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EVIDENCE FOR SINGLE ELECTRON TRANSFER IN THE REDUCTION OF ALCOHOLS WITH LITHIUM ALUMINUM HYDRIDE

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Summary: EPR evidence supporting a single electron transfer mechanism in the reduction of secondary and tertiary alcohols to hydrocarbons with $LiAlH_4$ is presented.

The reduction of ketones and alcohols to the corresponding hydrocarbons by hydrogen transfer from main-group metal hydrides is a useful synthetic reaction.[1-5] The mechanism of such hydrogen transfer is generally considered to be of a polar nature.[2-5] Recently we have presented both visible and EPR spectroscopic evidence demonstrating single electron transfer (SET) in the reduction of aromatic ketones,[6] alkyl halides[7] and polynuclear hydrocarbons[8] with simple and complex metal hydrides of the main-group elements for those systems studied. In view of these recent developments we decided to study the reduction of alcohols with $LiAlH_4$ in order to determine if SET is involved in this reaction as well. Interestingly, the reactions studied have been found to proceed via a SET pathway producing hydrocarbon radical intermediates which are then converted to the hydrocarbon products by hydrogen transfer from the metal hydrides. A preliminary account of these results is presented here.

Lithium aluminum hydride dissolved in THF was allowed to react with equimolar amounts of alcohols such as Ph_2CHOH, $(O\text{-Tolyl})_2CHOH$, $(\text{mesityl})_2CHOH$, Ph_3COH and $Bu^t_2(Pr^i)COH$. A vigorous reaction with hydrogen gas evolution was noticed in all the cases and the clear solutions of the corresponding alkoxyaluminum hydride was formed (IR;νAl-H, 1780 cm^{-1}). These solutions, in time, de-

$$R_2CHOH + LiAlH_4 \longrightarrow LiAlH_3(OCHR_2) + H_2 \qquad (1)$$

veloped an orange-red color and were found to be EPR active. The intensity of the EPR signal increases with time and reaches a maximum (estimated approximate amount of radical 10-20%), beyond which the intensity of the EPR signal decreases. The intensity of the radical intermediate is found to be dependent on (a) the alcohol used (b) the ratio of reactants (c) the concentration of the reaction and (d) the solvent. Thus when Ph_3COH was allowed to react with $LiAlH_4$ in 1:1 molar ratio in THF (conc· ≃ 0.06m), the radical intermediate reached a maximum in about 2 to 3 days (estimated intensity $\sim$20%). The EPR spectrum was found to be consistent with that of the trityl radical ($Ph_3C\cdot$), reported previously. Similarly Mes_2CHOH reacted with $LiAlH_4$ to produce about 15% of the corresponding radical ($Mes_2CH\cdot$) in 3 days (Fig. 1).

On the other hand when the above reactions were carried out in diethyl ether solvent, only a trace amount of radicals could be detected. The products of these reactions were also found to be the corresponding hydrocarbons which were continuously formed during the course of the reactions. In the case of Mes_2CHOH and Ph_3COH reactions with $LiAlH_4$ in THF under identical conditions, 70 and 85% yields of Mes_2CH_2 and Ph_3CH were formed in one week. In diethyl ether, the products were form-

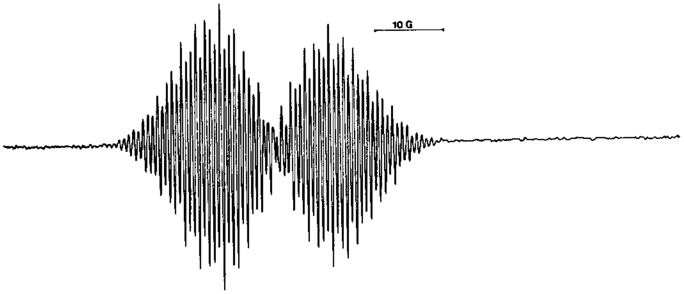
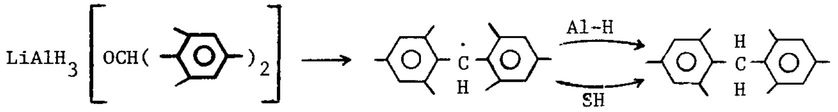


Figure 1: EPR spectrum of the radical intermediate ($\dot{\text{Mes}_2\text{C}}$H) formed in the reaction of $LiAlH_4$ with Mes_2CHOH in THF at R.T. (25°).

ed much more rapidly.

When the above reactions were carried out with $LiAlD_4$, the hydrocarbon products contained over 90% of the deuterium incorporated products i.e., Mes_2CHD and Ph_3CD, suggesting that the hydrogen (or deuterium) is being transferred predominently from the metal hydride (or deuteride) reagent. However, it appears that a small portion (< 10%) of the product is a result of hydrogen abstraction from the solvent, thus indicating further the presence of a radical intermediate. A proposed reaction pathway is outlined in the following scheme.



(2)

Preliminary studies involving similar reactions with other hydrides such as $NaAlH_4$ and AlH_3 suggest a similar SET pathway as above.

In conclusion, the above preliminary results represent the first spectroscopic evidence of radical intermediates in the reaction of $LiAlH_4$ and other metal hydrides with secondary and tertiary alcohols to form the corresponding hydrocarbons as reduction products. Detailed kinetic studies of these reactions are in progress.

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