Adamantylation and Adamantylalkylation of Amides, Nitriles and Ureas in Trifluoroacetic Acid

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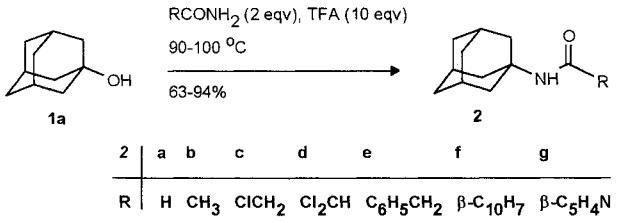
A new preparative method for *N*-adamantylation of carboxylic acid amides, ureas and for C5-adamantylation of barbituric acid in trifluoroacetic acid (TFA) is proposed. Tertiary 1-adamantanols and 1-(1-adamantyl)alkanols were used as adamantylating agents. The reaction of 1-(1-adamantyl)alkanols with nitriles in TFA solution was employed for the first time for the preparation of *N*-[1-(1-adamantyl)alkyl]amides.



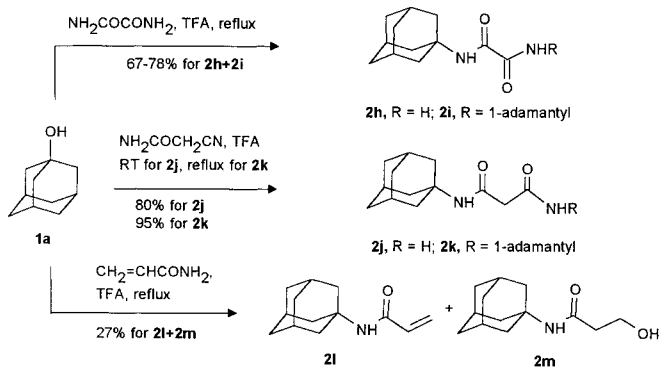
Recently much attention has been paid to the development of effective methods for the synthesis of *N*-adamantylamides and *N*-adamantylureas due to potential importance of these compounds in medicinal scientific fields.[1,2] Most frequently, *N*-(1-adamantyl)amides are obtained by one of two ways: by Ritter reaction of adamantane or its derivatives with nitriles[3,4] or by alkylation of amides with 1-adamantyl halides.[5] Condensation of adamantyliso(isothio)cyanates with amines[6] or, vice versa, condensation of aminoadamantanes with iso(isothio)cyanates[7] are universlly adopted methods for the synthesis of adamantylated ureas and thioureas.

On studying the novel nucleophilic substitution of the hydroxy group in adamantanols and 1-adamantylalkanols with different mild *C*-, *N*- and *P*-nucleophilic reagents in TFA solution,[8–12] we found that 1-adamantanol (**1a**) reacted with some nitriles to give the corresponding *N*-(1-adamantyl)amides[12] in good yields. Extending this work the present study deals with the interaction of 1-adamantanols and 1-(1-adamantyl)alkanols with different *N*-nucleophiles: carboxylic acid amides, nitriles, urea and thiourea. Some of the obtained nitrogen-containing adamantanes are hardly accessible by other methods and are expected to show interesting biological activity.

Amides, ureas and related compounds are ambident nucleophiles capable of *O*- or *N*-alkylation. Alkylation of amides with alcohols in acidic conditions is known to usually give products of *N*-substitution.[13] Rare data on amide adamantylation in acidic medium confirm this rule. Thus, a mixture of *N*-mono- and *N,N'*-diadamantylated derivatives is formed as a result of reaction of oxamide with adamantane in nitric acid.[2] In analogous conditions *N*-adamantyl- and *N*-alkyladamantylureas were obtained from urea and adamantane (or alkyladamantanes).[14]

We have found that 1-adamantanol (**1a**) reacts with primary amides in refluxing TFA to give *N*-(1-adamantyl)amides **2** in good yields (Table 1). A decrease of temperature of up to 50 °C leads to a lowering of product yields. At room temperature the adamantylation does not take place at all (Table 1, entry 2,3).

