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Alkylation of Adamantane with Alkyl Halides Catalyzed by Ruthenium Complexes

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Abstract—The feasibility of catalytic alkylation of adamantane and 1-bromoadamantane with alkyl halides in the presence of ruthenium-containing catalysts was revealed. The optimum molar ratios between the catalyst components and the reactants, as well as the reaction conditions for the selective synthesis of mono- and dialkylsubstituted adamantane derivatives with a 70–98% yield, were determined.

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Preparation of alkyl-substituted adamantanes is of great interest due to the fact that these compounds, possessing high thermal stability, satisfactory viscosity characteristics, and bactericidal properties, are widely used as valuable components of lubricating oils, gear and hydraulic fluids, effective heat-transfer media, etc. Alkyladamantanes are usually obtained via adamantane alkylation with olefins, alcohols, and alkanes in the presence of acid catalysts. At the same time, published data concerning the alkylation of adamantane and some of its functional derivatives (containing Cl, Br, and OH groups) with olefins, alcohols, or paraffins indicate that the reaction is difficult to initiate and the product yield is low [1]. In the presence of strong acid catalysts (H_2SO_4, HF, CF_3COOH, $AlCl_3$, $AlBr_3$), which are necessary for adamantane activation, olefins rapidly isomerize and polymerize and alcohols form the products of dehydration, oxidation, and polycondensation [2]. Alkyl halides are less effective as alkylating agents; the alkylation of adamantane and its derivatives with RX (X = Cl, Br) catalyzed by $AlCl_3$ proceeds nonselectively and is often accompanied by halogenation [3]. There is the example of catalytic alkylation of adamantane with *n*-butyl bromide in the presence of the zeolitic catalyst Zeokar-2, which was used in a 1 : 1 ratio relative to the hydrocarbon, at 310°C for 3 h [4]. In spite of the stringent reaction conditions, the conversion of adamantane was less than 100% and the total yield of 1-*n*-butyladamantane was 40%.

The aim of this work was to develop an effective process for the alkylation of adamantane and its derivatives with alkyl halides in the presence of metal-complex catalysts based on ruthenium compounds.

EXPERIMENTAL

Alkylation of adamantane and its derivatives was carried out in the presence of the ruthenium catalysts $RuCl_3$, $Ru(OH)Cl_3$, and $Ru(PPh_3)_3Cl_2$, which are commercially available chemicals. The catalysts were purified by standard procedures; for example, $Ru(PPh_3)_3Cl_2$ was prepared according to a known procedure [5].

The reaction was carried out in sealed glass ampules (V = 20 ml) or in stainless steel microautoclaves (V = 17 ml) (the results of parallel experiments were practically the same). Methylene chloride, alkyl halides (methyl iodide, ethyl bromide, *n*-propyl bromide, *n*-propyl chloride, *iso*-propyl bromide, *n*-butyl bromide, *n*-butyl chloride, *n*-butyl iodide, *iso*-butyl chloride, *tert*-butyl chloride), and bromobenzene used in the work were preliminarily purified and dried [6]. The reactants adamantane (**1**), 1-chloroadamantane (**2**), and 1-bromoadamantane (**3**) were of reagent grade and were used without additional purification.

Product Analysis

The purity of the synthesized compounds and the product composition were monitored by GLC on a Chrome-5 chromatograph with a column of 1.2 m × 3 mm packed with 5% SE-30-coated Chromaton N-AW-HMDS at a temperature programmed from 50 to 280°C at a rate of 8°C/min and helium as a carrier gas, using *n*-tridecane as an internal standard.

Infrared spectra were recorded on an IR-75 spectrometer (in a thin layer or nujol mull) in the range 550–3600 cm^{-1}.

^1H and ^{13}C NMR spectra were recorded on a JEOL FX 90Q instrument operating at 90 and 25.5 MHz, respectively, in $CDCl_3$ as a solvent; chemical shifts (δ) are given in ppm relative to TMS.

