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# Novel Approach to Trisubstituted Adamantanes

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***Abstract:*** The 2,5-diaryl-2-adamantanol and 2-(3-alkyl-1-adamantyl)-2-alkanol were found to produce the corresponding 2,5-diaryl-7- and 3,5-dialkyl-1-adamantanols in trifluoroacetic acid with high selectivity. This synthetic methodology is proposed as a perspective approach to 2,5,7- and 1,3,5-trisubstituted adamantanes.

The intensive progress in the adamantane chemistry was accompanied by the development of effective methods for functionalization of adamantane nucleus. Many reliable and convenient procedures for preparation of adamantane compounds have been proposed[1,2]. However, the majority of work dealt only with mono- and disubstituted adamantanes. Tri- and tetrasubstituted derivatives are still not easily available and their properties as well as synthetic potential required further exploration.

The described methods for synthesis of trisubstituted adamantanes are well elaborated only for compounds with functional groups attached to the bridgehead positions of adamantane moiety[3,4] and for 2,2,5-trisubstituted derivatives[5-7]. The former are prepared by direct or stepwise functionalization of bridgehead adamantane positions and the latter could be readily obtained by nucleophile attaching to carbonyl groups of 5-substituted 2-adamantanones. The other possible approaches consist in design of adamantane skeleton by cyclization of non-adamantane polycycles such as bicyclo[3.3.1]nonane derivatives[8] or by isomerization of perhydroaromatic hydrocarbons at the presence of aluminum trihalides[9].

We believe the alternative way to polysubstituted adamantanes employing selective rearrangements of more available adamantane derivatives to be very promising.

There are known two examples when disubstituted adamantanes were produced as a result of isomerization of 2-methyl-2-adamantanol[10] and 2-(1-adamantyl)-2-propanol[11] at the presence of sulfuric acid. These rearrangements included the transfer of reaction center to the bridgehead adamantane position and, however, were accompanied by the formation of by-products and gave low yields.

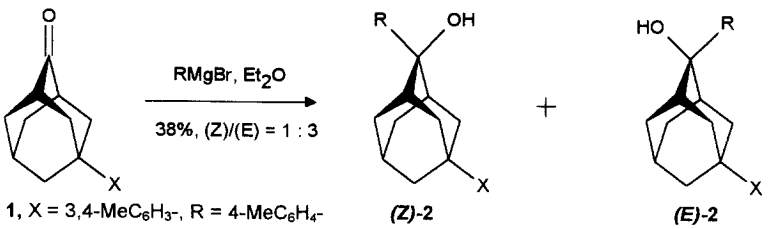
Some years ago we showed that tertiary 2-alkyl- and 2-aryl-2-adamantanols undergo regio- and stereoselective isomerization into corresponded 2-substituted-5-adamantanols in trifluoro-

acetic acid (TFA) medium[12-14]. The reaction was suggested to proceed *via* intermolecular hydride transfer.

Here we would like to suggest a new synthetic approach to 2,5,7- and 1,3,5-trisubstituted adamantanes based on the isomerization of tertiary alcohols with hydroxy group at the bridge position of adamantane nucleus or at α-position of alkyl chain attached to bridgehead adamantane carbon. This work deals with the transformations of 2-(4-methylphenyl)-5-(3,4-dimethylphenyl)-2-adamantanol and 2-(1-adamantyl)-2-alkanols in TFA solution.

## RESULTS AND DISCUSSION

The original alcohols *(Z)*- and *(E)*-**2** were prepared by action of the Grignard reagent on 5-(3,4-dimethylphenyl)-2-adamantanone **1**. This reaction proceeded stereoselectively with predominant formation of *(E)*-product *(E)*-**2** (Scheme 1). Selectivity ratio *(E)/(Z)* was determined by NMR measurements of the crude reaction mixture (76/24) and by the yields of isolated products (75/25).

