

## PREPARATION OF HIGHER ADAMANTANE HOMOLOGUES BY REACTION OF ADAMANTAN-1-OL WITH HEPTENES IN SULFURIC ACID

Luděk VODIČKA, Jiří BURKHARD and Josef JANKŮ

*Laboratory of Synthetic Fuels,*

*Prague Institute of Chemical Technology, 166 28 Prague 6*

Received March 19th, 1979

---

Reaction of adamantan-1-ol with heptenes in conc. sulfuric acid affords a complicated mixture of hydrocarbons, containing heptyladamantanes, diheptyladamantanes, tetradecyladamantanes, diadamantylheptanes and adamantyl-heptyladamantylheptanes. The reaction mixture can be separated into narrower fractions containing hydrocarbons of approximately equal molecular weight. The method can be utilized for the preparation of technical mixtures of high-boiling alkyladamantanes.

---

Lower homologues of adamantane, *e.g.* methyl- or ethylmethyladamantanes, can be obtained relatively easily by isomerisation of tricyclic perhydroaromatic compounds. The preparation of higher adamantane homologues, however, is substantially more difficult. One of the possible ways, leading to higher adamantane homologues, is the reaction of adamantane or its homologues with alcohols, described by Schneider and Warren<sup>1,2</sup>, and by Frid, Bagrii, Koshevnikov, Shishkin and Sanin<sup>3</sup>. These authors assume that in this reaction adamantane or its homologues are oxidized to the corresponding cation and the alcohol is dehydrated to olefin. The adamantyl cation is then added to the olefinic double bond under formation of an adamantylalkyl cation which is stabilized by reaction with adamantane to give alkyladamantane and adamantyl cation, and the reaction proceeds further by a chain mechanism. As side-products, monoalkyladamantanes with double length of the alkyl chain, diadamantylalkanes and dialkyladamantanes were observed. Schneider and Warren have also shown that it is possible to employ the corresponding olefins instead of alcohols.

In order to verify the applicability of this method to the preparation of higher alkyladamantanes, we studied the reaction of adamantan-1-ol with selected heptenes in sulfuric acid (96%). Adamantanol was used since it affords the cation more readily than the unsubstituted adamantane. In the model experiments adamantan-1-ol was treated with the following olefins: 1-heptene, 3-heptene, a mixture of 3-methyl-2-hexene and 2-methyl-3-hexene, 4-methyl-1-hexene and 2,3-dimethyl-2-pentene.

The reaction mixtures were analysed using a combination of gas-liquid chromatography on packed as well as capillary columns, gel permeation chromatography and mass spectrometry. The reaction of heptenes with adamantanol was shown to afford heptyladamantanes (mol.w. 234), diheptyladamantanes (mol.w. 332), tetradecyl-

adamantanes (mol.w. 332), diadamantylheptanes (mol.w. 368), and adamantane hydrocarbons of molecular weight 466 (probably (adamantylheptyl)adamantylheptanes Ad-C<sub>7</sub>H<sub>14</sub>-Ad-C<sub>7</sub>H<sub>15</sub>).

Yields of the reactions and ratio of the groups of compounds present in the volatile part of the product, as calculated from the chromatograms, are listed in Table I ("volatile part" of the reaction product represents those compounds which, under the conditions given in the Experimental, could be analysed by gas-liquid chromatography). A chromatogram of the reaction mixture from the reaction of adamantan-1-ol with 1-heptene is shown on Fig. 1. In addition to adamantane and unreacted adamantan-1-ol, the reaction mixture contains a distinctly separated group of heptyladamantanes. Chromatograms of other reaction mixtures are similar, all of them containing adamantane, adamantan-1-ol, the group of monoheptyladamantanes and the group of hydrocarbons of molecular weight 332 and 368. Product mixtures, arising from branched olefins and adamantan-1-ol, contained also butyl-, pentyl-, and hexyladamantanes.