Mass spectra were recorded with a Finnigan MAT-112S gas chromatograph–mass spectrometer in the electron ionization mode at an ionization energy of 70 eV and a source temperature of 22°C.

General Procedure for Adamantane Alkylation with Alkyl Halides

A stainless-steel microautoclave (V = 17 ml) or a glass ampoule (V = 20 ml) was charged with 0.25 mmol of a ruthenium catalyst ($RuCl_3$, $Ru(OH)Cl_3$, $Ru(PPh_3)_3Cl_2$), 25 mmol of adamantane (**1**) (or 1-chloroadamantane (**2**), or 1-bromoadamantane (**3**)), and 25–50 mmol of an alkyl halide in 5 ml of CH_2Cl_2 under argon, and the autoclave was tightly closed (the ampoule was sealed). The reaction was conducted under continuous agitation for 3–5 h at 150°C. Then, the autoclave was cooled to room temperature, the reaction mixture was passed through a silica gel column (l = 20 cm, d = 30 mm, 1 : 1 hexane–ether solvent blend), the solvent was evaporated, and the residue was distilled in vacuum.

The isolated products had the following characteristics:

1-Methyladamantane (4). Yield 97%, bp 83°C/10 torr. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.48 (6H, $3CH_2$), 1.92 (3H, 3CH), 1.68 (6H, $3CH_2$), 0.82 (CH_3). ^{13}C NMR ($CDCl_3$, δ, ppm): 29.72 (C^1), 44.65 (C^2, C^8, C^9), 28.90 (C^3, C^5, C^7), 36.94 (C^4, C^6, C^{10}), 31.28 (C_{11}). Mass spectrum, m/z, (J_{rel}, %): 150 $[M]^+$ (3), 135 (100). Found (%): C, 87.91; H, 12.09; $C_{11}H_{18}$. Calculated for $C_{11}H_{18}$: C, 87.92; H, 12.08. Published data: bp 98–101°C [7].

1-Ethyladamantane (5). Yield 95%, bp 95°C/10 torr, n_D^{20} = 1.4950. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.50 (6H, $3CH_2$), 2.00 (3H, 3CH), 1.74 (6H, $3CH_2$), 0.81 (3H, CH_3), 1.12 (2H, CH_2). ^{13}C NMR ($CDCl_3$, δ, ppm): 32.41 (C_1), 42.30 (C^2, C^8, C^9), 28.95 (C^3, C^5, C^7), 37.63 (C^4, C^6, C^{10}), 36.94 (C^{11}), 14.52 (C^{12}). Mass spectrum, m/z, (J_{rel}, %): 164 $[M]^+$ (4), 135 (100), 79 (21), 93 (15), 136 (11), 67 (9), 107 (7), 77 (6), 55 (6), 91 (5), 81 (5). Found (%): C, 87.69; H, 12.31; $C_{12}H_{20}$. Calculated for $C_{12}H_{20}$: C, 87.73; H, 12.27. Published data: bp 228°C/752 torr [8].

1-*n*-Propyladamantane (6). Yield 94%, bp 110–111°C/6 torr. n_D^{20} = 1.4908. ^{13}C NMR ($CDCl_3$, δ, ppm): 32.49 (C^1), 43.20 (C^2, C^8, C^9), 29.14 (C^3, C^5, C^7), 37.68 (C^4, C^6, C^{10}), 47.65 (C^{11}), 16.05 (C^{12}), 15.48 (C^{13}). Mass spectrum, m/z, (J_{rel}, %): 178 $[M]^+$ (3), 135 (100), 79 (14), 93 (12), 67 (6), 91 (6), 107 (6), 77 (5), 55 (4), 81 (4). Found (%): C, 87.02; H, 12.98; $C_{13}H_{22}$. Calculated for $C_{13}H_{22}$: C, 87.56; H, 12.44. Published data: bp 234°C [9].