The substitution reaction is likely to occur via the corresponding trifluoroacetates which are formed readily after reagent mixing. Probably, it is the low nucleophilicity of the trifluoroacetic ion that provides the facility of adamantyl-containing carbenium ions generation in TFA medium. Then, the solvated adamantyl cation is trapped by the NH_2-group of the amide to give *N*-(1-adamantyl)amide. TFA has excellent solvent power for all adamantanols, in general, and for *N*-nucleophilic reagents of present interest, the low boiling point of this acid permits it to separate facilely from the reaction mixture. The possibility of selective adamantylation of compounds with several *N*-nucleophilic centres is one of the main advantages of our method. Thus, in reaction with 1-adamantanol (**1a**) oxamide affords a mixture of mono- and diadamantylated amides **2h,i**. If the amounts of reagents are equal monoadamantyl amide **2h** is a dominant product of the reaction (**2h:2i** = 19:1). When triple excess of **1a** is used amide **2i** is formed in preference (**2h:2i** = 1:1.2). We have found that in comparison with amides, nitriles are alkylated considerably easier in TFA. This observation allows us to carry out the chemoselective *N*-adamantylation of cyanoacetic acid amide. Under mild conditions, only the more nucleophilic nitrile group is affected by 1-adamantanol, *N*-adamantylmalondiamide (**2j**) being produced in 80% yield (Table 1, entry 12). Under reflux, cyanoacetamide (1 equiv) interacts with **1a** (3 equiv) to yield *N,N'*-di(1-adamantyl)malondiamide (**2k**) quantitatively, that is, both nitrile and amide groups react. Interestingly, acrylamide has been shown to undergo not only the adamantylation of the amide centre but the addition of TFA to the carbon–carbon double bond. Separation of *N*-(1-adamantyl)acrylamide (**21**) and β-hydroxypropionic acid *N*-(1-adamantyl)amide (**2m**) in this case was performed by column chromatography on silica gel.



The products of *C*-adamantylation are not revealed in this case. This result seems to be in a good agreement with our earlier observation[8] that the presence of electron-withdrawing substituents in alkenes prevents the interaction of double bonds with the 1-adamantyl cation in TFA medium. Also the adamantylation of aromatic fragments of phenylacetic, α-naphthoic and nicotinic acid amides does not occur and *N*-(1-adamantyl) derivatives **2e–g** are the only products of the reaction.

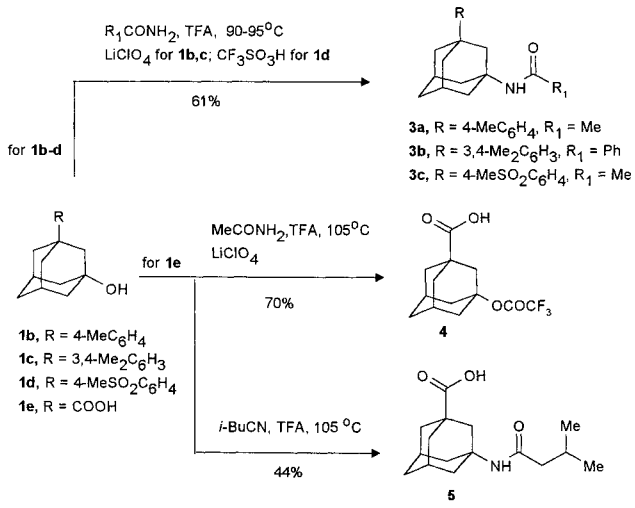
In contrast to sulfuric acid usually employed as a catalyst

Table 1. Reactions of 3-(*R*)-1-Adamantanols and 1-Adamantylalkanols with Amides, Nitriles and Ureas in TFA