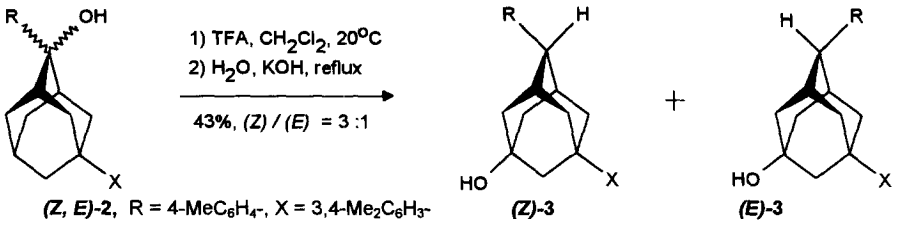



Scheme 1

Our results seem to be in good agreement with the data obtained earlier[15-18] in the study of stereochemical course of nucleophilic attack onto trigonal carbon in the different 5-substituted-2-adamantanones. The direction of preferential nucleophile attaching was found out to be determined by the electronic properties of the substituent at 5-position. Electron-withdrawing substituents, particularly the aryl groups, favor the *syn*-attack of nucleophile and formation of corresponding *(E)*-alcohols.

The isomerization experiments were carried out with 0.25 M solution of alcohol **2** in TFA-$CH_2Cl_2$ (1 : 1, vol.) solution at room temperature. We established that *(Z,E)*-2-(4-methylphenyl)-5-(3,4-dimethylphenyl)-2-adamantanol **2** underwent the rearrangement leaded to the 2-(4-methylphenyl)-5-(3,4-dimethylphenyl)-7-adamantanol **3** (Scheme 2). The reaction was followed by $^{13}C$ NMR spectrometry and the obtained results are presented in Table 1.

The isomerization of both *(Z)*- and *(E)*-isomer of **2** is likely to proceed with initial formation of identical carbocationic intermediates which could be weak-linked ion pairs and the stereochemical result of these transformations should not depend upon substrate configuration. To clarify this assumption we carried out the isomerization of the two isolated isomers of 2-(4-methylphenyl)-5-(3,4-dimethylphenyl)-2-adamantanol *(Z)*-**2** and *(E)*-**2** as well as their mixture *(Z,E)*-**2**. The selectivity of the reactions occurred to be almost independent on the configuration of a starting compound.

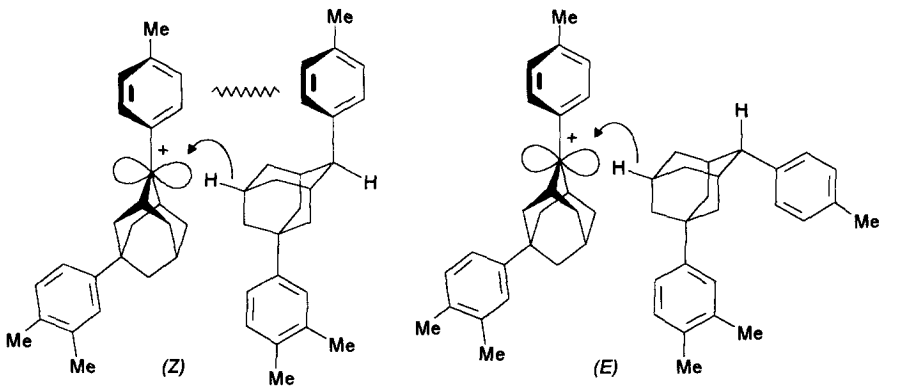



*(Z, E)*-**2**, R = 4-$MeC_6H_4$-, X = 3,4-$Me_2C_6H_3$- *(Z)*-**3** *(E)*-**3**

Scheme 2

This reaction seems to be accompanied by the intermolecular hydride shift between the initilal cationic intermediate and appropriate hydrocarbon (Scheme 3) as it was assumed earlier for disubstituted substrates[13,14]. The hydrocarbon could be generated by disproportion of starting alcohol and plays a key role in the isomerization process acting as hydride carrier and catalyst.

We believe that intrigued reaction stereoselectivity may be explained by specific interactions of the closely oriented aromatic moieties of the hydride donor and hydride acceptor in the transition state of hydride transfer reaction when the *(Z)*-isomer is formed (Scheme 3, *(Z)*). In the case of *(E)*-isomer the interaction of that kind could not be realized (Scheme 3, *(E)*). The thorough consideration of the nature of these interactions is going to be published in a forthcoming paper.




Scheme 3

In general, stereoselectivity and rate of isomerization in the case of trisubstituted alcohol **2** were somewhat lower in comparison with the disubstituted 2-aryl-2-adamantanols[13,14]. The remarkable 'conductivity' of adamantane skeleton to the electronic effects of substituents[19] seems to be responsible for this. The presence of 5-aryl substituent into starting cationic intermediate resulted in increased electrophilicity of cationic center and, hence, lowered selectivity. This methodology could be proposed as a perspective approach to the 2,5,7-trisubstituted adamantanes with three different substituents (not available before). To demonstrate this we prepared both individual *(Z)*- and *(E)*-2-(4-methylphenyl)-5-(3,4-dimethylphenyl)-7-adamantanols *(Z)*-**3** (33%) and *(E)*-**3** (10%).

