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Hydrogenolysis of Alkyl-Substituted Adamantanes, Diamantanes, and Triamantanes in the Gas Phase on a Nickel-Alumina Catalyst

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Dealkylation of several alkyladamantanes, diamantanes, and triamantanes has been observed in the gas phase with hydrogen at atmospheric pressure on a 30% nickel-alumina catalyst. Yield-temperature profiles show that the optimum temperature for obtaining the pure parent compound in high yield can be as low as 215 °C. The ease of removal of an alkyl substituent depends on whether it is secondary or tertiary on the diamondoid nucleus. Rupture of the diamondoid skeleton requires much higher temperatures (over 280 °C) than dealkylation. The hydrogenolytic degradation of diamantane to adamantane was examined with the aid of molecular mechanics calculations; likely pathways for C – C bond cleavage were deduced which are consistent with the several intermediates detected experimentally. The mechanism of dealkylation is discussed in terms of steric and thermodynamic factors and the nature of possible surface intermediates.

Hydrogenolyse von alkylsubstituierten Adamantanen, Diamantanen and Triamantanen mit Nickel-Aluminiumoxid-Katalysatoren in der Gasphase

Bei der Gasphasen-Hydrogenolyse verschiedener Alkyladamantane, Diamantane und Triamantane unter Normaldruck mit Wasserstoff an einem Nickel-Aluminiumoxid-Katalysator wurde glatte Dealkylierung beobachtet. Die optimale Temperatur zur Erzeugung des reinen Grundkörpers in guten Ausbeuten kann den Temperaturprofilen entnommen werden. Die optimale Dealkylierungstemperatur zeigt starke Abhängigkeit von der Position (sekundär oder tertiär) der Alkylgruppe am Käfigmolekül. Die Zerstörung des Käfig-Grundkörpers erfolgt erst bei wesentlich höheren Temperaturen als die Dealkylierung. Der hydrogenolytische Abbau des Diamantans zu Adamantan wurde untersucht, und der wahrscheinlichste Reaktionsweg wird mit der Hilfe von Kraft-Feld-Rechnungen diskutiert. Unter Berücksichtigung von sterischen und thermodynamischen Faktoren sowie der Natur möglicher Zwischenstufen an der Katalysatoroberfläche wird ein Dealkylierungs-Mechanismus vorgeschlagen.

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Few direct methods exist for the selective demethylation of alkanes, e. g.

$$R_3C-CH_3 + HX \rightarrow R_3C-H + CH_3X$$

Indirect methods such as oxidative cleavage¹⁾ are of very limited use because relative reactivity differences between primary, secondary, and tertiary carbon hydrogen bonds render methyl groups unreactive. Catalytic hydrogenolysis ($X = H$) offers an attractive direct approach to the problem, but the ease and selectivity of this process are strongly dependent on the alkane structure and the operating conditions. Unless present in strained rings²⁾ or otherwise activated (e. g. by aromatic rings³⁾), carbon-carbon single bonds are considered to be practically inert towards catalytic hydrogenation. The few exceptions known require high temperatures and drastic conditions⁴⁾. Nevertheless, as illustrated by the hydrogenolysis of ethane, C – C bond cleavage is exothermic⁵⁾:

$$H_3C-CH_3 + H_2 \rightarrow 2\,CH_4 \qquad \Delta H_R(25\,^\circ C) = -15\ \text{kcal mol}^{-1}$$

Catalytic hydrogenolysis of normal and branched acyclic alkanes plays an important role in some refinery operations where the process, known as "hydrocracking", is used to convert high-boiling petroleum fractions into lower molecular weight alkanes⁶⁾. Hydrocracking requires high temperatures and complex mixtures of alkanes are usually produced, the ultimate product being methane.

The selectivity of alkane hydrogenolysis is catalyst dependent. Platinum catalysts promote hydrocracking and isomerisation. *Kochloefl* and *Bažant*⁷⁾ have shown that the hydrogenolysis of octane, decane, and isooctane at very low conversions (< 10%) on nickel proceeds by the stepwise removal of methyl groups as methane. These workers also found that the alkyl groups of dialkylcyclohexanes were successively removed in hydrogen on nickel, again at very low conversions.

With cycloalkanes structural considerations are important; carbon-carbon bond cleavage occurs readily in systems containing substantial angle strain. Cyclopropane²⁾ undergoes ring-opening hydrogenolysis under mild conditions. Cyclobutane⁸⁾ also reacts with hydrogen catalytically, though less readily than cyclopropane. With polycyclic hydrocarbons containing an accumulation of small rings, e. g. cubane⁹⁾ and basketane¹⁰⁾, ring-opening hydrogenolysis occurs selectively in such a way as to maximise relief of strain. Catalytic hydrogenolysis of cyclopentane¹¹⁾ and larger rings requires high temperatures.

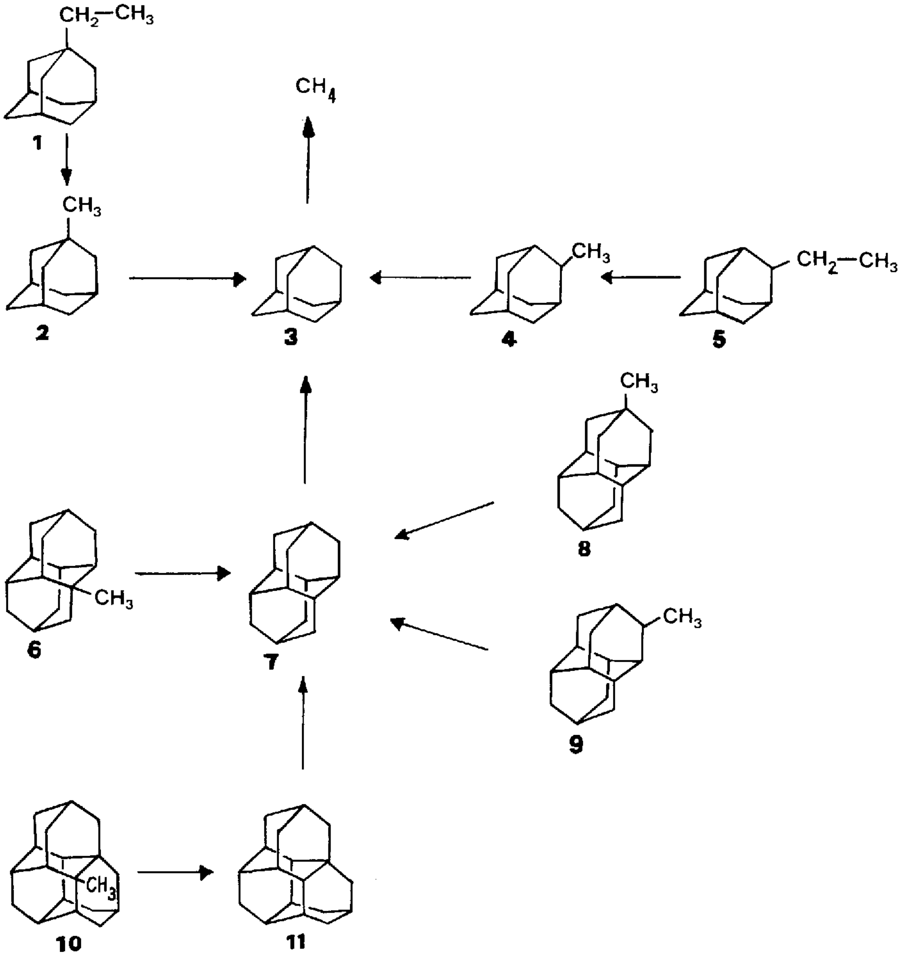
We have examined the catalytic hydrogenolysis of a series of alkyl-substituted adamantanes, diamantanes, and triamantanes (polymantanes) in the gas phase on nickel-alumina to determine if alkyl groups can be removed selectively leaving the diamond nucleus intact; a preliminary communication has been published¹²⁾. The polymantane series contains bridged cyclohexane rings with carbon atoms interlocked in the tetrahedral diamond-lattice arrangement. The series is characterised by resistance to chemical degradation and high thermodynamic stability relative to isomeric structures.