1-*iso*-Propyladamantane (7). Yield 86%, bp 108–109°C/6 torr. n_D^{20} = 1.4884. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.52 (6H, $3CH_2$), 2.00 (3H, 3CH), 1.69 (6H, $3CH_2$), 0.80 (CH_3), 1.10 (CH). ^{13}C NMR ($CDCl_3$, δ, ppm): 34.62 (C^1), 39.64 (C^2, C^8, C^9), 29.20 (C^3, C^5, C^7), 37.67 (C^4, C^6, C^{10}), 38.02 (C^{11}), 16.50 (C^{12}, C^{13}). Mass spectrum, m/z, (J_{rel}, %): 178 $[M]^+$ (14), 135 (100), 79 (17), 93 (15), 136 (14), 67 (13), 81 (7), 55 (7), 91 (6), 107 (5). Found (%): C, 87.32; H, 12.68; $C_{13}H_{22}$. Calculated for $C_{13}H_{22}$: C, 87.56; H, 12.44.

1-*n*-Butyladamantane (8). Yield 94%, bp 117–118°C/6 torr. n_D^{20} = 1.4912. ^{13}C NMR ($CDCl_3$, δ, ppm): 32.41 (C^1), 42.80 (C^2, C^8, C^9), 29.15 (C^3, C^5, C^7), 37.64 (C^4, C^6, C^{10}), 44.81 (C^{11}), 25.02 (C^{12}), 23.97 (C^{13}), 14.30 (C^{14}). Mass spectrum, m/z, (J_{rel}, %): 192 $[M]^+$ (2), 135 (100), 79 (14), 93 (12), 67 (7), 55 (7), 107 (6), 91 (6), 77 (5). Found (%): C, 86.88; H, 13.12; $C_{14}H_{24}$. Calculated for $C_{14}H_{24}$: C, 87.56; H, 12.44. Published data: bp 254°C [10].

1-*iso*-Butyladamantane (9). Yield 82%, bp 114–115°C/6 torr. n_D^{20} = 1.4884. ^{13}C NMR ($CDCl_3$, δ, ppm): 33.34 (C^1), 43.30 (C^2, C^8, C^9), 29.03 (C^3, C^5, C^7), 37.55 (C^4, C^6, C^{10}), 54.48 (C^{11}), 22.81 (C^{12}), 16.02 (C^{13}, C^{14}). Mass spectrum, m/z, (J_{rel}, %): 192 $[M]^+$ (2), 135 (100), 79 (12), 93 (12), 136 (11), 67 (6), 107 (6), 91 (5), 77 (5), 81 (4), 55 (4). Found (%): C, 86.92; H, 13.08; $C_{14}H_{24}$. Calculated for $C_{14}H_{24}$: C, 87.43; H, 12.57. Published data: bp 248°C [10].

1-*tert*-Butyladamantane (10). Yield 98%, mp 112–112.5°C (in a sealed capillary). ^{13}C NMR ($CDCl_3$, δ, ppm): 32.40 (C^1), 42.85 (C^2, C^8, C^9), 29.15 (C^3, C^5, C^7), 37.62 (C^4, C^6, C^{10}), 44.86 (C^{11}), 34.40 (C^{12}, C^{13}, C^{14}). Mass spectrum, m/z, (J_{rel}, %): 192 $[M]^+$ (abs), 135 (100), 79 (11), 136 (11), 93 (10), 67 (5), 107 (6), 91 (4), 55 (4), 77 (4), 81 (4). Found (%): C, 87.31; H, 12.69; $C_{14}H_{24}$. Calculated for $C_{14}H_{24}$: C, 87.42; H, 12.58. Published data: mp 111.7–113.0°C [9].