Entry	Alcohol	Reagent	Reagent Equiv	TFA Equiv	Time (h), Temp. (°C)	Product, Yield,[a] %	mp, °C; R_f (silica gel)
1	**1a**	$HCONH_2$	2	10	8, 90–95	**2a**, 94	137–139 (hexane);[25] 0.38 ($CHCl_3/Me_2CO$, 20:1)
2	**1a**	$MeCONH_2$	2	10	72, r.t.	–	
3	**1a**	$MeCONH_2$	2	10	12, 50–55	**2b**, 42	147–149 (hexane);[26] 0.42 ($CHCl_3/Me_2CO$, 20:1)
4	**1a**	$MeCONH_2$	2	10	6, 90–95	**2b**, 83	147–149 (hexane)[26]
5	**1a**	$ClCH_2CONH_2$	2	10	8, 90–95	**2c**, 80	177–178 ($EtOH/H_2O$, 1:1);[4] 0.74 ($CHCl_3/Me_2CO$, 20:1)
6	**1a**	$Cl_2CHCONH_2$	2	10	12, 90–95	**2d**, 70	137–139 ($EtOH/H_2O$, 1:1); 0.66 ($CHCl_3$)
7	**1a**	$PhCH_2CONH_2$	2	10	11, 90–95	**2e**, 68	178–179 (isooctane);[27] 0.38 ($CHCl_3/Me_2CO$, 20:1)
8	**1a**	1-naphthylCONH$_2$	2	10	13, 95–100	**2f**, 70	209–210 (EtOH)
9	**1a**	3-pyridylCONH$_2$	2	10	9, 95–100	**2g**, 64	165–166 (hexane/EtOH);[12] 0.21 ($CHCl_3/Me_2CO$, 20:1)
10	**1a**	$(CONH_2)_2$	2	36	9, 90–95	**2h**, 63	183–185;[2] 0.18 ($CHCl_3$)
						2i, 4	233–234;[2] 0.78 ($CHCl_3$)
11	**1a**	$(CONH_2)_2$	0.3	12	22, 90–95	**2h**, 35	183–185[2]
						2i, 43	233–234[2]
12	**1a**	$NCCH_2CONH_2$	1	10	4, r.t.	**2j**, 80	170–172 (heptane: Me_2CO); 0.14 ($CHCl_3$/EtOH 20:1)
13	**1a**	$NCCH_2CONH_2$	0.3	3.5	8, 90–95	**2k**, 95	245–247; 0.66 ($CHCl_3/Me_2CO$ 20:1)
14	**1a**	$CH_2=CHCONH_2$	2	10	8, 90–95	**2l**, 19	140–142;[28] 0.73 ($CHCl_3$/MeCO 20:1)
						2m, 8	145–147; 0.26 ($CHCl_3$/EtOH 20:1)
15	**1b**	$MeCONH_2$	3	15[b]	10, 100–105	**3a**, 56	162–164 (octane); 0.50 ($CHCl_3$)
16	**1c**	$PhCONH_2$	3	15[b]	10, 100–105	**3b**, 41	159–161 (heptane); 0.45 ($CHCl_3$)
17	**1d**	$MeCONH_2$	2	15[b]	12, 90–95	**3c**, 10	167–168; 0.33 ($CHCl_3/Me_2CO$, 20:1)
18	**1d**	$MeCONH_2$	2	10[c]	12, 90–95	**3c**, 61	167–168
19	**1e**	$MeCONH_2$	2	15[b]	16, 75–80	**4**, 70	158–160; 0.41 ($CHCl_3/Me_2CO$, 20:1)
20	**1e**	$PhCH_2CONH_2$	2	15[b]	12, 100–105	**4**, 75	158–160
21	**1c**	Me_2CHCH_2CN	2	20	7, 100–105	**5**, 44	202–203; 0.53 ($CHCl_3/Me_2CO$, 20:1)
22	**1a**	NH_2CONH_2	2	10	7, 45–50	**6a**, 80	270–272[15]
23	**1a**	NH_2CONH_2	2	10	7, 75–80	**6a**, 78	270–272[15]
24	**1a**	NH_2CONH_2	0.3	10	17, 75–80	**6a**, 82	270–272[15]
25	**1a**	NH_2CSNH_2	1.5	10	11, 45–50	**7a**, 90	205–206[7]
26	**1a**	NH_2CSNH_2	1.5	10	15, 100–105	**7a**, 85	205–206[7]
27	**1a**	NH_2CONH_2	2	10	7, 110–115	**8a**, 83	350 dec
28	**1d**	NH_2CONH_2	1.5	15	9, 110–115	**8b**, 31	162–165
29	**1d**	NH_2CSNH_2	2	20	12, 100–105	**7b**, 58	235–240; 0.47 ($CHCl_3$/EtOH, 20:1)
30	**1a**	barbituric acid	0.5	29	5, 90–95	**9**, 92	> 320 (HOAc); 0.47 ($CHCl_3$/EtOH, 20:1)
31	**10a**	PhCN	2	10[c]	10, 95–100	–	–
32	**10b**	$PhCH_2CONH_2$	2	15[b]	15, 95–100	–	–
33	**10b**	$PhCH_2CONH_2$	2	15[c]	22, 95–100	**11**, 20	114–115; 0.47 ($CHCl_3$)
34	**10b**	NH_2CONH_2	2	20	20, 100–105	–	
35	**10b**	$ClCH_2CN$	3	15	7, 90–95	**12a**, 57	107–108 (hexane)
36	**10b**	3-pyridylCN	2	15[b]	8, 90–95	**12b**, 70	144–145 ($EtOH/H_2O$, 2:1)
37	**10b**	$ClC_6H_4CH_2CN$	1.5	15	9, 100	**12c**, 83	144–145 ($EtOH/H_2O$, 6:1)
38	**10b**	MeCN	5	8.5	5, 65–70	**12d**, 81	134–136 (heptane); 0.28 ($CHCl_3$/PhH, 3:1)
39	**10c**	$ClCH_2CN$	3	15	10, 90–95	**12e**, 80	116–117 (hexane)
40	**10d**	MeCN	5	8.5	9, 90–95	**12f**, 78	179–181 (isooctane); 0.40 ($CHCl_3$/PhH, 3:1)
41	**13a**	$HCONH_2$	2	10	7, 54–50	**14a**, 40	154–156 (heptane); 0.27 ($CHCl_3$)
42	**13a**	$PhCH_2CONH_2$	2	10	7, 95–100	**15a**, 58	136–137 (heptane); 0.60 ($CHCl_3$)
43	**13a**	$PhCH_2CONH_2$	1.5	16	20, 50	**15a**, 45	136–137 (heptane)
44	**13a**	$MeCONH_2$	2	10	13, 90–95	**15b**, 67	97–100, 0.13 ($CHCl_3$)
45	**13a**	$ClCH_2CONH_2$	2	10	13, 90–95	**15c**, 60	95–98; 0.65 ($CHCl_3/Me_2CO$, 20:1)
46	**13a**	$Cl_2CHCONH_2$	2	10	13, 90–95	**15d**, 44	117–119; 0.70 ($CHCl_3/Me_2CO$, 20:1)
47	**13a**	$CH_2=CHCONH_2$	2	10	6, 95–100	**15e**, 28	148–149; 0.23 ($CHCl_3$)
						15f, 25	97–99; 0.17 ($CHCl_3$)
48	**13a**	NH_2CONH_2	2	10	20, 75–80	**16**, 64	179–182
49	**13a**	barbituric acid	2	65	11, 90–95	**17**, 67	183–185 (heptane/Me_2CO)
50	**13a**	NH_2CONH_2CN	1	10	20, r.t.	**14b**, 95	252–253 (EtOH); 0.21 ($CHCl_3$/EtOH, 20:1)
51	**13b**	MeCN	5	8.5	2, 35–40	**14c**, 63	115–117; 0.34 (hexane/Et_2O, 1:1)
52	**18**	$PhCH_2CONH_2$	2	10	6, 95–100	**19**, 16	103
53	**20**	$MeCONH_2$	2	10	8, 40–45	**21**, 87	153–155