Our work is based on the observations of *Weidenhoffer, Hála,* and *Landa*¹³⁾ 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 alkyladamantanes were obtained. Suitable reaction temperatures of 410 – 420°C were suggested; at higher temperatures loss of material through destructive side reactions occurred.

We have improved and have extented this process significantly. With a more active catalyst and longer contact times, the optimum reaction temperature can be decreased greatly, to as low as 150°C and generally in the 250°C range. At these lower temperatures the reaction selectivity is increased, and product purities as well as yields approach 100% in favorable instances.

The reactions are easy to carry out. Coprecipitated nickel and aluminum hydroxides are dried, introduced into the apparatus (see figure 10), and reduced at 425 °C 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 (±1 °C) 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.

Scheme 1. Dealkylation of alkyladamantanes, methyldiamantanes, and methyltriamantane



The results obtained with 1- and 2-methyladamantane (**2** and **4**) are presented in figure 1; yields of adamantane (**3**) are a function of reaction temperature. It is immediately clear that the methyl group can be selectively removed very readily by hydrogen. At 235 °C, 2-methyladamantane (**4**) gives adamantane (**3**) in 97% yield (table 1).

Table 1. Catalytic hydrogenolysis of cage hydrocarbons[a]

Starting material	Optimum temperature[b]	Total product yield (%)	Product composition (GC-Analysis) (%)	
1-Methyladamantane (**2**)	280	81	Adamantane	98
			1-Methyladamantane	2
2-Methyladamantane (**4**)	235	100	Adamantane	97
			2-Methyladamantane	3
2-Ethyladamantane (**5**)	190	99	2-Methyladamantane	79
			2-Ethyladamantane	13
			Adamantane	8
2-Ethyladamantane (**5**)	245	95	Adamantane	99
			1-Methyladamantane	1
1-Ethyladamantane (**1**)	220	100	1-Methyladamantane	98
			Adamantane	2
1-Methyldiamantane (**6**)	255	98	Diamantane	72
			1-Methyldiamantane	16
			Adamantane	12
4-Methyldiamantane (**8**)	245	99	Diamantane	81
			4-Methyldiamantane	13
			Adamantane	6
3-Methyldiamantane (**9**)	215	100	Diamantane	100
2-Methyltriamantane (**10**)	240	100	Triamantane	46
			Diamantane	18
			1-Methyldiamantane	15
			2-Methyldiamantane	13
			Dimethyldiamantane	8
1-n-Butyladamantane (**12**)	210	100	1-Methyladamantane	81
			Adamantane	17
			1-Ethyladamantane	2
2-n-Butyladamantane (**14**)	180	100	2-Methyladamantane	70
			2-Ethyladamantane	9
			2-Propyladamantane	8
			Adamantane	6
Adamantylideneadamantane (**27**)	260	21	Adamantane	95
			2-Methyladamantane	5
1,1′-Biadamantane (**28**)	250		little reaction	
	300	20	1-Methyladamantane	65
			Adamantane	35

[a] For other reaction conditions, see text. – [b] Optimum reaction temperature (°C) for the major product.

Demethylation of **4** was detected at temperatures as low as ca. 190 °C. At temperatures above 235 °C the yield of adamantane gradually diminished due to hydrogenolytic degradation of the nucleus, the major product of which was shown to be methane (scheme 1). The yield vs. temperature profile for 1-methyladamantane (**2**) is signifi-

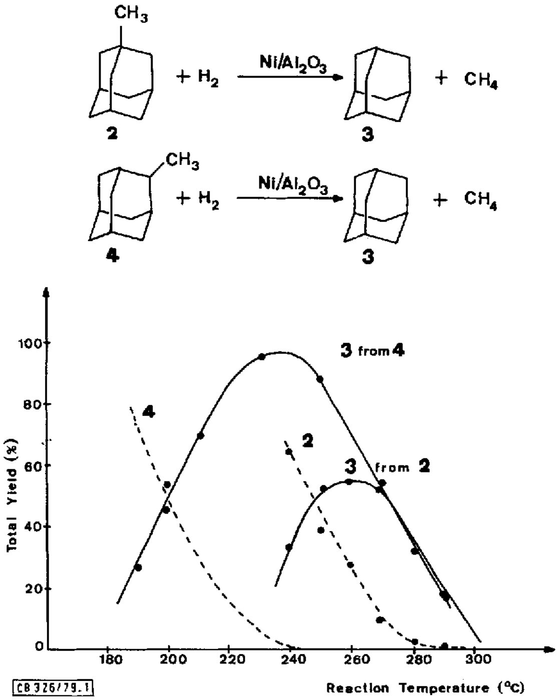


Figure 1. Yield-temperature profile for 1- and 2-methyladamantane (2 and 4)