1-Phenyladamantane (11). Yield 85%, mp 79–80°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.90 (6H, $3CH_2$), 2.04 (3H, 3CH), 1.75 (6H, $3CH_2$), 7.11 (aromatic protons). ^{13}C NMR ($CDCl_3$, δ, ppm): 36.11 (C^1), 43.18 (C^2, C^8, C^9), 29.05 (C^3, C^5, C^7), 36.82 (C^4, C^6, C^{10}), 151.12 (C^{11}), 125.28 (C^{12}, $C^{12'}$), 128.16 (C^{13}, $C^{13'}$), 125.17 (C^{14}). Found (%): C, 89.84; H, 10.16; $C_{16}H_{20}$. Calculated for $C_{16}H_{20}$: C, 90.50; H, 9.50. Published data: mp 80°C [11].

1,3-Dimethyladamantane (12). Yield 79%, bp 84°C/6 torr. ^{13}C NMR ($CDCl_3$, δ, ppm): 30.64 (C^1, C^3), 51.80 (C^2), 44.15 (C^4, C^8, C^9, C^{10}), 29.56 (C^5, C^7), 36.41 (C^6), 31.02 (C^{11}, C^{12}). Found (%): C, 87.12; H, 12.88; $C_{12}H_{20}$. Calculated for $C_{12}H_{20}$: C, 87.73; H, 12.27. Published data: bp 100–105°C/25 torr [12].

1,3-Diethyladamantane (13). Yield 75%, bp 113–114°C/6 torr. n_D^{20} = 1.4855. ^{13}C NMR ($CDCl_3$, δ, ppm): 33.29 (C^1, C^3), 48.92 (C^2), 43.50 (C^4, C^8, C^9, C^{10}), 29.52 (C^5, C^7), 36.41 (C^6), 31.92 (C^{11}, C^{13}), 14.50 (C^{12}, C^{14}). Mass spectrum, m/z, (J_{rel}, %): 192 $[M]^+$ (abs), 163 $[M\text{-}C_2H_5]^+$ (100), 93 (28), 107 (13), 79 (9), 55 (7), 81

Influence of the reaction conditions and alkyl halide structure on the alkylation of adamantane

Catalyst	RX	[cat] : [AdH] : [RX] mole ratio	Reaction conditions		Product	Yield	
			T, °C	time, h		Ad-R	Ad-R_2
$RuCl_3$	MeI	1 : 100 : 100	100	5	4	30	–
	″	″	150	3	″	42	–
$Ru(OH)Cl_3$	″	″	100	5	″	63	–
$Ru(PPh_3)_3Cl$	″	″	″	″	″	97	–
	″	″	150	3	″	95	–
	″	1 : 100 : 200	150	3	4; 12	21	79
$Ru(OH)C_3$	EtBr	1 : 100 : 100	150	3	5	87	–
$Ru(PPh_3)_3Cl$	″	″	″	″	″	95	–
	″	1 : 100 : 200	″	″	5; 13	25	75
	n-PrI	1 : 100 : 100	100	5	6	68	–
	n-PrBr	″	″	″	″	72	–
	n-PrCl	″	″	″	″	89	–
	″	″	150	3	″	94	–
	″	1 : 100 : 200	″	″	6; 14	27	73
	iso-PrCl	1 : 100 : 100	″	″	7	86	–
	BuCl	″	″	″	8	94	–
	iso-BuCl	″	″	″	9	82	–
	tert-BuCl	″	″	″	10	98	–
	PhCl	″	″	″	11	85	–
	AdBr	″	″	″	15	80	–

(7), 121 (5), 77 (5), 53 (4). Found (%): C, 87.35; H, 12.65; $C_{14}H_{24}$. Calculated for $C_{14}H_{24}$: C, 87.42; H, 12.58.