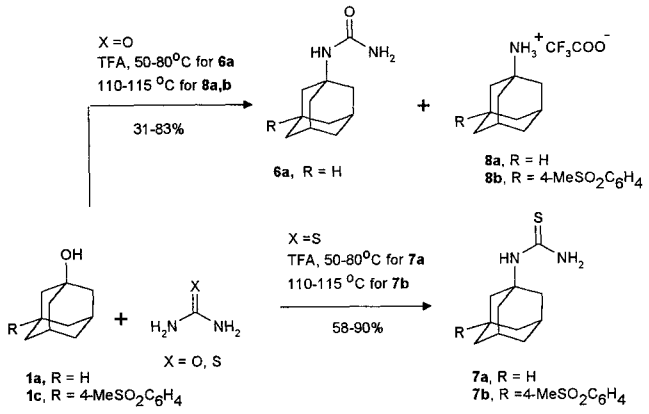
[a] Yield of isolated product. [b] 0.05 equiv. $LiClO_4$ was added. [c] 0.5 equiv. CF_3SO_3H was added.

for preparation of alkylated amides, TFA utilisation avoids competing oxidation, sulfonation, polymerization and unselective rearrangements. For example, we used as alkylating compounds 3-(4-tolyl)- and 3-(3,4-dimethylphenyl)-1-adamantanols **1b,c** which could be sulfonated in sulfuric acid. However, it should be noted that in these cases the yields of isolated *N*-(3-*R*-1-adamantyl)amides were moderate and the use of catalytic amounts of lithium perchlorate was required to increase them. These results emphasize the crucial influence of electron-withdrawing substituents in the adamantane nucleus on the carbenium ion's electrophilic reactivity. Indeed, the presence of strong electron-withdrawing substituents in 3-(4-methylsulfonylphenyl)-1-adamantanol **(1d)** and 3-carboxy-1-adamantanol **(1e)** is likely to be responsible for the retardation of their amidation. We succeeded in the preparation of *N*-[3-(4-methylsulfonylphenyl)-1-adamantyl]-acetamide **(3c)** in good yield (61%) only by adding a 0.5 equiv. of trifluoromethanesulfonic (triflic) acid to the reaction mixture. Alcohol **1e** bearing a carboxy group at the 3 position of the adamantane nucleus completely loses the alkylating power. 3-Carboxy-1-trifluoroacetoxyadamantane **(4)** was the sole isolated product of the reaction performed without catalyst or in the presence of lithium perchlorate. If triflic acid was added to the reaction sphere, a hard to separate mixture of compounds was formed. At the same time acylated γ-amino acid **5** was obtained in 44% yield by reaction of hydroxy acid **1e** with the more nucleophilic isovaleronitrile.