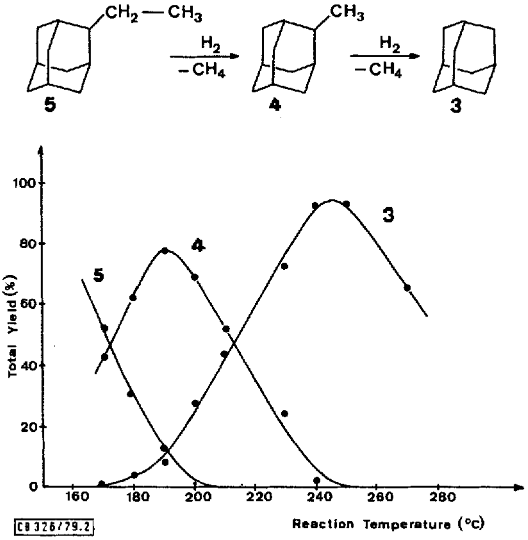


Figure 2. Stepwise dealkylation of 2-ethyladamantane (5)

cantly different from that for the 2-methyl isomer (figure 1). Not only is the maximum yield of adamantane (3) lower (55%) but the temperature required to realise this yield is higher (260 °C). Furthermore, demethylation of the 1-methyl isomer was not observed at temperatures below *ca.* 230 °C. That this difference in reactivity between 1- and 2-methyladamantane was not due to small differences in the operating conditions of the two sets of experiments was established by exposing an equimolar mixture of the two isomers to hydrogen at 240 °C. Analysis of the products showed that whereas only 2% of the 2-methyl isomer remained, there was 29% of unreacted 1-methyladamantane. With higher hydrogen flow rates at 280 °C, a 79% yield of adamantane was obtained from 1-methyladamantane (table 1).

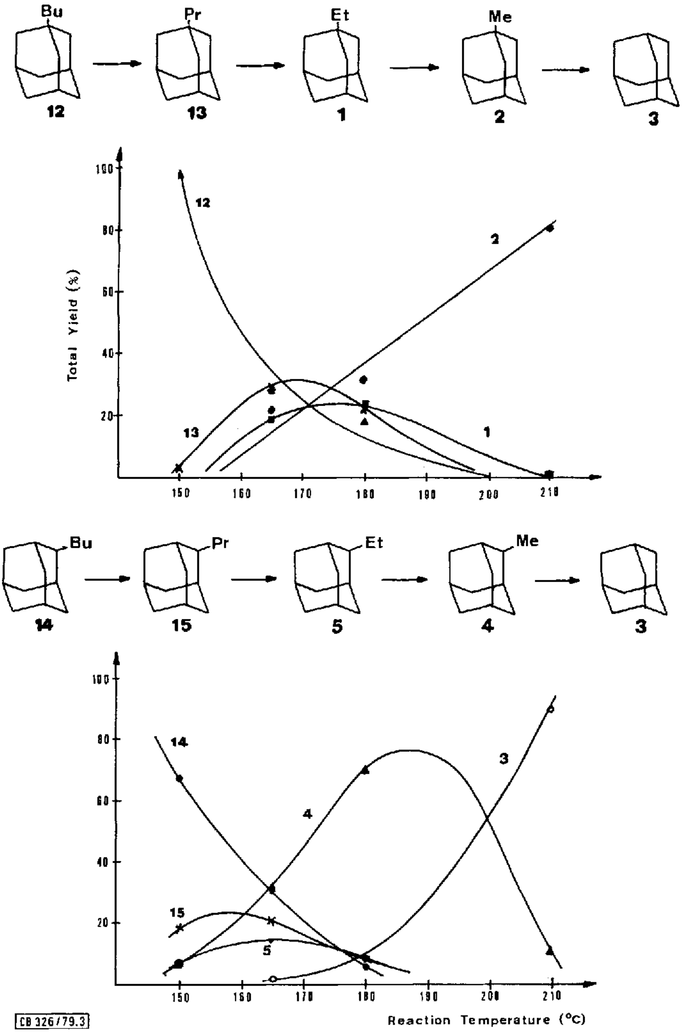


Figure 3. Hydrogenolysis of 1- and 2-n-butyladamantanes (**12** and **14**)

Hydrogenolysis of 2-ethyladamantane (**5**) was observed at temperatures down to 170°C. Figure 2 illustrates the stepwise character of the reaction of **5** and the selectivity which can be achieved by means of temperature control. The optimum temperatures are 190°C for the obtention of 2-methyladamantane (**4**) and 245°C for adamantane (**3**). The former is contaminated with some adamantane and some starting material, but the latter is produced practically pure (table 1).

Hydrogenolysis of 1-ethyladamantane (**1**) required higher temperatures than of the 2-isomer; at 220°C the product was 98% 1-methyladamantane. A competitive experiment using equal amounts of the 1- and 2-ethyl isomers showed that at 190°C all of the adamantane produced arose from hydrogenolysis of the 2-isomer. Hydrogenolysis of 1- and 2-n-butyladamantane (**12** and **14**) was detected at temperatures as low as 150°C. Again the 2-isomer was the more reactive of the two. The yield-temperature profile for both isomers is shown in figure 3. The main features of these reactions are the low concentrations of ethyl- and propyladamantanes at temperatures between 150 and 190°C. This is consistent with a stepwise degradation of the side chain giving 1- and 2-methyladamantane and ultimately adamantane. The difference in behaviour between the isomeric methyl and ethyl adamantanes is even apparent with the 1- vs. the 2-butyl isomers: nonbridgehead isomers are the more reactive towards hydrogenolytic cleavage.

That the ease of cleavage of a methyl group depends on the position of substitution was also observed in the behaviour of the methyldiamantanes (scheme 1), isomers **6**, **8**, and **9**. 1- and 4-methyldiamantane (**6** and **8**) have tertiary (bridgehead) substituents while the 3-isomer (**9**) has a secondary substituent. Yields of diamantane (**7**) as a function of temperature from each of the three isomers are summarized in figure 4. As with the methyladamantanes, demethylation of the methyldiamantanes occurs most readily with the secondary isomer, **9**. In fact, the selectivity of this reaction is quite striking for it is possible to convert 3-methyldiamantane (**9**) into diamantane (**7**) in 99% yield by ca-

