# **Free-Radical Alkylation of Adamantanes**

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Adamantane and dimethyladamantane were alkylated exclusively at the bridgehead position with olefin in the free-radical chain reaction initiated by di-*tert*- butyl peroxide. *n*-Hexyl-, *n*- octyl-, cyclohexyl-, or cyclooctyladamantane was prepared in moderate yield based on consumed olefin. The major by-product isolated was that of allylic coupling. Treatment of an adamantane with ethylene gave the corresponding bridgehead ethyladamantane in practically quantitative yield when the initial pressure of ethylene was low. With higher ethylene pressure, *n*butyl- and *n*-hexyladamantanes were also formed.

Adamantane often serves as an excellent probe for the investigation of aliphatic substitution because of its skeletal stability<sup>1</sup> and its resistance to intramolecular rearrangement.<sup>2</sup> Thus, the synthetic applications of many cationic and some free-radical<sup>3–6</sup> substitutions for the functionalization of adamantanes are very successful.

The free-radical alkylation of dimethyladamantane<sup>7</sup> with an olefin in the presence of di-tert-butyl peroxide gave the corresponding 1-alkyl-3,5-dimethyladamantane as the major product. Results are summarized in Table I. The important by-products obtained were the corresponding 1: 2 adduct and the coupling product derived from the allylic radical. Thus, the radical alkylation was extended to ethylation of 1,3-dimethyladamantane with ethylene, which bears no allylic hydrogen (excluding the possibility of the formation of the allylic coupling product) but has a moderate tendency toward radical telomerization depending on the pressure of ethylene. The results are shown in Table II. Yield of the ethylation of 1,3-dimethyladamantane (based on dimethyladamantane consumed) was excellent (89%) at low ethylene pressure  $(2 \text{ kg/cm}^2)$ . The telomerization (higher alkylation) became more important with the increase in ethylene pressure, and 1-n- butyl-3,5-dimethyladamantane, 1-n-hexyl-3,5-dimethyladamantane, and 1-noctyl-3,5-dimethyladamantane were obtained with moderate ethylene pressure  $(2-10 \text{ kg/cm}^2)$ . Similar results were also obtained for adamantane (see Table III).

Thus, the direct free-radical alkylation of 1,3-dimethyladamantane with an appropriate olefin is an excellent procedure. Other alkylation procedures of adamantane in the literature are (1) the Wurtz type synthesis<sup>8</sup> giving alkyladamantanes only in poor yield, (2) the Grignard coupling of adamantyl bromide with alkylmagnesium bromide<sup>9</sup> giving methyladamantane in excellent yield but considerably reduced yields with higher alkyl groups, and (3) the Friedel–Crafts type syntheses<sup>10–14</sup> with moderate to excellent yields, but often accompanied by skeletal rearrangement of an alkyl group.

The characteristics of the present alkylation are its regiospecificity producing almost exclusively bridgehead radical from 1,3-dimethyladamantane or adamantane and the very efficient chain transfer from the growing chain to 1,3dimethyladamantane or adamantane.

The observed regiospecificity was interpreted by the bulkiness of the attacking (abstracting) radical.<sup>15</sup>

A bulky attacking radical was observed to increase the bridgehead of reduced bridge reactivity ratio as shown in Table IV, because of reduced bridge reactivity, probably by the steric repulsion in a transition state. An intermediate radical derived from adamantyl and an olefin (1) is that of the secondary structure (except for the ethylene addition),

Table I
1:1 Adducts of the Radical Addition of
1,3-Dimethyladamantane with Various Olefins

l:1 adduct R	Olefin used	Registry no.	Molar ratio <sup>c</sup>	Yields of <sup>b</sup> l:1 adduct, %	Yields of <sup>b</sup> olefin dimer, %
$C_6H_{13}$	Hexene-1	592-41-6	1	9	0
			10	20	0
$C_{8}H_{17}$	Octene -1	111-66-0	5	15	0
0 11			10	17	0
$C_{\beta}H_{11}$	Cyclohexene	110-83-8	10	5	9
$C_8H_{15}$	Cyclooctene	931-88-4	5	15	1
5 10	-		10	<b>26</b>	2

<sup>a</sup> Reactions were initiated by DTBP at 150° and kept for 5 hr. <sup>b</sup> Yields were determined based upon the converted olefins. The yield of the 1:1 adduct based on dimethyladamantane was practically quantitative.<sup>c</sup> The ratio of dimethyladamantane to olefin.