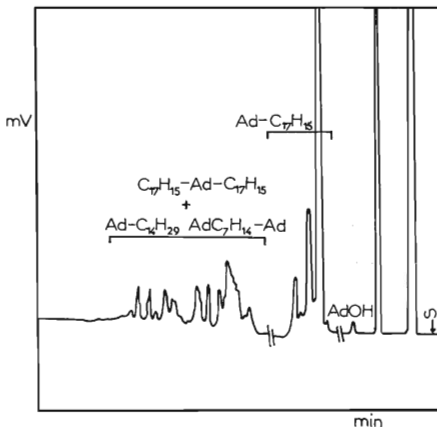


FIG. 1

Chromatogram of the Reaction Mixture from Adamantan-1-ol and 1-Heptene

The formulae should be as follows (read from the top): Ad-C<sub>7</sub>-H<sub>15</sub>; C<sub>7</sub>H<sub>15</sub>-Ad-C<sub>7</sub>H<sub>15</sub>; Ad-C<sub>14</sub>H<sub>29</sub> + Ad-C<sub>7</sub>H<sub>14</sub>-Ad. The second peak from right: Ad-H.

Hydrocarbons with molecular weight higher than 368 were already not detectable by gas-liquid chromatography and therefore the product of the reaction of adamantan-1-ol with 1-heptene was distilled *in vacuo*, affording three relatively narrow-boiling fractions and a distillation residue. The first fraction contained mainly heptyladamantanes, the second fraction consisted of hydrocarbons of molecular weight 332 and 368, whereas the third one contained mainly hydrocarbons of molecular weight 466. The mean molecular weight of the distillation residue was 988; it contained mainly polymers of the starting olefin and small amount (10–20% wt) of alkyladamantanes of molecular weight 466 and higher.

Composition of the heptyladamantyl portions was studied in more detail. Retention indexes of the more significant components of the heptyladamantane portions from reactions with all the studied olefins, together with the retention indexes of the synthesized four possible adamantyl-*n*-heptanes, were measured on the capillary column (Table II). The reaction mixtures were shown to contain five significant components of molecular weight 234. Only two of these compounds (No 3 and 5) had retention indexes identical with those of two standard adamantyl-*n*-heptanes. Both were found in minor quantities only in the reaction mixture from 1-heptene and 3-heptene. It thus follows that adamantyl-*n*-heptanes cannot be prepared by the reaction of adamantan-1-ol with *n*-heptenes because the reaction is accompanied with isomerisation of the alkane chain, most probably in the adamantylheptyl cation stage. The compound 1 is present only in the reaction mixture from branched

TABLE I  
Products of Reaction of Heptenes with Adamantan-1-ol

Olefin	Yield g/0.01 mol AdOH <sup>a</sup>	Product composition %, wt.			
		AdH <sup>a</sup>	AdOH <sup>a</sup>	M.w. 234	M.w. 332+368
1-Heptene	1.85	18.2	2.6	58.8	20.4
3-Heptene	2.15	5.8	2.5	76.1	15.6
4-Methyl-1-hexene <sup>b</sup>	2.10	25.4	2.6	33.0	39.0
3-Methyl-2-hexene and 3-Methyl-3-hexene <sup>b</sup>	2.00	23.6	21.2	23.0	32.2
2,3-Dimethyl-2-pentene <sup>b</sup>	1.90	16.9	16.4	28.1	38.6

<sup>a</sup> Ad adamantyl; <sup>b</sup> the reaction mixture contained also alkyladamantanes with 1–3 carbon atoms less than corresponding to m.w. 234; they are included in the percentage of species of m.w. 234.