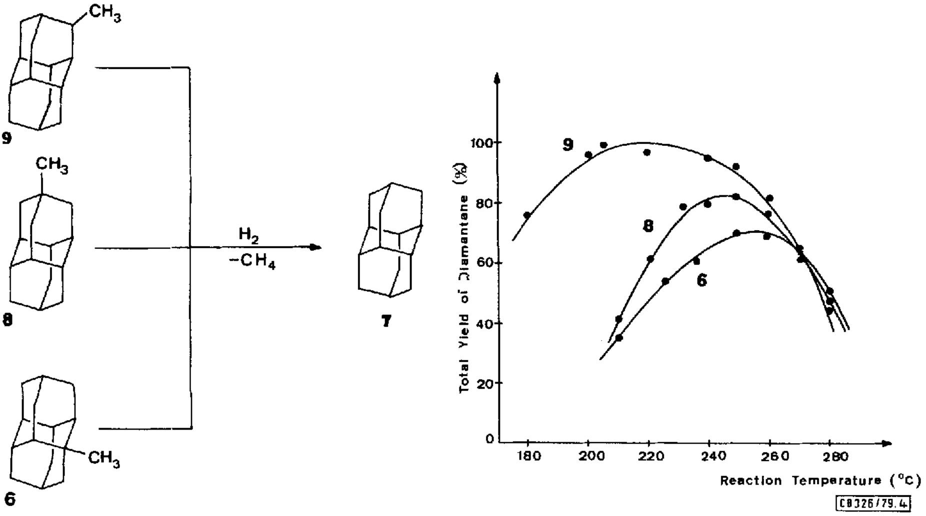


Figure 4. Yield-temperature profile for the methyldiamantanes **6**, **8**, **9**

talytic hydrogenolysis at 215 °C (table 1). The bridgehead isomers, **6** and **8**, are less reactive than the secondary isomer, **9**, and higher temperatures are required to achieve maximum selectivity of removal of the methyl group (table 1). Irrespective of the methylpolymantane isomer employed, it is clear from figures 1 and 4 that the diamondoid nucleus itself becomes susceptible to hydrogenolytic cleavage as the temperature is increased. Demethylation of the methyladamantanes was followed by cleavage of the nucleus. Mass spectroscopic investigation showed a trace of ethane to be present, but other products such as propane, the butanes, etc., could not be detected. With the methyldiamantanes, however, stepwise fragmentation to adamantane was observed (figures 5 – 7).

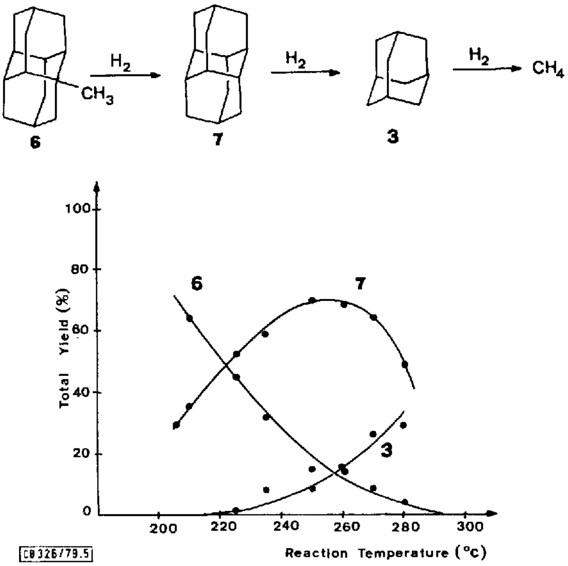


Figure 5. Hydrogenolysis of 1-methyldiamantane (**6**)

Hydrogenolysis of 2-methyltriamantane (**10**) on nickel is somewhat more complex than that of the methyldiamantanes, although selective removal of the methyl group is again observed (table 1). The product temperature profile is shown in figure 8. Triamantane (**11**) formation reaches a maximum at 240 °C and then falls off at higher temperatures in favor of diamantane (**7**) and adamantane (**3**). Trace amounts of several intermediates were detected; these include $C_{17}H_{26}$, $C_{16}H_{24}$, $C_{15}H_{22}$, $C_{14}H_{20}$, $C_{14}H_{22}$, $C_{13}H_{22}$, $C_{12}H_{20}$, and $C_{11}H_{18}$.

1-Methyldiamantane (**6**) was chosen for a more detailed study of the fragmentation process. Using a relatively fast hydrogen flow rate and a catalyst temperature of 245 °C, **6** gave, in order of decreasing glc retention time: diamantane (**7**), six hydrocarbon intermediates of molecular formula $C_{14}H_{22}$, $C_{13}H_{20}$, $C_{13}H_{22}$, $C_{12}H_{20}$, $C_{12}H_{20}$, and $C_{11}H_{18}$, respectively, and finally adamantane (**3**). Diamantane and adamantane were by far the major products of the reaction, the other six hydrocarbons amounting to not more than 1% of the total (figure 9).

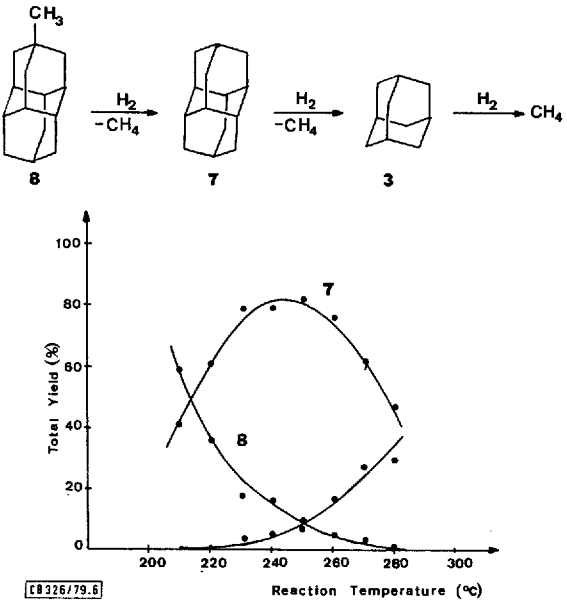


Figure 6. Hydrogenolysis of 4-methyldiamantane (8)

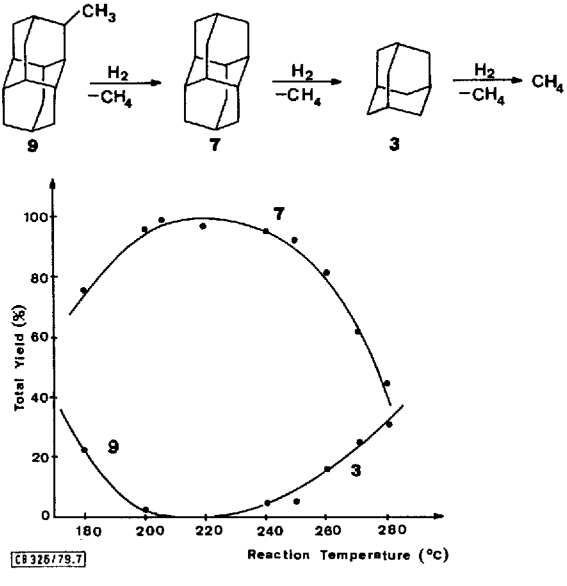


Figure 7. Hydrogenolysis of 3-methyldiamantane (9)

