Formation of Alcohols from Alkenes by Reaction with $SnCl_4$–$NaBH_4$

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Summary Treatment of alkenes with a combination of $SnCl_4$ and $NaBH_4$ gave the corresponding alcohols, the hydroxy-group of which was introduced in the anti-Markownikov direction.

THE combination of metal halides and $NaBH_4$ such as $AlCl_3$–$NaBH_4$[1] and $CoCl_2$–$NaBH_4$[2,3] has been applied to reduction of functional groups, including the conversion of alkenes into alkanes.[3] We have investigated the synthetic applications of the combination $SnCl_4$–$NaBH_4$[4] as a reducing reagent. Nitro, nitrile, and amide derivatives were reduced to amines with this reagent, and carboxylic acids and acid anhydrides were reduced to alcohols; esters and halogenobenzene derivatives remained unchanged.† We now report the novel reactivity of $SnCl_4$–$NaBH_4$ with olefins, leading to alcohols. *trans*-Stilbene was treated for 5 h with $SnCl_4$–$NaBH_4$, prepared by mixing $SnCl_4$ (1 equiv.) and $NaBH_4$ (4 equiv.) in tetrahydrofuran (THF) at room temperature. Decomposition of the resulting mixture with H_2O led to vigorous effervescence and 1,2-diphenylethanol (53%)‡ was obtained. In similar reactions, 2-phenylpropan-1-ol (58%) and 1-hydroxyacenaphthene (60%; together with acenaphthene, 15%), respectively, were obtained by the reaction of α-methylstyrene and acenaphthylene with $SnCl_4$–$NaBH_4$. Thus, alkenes were easily converted into alcohols, the hydroxy-group of which was introduced in an anti-Markownikov manner.§ This reaction was applied to the synthesis of (±)-isopinocampheol (40%)[5] and (±)-*cis*-myrtanol (43%)[5] from (±)-α-pinene and (±)-β-pinene, respectively. However, the reaction of $SnCl_4$–$NaBH_4$ with dienes such as limonene and cyclo-octa-1,5-diene showed complicated results.

Finally, the reactivity of $SnCl_4$–$NaBH_4$ towards carbon–carbon triple bonds was investigated. Phenylacetylene was treated with $SnCl_4$–$NaBH_4$ to give 2-phenyl- (50%) and 1-phenyl-ethanol (15%).

(Received, 19th April 1979; *Com.* 415.)

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† As typical illustrations, *p*-nitrotoluene, phenylacetonitrile, and *N*-acetyl-2-phenylethylamine were reduced with $SnCl_4$–$NaBH_4$ for 7 h to give *p*-toluidine, 2-phenylethylamine, and *N*-ethyl-2-phenylethylamine, respectively, in nearly quantitative yields. *o*-Bromobenzoic acid and *o*-iodobenzoic acid were reduced to *o*-bromobenzyl alcohol and *o*-iodobenzyl alcohol, respectively (each *ca.* 100%). Ethyl benzoate and the ethyl phenylpropionates were not reduced and starting material (100%) was recovered.

‡ All products in this paper were identified by direct comparison with authentic samples. In all cases, products were isolated by column chromatography on silica gel and no starting material was recovered. A white crystalline contaminant was sometimes present in the crude products.

§ Formation of alcohols might proceed through air oxidation of hydrometallated intermediates during work-up, though the mechanism leading to alcohols is uncertain.

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