Table II Products of the Radical Addition of Ethylene to 1,3-Dimethyladamantane<sup>a</sup>

$\bigcap$	
Me	+ $CH_2 = CH_2 \xrightarrow{\text{DTBP}} Me \xrightarrow{(CH_2CH_2)_n} H$
Me	Me

	Experiment		
	1	2	3
Ethylene pressure, kg/cm <sup>2</sup> Conversion of dimethyl-	2 22.5	5 29.6	10 25.3
adamantane (%)			

Products		Yield, <sup>b</sup> mol %	
1-Ethyl-3,5-dimethyl- adamantane $(n = 1)$	89.0	69.7	33.5
1-Butyl-3,5-dimethyl- adamantane $(n = 2)$	10.5	17.0	23.9
1-Hexyl-3,5-dimethyl- adamantane $(n = 3)$	0.5	1.8	4.8
$\begin{array}{l} 1 \text{-Octyl}-3,5 \text{-dimethyl}-\\ \text{adamantane} \ (n = 4)\\ (n = 5) \end{array}$	0	0.4	1.1

 $^a$  Reactions were initiated by DTBP at 130° and kept at a constant pressure of ethylene for 5 hr.  $^b$  Yields were calculated based upon dimethyladamantane consumed.

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Table III
Alkylation of Adamantane with Ethylene in Benzene
$(50 \text{ ml})$ in the Presence of DTBP $(0.73 \text{ g})$ at $150^{\circ}$
for 2 hr

<u>, , , , , , , , , , , , , , , , , , , </u>	<ul> <li>Initial pressure of ethylene,</li> </ul>		e, kg/cm <sup>2</sup> ~
	5	10	20
Adamantane, g			
used	13.65	13.61	13.65
recovered	11.63	a	а
Product, g			
1 -ethyladamantane	1.18	0.58	0.25
1-n-butyladamantane	0.46	0.51	0.33
1 -n -hexyladamantane		0.034	0.051

<sup>a</sup> Recovery was practically quantitative.

 Table IV

 Effect of Bulkiness of an Abstracting Radical in

 Simple Brominations<sup>6</sup>

Brominating reagent	Abstracting radical	Bridgehead to bridge react, ratio	
$\mathrm{Br}_2 \ \mathrm{CH}_2\mathrm{Br}_2 \ \mathrm{Br}\mathrm{CCl}_3$	$\cdot Br$ $\cdot CH_2Br$ $\cdot CCl_3$	2.5 9 27	

favoring the hydrogen abstraction from the bridgehead position of 1,3-dimethyladamantane or adamantane.

$$1,3-R_2AdH + 3,5-R_2Ad^{(1)}CHR'CHR' \rightarrow$$

$$3,5-R_2Ad^{(1)}$$
 (major) +  $3,5-R_2Ad^{(1)}CHR'CH_2R''$   
1  
 $R = H \text{ or } CH_3$ 

A substituent at the bridgehead (1 position) lowers the reactivity of the 2 position *profoundly* and that of the 4 position *moderately*.<sup>16</sup> While the reactivity of the 3 position was less affected by a substituent, actually a small *acceleration* by methyl was observed for the bromination with NBS or the chlorination with CCl<sub>4</sub>.

For 1,3-dimethyladamantane, most of the bridge hydrogens are *doubly* deactivated, so that the reasonable assumption should be made that the abstraction of a bridgehead hydrogen prevails over that of a bridge hydrogen.