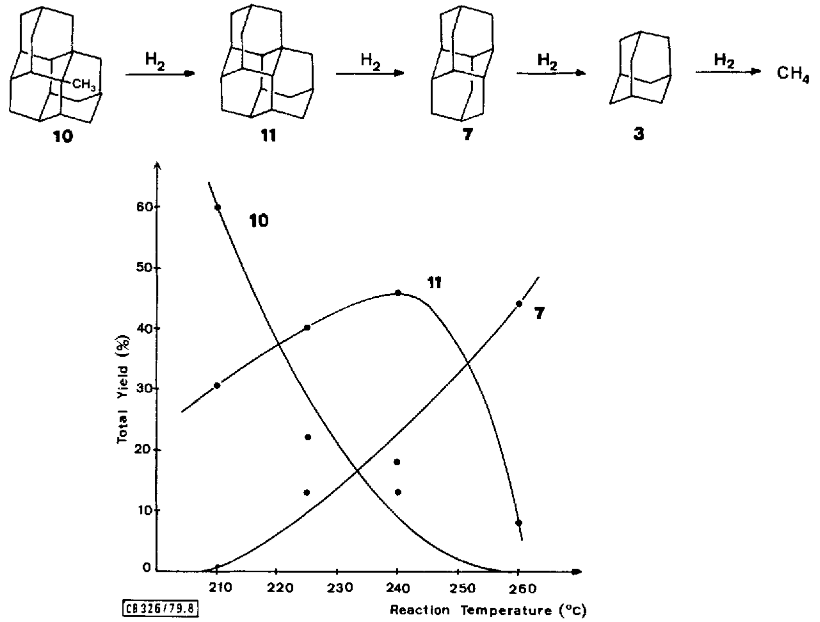


Figure 8. Hydrogenolysis of 2-methyltriamantane (**10**)

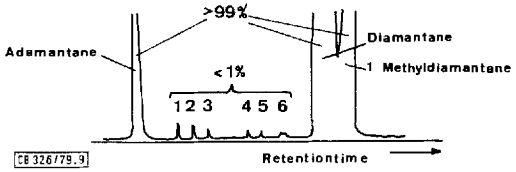
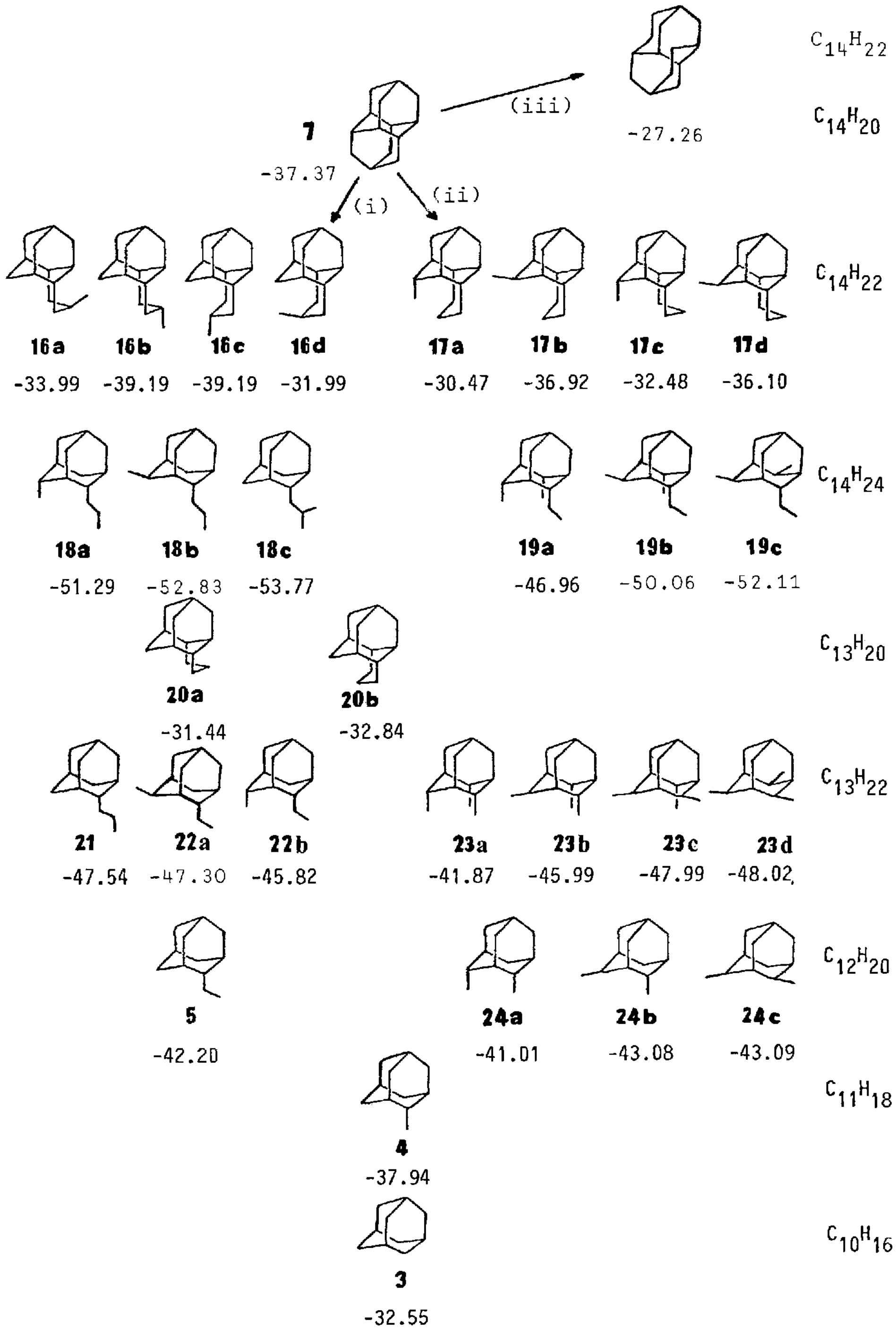


Figure 9. Glc of the products from the hydrogenolysis of 1-methyldiamantane (**6**). Peak 1 is due to 2-methyladamantane (**4**); similarly peaks 2, 3 correspond to 2,4-dimethyladamantane isomers (**24**), 4 to 2,4,9-trimethyladamantane (**23**), 5 to 2,4-trimethyleneadamantane (**20**), and the multiple peak 6 is assigned to methyl-2,4-trimethyleneadamantane isomers (**16** and/or **17**)