**Table 1.** Isomerization of 2-(4-methylphenyl)-5-(3,4-dimethylphenyl)-2-adamantanol **2** (0.25 M soln. in TFA-$CH_2Cl_2$ (1:1, vol.); 20°C, 120 h)

| Substrate | **2**, *(Z)/(E)*[a] | Yield, **3**, % | *(Z)/(E)*[a], **3** |
|---|---|---|---|
| *(Z)*-**2** | 100/0 | -[b] | 76/24 |
| *(E)*-**2** | 0/100 | -[b] | 79/21 |
| *(Z,E)*-**2** | 24/76 | 43.4[c] | 75/25 |

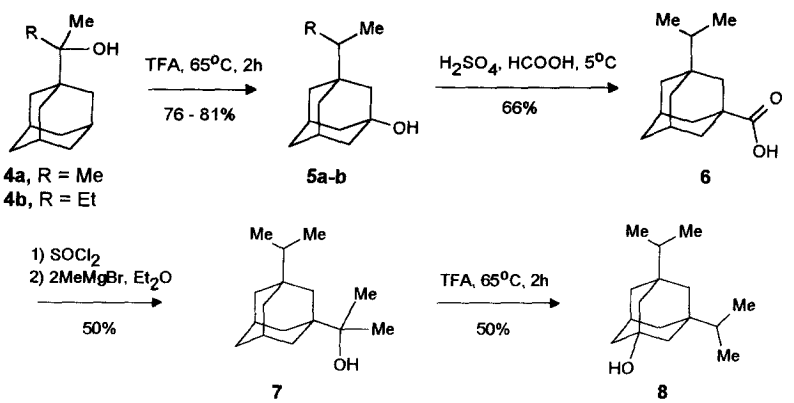
[a] $^{13}C$ NMR data;

[b] The reaction was carried out in NMR tube in $CF_3COOD$;

[c] Yield of isolated product.

The rearrangement described above, therefore, allows to get a new type of trisubstituted adamantanes from more available derivatives that, however, have three substituents too. The another part of our work was devoted to the study of mono- and disubstituted adamantane derivatives bearing hydroxy function at the α-position of side chain, *i. e.* 2-(1-adamantyl)-2-alkanols **4a,b** and **7**. Their transformations in TFA solution are potential to result in transfer of reaction center into adamantane moiety[11]. This is a way by which bridgehead di- and trisubstituted adamantanes could be achieved.

Isomerization experiments were carried out under heating in TFA solution. The alcohols **4a,b** formed correspondent 3-alkyl-1-adamantanols **5a,b** in high yield and selectivity. To our opinion, this way appeared to be more convenient than that of described in[11], especially for the compounds that might contain functional groups sensitive to sulfuric acid. And finally, we succeeded to obtain a new 1,3,5-trisubstituted adamantane **8** from 1-adamantylalkanol **7** by the further use of such a process (Scheme 4).

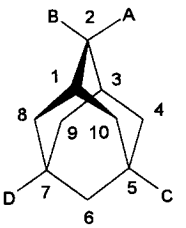



Scheme 4

For the reason that each of trisubstituted alcohols **2** and **3** could be one of two possible diastereomers, the determination of their structures have required thorough analysis of $^{13}C$ NMR spectra followed by comparison of experimental data with ones calculated on the base of additivity of $^{13}C$ substituents chemical shifts (SCS) (Table 2).

The $^{13}C$ peak assignments were based on APT technique and different signal intensities according to the symmetry of alcohols **2** and **3**. To calculate $^{13}C$ NMR chemical shifts of adamantane carbons in compounds **1-3** we employ 2-adamantanone, 2-(4-methylphenyl)-2-adamantanol, 1-(3,4-dimethylphenyl)-3-adamantanol, *(Z)*- and *(E)*-2-(4-methylphenyl)-5-adamantanols as model compounds[13,20,21] and known[20] SCS of 1-(3,4-dimethylphenyl)- and 2-(4-methylphenyl)- groups.

