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HYDROGENOLYSIS OF UNSTRAINED C-C SINGLE BONDS. DEALKYLATION OF CAGE HYDROCARBONS.

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Unless present in strained rings[1] or otherwise activated (e.g. by aromatic rings),[2] carbon-carbon single bonds are considered to be practically inert towards catalytic hydrogenation. The few exceptions known require high temperatures and drastic conditions.[3] Nevertheless, as illustrated by the hydrogenolysis of ethane, C-C bond cleavage in alkanes is quite exothermic:[4]

$$CH_3\text{-}CH_3 + H_2 \longrightarrow 2CH_4 \qquad \Delta H^{o}_{25^{o}C} = -\ 15.4\ \text{kcal/mole}$$

We have developed this type of reaction into a synthetically useful process.

Our work is based on the observations of Weidenhoffer, Hâla, and Landa[5] that 1-ethyl and various polyalkyladamantanes can be dealkylated with hydrogen at atmospheric pressure in the gas phase over an easily prepared Ni/Al_2O_3 catalyst. The reactions proceeded stepwise, and mixtures of adamantane and lower alkyl adamantanes were obtained. Suitable reaction temperatures of 410-420° were suggested; at higher temperatures loss of material through destructive side reactions occurred.

We have improved and have extended this process significantly. By passing the substrate over the catalyst bed more slowly, the optimum reaction temperature can be decreased greatly, to as low as 190° and generally in the 250° range (Table). At these lower temperatures the reaction selectivity is increased, and product purities as well as yields approach 100% in favorable instances (Table).

The reactions are easy to carry out. Coprecipitated nickel and aluminum hydroxides are dried, introduced into the apparatus, and reduced at 425° in a stream of H_2; a ~30% Ni (on Al_2O_3) catalyst was employed in our work. A slow stream of H_2 (approximately 20 ml/min) passes over the substrate in a U tube heated in an oil bath and then through a heated pyrex tube packed with the catalyst; the products are collected in cooled U tubes. Reaction temperature control is critical; a furnace capable of maintaining constant temperature ($\pm 1^{\circ}$) facilitates the determination of the optimum reaction conditions for the formation of the desired product from each substrate. At lower temperatures the reactions are incomplete, at higher temperatures side reactions compete. As many as thirty experiments have been carried out with the same catalyst without noting any significant decrease in activity.

The Figure illustrates the stepwise character of the reaction of 2-ethyladamantane and the selectivity which can be achieved by means of temperature control. The optimum temperatures are 190° for the obtention of 2-methyladamantane and 245° for adamantane. The former is contaminated with some adamantane and some starting material, but the latter is produced practically pure (Table).

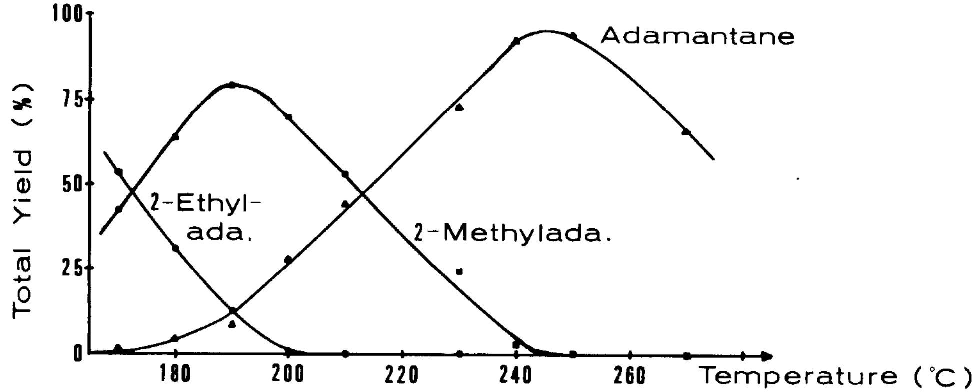


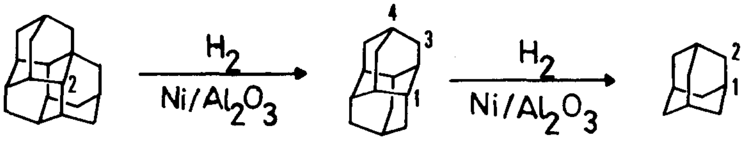
Figure. Temperature dependence of 2-ethyladamantane hydrogenolysis.

The ease of cleavage depends on the position of alkyl substitution. Thus, the order both with regard to optimum temperature and to product yield is 3-methyldiamantane > 4-methyldiamantane > 1-methyldiamantane. The extent of substitution of the CC bond, the amount of strain relief during reaction, and the degree of crowding at the reaction site are factors determining such preferences. Thus, 2-methyladamantane is more reactive than 1-methyladamantane, and the highly crowded 2-methyltriamantane gives the lowest yield of methyl cleavage product in the Table.

Table. Catalytic Hydrogenolysis of Cage Hydrocarbons[a]

Starting material[b]	Optimum Temperature[c]	Total product yield	Product composition (GLC Analysis)
1-Methyladamantane	280°	81%	Adamantane 98% 1-Methyladamantane 2%
2-Methyladamantane	235°	100%	Adamantane 97% 2-Methyladamantane 3%
2-Ethyladamantane	190°	99%	2-Methyladamantane 79% 2-Ethyladamantane 13% Adamantane 8%
2-Ethyladamantane	245°	95%	Adamantane 99% 1-Methyladamantane 1%
1-Methyldiamantane	255°	98%	Diamantane 72% 1-Methyldiamantane 16% Adamantane 12%
4-Methyldiamantane	245°	99%	Diamantane 81% 4-Methyldiamantane 13% Adamantane 6%
3-Methyldiamantane	215°	100%	Diamantane 100%
2-Methyltriamantane	240°	99%	Triamantane 46% Diamantane 18% 1-Methyldiamantane 15% 2-Methyltriamantane 13% Dimethyldiamantane 8%

[a] For other reaction conditions, see text. [b] For numbering of the positions of substitution, see I-III. [c] Optimum reaction temperature (°C) for the major product.



III II I

At higher temperatures, skeletal bonds are cleaved, and some amazing degradation are observed. Diamantane (II) gives adamantane (I) (in as much as 30% yield, even under nonoptimum conditions), and triamantane (III) gives both diamantane and adamantane. Additional examples may be found in the Table. Analysis (GC-MS) of the structures of the trace solid byproducts indicates that the bonds of one of the adamantane units are cleaved sequentially until the next lower diamandoid structure is obtained. Such entities have a higher stability towards further reaction. The gaseous products in these degradation reactions consist only of methane with a trace of ethane.

We have also examined the behavior of other types of hydrocarbons. For example, methyl groups can be removed from methylcyclohexane and from methylnaphthalene, but cholestane gives a dreadful mixture of products. We will report the details of these reactions and those involving functionalized substrates subsequentially.

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