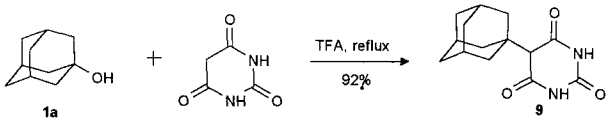
Furthermore, we have examined the methods of urea and thiourea transformation under our conditions. Since urea and, particularly, thiourea have stronger nucleophilic properties than carboxylic acid amides it should be expected that the adamantylation of such compounds would proceed more easily. In reality, it appears that *N*-(1-adamantyl)urea **(6a)** is formed at 50 °C in 80% yield (Table 1, entry 22). Thiourea is adamantylated even at room temperature to afford *N*-(1-adamantyl)thiourea **(7a)** in 22% yield. Heating to 50 °C raises the yield of **7a** to 90%.

The alkylation of urea at 110–115 °C leads to immediate quantitative formation of 1-aminoadamantane **(8a)**.



N-(1-adamantyl)urea **(6a)** is also decarboxylated by heating in TFA at such a temperature to be converted into amine **8a**. It is to be noted that the preparation of 1-aminoadamantanes from 1-bromoadamantanes and ureas at 170–190 °C is reported in literature.[15] Interestingly, when using thiourea as the starting material only compound **7a** is produced at high temperature in 85% yield. 3-(4-Methylsulfonylphenyl)-1-adamantanol **(1d)** reacts with urea and thiourea under intensive TFA refluxing in the presence of lithium perchlorate to give proper amine **8b** in the first case and *N*-[3-(4-methylsulfonylphenyl)-1-adamantyl]thiourea **(7b)** in the second case.

Barbituric acid having *N*-, *C*- and *O*-nucleophilic centres was chosen as the next subject of adamantylation. Because of the lower nucleophilicity of the nitrogen atom in this reagent in comparison with that in carboxylic acid amides and urea the formation of *C*- and *O*-alkylated products should be expected. C5-Adamantylation of the pyrimidine ring is proved to be the only direction of the process, hitherto unknown 5-(1-adamantyl)barbituric acid **(9)** was isolated in 92% yield (Table 1, entry 30).

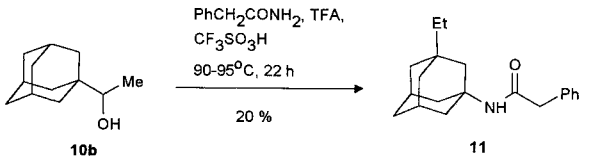


It is common knowledge that barbituric acid is readily chlorinated, brominated, nitrated and nitrosated at the 5 position of the pyrimidine nucleus.[16] To the best of our knowledge there are no data on C5-alkylation of this compound in acidic conditions. The interaction of primary alcohols with barbituric acid as well as with N^1,N^2-dimethylbarbituric acid in concentrated sulfuric and hydrochloric acid and boron trifluoride–diethyl ether complex medium affords 6-alkoxyuracils.[17] The earlier obtained derivatives of 5-adamantylbarbituric acid were synthesized from proper adamantylmalonic esters and urea.[18]

One-step hydroxy substitution of 1-(1-adamantyl) alcohols with *N*-nucleophiles in acidic medium is practically unknown. Nevertheless adamantane derivatives with nitrogen-containing functional groups on the side chain are of considerable interest. Examining the scope and limitation of *N*-alkylation procedure in TFA for this type

of alcohol, we revealed that the reaction course depends to a large extent on both the structure of the alkylating substrate and on the type of *N*-nucleophile.

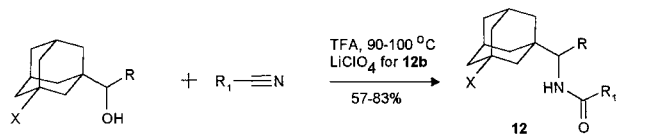
Primary 1-adamantylmethanol **(10a)** does not react with studied *N*-nucleophiles even in the presence of triflic acid. It is to be noted that compound **10a** is the only alcohol among applied carbinols that does not afford the corresponding trifluoroacetate under the reaction conditions. In the absence of catalyst, secondary 1-(1-adamantyl)-ethanol **(10b)** does not react with amides and ureas either. We succeeded in the amidation of **10b** only by adding triflic acid to the reaction mixture, amidation by phenylacetic amide being accompanied with isomerisation of the starting alcohol and with the formation of 1,3-disubstituted adamantanes **11**.