#### **Experimental Section**

Materials and Apparatus. Commercially available 1,3-dimethyladamantane, adamantane, olefins (ethylene, hexene-1, octene-1, cyclohexene, and cyclooctene), and di-*tert*-butyl peroxide were used. All the materials except ethylene were purified by usual distillation. Commercially available ethylene (99% pure) was used without further purification.

Nmr spectra were measured with a Varian EM 360, 60 MHz, using TMS as an internal standard in CCl<sub>4</sub> solvent. Infrared spectra were measured with a Hitachi 215 spectrophotometer. Glc analysis was performed using a  $0.3 \times 200$  cm column (Apiezon grease L, 5 and 10%).

1-Alkyl-3,5-dimethyladamantane from Ethylene and 1,3-Dimethyladamantane. A mixture of 1,3-dimethyladamantane (16.435 g; 0.1 mol) and di-*tert*- butyl peroxide (0.730 g, 5 mmol) was placed in a 100-ml autoclave. After the replacement of air with ethylene, the initial pressure of ethylene was adjusted to 5 kg/cm<sup>2</sup> and the mixture was stirred at 130° for 5 hr. After cooling, the reaction products were isolated by distillation *in vacuo* and/or preparative gas chromatography. Four products (determined as 1ethyl-, 1-butyl-, 1-hexyl-, and 1-octyl-3,5-dimethyladamantane) were obtained, which amounted to 3.976, 1.110, 0.128, and 0.040 g, respectively (mol %: 69.7, 17.0, 1.8, and 0.4) and the combined yield was 89% based on adamantane consumed, determined by analytical glc. A higher homolog ( $n \ge 5$ ) could not be isolated but in some cases was obtained as a white precipitate, probably admixed with high polymer. Similarly, the alkylations of 1,3-dimethyladamantane with higher initial pressures of ethylene were carried out.

Alkylation of Adamantane with Ethylene. Similar alkylation was applied to 13.6 g (0.1 mol) of adamantane dissolved in 50 ml of benzene with ethylene of the initial pressure of 5 kg'cm<sup>2</sup> in the presence of 0.73 g (5  $\times$  10<sup>-3</sup> mol) of di-tert- butyl peroxide at 150° for 2 hr. Together with 11.63 g of recovered adamantane, 1.18 g of 1-ethyladamantane (50% based on adamantane consumed) and 0.46 g of 1-n-butyladamantane (17% based on reacted adamantane) were obtained. The combined yield of the alkylation based on ethylene was practically quantitative. Higher 1-alkyl homologs were present in the product only in trace amounts under the present condition. 1-Ethyl-, 1-n-butyl-, and 1-n-hexyladamantanes were identified with those from the relevant syntheses: 1-ethylfrom 1-bromoadamantane and ethylmagnesium bromide,9 1-nbutyl- from 1-bromoadamantane and thiophene with stannic chloride followed by the Raney Ni hydrogenolysis,<sup>14</sup> and 1-n-hexyladamantane from adamantane and 1-hexene in the presence of di-tert- butyl peroxide.

Alkylation of adamantane at higher initial ethylene pressure under similar reaction conditions gave the following results: at 10 kg/cm<sup>2</sup>, ethylene, 1-ethyladamantane, 1-*n*-butyladamantane, and 1-*n*-hexyladamantane in a molar ratio of 23:17:1, the combined yield of alkyladamantanes based on reacted adamantane was practically quantitative; at 20 kg/cm<sup>2</sup>, ethylene, 1-ethyladamantane, 1-*n*-butyladamantane, and 1-*n*-hexyladamantane in a molar ratio of 6.5:7.4:1, the combined yield was again practically quantitative.

