Heterogeneous Catalysis, VI

Direct Reduction of Alcohols to Hydrocarbons [1]

Wilhelm F. Maier+, Irina Thies,
and Paul von Ragué Schleyer*

Institut für Organische Chemie
der Friedrich-Alexander-Universität
Erlangen–Nürnberg, Henkestraße 42,
D-8520 Erlangen, Federal Republic of Germany

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Gas Phase Hydrogenolysis,
Homoadamantane Preparation

Secondary and tertiary alcohols are converted cleanly to the parent hydrocarbons in the gas phase with H_2 in the presence of a Ni/Al_2O_3 catalyst at 190 °C. Primary alcohols are dehydroxymethylated; *e.g.*, 1-hydroxymethyladamantane (**4**) gives adamantane (**1**). Alumina alone, in the absence of Ni, results in the formation of homoadamantane (**5**) from **4**.

The conversion of alcohols to the corresponding hydrocarbons, a transformation frequently encountered in organic synthesis, is usually achieved by two-step procedures [2, 3]. The hydroxyl function can be converted to a more suitable leaving group, *e.g.*, a sulfonate [4] or halide [5], before reduction. Dehydration of an alcohol to an olefin followed by hydrogenation requires the presence of suitable β-hydrogen; the possibility of rearrangement is a major drawback [6]. Direct one-step reduction by catalytic hydrogenolysis requires high temperatures and pressures; only benzyl and allyl alcohols are reduced easily [7]. However, such reactions should be realizable under milder conditions as they are thermodynamically favorable; representative data are given below [8]. Alcohol hydrogenolysis is quite exothermic, although the thermodynamic driving force decreases with increasing substitution. (Since the reaction entropy is nearly zero, the temperature dependence of the free enthalpy is negligible.)

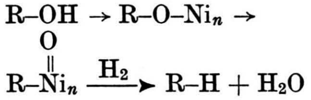
$$ROH + H_2 \rightarrow RH + H_2O$$

R	$\Delta G°_{500°}$ reaction kcal/mol
CH_3	—28.1
CH_3CH_2	—22.4
$(CH_3)_2CH$	—19.5
$(CH_3)_3C$	—15.1

We have already observed such reactions. In our study of the defunctionalization of substituted adamantanes by gas phase hydrogenolysis in the presence of Ni/Al_2O_3 catalysts, both 1- and 2-adamantanol were deoxygenated in high yield [1 b]. Such reactions have now been explored more generally; Table I summarizes the experimental results with a representative collection of alcohols.

A simple flow apparatus with hydrogen as carrier gas (at one atm pressure) and a Ni/Al_2O_3 catalyst is employed [1 a]. The reaction temperatures should not exceed 190 °C. Above this temperature cleavage of unactivated C–C bonds begins to occur with our catalyst [1 a]; yields and selectivities are decreased. The results in Table I demonstrate that acyclic and cyclic secondary and tertiary alcohols can be reduced to the present hydrocarbons in high yields.

Since 1- and 2-adamantanol, which are not likely to be converted to olefins, are reduced cleanly to adamantane (**1**), α,β-adsorption, the dominant mechanistic feature of other hydrogenolysis reactions with this Ni catalyst [1], may not be important for the cleavage of hydroxyl groups. Another mechanism, similar to that proposed for the demethylation of 1-methyladamantane [1 a], may be favored instead. The formulation shown below ("Ni_n" represents a nickel surface or cluster) is supported by the facile reduction of the sterically hindered alcohols, diethyl-*t*-butylcarbinol (2) and ethyldi-*t*-butylcarbinol (3). In both cases, α,β-adsorption should be precluded by the bulky alkyl groups.



$$R\text{–}OH \rightarrow R\text{–}O\text{–}Ni_n \rightarrow \overset{\overset{\displaystyle O}{\|}}{R\text{–}Ni_n} \xrightarrow{H_2} R\text{–}H + H_2O$$

The reduction of **2** and **3** have particular synthetic significance; it is often difficult to prepare such crowded hydrocarbons in other ways [9].

Primary alcohols react differently: dehydromethylation occurs. For example, 1-hydroxymethyladamantane (4) is converted to adamantane (**1**) nearly quantitatively and *n*-hexanol gives pentane predominately (94%) with only a minor amount (6%) of hexane by-product. Stepwise reduction (to the parent hydrocarbon followed by hydrogenolysis of the methyl group) cannot be involved as, *e.g.*, 1-methyladamantane does not react under the deoxygenation conditions. Hydrogenolytic dehydroxymethylation, the "reverse" of the commercially important hydroxymethylation [10], is thermodynamically favorable [8] especially when methane and water (the products observed) are formed, *e.g.*,

	$\Delta G°_{500°}$ (rxn) kcal/mol
$CH_3CH_2CH_2OH + 2\ H_2 \rightarrow C_2H_6 + CH_4 + H_2O$	—36.3
$CH_3CH_2CH_2OH + H_2 \rightarrow C_2H_6 + CH_3OH$	— 8.2

+ *Present address:* Professor W. F. Maier, Department of Chemistry, University of California, Berkeley, California 94720.

* Reprint requests to Professor P. v. R. Schleyer.

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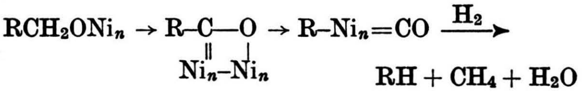
Table. Gas phase hydrogenolysis of alcohols with H_2 in the Presence of a Ni/Al_2O_3 Catalyst[a].