10b **11**

This is the first example of a rearrangement of a secondary 1-(1-adamantyl)alkanol in TFA medium. It should be emphasized that 1-(1-adamantyl)ethanol polymerizes in the absence of amide (**10b**: TFA : CF_3SO_3H = 1 : 15 : 0.1, 95 °C, 0.5 h). The reaction of nicotinamide with **10b** does not occur even in the presence of catalysts.

In contrast to amides, more nucleophilic carboxylic acid nitriles react with secondary 1-(1-adamantyl)alkanols **10b–d** sufficiently easily. These yield *N*-[1-(1-adamantyl)alkyl]amides **12**, with the structure of the starting alcohols retained.

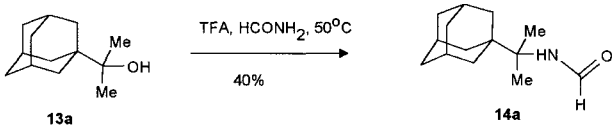


10b, R = Me, X = H
10c, R = Et, X = H
10d, R = Et, X = 4-MeC_6H_4

12	a	b	c	d	e	f
R	Me	Me	Me	Et	Et	Et
X	H	H	H	H	H	4-MeC_6H_4
R_1	CH_2Cl	3-C_5H_4N	4-$ClC_6H_4CH_2$	Me	CH_2Cl	Me

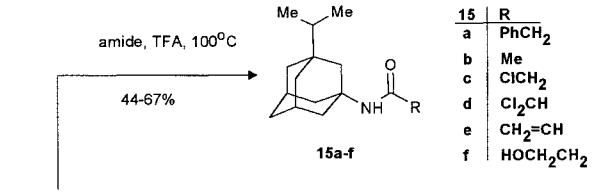
Secondary 1-(1-adamantyl)alkanols could be readily obtained from 1-adamantanol and α-alkenes in TFA,[8] therefore, the possibility of their amidation allows a novel convenient route to practically important α-(1-adamantyl)alkylamines and their derivatives. It is to be stressed that sulfuric acid, classically used in the Ritter reaction, is not suitable for this goal since in this case the formation of γ-homoadamantylsultones becomes the major direction of 1-(1-adamantyl)alkanol transformations.[19]

Recently[20] we have shown that tertiary 2-(1-adamantyl)propan-2-ol **(13a)** isomerized completely to 3-isopropyl-1-adamantanol in TFA solution. In the presence of low nucleophilic phosphorus trichloride such isomerization is partially suppressed,[11] a mixture of 3-isopropyl-1-adamantyl- and 2-(1-adamantyl)-2-propylphosphonic acid dichlorides was isolated. Using alcohol **13a** as an alkylating agent for different *N*-nucleophiles we have obtained *N*-containing admantane derivatives with a structure similar to that of the starting alcohol as well as to that of isomerized 3-isopropyl-1-adamantanol according to nucleophile activity. Reaction of **13a** with formamide at 50 °C gives unrearranged *N*-[2-(1-adamantyl)-propyl]-2-formamide **14a** as the only reaction product.

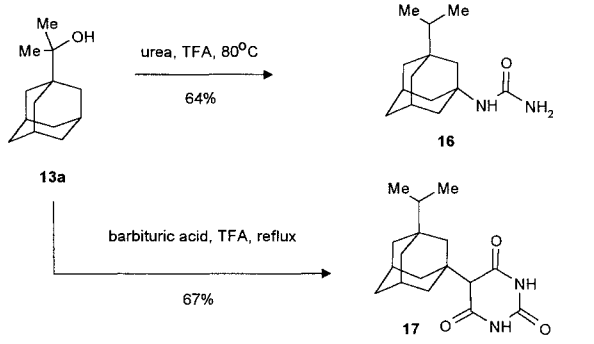


13a **14a**

Surprisingly, alcohol **13a** reacts with phenylacetamide under analogous conditions to afford isomerized *N*-[3-isopropyl-1-adamantyl)]amide **(15a)** only. Nucleophilicity of phenylacetamide is likely to decrease in comparison with formamide so that the rate of the isomerization reaction considerably exceeds the rate of alkylation. Analogously *N*-[3-isopropyl-1-adamantyl)]amides **15b–f** were isolated after refluxing a TFA solution of **13a** and different amides. Similar to 1-adamantanol, alcohol **13a** in reaction with acrylamide gives a mixture of two products: **15e** (R = CH_2=CH) and **15f** (R = $HOCH_2CH_2$) in ratio 1 : 1 in a total 53 % yield, that is the addition of TFA to the double bond takes place together with alcohol isomerization and *N*-adamantylation. Reaction of compound **13a** with urea and barbituric acid is accompanied by isomerization and production of disubstituted adamantanes **16, 17**.