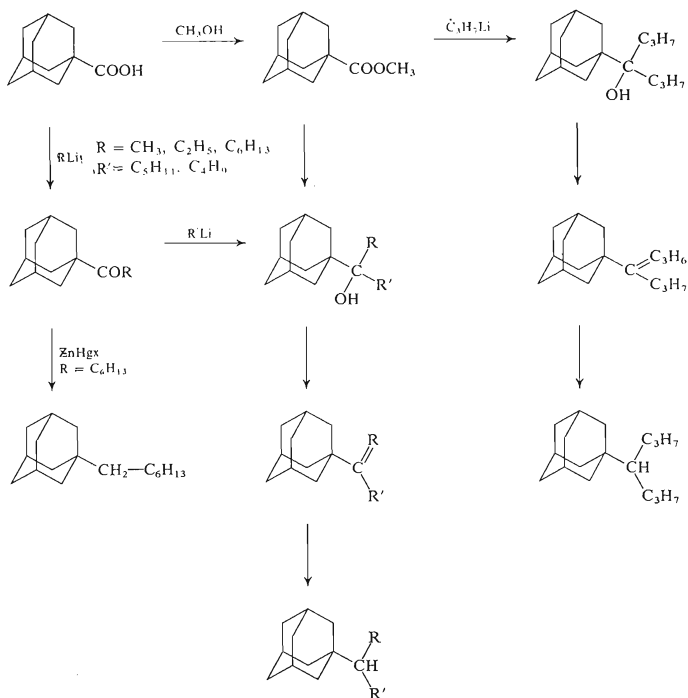
TABLE II  
Retention Indexes (R.I.) and Composition of the Heptyladamantane Portion from the Reaction Mixtures and of Authentic Adamantyl-*n*-heptanes.

	R.I. (200°C/180°C)										Composition, % wt						
	1	a	2	3	4	5	b	1	2	3	4	5					
Heptyladamantane portion from the reaction of adamantan-1-ol																	
with olefin:																	
1-Heptene	—	—	1 736	1 747	—	1 773	—	—	96.2	3.1	—	—	0.7				
			1 718	1 732		1 754											
3-Heptene	—	—	1 736	—	—	1 772	—	—	93.2	—	—	—	6.8				
			1 719			1 754											
3-Methyl-2-hexene and 3-methyl-3-hexene	1 730	—	1 736	—	—	—	—	87.2	12.8	—	—	—	—				
	1 712		1 719														
4-Methyl-1-hexene	1 729	—	1 736	1 751	—	—	—	10.6	1.1	—	—	—	88.3				
	1 710		1 717	1 731													
2,3-Dimethyl-2-pentene	1 731	—	—	—	—	—	—	100	—	—	—	—	—				
	1 710																
Authentic heptyladamantanes																	
4-(1-Adamantyl)heptane	—	1 732	—	—	—	—	—	—	—	—	—	—	—				
3-(1-Adamantyl)heptane	—	—	—	1 748	—	—	—	—	—	—	—	—	—				
				1 731													
2-(1-Adamantyl)heptane	—	—	—	—	—	1 773	—	—	—	—	—	—	—				
						1 755											
1-(1-Adamantyl)heptane	—	—	—	—	—	—	—	—	—	—	—	—	—				
								1 783									
								1 766									

<sup>a</sup> R. I.: 4-(1-Adamantyl)heptane; <sup>b</sup> 1-(1-Adamantyl)heptane.

heptenes and in the case of 2,3-dimethyl-2-pentene it is the only significant component of the heptyladamantane fraction. This indicates that compound 1 is a heptyladamantane containing a doubly branched substituent. The compounds 2 and 4 have probably only singly branched substituent.

It follows from the found results that in the reaction of adamantan-1-ol with heptenes in sulfuric acid following reactions take place: shift of the double bond in the olefin molecule, partial fragmentation of the olefin, and dimerization or even polymerisation of the olefins present in the reaction mixture. The adamantyl cation, formed from adamantanol, reacts with all types of olefins present by the mechanism suggested by Schneider and Warren<sup>1</sup>, the result being a relatively complex mixture



containing adamantane hydrocarbons of the mentioned types whose ratio depends on the structure of the olefin employed. Polymers of the starting olefin, or products of its fragmentation or isomerisation, are side products. The reaction can be used for preparation of mixtures of higher alkyladamantanes but it is not suitable for the synthesis of individual alkyladamantanes.