1,3-Di-*n*-propyladamantane (14). Yield 73%, bp 139–140°C/6 torr. n_D^{20} = 1.4880. ^{13}C NMR ($CDCl_3$, δ, ppm): 33.31 (C^1, C^3), 47.95 (C^2), 42.56 (C^4, C^8, C^9, C^{10}), 29.48 (C^5, C^7), 37.30 (C^6), 47.32 (C^{11}, C^{14}), 16.02 (C^{12}, C^{15}), 15.34 (C^{13}, C^{16}). Mass spectrum, *m*/*z*, (J_{rel}, %): 220 $[M]^+$ (2), 177 (100), 93 (15), 178 (12), 79 (11), 121 (10), 135 (10), 81 (7), 55 (7), 91 (7), 107 (6). Found (%): C, 87.11; H, 12.89; $C_{16}H_{28}$. Calculated for $C_{16}H_{28}$: C, 87.19; H, 12.81. Published data: bp 275°C [10].

1,1-Diadamantyl (15). Yield 80%, subp 72°C/10 torr. ^{13}C NMR ($CDCl_3$, δ, ppm): 36.12 (C^1, $C^{1'}$), 35.20 (C^2, C^8, C^{10}, $C^{2'}$, $C^{8'}$, $C^{10'}$), 28.83 (C^3, C^5, C^7, $C^{3'}$, $C^{5'}$, $C^{7'}$), 37.46 (C^4, C^6, C^9, $C^{4'}$, $C^{6'}$, $C^{9'}$). Found (%): C, 88.74; H, 11.26; $C_{20}H_{30}$. Calculated for $C_{20}H_{30}$: C, 88.82; H, 11.18. Mass spectrum, *m*/*z*: 270 $[M]^+$.

1-But-2-enyladamantane (16). Yield 25%, mp 35–36°C (bp 70–71°C/2 torr). ^{13}C NMR ($CDCl_3$, δ, ppm): 33.20 (C^1), 42.24 (C^2, C^8, C^9), 28.33 (C^3, C^5, C^7), 37.60 (C^4, C^6, C^{10}), 37.74 (C^{11}), 42.51 (C^{12}), 138.04 (C^{13}), 114.89 (C^{14}).

RESULTS AND DISCUSSION

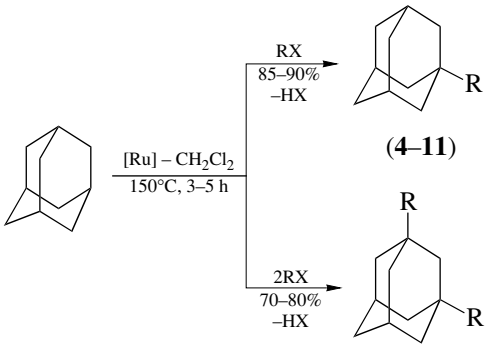
Searching for convenient preparative methods of selective introduction of alkyl substituents into the adamantane (**1**) molecule, we studied its reaction with alkyl halides in the presence of metal-complex catalysts based on platinum, rhodium, palladium, and ruthenium compounds, which are known to activate C–H and C–Hal bonds.

It was found that, of the variety of examined catalysts, the ruthenium complexes exhibit noticeable activity in the alkylation of adamantane **1** with alkyl halides.

For example, the reaction of adamantane with chloro-, bromo-, and iodoalkanes in the presence of ruthenium compounds ($[RuCl_3$, $Ru(OH)Cl_3$, $Ru(PPh_3)_3Cl_2$) taken in a molar ratio of [Ru] : [AdH] : [RX] = 1 : 100 : 100 in a CH_2Cl_2 medium resulted in the formation of alkyladamantanes with a total yield of 70–98%.

The process is highly regioselective: alkylation proceeds exclusively at the bridgehead (tertiary) carbon atom of adamantane, with the yields of 1-alkyl- (**4**–**11**) and 1,3-dialkyladamantanes (**12**–**14**) depending on the length and branching of the alkyl radical in a halogenalkane and on the reaction time.