1-Alkyl-3,5-dimethyladamantanes from 1,3-Dimethyladamantane and Olefins. A mixture of 1,3-dimethyladamantane, an olefin, and di-tert- butyl peroxide was placed in a flask and heated at a given temperature (between 110 and  $150^{\circ}$ ). The initial molar ratio of dimethyladamantane to an olefin was in the range of 1–10 and the amount of the initiator added was 5–50 mol % of the olefin. After the usual work-up, the 1:1 adduct was isolated by the preparative gas chromatography. Table I shows the results obtained for hexene-1, octene-1, cyclohexene, and cyclooctene. In the case of cyclooctene, the products consisted of two components (in a ratio of 3:1); the major one was found to be 1-cyclooctyl-3,5-dimethyladamantane, but the structure of the minor one has not yet been determined.

Physical and Spectral Properties of 1-Alkyl-3,5-dimethyladamantanes. 1-Ethyl-3,5-dimethyladamantane: bp 65-67° (5 mm);  $n^{25}$ D 1.4804; nmr  $\delta$  0.80 (s, 6 H, CH<sub>3</sub>, CH<sub>3</sub>), 0.80 (t, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 2.00 (br, 1 H, bridgehead proton), and 0.9-1.7 ppm (m, 12 H, remaining adamantyl protons); mass spectrum, m/e (relative intensity) 192 (M<sup>+</sup>, 2), 177 (M - 15, 11), 163 (M - 29, 100), 107 (M - 85, 70).

**1-***n***-Butyl-3,5-dimethyladamantane:** bp 123-124° (9 mm);  $n^{25}$ D 1.4813; nmr  $\delta$  0.80 (s, 6 H, two CH<sub>3</sub>), 0.89 (t, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 2.00 (br, 1 H, bridgehead proton), and 1.0-1.5 ppm (three sharp peaks centered at 1.09, 1.27, and 1.30, 18 H, remaining alkyl and adamantyl protons); mass spectrum, m/e 220 (M<sup>+</sup>, 1), 205 (M – 15, 6), 163 (M – 57, 100), 107 (M – 113, 43).

1-n-Hexyl-3,5-dimethyladamantane: bp 108–108.5° (0.9 mm);  $n^{25}$  D 1.4807; nmr  $\delta$  0.80 (s, 6 H, two CH<sub>3</sub>'s), 2.00 (br, 1 H, bridgehead proton); mass spectrum, m/e 248 (M<sup>+</sup>, 1), 233 (M – 15, 6), 163 (M – 85, 100), 107 (M – 141, 67).

1-n-Octyl-3,5-dimethyladamantane:  $n^{25}$ D 1.4802; nmr  $\delta$  0.76 (t, 3 H, (CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>), 0.78 (s, 6 H, two CH<sub>3</sub>), 2.00 (br, 1 H, bridgehead proton), 0.9–1.6 ppm (m, 26 H, remaining alkyl and adamantyl protons); mass spectrum, m/e 276 (M<sup>+</sup>, 1), 231 (M – 15, 1), 163 (M – 83, 100), 107 (M – 169, 34).

1-Cyclohexyl-3,5-dimethyladamantane:  $n^{25}$  D 1.5137; nmr  $\delta$  0.80 (s, 6 H, two CH<sub>3</sub>), 1.73 (br, 1 H, cyclohexyl tertiary proton), 2.00 (br, 1 H, bridgehead proton), 0.9–1.5 ppm (m, 24 H, remaining alkyl and adamantyl protons); mass spectrum, m/e 246 (M<sup>+</sup>, 1), 244 (M - 2, 1), 231 (M - 15, 1), 163 (M - 83, 100), 107 (M - 139, 34).

1-Cyclooctyl-1,5-dimethyladamantane. This compound was contaminated with a small amount of an impurity assumed to be 1-cyclooctenyl-1,5-dimethyladamantane. Gas chromatographic separation gave the titled compound in a practically pure state:  $n^{25}D$  1.5175; nmr  $\delta$  0.80 (6 H, two CH<sub>3</sub>), multiplets centered at 1.11, 1.30, 1.56, and 2.08 ppm; mass spectrum, m/e 274 (M<sup>+</sup>, 2), 272 (M - 2, 2), 244 (M - 30, 5), 163 (M - 111, 100), 149 (M - 125, 5), 135 (M - 139, 25), 107 (M - 167, 34).