## EXPERIMENTAL

### Preparation of Olefins

The monoalkylethylenes were prepared by reaction of alkylmagnesium bromide with allyl bromide. Ether was distilled off on a Vigreux column and the residue fractionated on a column packed with Berl saddles (15 TP). Fractions purer than 98% (wt/wt) were used in further reactions. 1-Heptene was prepared from butylmagnesium bromide and allyl bromide in 33% yield; b.p. 92–94.5°C. 4-Methyl-1-hexene was synthesized from 2-butylmagnesium bromide and allyl bromide; yield 49%, b.p. 85–85.5°C. Di-, tri- and tetraalkylethylenes were prepared by Grignard reaction from the appropriate aldehydes and ketones. The crude secondary or tertiary alcohols were dehydrated by boiling with *p*-toluenesulfonic acid (5%) with simultaneous distillation of the water formed. The crude olefin, distilled from the reaction mixture, was dried and fractionated on a column packed with Berl saddles (15 TP). Fractions purer than 98% were used in further reactions. 3-Heptene was prepared from butyraldehyde and propylmagnesium bromide in 46% yield; b.p. 94.5–95°C. A mixture of 3-methyl-2-hexene and 3-methyl-3-hexene was obtained from methyl ethyl ketone and propylmagnesium bromide; b.p. 88–93°C, yield 39%. 2,3-Dimethyl-2-pentene was prepared from acetone and 2-butylmagnesium bromide; b.p. 94 to 96.5°C, yield 12%.

### Preparation of Standard Adamantyl-*n*-heptanes

The title compounds were prepared starting from 1-adamantanecarboxylic acid as depicted in Scheme 1. The reaction of 1-adamantanecarboxylic acid with alkyllithium was carried out according to the described procedure<sup>4</sup>. Hexyl 1-adamantyl ketone was reduced with amalgamated zinc in a mixture of azeotropic hydrochloric acid and ethanol (1 : 1). The isolated crude 1-heptyladamantane was purified by elution chromatography on alumina (Brockmann activity II, separated compound: adsorbent 1 : 20). Adamantylheptanols were prepared from alkyl adamantyl ketones or methyl 1-adamantanecarboxylate using alkyllithium rather than alkylmagnesium bromide (which afforded only about 30% yields of the desired products). The crude tertiary alcohols were dehydrated by heating with *p*-toluenesulfonic acid (5%), the reaction mixture was extracted with pentane, the pentane extract applied to an alumina column (*vide supra*) and the olefins eluted with pentane. The olefins were hydrogenated in ether over Adams catalyst at 20°C and atmospheric pressure. The reaction course and purity of the intermediates were followed by gas-liquid chromatography, the structure of the prepared adamantyl-*n*-heptanes was confirmed by mass spectrometry.

### Reactions of Adamantan-1-ol with Heptenes

The reactions were carried out in a three-necked flask equipped with stirrer and dropping funnel and immersed in an ice-water cooling bath. Adamantan-1-ol (1.52 g; 0.01 mol) was added to 96% sulfuric acid (20.4 g; 0.20 mol), the mixture was cooled to 0°C and the corresponding heptene

0.18 g; 0.012 mol) was added in one portion. The reaction mixture was stirred at 0°C for 1 h, poured on ice and extracted three times with ether. The ethereal extract was washed with water, aqueous solution of potassium hydrogen carbonate, again with water, dried and taken down. Traces of solvents were then removed *in vacuo* and the product was analysed by gas-liquid chromatography and mass spectrometry. Yields and composition of the products of the reaction of adamantan-1-ol with heptenes are given in Table I. The reaction product of adamantan-1-ol with 1-heptene was further separated by distillation and gel permeation chromatography. Products of several experiments were combined (9.9 g) and distilled *in vacuo* (1.33 kPa), affording three fractions: 145–156°C (2.05 g), 186–198°C (1.00 g) and 248–258°C (0.50 g). The dark distillation residue (5.70 g) was dissolved in hexane and purified by chromatography on alumina (100 g, activity II according to Brockmann), affording a viscous oil (4.8 g). Composition of the distillation fractions was followed by gas-liquid chromatography and mass spectrometry. Mean molecular weight of the distillation residue was 988 and the residue was analysed by gel permeation chromatography and mass spectrometry.