The activity of C_1–C_3 alkyl halides in this reaction is practically the same; they alkylate adamantane within 3 h at 150°C giving monoalkyladamantanes **4**–**6** with quantitative yields. An increase in the length of the alkyl radical in RX gradually decreases the activity of alkyl halide. The reaction of adamantane with *n*-butyl chloride over 3 h at 150°C afforded 1-*n*-butyladamantane (**8**) in a yield of 72%; an increase of the reaction time to 5 h increased the yield of **8** to 94%. The reaction of adamantane with *tert*-butyl chloride proceeds twice as slowly: the yields of **10** in 3, 5, and 10 h were 54, 71, and 98%, respectively.

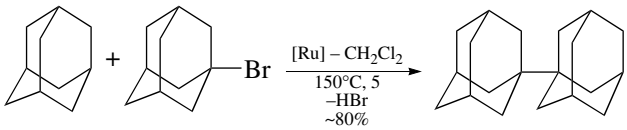


R = Me (**4**, **12**); Et (**5**, **13**); *n*-Pr (**6**, **14**); *iso*-Pr (**7**); *n*-Bu (**8**); *iso*-Bu (**9**); *tret*-Bu (**10**); Pb (**11**).
X = Cl, Br, I

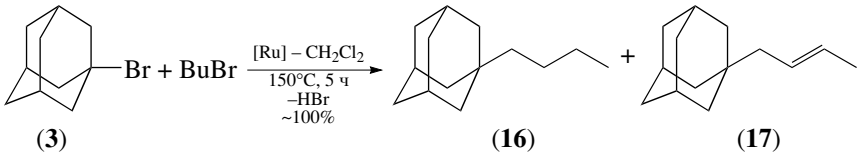
Adamantane alkylation with alkyl bromides and alkyl iodides proceeds more rapidly and more readily; however, the yields of alkyladamantanes are considerably lower because of the formation of high-molecular-mass compounds. A GC–MS analysis and titration of the reaction mixture with a NaOH solution showed that the reaction mixture contained hydrogen halides (HCl, HBr, HI) along with alkylated adamantanes, thus indicating that alkylation proceeds via the substitution of alkyl for the bridgehead hydrogen of adamantane.

An increase in alkyl halide concentration increases the degree of adamantane alkylation. For example, a two-fold excess of RX ([AdH] : [RX] = 1 : 2) results in replacement of two bridgehead hydrogen atoms in the adamantane molecule and the formation of 1,3- dialkyladamantanes.

The alkylation of adamantane **1** with 1-chloroadamantane **2** is difficult and results in low yields of the product (3 h, 30%) even with an increase in the reaction time (5 h, 44%). However, the use of 1-bromoadamantane **3** instead of 1-chloroadamantane **2** resulted in an 80% yield of 1,1'-diadamantyl (**15**) in the reaction at 150°C for 5 h in a CH_2Cl_2 solution at a reactant molar ratio of [Ru] : [AdH] : [RX] = 1 : 100 : 100.



In turn, 1-bromoadamantane **3** is also alkylated with alkyl halides, in particular, *n*-butyl bromide, but the product contains 1-but-2-enyladamantane (**16**) along with 1-*n*-butyladamantane **8**, where **16** is presumably formed via HBr elimination from the side chain.



An attempt to involve 1,3-dibromoadamantane in the reaction in question was unsuccessful. In this case, we observed the formation of a mixture of isomeric monobromodichloro- and monobromotrichloroadamantanes, which were obviously due to the direct participation of CH_2Cl_2 in the chlorination of the adamantane ring and the replacement of bromine by chlorine in the reactant 1,3-dibromoadamantane molecule. The structure of the obtained 1-alkyl- and 1,3-dialkyladamantanes (**4**–**16**) was determined by spectral methods, as well as by comparison with authentic compounds.

The proposed method for the synthesis of alkyladamantanes in the presence of ruthenium-containing catalysts is simple and ensures a high yield of the desired products and high selectivity.

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