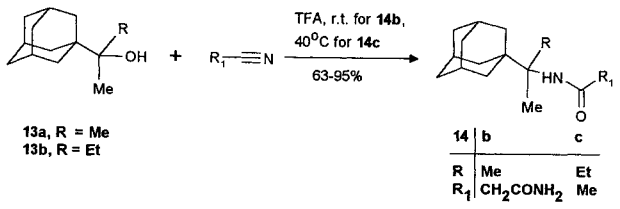


15	R
a	$PhCH_2$
b	Me
c	$ClCH_2$
d	Cl_2CH
e	CH_2=CH
f	$HOCH_2CH_2$



In order to obtain amines **14** with a *N*-containing group on the side chain it is necessary to use nitriles as *N*-nucleophiles. Thus, cyanoacetamide reacts with **13a** even at room temperature yielding the product of *N*-alkylation of the more nucleophilic nitrile group **14b** quantitatively.

In the present work, the possibility of carboxylic acid amide alkylation by alcohols not containing an adamantane fragment was examined as well. We chose alcohols



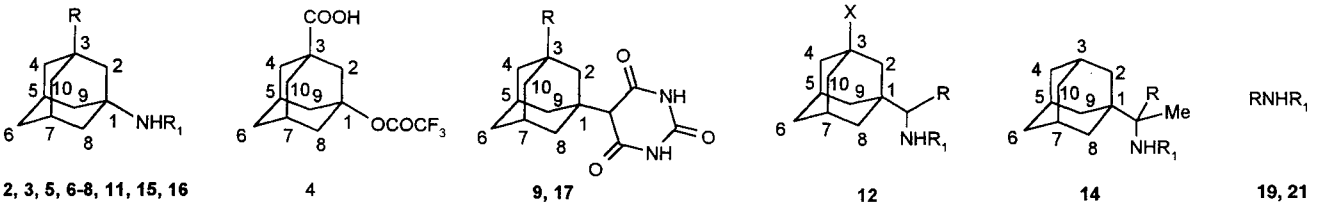
capable of forming carbocations in TFA: *tert*-butanol, di- and triphenylmethanols. It was found that although *tert*-butanol **18** reacts with phenylacetamide, the yield of the corresponding amide **19** is low (16%). More active diphenylmethanol **20** reacts with acetamide to give *N*-diphenylmethyl derivatives **21** in 87% yield at room temperature. However, triphenylmethanol does not alkylate acetamide even in harsh conditions (alcohol:amide: TFA = 1:2:10, 100°C, 11 h).

The structures of all the products summarised in Table 1 were determined on the basis of their ^{13}CNMR spectra presented in Table 2 and were confirmed by microanalyses. Typically, *C*-NHr amide carbon atoms in the ^{13}C NMR spectra gave a signal around $\delta = 49-54$ for the *N*-adamantylated amides, ureas, thioureas and amines **2**, **3**, **5–8**, **11**, **15** and $\delta = 56-60$ for the *N*-adamantylalkylamides **12** and **14**, respectively. In the case of adamantylated barbituric acids **9**, **17** chemical shifts of adamantane quaternary carbon atoms bound to the heterocyclic ring are typical for a C–C bond ($\delta = 37.88$ and 40.03, respectively). The presence in the ^{13}C NMR spectrum of CH signals at $\delta = 61-63$ belonging to the heterocyclic fragment also confirmed the C5-adamantylation. The ^{13}C peak assignments were based on APT technique and different signal intensities according to the symmetry of obtained adamantyl derivatives. The additivity of ^{13}C substituents chemical shifts (SCS) was successfully applied for the unambiguous assignment of signals in 1,3-disubstituted adamantanes **3–5**, **7b**, **8b**, **11**, **15–17**.

Melting points are uncorrected. ^{13}C NMR spectra were recorded with Varian VRX-300 spectrometer in $CDCl_3$. Preparative column chromatography separations were performed on silica gel L 40/100 (Chemapol Praha). Precoated silica gel plates (Silufol UV-254) were used for analytical TLC. 3-(4-Methylphenyl)-1-adamantanol (**1b**),[21] 3-(3,4-dimethylphenyl)-1-adamantanol (**1c**),[21] 3-(4-methylsulfonylphenyl)-1-adamantanol (**1d**),[11] 3-carboxy-1-adamantanol (**1e**),[22] 1-(1-adamantyl)ethanol (**10b**),[23] 1-(1-adamantyl)propanol (**10c**),[8] 2-(1-adamantyl)propan-2-ol (**13a**)[24] and 2-(1-adamantyl)butan-2-ol[24] (**13b**) were prepared as reported.