**Table 2.** Calculated ($\delta_{cal.}$) and Experimental ($\delta_{exp.}$) $^{13}C$ NMR Chemical Shifts of Adamantane Fragment in 2,5,7-Trisubstituted Adamantanes **1-3** (δ, ppm; $CDCl_3$, 20°C)




| Entry | Substituents | | $C_{1,3}$ | $C_2$ | $C_{4,10}$ | $C_5$ | $C_6$ | $C_7$ | $C_{8,9}$ |
|---|---|---|---|---|---|---|---|---|---|
| **1** | A = B = O | $\delta_{cal.}$ | 47.12 | 216.59 | 44.25 | 34.30 | 41.29 | 27.64 | 37.84 |
| | C = 3,4-$Me_2C_6H_3$ | $\delta_{exp.}$ | 46.63 | 217.86 | 44.39 | 35.55 | 42.02 | 28.11 | 38.43 |
| | D = H | Δ[a] | -0.49 | 1.27 | 0.14 | 1.25 | 0.73 | 0.47 | 0.59 |
| *(Z)*-**2** | A = HO, D = H | $\delta_{cal.}$ | 35.67 | 73.65 | 37.83 | 33.75 | 42.66 | 27.61 | 33.38 |
| | B = 4-$MeC_6H_4$ | $\delta_{exp.}$ | 36.41 | 74.58 | 38.48 | 34.74 | 43.10 | 28.05 | 33.99 |
| | C = 3,4-$Me_2C_6H_3$ | Δ | 0.74 | 0.93 | 0.65 | 0.99 | 0.44 | 0.44 | 0.61 |
| *(E)*-**2** | A = 4-$MeC_6H_4$ | $\delta_{cal.}$ | 35.67 | 73.65 | 39.79 | 34.27 | 42.66 | 27.09 | 31.42 |
| | B = HO, D = H | $\delta_{exp.}$ | 36.08 | 74.79 | 40.09 | 35.29 | 43.62 | 27.62 | 32.00 |
| | C = 3,4-$Me_2C_6H_3$ | Δ | 0.41 | 1.14 | 0.30 | 1.02 | 0.96 | 0.53 | 0.58 |
| *(Z)*-**3** | A = H, D = HO | $\delta_{cal.}$ | 34.00 | 44.00 | 42.82 | 39.06 | 50.50 | 69.36 | 39.23 |
| | B = 4-$MeC_6H_4$ | $\delta_{exp.}$ | 34.00 | 44.28 | 43.38 | 39.25 | 51.03 | 69.39 | 39.21 |
| | C = 3,4-$Me_2C_6H_3$ | Δ | 0.00 | 0.28 | 0.56 | 0.19 | 0.53 | 0.03 | -0.02 |
| *(E)*-**3** | A = 4-$MeC_6H_4$ | $\delta_{cal.}$ | 34.50 | 44.37 | 35.88 | 39.07 | 50.79 | 69.11 | 45.45 |
| | B = H, D = HO | $\delta_{exp.}$ | 33.73 | 44.48 | 36.31 | 39.35 | 51.03 | 69.09 | 45.41 |
| | C = 3,4-$Me_2C_6H_3$ | Δ | -0.77 | 0.11 | 0.43 | 0.28 | 0.24 | -0.02 | -0.04 |

[a] $D = d_{exp.} - d_{cal.}$

In conclusion, the rearrangements of tertiary adamantanols with hydroxy groups at bridge or α-side chain positions in TFA solution resulted in the intermolecular transfer of cationic center to the farthest adamantane bridgehead carbon. We suggest this synthetic approach to be used in preparing of different polysubstituted adamantanes including 1,3,5- and 2,5,7-trisubstituted

derivatives. Notably, that reactions of 2-arylsubstituted adamantanols were remarkable for stereoselectivity, and predominant formation of *(Z)*-isomers of products were observed in all cases.

## EXPERIMENTAL

Melting points are uncorrected. $^{13}C$ NMR spectra were recorded with Varian VRX-300 spectrometer in $CDCl_3$ and, in the case of isomerization experiments, in $CF_3COOD$. Preparative column chromatography separations were performed on silica gel L 40/100 (*Chemapol*®), and precoated silica gel plates (*Silufol*® *UV-254*) were used for analytical TLC. HPLC analyses were carried out using *Milichrom*® instrument supplied with *Seaparon*®-*CGX* column. Eluent: *n*-heptane-dichloromethane-2-propanol (70:29:1, vol. %). 5-Bromo-2-adamantanone, 2-(1-adamantyl)-2-propanol and 2-(1-adamantyl)-2-butanol were obtained according to literature procedures[11,16]. All species were characterized by microanalysis.