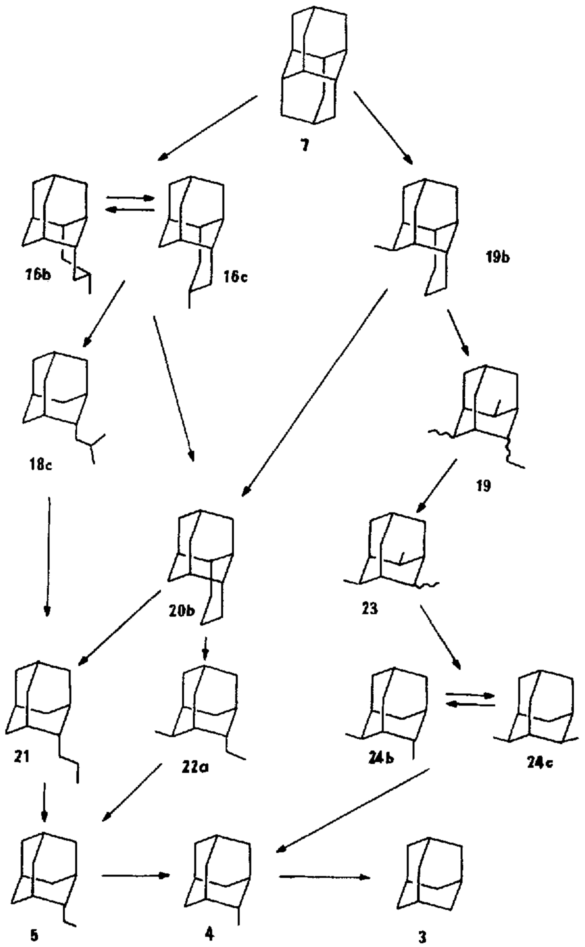
All the available evidence suggests that the six intermediates are derived from diamantane, i. e., methyl loss from 1-methyldiamantane is the first step. Of the six intermediates, the $C_{11}H_{18}$ product was positively identified as 2-methyladamantane (**4**) and the $C_{13}H_{20}$ product as 2,4-trimethyleneadamantane (**20**)[14a]; tentative structures for the others are based on mass spectrometry. All possessed methyl groups (M − 15 peaks are prominent) but not higher alkyls. Scheme 2, based on the assumption that degradation of the diamantane skeleton occurs by stepwise breaking of one carbon-carbon bond at a time, summarizes the possibilities. Geometrical and or conformational isomers are shown along with their calculated gas phase heats of formation (EAS force field)[14b] Although the operation of thermodynamic control in such hydrogenolytic degradations has not been established, the calculated energies provide useful insights into the relative stabilities of the various possible intermediates.

Scheme 2. ΔH_f^0 (kcal/mol) of decomposition intermediates from diamantane (**7**) to adamantane (**3**), calculated by the EAS-force-field[14b]



The $C_{14}H_{22}$ product results from cleavage of a single carbon-carbon bond in diamantane, a process that can occur in the three ways indicated by (i), (ii), and (iii) in scheme 2. Cleavage (iii) is very endothermic and is the least likely since both adamantane cages are ruptured. Cleavage (i) produces disubstituted adamantanes **16** for which four stereochemical forms, **16a – d**, have been calculated. Cleavage (ii) gives trisubstituted adamantanes **17**, also examined in four stereochemical forms (**17a – d**). The mass spectrum of the $C_{14}H_{22}$ product does not distinguish among structures **16** or **17**, although the enthalpy calculations suggest that **16b** and/or **16c** may be preferred. No $C_{14}H_{24}$ intermediates resulting from cleavage of the cyclohexane ring of **16** or **17** were detected. This is not surprising since such intermediates (e. g., **18a – c** and **19a – c** in scheme 2) have at least one substituent larger than a methyl group. Notwithstanding the 50% lower hydrogen flow rate, the behaviour of 2-methyladamantane (**4**) (figure 2) and of 2-n-

Scheme 3. Proposed pathways from diamantane (7) to adamantane (3), consistent with intermediates observed and the most favourable calculated enthalpy (ΔH^0) differences

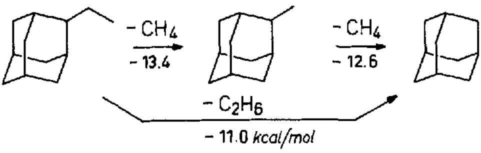


butyladamantane (**14**) (figure 3) suggests that at 245 °C intermediates with ethyl or larger groups should react very rapidly. Loss of a methyl group from **16** or **17** gives the $C_{13}H_{20}$ product, **20**[14a)]. A single $C_{13}H_{22}$ glc peak was found. Its mass spectrum indicates a 2,4,6-trimethyladamantane structure (i. e., **23a – d**). The alternative $C_{13}H_{22}$ isomers, 2-propyladamantane (**21**) and the 2-ethyl-4-methyladamantanes (e. g., **22a**, **b**), could also arise from **16** and **18**, but prominant M – 29 or M – 43 peaks were not observed. The identification of a 2,4,6-trimethyladamantane (**23**) confirms that its immediate precursor must also have been a trisubstituted adamantane, i. e., **19**. This in turn establishes that at least part of the fragmentation process follows pathway (ii). Pathway (i) cannot be excluded since this route can also lead to intermediate **20**.

The two $C_{12}H_{20}$ products were indicated by mass spectroscopy both to be 2,4-dimethyladamantane isomers (e. g., **24a – c**). These evidently arose by further loss of a methyl from **23**. The obtention of only two **24** isomers can be explained by *endo-exo* methyl epimerization of thermodynamically less stable **24a** which would relieve the methyl crowding. Such methyl group epimerizations have been observed on nickel[7)] and on palladium[15)] catalysts. Further sequential loss of methyl groups from **24b**, **c** gives 2-methyladamantane (**4**) and finally adamantane (**3**). Pathways from diamantane to adamantane, consistent with the intermediates observed and also with favorable enthalpy changes, are summarized in scheme 3.