Alcohol	Product	Yield [%]	Reaction temperature [°C]
2-Hexanol	Hexane	91	180
1-Phenylethanol	Ethylcyclohexane	99	120
Cycloheptanol	Cycloheptane	76	150
Cyclopentanol[b]	Cyclopentane[b]	95	180
Cyclohexanol	Cyclohexane	99	180
2-Adamantanol	Adamantane (**1**)	99	170
Borneol (**6**)	Camphane (**7**)	52	150
	Isocamphane (**8**)	35	
1-Adamantanol	Adamantane (**1**)	99	180
2-Methyl-2-adamantanol	2-Methyladamantane	86	150
Diethyl-butyl-carbinol (**2**)	2,2-Dimethyl-3-ethylpentane	64	150
Ethyl-di-*t*-butyl-carbinol (**3**)	2,2,4,4-Tetramethyl-3-ethylpentane	54	120
	Rearranged hydrocarbon	9	
1-Hexanol	Pentane	94	120
	Hexane	5	
1-Hydroxymethyladamantane (**4**)	Adamantane (**1**)[c]	96	200
2-Phenylethanol	Ethylcyclohexane	56	150
	Methylcyclohexane	43	

[a] Conditions: H_2 flow rate 35 ml/min at 1 atmosphere pressure; [b] the Ni catalyst described in [1 a] was employed; [c] homoadamantane (**5**) is the product in the presence of an alumina catalyst (see text).

These are precedents for such exceptional behaviour of primary derivatives under similar catalytic conditions. Thus, while nitriles are generally reduced to hydrocarbons with the same carbon content (RCN gives RCH_3), primary nitriles tend to lose the CN group completely (RCN gives RH) [1 c]. A speculative dehydroxymethylation mechanism involves multisite adsorption and the formation of nickel-complexed carbon monoxide as key steps:



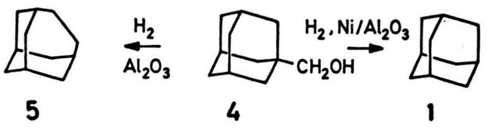
$$RCH_2ONi_n \rightarrow \underset{\substack{\|\quad| \\ Ni_n-Ni_n}}{R-C-O} \rightarrow R-Ni_n{=}CO \xrightarrow{H_2} RH + CH_4 + H_2O$$

We have reported that unactivated carboxylic acids can be decarboxylated with the Ni/Al_2O_3 catalyst, but much higher temperatures (*ca.* 300 °C) are needed [1 d]. Dehydroxymethylation may afford an alternative, milder route to accomplish the same objective but reduction of $-COOH$ to $-CH_2OH$ must be carried out separately. Similarly, ketones can be reduced catalytically to hydrocarbons directly [1 e], but less readily than the corresponding alcohols.

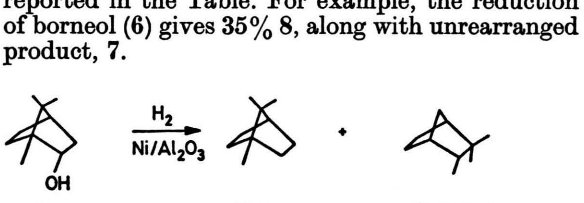
Another feature of these reactions requires discussion. We have observed that some of these alcohols (*e.g.*, 1-adamantanol) are reduced to hydrocarbon when only the support, Al_2O_3 (Woelm, neutral, activity 1), is present, *without any nickel at all!* In such instances, carbonium ion intermediates are implicated:

$$ROH \xrightarrow{Al_2O_3} R^+ \xrightarrow{H_2} RH$$

Alumina is a strong Lewis acid at higher temperatures [11] and carbocations are known to be reduced with hydrogen [12]. However, alcohols which can form stable olefins underwent dehydration with alumina [13] rather than reduction. Rearrangements characterize carbonium ion processes. A decisive experiment establishes the mechanistic differences when nickel is present. While 1-hydroxymethyladamantane (**4**) is reduced cleanly to adamantane (**1**) in the presence of Ni/Al_2O_3, homoadamantane (**5**) [14] is the sole product with alumina in the absence of nickel. The high yield of homoadamantane (83%) and the simple procedure involved makes this an attractive synthetic route.



In some instances, the ionic Al_2O_3-promoted mechanism may be able to compete with nickel reduction and give rise to the rearrangement by-products reported in the Table. For example, the reduction of borneol (**6**) gives 35% **8**, along with unrearranged product, **7**.



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Experimental

Most compounds are commercially available or were prepared by standard methods. The hindered alcohols 2 and 3 and the parent hydrocarbons were supplied by Professor Rüchardt. Products were identified by NMR and direct GC-comparison with the authentic materials. The GC-analysis employed a Perkin-Elmer Sigma I and capillary columns (50 m SE 30 and 20 m Carbowax 20 M). Total yields were calculated from the total amount of product obtained and its uncorrected concentration from GC-integration. The flow apparatus and the catalysts have already been described [1a].

Typical Procedure

Ca. 4 g of the reduced Ni-alumina catalyst was placed in the reactor tube and activated in a stream of hydrogen (*ca.* 30 ml/min) at 400 °C for 30 min. The substrate *e.g.*, 300 mg of 1-adamantanol, was heated in a U-tube with an oil bath at 100 °C. The reactor temperature was maintained at 150 °C and the hydrogen flow rate at 30 ml/min. The product was collected in a cooled (—80 °C) U-tube placed after the reactor. One hour after that starting material had disappeared (normally 3–6 h), the U-tube with the product which had to be separated carefully from the water by-product was weighed and dissolved in carbon tetrachloride. ^{1}H NMR and GC comparisons proved adamantane to be the only organic product. The yield, 260 mg of 99% pure adamantane, was 99%.

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