### Gas-Liquid Chromatography

The analyses were performed on a Chrom 4 chromatograph, equipped with an IT 1 integrator (Laboratorní přístroje, Prague). The reaction mixtures were analyzed on a stainless column (3600 × 3 mm) packed with SE-52 silicone elastomer (2%) on Chromaton N AW-DMCS (0.125–0.150 mm); starting temperature 110°C, programme 2°C/min up to 270°C (Fig. 1). Retention indexes of the standard adamantyl-n-heptanes were measured on a stainless capillary column (50 m) coated with OV 101; temperature 200°C and 180°C, carrier gas nitrogen. Flow rate of the carrier gas was chosen so as to achieve the maximum column efficiency (230 000 TP for n-octadecane at 180°C). The retention index of each compound was calculated as a mean of three runs and was rounded off to whole units. Chromatograms of analyses carried out on the capillary column were also used for determination of the retention indexes and of the ratio of principal components of molecular weight 234 (Table II).

### Mass Spectrometry

The analyses were performed on an LKB 9000 instrument (combination of gas-liquid chromatograph with mass spectrometer). Heated inlet was used in measurements of spectra of the standard alkyladamantanes. In analyses of the reaction mixtures, the samples were first separated on the chromatographic column and spectra of the single components were taken at the maxima of the chromatographic peaks. Complete separation of the reaction mixture components was achieved only in the region of molecular weights 234. Mixtures of compounds of higher molecular weight were separated only incompletely and, save some exceptions, several compounds were eluted in one peak. The spectra of higher-boiling distillation or gel chromatographic fractions were taken using direct inlet.

Mass spectra of heptyladamantanes (standards as well as reaction products) exhibit: molecular ion ( $m/e$  332, <1% rel.); "base peak"  $m/e$  135.

Spectra of diheptyladamantanes display practically no molecular ion, "base peak"  $m/e$  149 ( $M - C_7H_{15} - C_6H_{12}$ ); the second most abundant one  $m/e$  233 ( $M - C_7H_{15}$ ).

Mass spectrum of diadamantylheptenes: molecular ion  $m/e$  368 (about 5% rel.), "base peak"  $m/e$  135, further ions  $m/e$  149 (about 20–30% rel.) and  $m/e$  233 (5% rel.,  $M - 135$ ).

We were not able to obtain mass spectra of individual hydrocarbons of higher molecular weight. The presence of hydrocarbons of mol. w. 466 is indicated by the corresponding molecular ion in the spectra of higher-boiling fractions of the reaction mixtures.

### Gel Permeation Chromatography

The distillation residue was separated on a styrenedivinyl-benzene gel S-GEL-832 (prepared at the Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague), particle size 32–48  $\mu\text{m}$ , exclusion limit 1000 mol.w. units. The separation was performed on a gel chromatograph LC-1 (Development Center of Natural Sciences Department, Charles University, Prague) equipped with a series of five stainless columns (8  $\times$  1200 mm; total length 6000 mm); mobile phase tetrahydrofuran. The efficiency, determined by cyclohexane and expressed as HETP, was 0.25 mm.

### REFERENCES

1. Schneider A., Warren R. V.: *J. Amer. Chem. Soc., Div. Petrol. Chem., Prepr.* 1970, 15/2 B 56.
2. Schneider A.: U.S. 3 282 288.
3. Frid T. Yu., Bagrii E. I., Koshevnik A. Yu, Shishkin M. V., Sanin P. I.: *Neftekhimiya* 12, 511 (1972).
4. Landa S., Burkhard J., Vais J.: *Neftekhimiya* 8, 323 (1968).

Translated by M. Tichý.