*5-(3,4-dimethylphenyl)-2-adamantanone* ***1***

Mixture of 3.00 g (13.1 mmol) of 5-bromo-2-adamantanone, 7.00 g (26.3 mmol) of aluminum bromide, and 25 mL (21.8 g, 204 mmol) of *o*-xylene was kept for 3 h at 100°C. Then mixture was poured on ice, extracted by dichloromethane, washed by water, and dried over $MgSO_4$. The residue after evaporation was twice recrystallized.

Yield of **1**: 2.40 g, (9.4 mmol, 72%); mp 151-152°C (*n*-hexane); $R_f$ 0.63 (*n*-hexane-ether, 1:1); Found, %: C 84.56; H 9.09. $C_{18}H_{22}O$; Calcd., %: C 84.99; H 8.72.

*(Z)- and (E)-2-(4-methylphenyl)-5-(3,4-dimethylphenyl)-2-adamantanols* ***2***

Solution of 1.37 g (8.00 mmol) of 4-bromotoluene was added dropwise to 0.21 g (8.8 mmol) of magnesium turnings in 10 mL of absolute ether at stirring. After magnesium being dissolved, the solution of 1.02 g (4.0 mmol) of 5-(3,4-dimethylphenyl)-2-adamantanone **1** was added and refluxing continued for 3 h. The mixture was kept overnight at room temperature, treated with saturated water solution of ammonium chloride and extracted by ether. Organic layer was washed, dried over $MgSO_4$, and evaporated. The residue was chromatographed over silica gel (eluent: *n*-hexane - ether, 4:1). Stereoselectivity of the reaction was determined on the base of $^{13}C$ NMR spectra of unseparated mixture of isomers (*(Z)/(E)*=24/76).

Yield of *(Z)*-**2**: 0.18 g, (0.52 mmol, 13.0%); mp 138-139°C (*n*-heptane); $R_f$ 0.63 (*n*-hexane-ether, 1:1); Found, %: C, 86.34; H, 8.90; $C_{25}H_{30}O$; Calcd., %: C, 86.67; H, 8.73.

Yield of *(E)*-**2**: 0.46 g, (1.33 mmol, 33.2 %); mp 132-134°C (*n*-heptane); $R_f$ 0.70 (*n*-hexane-ether, 1:1); Found, %: C, 86.21; H, 9.09; $C_{25}H_{30}O$; Calcd., %: C, 86.67; H, 8.73.

*(Z)- and (E)-2-(4-methylphenyl)-5-(3,4-dimethylphenyl)-7-adamantanols* ***3***

The mixture of alcohols *(Z)*-**2** and *(E)*-**2** 0.69 g (2 mmol) was dissolved in TFA-$CH_2Cl_2$ (1:1, vol. 8 mL), solution was kept for 120 h at room temperature until isomerization was finished. The reaction was followed by HPLC. Then, 25 mL 20% aqueous solution of KOH was added, mixture was kept at reflux for 2 h and extracted by dichloromethane. The organic layer was washed by water, dried over $MgSO_4$, and evaporated. The residue was chromatographed

over silica gel (eluent: *n*-hexane - ether, 4:1). Stereoselectivity of the reaction was determined on the base of $^{13}C$ NMR spectra of unseparated mixture of isomers (*(Z)/(E)*=75/25).

Yield of *(Z)*-**3**: 0.23 g, (0.66 mmol, 33.3%); mp 135-137°C (*n*-heptane); $R_f$ 0.25 (*n*-hexane-ether, 1 : 1); Found, %: C, 86.20; H, 8.65; $C_{25}H_{30}O$; Calcd., %: C, 86.67; H, 8.73.

Yield of *(E)*-**3**: 0.07 g, (0.20 mmol, 10.1 %); mp 174-177°C (*n*-heptane); $R_f$ 0.17 (*n*-hexane-ether, 1:1); Found, %: C, 86.41; H, 9.01; $C_{25}H_{30}O$; Calcd., %: C, 86.67; H, 8.73.

