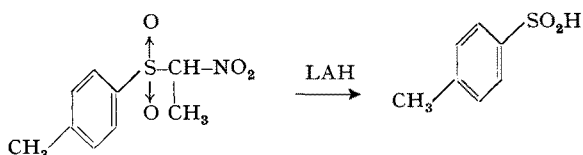


LAH reduction of the corresponding sulfone yields p-toluenesulfonic acid in good yield.



In these cases, scission of the C-S bond in an -N-C-S- grouping has occurred under the influence of LAH.

Although it might not be pertinent in this consideration of singly bonded groupings, it is of interest to note that thiocyanates, containing the grouping $\text{-S-C}\equiv\text{N}$, are reduced by LAH to thiols indicating, as above, cleavage of the C-S bond¹.

Due to the lack of additional types of compounds containing the -NCS- grouping and the possible effect of the nitro group, a generalization cannot with justification be made in this case although the reported results appear to fall within the scope of this discussion.

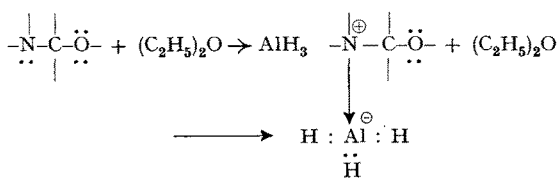
Mechanism

Paddock has shown that ether plays an essential part in LAH reductions². The analogy with the GRIGNARD reagent has been extended to show the necessity for a donor solvent and evidence for monoetherate formation has been obtained. On this basis, PADDOCK has suggested that there is an equilibrium in solution



and that the ether coordinates with the AlH_3 and the active entity in LAH reactions is the hydride ion.

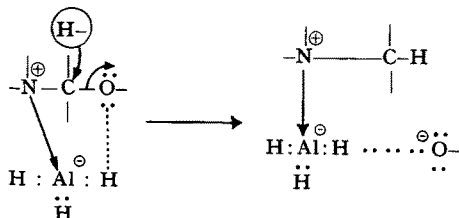
If we utilize this suggestion we see that the cleavages and non-cleavages discussed above can be explained by analogy with GRIGNARD reactions. Thus, in the case of the -N-C-O- grouping coordination of the available electron pair on nitrogen can occur with AlH_3



¹ M. MOUSSERON and M. CANET, Bull. Soc. chim. France [5] 18, 792 (1951). - J. STRATING and H. J. BACKER, Rec. Trav. chim. 69, 638 (1950); 69, 909 (1950). - J. STRATING, U. S. Patent 2,549,991 (April 24, 1951); German Patent 820,435 (November 12, 1951).

² N. L. PADDOCK, Nature 167, 1070 (1951).

The tendency for the electron pair on oxygen to take part in hydrogen bonding results in the formation of a quasi ring such as has been postulated in many GRIGNARD reactions. The electron deficient nitrogen would tend to withdraw electrons from the adjacent carbon giving the latter a positive character. The hydride ion present in the solution, according to PADDOCK's postulation, could displace the ethereal oxygen resulting in cleavage of the C-O bond:



In the case of the -O-C-O- grouping there is no reason to believe that the electron pair on oxygen should displace the electron pair on oxygen in the weakly acidic aluminium hydride monoetherate. The fact that cleavage of the spirostanes can be induced by carrying out the LAH reduction in the presence of hydrogen chloride¹ supports this view. In the case of the -S-C-O- grouping the same considerations hold.

Zusammenfassung

Unter den gewöhnlichen Reaktionsbedingungen bleiben -O-C-O- und -S-C-O- Gruppen durch LiAlH_4 unverändert, während -N-C-O- und möglicherweise auch -N-C-S- Gruppen an der C-O- bzw. C-S-Bindung gespalten werden. Diese Verallgemeinerungen, die sich auf aliphatische und aromatische Verbindungen, Zucker und Steroide, anwenden lassen, werden zur Bestätigung kürzlich aufgestellter Steroid- und Alkaloidformeln herangezogen. Es wird ein Reaktionsmechanismus vorgeschlagen.

¹ H. M. DOUKAS and T. D. FONTAINE, J. Amer. Chem. Soc. 73, 5917 (1951).

Corrigendum

P. LOUIS, *Recherches sur la fraction Y des protéines de muscles de Lapin*, Exper. 10, 258 (1954).

Dans la figure 1, fraction Y après 20640 s d'électrophorèse à 4,12 V/cm, μ 0,10, pH 7,6, la partie supérieure du cliché représente la frontière descendante et la partie inférieure la frontière ascendante.