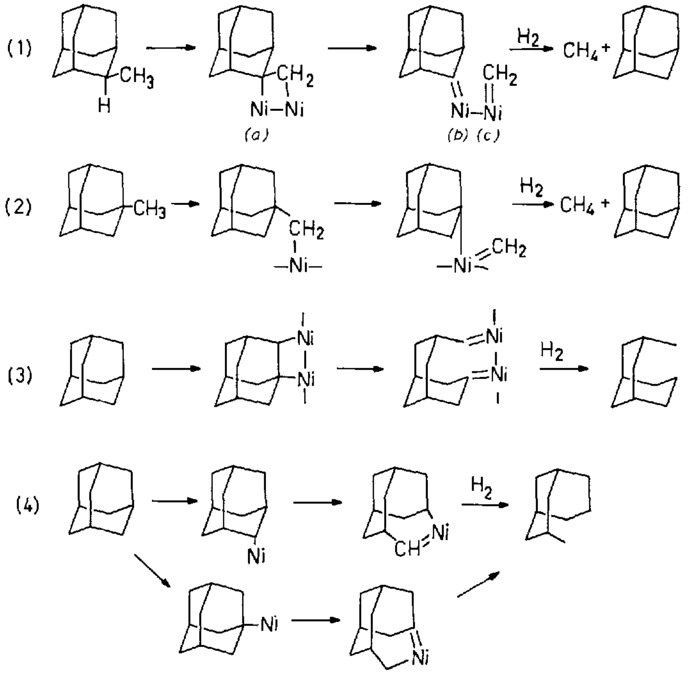
Our conclusions are in accord with the observation of *Kochloefl* and *Bažant*[7)] on the catalytic hydrogenolysis of alkanes and alkylcycloalkanes on nickel at 220 °C. These workers found that the predominant reactions of alkanes at low conversions (<10%) were successive degradation to methane and a hydrocarbon containing one carbon atom less than the starting material. With branched alkanes, only methyl groups bonded to secondary and tertiary carbon atoms and not those to quaternary carbon atoms were split off, cf. the behaviour of 1- and 2-methyladamantane.

With dialkylcyclohexanes, the alkyl groups were successively removed. Thus at 7 – 20% conversions ethylmethylcyclohexanes gave dimethylcyclohexanes exclusively. Stepwise removal of carbon atoms as methane is also the more favourable process thermodynamically as is shown by the following alternatives for dealkylation of 2-ethyladamantane: demethylation is more favourable than cleavage of the ethyl group.

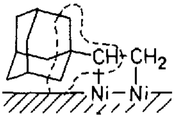


To help elucidate the mechanisms of these hydrogenolytic reactions we examined the behaviour of 1- and 2-methyladamantane and of 1-ethyladamantane towards deuterium/hydrogen exchange on the same nickel catalyst[16)]. Such exchange can be observed at temperatures much lower than those required for hydrogenolytic dealkylation. Thus the positions at which such exchange reactions occur in the molecule may not necessarily be those at which carbon-carbon bond cleavage takes place at the higher temperatures. Nevertheless they do provide a qualitative indication of the most likely sites for initial chemisorption of the molecule on the catalyst surface. The striking ease with which 2-methyladamantane is hydrogenolysed relative to 1-methyladamantane is reflected in the deuterium/hydrogen exchange results: at 150 °C the hydrogen atoms of the methyl group exchange much more readily in the 2-position than in 1-position. When, however, the bridgehead substituent contains an additional methylene group as in 1-ethyladamantane, deuterium/hydrogen exchange occurs readily. Thus deuterium/hydrogen exchange in alkyladamantanes is found at C – H positions which have at least one neighbouring C – H bond. This is in accord with the result of numerous deuterium/hydrogen exchanges studied with acyclic and alicyclic alkanes[17]. Our results and those of *Kochloefl* and *Bažant*[7] indicate that the adsorbed reactants form a species bonded to the catalyst surface by both terminal and neighbouring groups; hydrogenolysis then yields methane and the next lower homologue of the alkane. Although details, such as the nature of the bonding to the surface and the number of nickel atoms actually involved, are unknown, we suggest for the hydrogenolysis of 2-methyladamantane process (1) in scheme 4. Loss of two contiguous hydrogen atoms produces the surface species (a) bonded to two nickel atoms. Cleavage of the C – C bond yields the surface bonded carbenes (b) and (c) which are hydrogenated to the observed products. This mechanism is also applicable to the ethyl and to the n-butyladamantanes but not to 1-methyladamantane which cannot form a 1,2-diadsorbed intermediate. To account for the demethylation of the 1-methyl isomer, we propose the novel heterogeneous mechanism of a retro carbene insertion reaction (process (2) in scheme 4).

Scheme 4. Proposed reaction mechanisms for C – C hydrogenolysis



Process (2) should be more difficult than process (1), as indicated by deuterium/hydrogen exchange of 1-methyladamantane relative to its nonbridgehead isomer. An example of a retro carbene insertion in a homogeneous nickel alkyl intermediate has been reported by *Grubbs*[18]. Process (1) is applicable to both 1- and 2-ethyladamantane but it does not explain the greater ease of demethylation of the nonbridgehead isomer. In fact, demethylation of 1-ethyladamantane is more exothermic than is demethylation of 2-ethyladamantane ($\Delta H^0_R = -14.4$ and -13.4 kcal/mol, respectively). We suggest that unfavourable steric effects may hinder the formation of the 1,2-diadsorbed intermediate (**25**) in the bridgehead isomer. In this intermediate one nickel atom is attached to a bulky neopentyl-like system whereas in the nonbridgehead isomer the arrangement is that of an isobutyl system (**26**). Steric effects appear to influence some of the other systems. For example, the difficulty of removal of the substituent in 2-methyltriamantane relative to 1-methyladamantane may be associated with the considerable steric shielding of the substituent in the former. With the isomeric diamantanes the nonbridgehead substituent is removed most readily. This is consistent with the mechanisms in scheme 4, but the two bridgehead isomers differ in that the 1-methyl compound is more difficult to demethylate than the 4-methyl compound. Sterically, a substituent at position 4 is more accessible than at position 1; in the latter the substituent is encumbered by 1,3-axial-axial interactions with hydrogen atoms. Both 1,1'-biadamantane (**28**) and adamantylideneadamantane (**27**) underwent hydrogenolytic cleavage only with difficulty. In both cases degradation did *not* initiate with cleavage of the conjoining bond. The formation of methyladamantane indicated that one of the adamantyl cages had been degraded. Steric effects may prevent chemisorption of the central C – C bond on the catalyst surface. With the two exceptions just noted, cleavage of the first C – C bond in the diamondoid cage is the slowest process of all. The behaviour of triamantane and diamantane indicate that once the first rupture of the cage has occurred rapid and extensive degradation then ensues until the next lower diamondoid homologue is reached. This behaviour is associated with the high thermodynamic stability of the diamondoid nucleus. Mechanistic difficulties associated with the breaking of the first C – C bond may also be important to the resistance to degradation. Two proposals, processes (3) and (4), for the initial cleavage are summarized in scheme 4. In (3) the 1,2-diadsorbed species utilising two nickel atoms is formed at the 1,2 positions of adamantane. Subsequent cleavage of the 1,2 C – C bond requires these two



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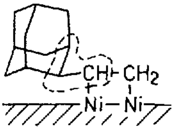

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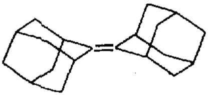

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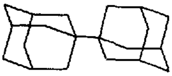

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carbon atoms to move apart thus increasing the overall ring strain. In (4) one nickel atom is involved in a retro-carbene insertion reaction. Insertion of the metal into the ring in this fashion is formally analogous to the conversion of methyladamantane into homoadamantane, an energetically unfavourable process (ΔH_f^0 increase 12 – 15 kcal/mol)[14a]. Accordingly, rupture of the diamondoid cage should be difficult relative to hydrogenolysis of alkyl substituents.