*3-Isopropyl-1-adamantanol* ***5a****, 3-(2-butyl)-1-adamantanol* ***5b****, and 3,5-di(isopropyl)-1-adamantanol* ***8***

The mixture of alcohol **4a, 4b,** or **7** (26 mmol) and 15 mL (200 mmol) of TFA was kept for 2 h at 60-65°C. Then, a saturated aqueous solution of sodium carbonate was added. Mixture was refluxed for 2h and extracted by ether. Organic layer was washed by water, dried over $MgSO_4$, and evaporated. The residue was chromatographed over silica gel (eluent: *n*-hexane - ether, 2 : 1).

Yield of **5a**: 76%; oil, Found, %: C, 80.12; H, 11.45; $C_{13}H_{22}O$; Cald., %: C, 80.41; H, 11.34; $^1H$ NMR (δ, ppm, $CCl_4$): 0.80 (d, 6H), 1.21-1.79 (m, 13H), 2.22 (br.s, 2H), 3.63 (s, 1H); $^{13}C$ NMR (δ, ppm, $CHCl_3$): 69.14 ($C_1^{Ad}$), 46.92 ($C_2^{Ad}$), 38.35 ($C_3^{Ad}$), 37.77 ($C_{4,9}^{Ad}$), 30.66 ($C_{5,7}^{Ad}$), 35.76 ($C_6^{Ad}$), 44.90 ($C_{8,10}^{Ad}$);

Yield of **5b:** 81%; oil, Found, %: C, 80.12; H, 11.45; $C_{13}H_{22}O$; Cald., %: C, 80.41; H, 11.34; $^1H$ NMR (δ, ppm, $CCl_4$): 0.80 (d, 6H), 1.21-1.79 (m, 13H), 2.22 (br.s, 2H), 3.63 (s, 1H); $^{13}C$ NMR (δ, ppm, $CHCl_3$): 68.41 ($C_1^{Ad}$), 46.72 ($C_2^{Ad}$), 36.51 ($C_3^{Ad}$), 37.50 ($C_{4,9}^{Ad}$), 31.01 ($C_{5,7}^{Ad}$), 35.60 ($C_6^{Ad}$), 44.82 ($C_{8,10}^{Ad}$);

Yield of **8**: 76%; oil, Found, %: C, 80.12; H, 11.45; $C_{13}H_{22}O$; Cald., %: C, 80.41; H, 11.34; $^1H$ NMR (δ, ppm, $CCl_4$): 0.81(d, 6H), 1.10-1.49 (m, 12H), 2.12 (br.s, 1H), 2.50 (s, 1H); $^{13}C$ NMR (δ, ppm, $CHCl_3$): 68.91 ($C_1^{Ad}$), 46.42 ($C_2^{Ad}$), 37.01 ($C_3^{Ad}$), 39.10 ($C_4^{Ad}$), 37.01 ($C_5^{Ad}$), 37.20 ($C_6^{Ad}$), 31.51 ($C_7^{Ad}$), 44.52 ($C_8^{Ad}$), 37.20 ($C_9^{Ad}$), 46.42 ($C_{10}^{Ad}$);

*3-Isopropyl-1-adamantanecarboxylic acid* ***6***

The flat-bottomed flask equipped with magnetic stirrer was loaded with 9.7 g (50 mmol) of 1-isopropyl-3-adamantanol **5a** and 65 mL (1200 mmol) of 98% sulfuric acid. The mixture was cooled with ice-water bath and 2.5 mL (55 mmol) of anhydrous formic were added dropwise at 5-7°C. Then cooling bath was removed and stirring was continued for 24 h at room temperature. The reaction mixture was poured on ice. The formed precipitate was filtered and twice reprecipitated by action of water solution of sodium bicarbonate and hydrochloric acid. Obtained product was washed with water and dried.

Yield of **6**: 7.3 g (33 mmol, 66%); mp 115-117°C[11];

*2-(3-Isopropyl-1-adamantyl)propanol* ***7***

The three-neck round-bottom flask equipped with effective stirrer and condenser was loaded with 11.1 g (50 mmol) of 3-isopropyl-1-adamantanecarboxylic acid **6** and 18 mL (29.8 g, 250 mmol) of thionyl chloride. The mixture was heated on boiling water bath for 45 min until acid being dissolved. After cooling, 30 mL of dry benzene was added and excess of thionyl

chloride was removed by evaporation under reduced pressure. This procedure was repeated four times. Obtained 3-isopropyl-1-adamantanecarboxylchloride was dissolved in dry diethyl ether and used in the following procedure without further purification.

