hydride donation to C-3 *via* a six-membered transition state might be expected in a prop-2-ynyl system, no such problem is expected with an allylic substrate. Moreover, while the presence of tervalent aluminium (adventitious or added) appears necessary for directing attack to C-3 of a prop-2-ynyl system,[1] experimentally the addition of $AlCl_3$ has the same inhibitory effect on the reaction of (**I**) as it has on the reduction of 3-phenyl substituted allylic alcohols.[1,8] Thus, no reduction of (**I**) is observed after 15 min in refluxing THF with $LiAlH_4$ (2·2 mol) when $AlCl_3$ (0·05 mol) is added; without added $AlCl_3$, the conversion of (**I**) into (**II**) is complete under these conditions.



A stereochemical study now in progress is expected to show unequivocally whether the reaction of 2-phenylallylic alcohols with $LiAlH_4$ proceeds by intramolecular hydride donation, as in the 3-phenylallylic system, or intermolecularly, as we have suggested for the reaction of alkyl substituted prop-2-ynyl alcohols in the presence of tervalent aluminium.[1]

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† All new compounds gave acceptable elemental analyses and had spectra consistent with the suggested structures.

‡ In order to confirm the expected *trans* disposition of the phenyl and t-butyl group in (**II**), we sought to prepare the other isomer for comparison. Hydrogenation of (**I**) over a 5% rhodium on alumina catalyst gave a 3:2 mixture of the diastereomeric saturated alcohols, which could be separated by preparative g.l.c. on a 10 ft × 3/8 in column of 20% SE-30. The alcohols were converted into the xanthates, which were pyrolysed at 325° in a flow system. From the major diastereomer, (**II**) was produced in excellent yield as the only product. From pyrolysis of the minor diastereomer, only trace amounts of material, showing no olefinic protons, were obtained. These results support the assignment of the more stable *trans* stereochemistry to (**II**).

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