Conclusions

The main conclusions to be drawn are:

a) Methyl, ethyl, and butyl groups can be cleaved from adamantane and diamantane nucleus with high efficiency and high selectivity by catalytic hydrogenolysis. Alkyl groups are degraded in a stepwise fashion with consecutive loss of carbon atoms until an adamantanoid or diamondoid nucleus is reached. Preparative yields of hydrogenolysis products can be obtained at temperatures as low as 190 °C, although typical temperatures are 30 – 60 °C higher.

b) The ease of cleavage of an alkyl substituent depends on its point of attachment. Thus, the order with regard to optimum temperature and product yield is 2-methyladamantane > 1-methyladamantane; 2-ethyladamantane > 1-ethyladamantane; 2-n-butyladamantane > 1-n-butyladamantane; and 3-methyldiamantane > 4-methyldiamantane > 1-methyladamantane. The extent of substitution of the C – C bond, the amount of strain relief during the reaction, and the degree of crowding at the reaction site may be factors determining such preferences. Thus, the highly crowded 2-methyltriamantane (**10**) gives the lowest yield of methyl cleavage products (table 1).

c) Hydrogenolytic degradation of the diamondoid skeleton is difficult and requires higher temperatures than does the removal of substituents. Skeletal degradation also appears to occur in a stepwise manner but occurs rapidly until the next lower diamondoid nucleus is reached (e. g., adamantane (**3**) from diamantane (**7**)). Essentially only methane is produced as a by-product.

Experimental Part

Mass spectra: Varian CH 4B MAT and Varian 311A MAT, 70 eV. – GC-MS analyses: Finnigan 3200 E instrument (50 m capillary column, silicon gum rubber OV 1, 70 eV). – Gas chromatographic analyses: Perkin Elmer 990 and Hewlett Packard 5750 G flame ionization gaschromatographs equipped with a 50 m capillary column silicon gum rubber OV 1, a 50 m capillary column Carbowax 20 m, or a 2 m Porapak Q column (80 – 100 mesh).

Materials: Pure samples of adamantane[19], 1-methyladamantane[20], 2-methyladamantane[21], 1-ethyladamantane[22], 2-ethyladamantane[23], 1-n-butyladamantane[25], diamantane[25], 1-methyldiamantane[24], 3-methyldiamantane[26], 4-methyldiamantane[26], triamantane[27], and 2-methyltriamantane[28] were prepared by literature procedures. Hydrogen (Linde A.G.) with 99.999% purity was used without further purification. The purity of all hydrocarbons used was checked by gas chromatography.

Catalyst: To 220.5 g $Al(NO_3)_3 \cdot 9\ H_2O$ and 99.0 g $Ni(NO_3)_2 \cdot 6\ H_2O$, dissolved in 3.2 l water, was added 137.4 g KOH in 1.4 l water. The resulting nickel- and aluminium hydroxides were allowed to settle for several days; the clear solution was then decanted twice and water added to the residue. The hydroxides were filtered (a lengthy process!), added to 5 l water, filtered again, and washed several times with water. The wet hydroxides were dried at 130 °C for 48 hours and ground in a powder mill; 163 g of a pale green powder resulted.

This material was packed between glass wool plugs in a pyrex tube (see figure 10) and reduced by means of hydrogen (flow rate 20 – 30 ml/min). The temperature was increased from 25 to 425 °C (2 hours) and then held at 425 °C for 3 hours. The resulting Ni/Al_2O_3-catalyst (Ni content ca. 30%) could be used for thirty experiments without significant decrease in activity. (Improvements in catalyst preparation will be reported subsequently.)

Apparatus and experimental Procedure: The dealkylation of the various hydrocarbons was carried out in a flow apparatus (see figure 10). A general demethylation procedure is described for 3-methyldiamantane[12]. Other experimental details are given in table 2.

Table 2. Experimental details[b] of catalytic hydrogenolysis of cage compounds

Starting material	Starting material was heated to (°C)	Flow rate (ml H_2/min)	Optimum catalyst temperature[a] (°C)	Reaction time (h)
1-Methyladamantane (**2**)	70	24	280	2.5
2-Methyladamantane (**4**)	70	19	235	4.0
2-Ethyladamantane (**5**)	90	19	190	3.5
2-Ethyladamantane (**5**)	90	19	245	3.5
1-Ethyladamantane (**1**)	90	19	220	3.5
1-n-Butyladamantane (**12**)	120	22	220	4.5
2-n-Butyladamantane (**14**)	120	22	190	4.5
Adamantylidene-adamantane (**27**)	225	28	260	8.0
1,1′-Biadamantane (**28**)	225	28	300	8.0
1-Methyldiamantane (**6**)	125	21	225	5.5
4-Methyldiamantane (**8**)	125	21	245	5.5
3-Methyldiamantane (**9**)	125	21	215	5.5

[a] Optimum catalyst temperature (°C) for the major product. – [b] Product composition for glc analysis and total product yield are given in table 1.

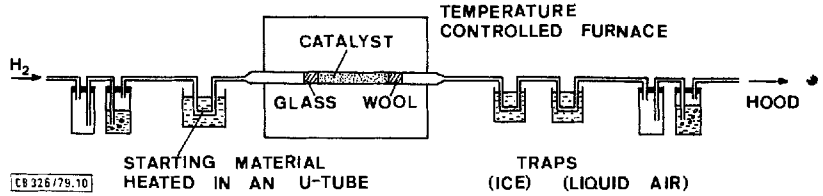

Figure 10. Flow apparatus for dealkylation

125.5 mg of 3-methyldiamantane (**9**) was placed in a U-tube (figure 10) and heated in an oil bath for 5.5 hours at 125 °C. A slow stream of hydrogen carrier gas (21 ml/min) was used to pass 3-methyldiamantane through a pyrex tube packed with 5 g catalyst and heated to 205 °C. The furnace, capable of maintaining a constant reaction temperature of ± 1 °C for several hours, was controlled by a Fischer Proportionalregler 0120. The product (116.6 mg; 100% yield) was collected in two weighed U-tubes, cooled in ice and in liquid air. The product was dissolved in pentane; glc analysis showed pure diamantane (**7**) to be present and no starting material to be left.

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