The Grignard reagent was prepared from 1.8 g (75 mmol) of magnesium turnings and 4.67 mL (10.7 g, 75 mmol) of methyl iodide in dry diethyl ether. This solution was added dropwise to the soln. of 50 mmol of 3-isopropyl-1-adamantanecarboxylchloride in 150 mL of diethyl ether. The reaction mixture was stirred and refluxed for 3 h, cooled, and quenched with saturated soln. of ammonium chloride. Organic layer was separated and water phase was extracted with diethyl ether. Combined ether phases were washed by water and dried over $MgSO_4$ and evaporated. The residue was chromatographed over silica gel (eluent: *n*-hexane - ether, 1 : 1).

Yield of **7**: 5.9 g (25 mmol, 50%); oil; Found, %: C, 81.22; H, 12.05; $C_{16}H_{28}O$; Cald., %: C, 81.29; H, 11.94;

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## REFERENCES

1. Fort, R. C.; Schleyer, P. R. Chem. Rev., **1964**, *64*, 277-300.
2. Bingham, R. C.; Schleyer, P. R. Chemisty of Adamantenes. *In: Topics in Current Chem.*, **1971**, 3-102.
3. Stetter, H.; Krause, M.; Last, W. *Chem. Ber.*, **1969**, *102*, 3357-3359.
4. Stetter, H.; Wulf, C. Baughman, *Chem. Ber.*, **1960**, *23*, 1366-1367.
5. Cheung, C.; Tseng, L.; Lin, M.-H.; Srivastava,S.; Le Noble, W. J. *J. Am. Chem. Soc.*, **1986**, *108*, 1598-1605.
6. Vodicka, L.; Hlavaty, J. *Coll. Czech. Chem. Commun.*, **1979**, *11*, 3296-3300.
7. Giddings, M. R.; Hudes, J. *Can. J. Chem.*, **1981**, *59*, 459-467.
8. Krasutsky, P. A.; Fokin, A. A.; Skoba, E. D.; Yurchenko, A. G. *Zh. Org. Khim.*, **1986**, *22*, 460-461.
9. Schneider, A.; Warren, R. Janoski, E. *Trans. N. Y. Acad. Sci.*, **1967**, *30*, 3.
10. McKervey, M.; Alford, J.; McGarrity, J.; Rea, E. *Tetrahedron Lett.*, **1968**, *(50)*, 5165-516.
11. Raber, D.; Fort, R.; Wiskott, E.; Woodworth, C.; Schleyer, P. *Tetrahedron*, **1971**, *27*, 3-18.
12. Kovalev, V. V.; Rozov, A. K.; Shokova, E. A. **SU** 1,502,558, 23 Aug 1989, Appl. 4,309,237 23 Sep 1987, *Ch.Abs.* **1990**, *112*, P 76470.
13. Kovalev, V. V.; Rozov, A. K.; Luzikov, Yu. N.; Savelyev, Yu. I.; Shokova, E. A. *Zh. Org. Khim.*, **1989**, *25*, 517-521.
14. Kovalev, V. V.; Rozov, A. K.; Shokova, E. A. *Synlett*, **1990**, *12*, 739-740.
15. Bone, J.; Pritt, J.; Whiting, H. *J. Chem. Soc., Per. Trans. 1*, **1972**, *21*, 2644-2647.
16. Cheung, C.; Tseng, L.; Lin, M.-H.; Srivastava, S.; le Noble, W. J. *J. Am. Chem. Soc.*, **1986**, *108*, 1598-1605.
17. Lin, M.-H.; Silver, J. E.; le Noble, W. J. *J. Ogr. Chem.*, **1988**, *53*, 5155-5158.
18. Xie, M.; le Noble, W. J. *J.Org.Chem.*, **1989**, *54*, 38361-3839.
19. Grob, C. A.; Grundel, M.; Sawlewicz, P. *Helv. Chim. Acta*, **1988**, *71*, 1502-1507.
20. Kovalev, V. V.; Lusikov., Yi. N.; Saveljev, Yi. I. *Neftekhimija*, **1989**, *29*, 628. *Chem. Abstr.*, **1990**, *113*, 5567b.
21. Duddek, H.; Hollowood, F.; Karim, A.; McKervey, M. A. *J. Chem. Soc. Perkin Trans. II.*, **1979**, *(3)*, 360-365.

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