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Registry No.-1,3-Dimethyladamantane, 702-79-4; ethylene, 74-85-1; 1-ethyl-3,5-dimethyladamantane, 1687-35-0; 1-n-butyl-3,5-dimethyladamantane, 52826-28-5; 1-n-hexyl-3,5-dimethyladamantane. 52873-50-4: 1-n-octyl-3,5-dimethyladamantane, 52855-93-3; 1-cyclohexyl-3,5-dimethyladamantane, 19385-91-2; 1cyclooctyl-3,5-dimethyladamantane, 52826-29-6; adamantane, 281-23-2.

## **References and Notes**

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$$\mathrm{Ad}^{(2)} \xrightarrow{\mathrm{SH}} \mathrm{AdH} \xrightarrow{\mathrm{R}^{+}} \mathrm{Ad}^{(1)} \xrightarrow{\mathrm{Y-X}} \mathrm{Ad}^{(1)} \xrightarrow{\mathrm{Y-X}} \mathrm{Ad}^{(1)} \xrightarrow{\mathrm{Y-X}}$$

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# Stable Carbocations. CLXXII.<sup>1</sup> 2-Adamantyl Cations

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A series of 2-alkyl-, 2-phenyl-, and 2-halo-substituted 2-adamantyl cations were obtained in FSO<sub>3</sub>H, FSO<sub>3</sub>H.  $SbF_5$ , and  $SbF_5$  (SO<sub>2</sub>ClF or SO<sub>2</sub>) solutions at  $-78^\circ$  and their <sup>1</sup>H and <sup>13</sup>C nmr spectra were studied. Tertiary 2adamantyl cations, unlike the parent secondary 2-adamantyl cation which immediately undergoes intermolecular rearrangement to the bridgehead 1-adamantyl cation, show no skeletal rearrangement in superacidic media.  $2p-\pi$ conjugation between the phenyl  $\pi$  system and the empty 2p orbital at the carbenium center in 2-phenyl-2-adamantyl cation was found important. Halogen back donation (n-2p conjugation) induced by the halogen unshared electron pairs in 2-halo-2-adamantyl cations was found to increase in accordance with the increasing order of halogen electronegativity Br < Cl < F.

The observation and study of 1-adamantyl cations<sup>2</sup> in strongly acidic media in our laboratory prompted interest in the study of 2-adamantyl cations. These ions have similar rigidity but bear positive charge at the secondary, nonbridgehead position of the adamantane system. The parent 2-adamantyl cation 1–H has thus far not been directly observed. The reason is that fast intermolecular hydride shift takes place immediately after the relatively unstable secondary ion 1–H is formed, giving the more stable tertiary bridgehead 1-adamantyl cation 2.<sup>3,4</sup>



X = OH, Cl, Br or F

2-Methyl-2-adamantyl cation is, however, stable in strong acid solutions (in H<sub>2</sub>SO<sub>4</sub>, FSO<sub>3</sub>H, or FSO<sub>3</sub>H-SbF<sub>5</sub>) and shows no tendency to interconvert.<sup>5</sup> Many rearrangements involving apparent 1,2-hydride shifts in adamantane systems are now known to take place intermolecularly.<sup>3,4,6</sup> The interconversion of 2-methyl- and 1-methyladamantane, however, was shown to proceed intramolecularly involving rearrangement of 2-methyl-2-adamantyl cation to the 4-protoadamantyl cation followed by a rearrangement back to the adamantyl skeleton.<sup>4b</sup>

Although a series of 1-adamantyl cations have been prepared and characterized,<sup>2</sup> 2-substituted-2-adamantyl cations have not yet been reported in the literature. We, therefore, undertook the preparation of a series of 2-substituted-2-adamantyl cations and the study of their structure and stability in superacidic media. Proton and carbon-13 nmr spectra of 2-adamantyl cations including 2-alkyl-, 2phenyl-, and 2-halo-substituted ions were obtained.