All other chemicals were commercially available and were used without further purification.

Table 2. ^{13}C NMR Spectral Data of Obtained Compounds



Product	R (X for **12**)	R_1	δ, ^{13}C[a]
2a	H	HCO	**C(Ad):** 51.60 (C_1), 43.48 ($C_{2,8,9}$), 29.06 ($C_{3,5,7}$), 35.58 ($C_{4,6,10}$); **C(R_1):** 161.5 (CO), 163.3 (CO)
2b	H	MeCO	**C(Ad):** 51.54 (C_1), 41.33 ($C_{2,8,9}$), 29.19 ($C_{3,5,7}$), 36.14 ($C_{4,6,10}$); **C(R_1):** 169.17 (CO), 24.35 (Me)
2c	H	$ClCH_2CO$	**C(Ad):** 52.18 ($C_{2,8,9}$), 29.12 ($C_{3,5,7}$), 36.04 ($C_{4,6,10}$); **C(R_1):** 164.40 (CO), 24.35 (CH_2Cl)
2d	H	Cl_2CHCO	**C(Ad):** 52.69 (C_1), 40.77 ($C_{2,8,9}$), 29.17 ($C_{3,5,7}$), 35.97 ($C_{4,6,10}$); **C(R_1):** 162.56 (CO), 66.96 ($CHCl_2$)
2e	H	$C_6H_5CH_2CO$	**C(Ad):** 51.68 (C_1), 41.27 ($C_{2,8,9}$), 29.20 ($C_{3,5,7}$), 36.11 ($C_{4,6,10}$); **C(R_1):** 169.84 (CO), 44.71 (CH_2)$_2$, 135.40 (C_{Ar}), 129.04 (2CH_{Ar}), 128.62 (2CH_{Ar}), 126.83 (CH_{Ar})
2f	H	2-$C_{10}H_7CO$	**C(Ad):** 52.60 (C_1), 41.54 ($C_{2,8,9}$), 29.37 ($C_{3,5,7}$), 36.23 ($C_{4,6,10}$); **C(R_1):** 168.70 (CO), 135.83 (C_{Ar}), 133.45 (C_{Ar}), 129.85 (C_{Ar}), 129.73 (CH_{Ar}), 128.05 (CH_{Ar}), 126.68 (CH_{Ar}), 126.08 (CH_{Ar}), 125.23 (CH_{Ar}), 124.58 (CH_{Ar}), 124.22 (CH_{Ar})
2g	H	3-C_5H_4NCO	**C(Ad):** 52.54 (C_1), 41.39 ($C_{2,8,9}$), 29.37 ($C_{3,5,7}$), 36.11 ($C_{4,6,10}$); **C(R_1):** 164.51 (CO), 151.51 (CH_{Py}), 147.60 (CH_{Py}), 134.65 (CH_{Py}), 131.39 (C_{Py}), 123.11 (CH_{Py})
2h	H	NH_2COCO	**C(Ad):** 51.97 (C_1), 40.79 ($C_{2,8,9}$), 29.10 ($C_{3,5,7}$), 35.99 ($C_{4,6,10}$); **C(R_1):** 163.05 (CO), 157.94 (CO)
2i	H	N-(1-Ad)NHCO	**C(Ad):** 51.76 (C_1), 40.84 ($C_{2,8,9}$), 29.16 ($C_{3,5,7}$), 36.07 ($C_{4,6,10}$); **C(R_1):** 159.18 (CO)
2j	H	N-(1-Ad)-$NHCOCH_2CO$	**C(Ad):** 54.05 (C_1), 40.53 ($C_{2,8,9}$), 29.18 ($C_{3,5,7}$), 35.94 ($C_{4,6,10}$); **C(R_1):** 168.12 (CO), 43.11 (CH_2, brs)
2k[b]	H	NH_2COCH_2CO	**C(Ad):** 50.78 (C_1), 40.94 ($C_{2,8,9}$), 28.81 ($C_{3,5,7}$), 36.01 ($C_{4,6,10}$); **C(R_1):** 169.74 (CO), 166.07 (CO), 43.78 (CH_2)
2l	H	CH_2=CHCO	**C(Ad):** 51.75 (C_1), 41.26 ($C_{2,8,9}$), 29.17 ($C_{3,5,7}$), 36.11 ($C_{4,6,10}$); **C(R_1):** 164.42 (CO), 132.07 (CH=), 125.03 (=CH_2)
2m	H	$HOCH_2CH_2CO$	**C(Ad):** 51.95 (C_1), 41.49 ($C_{2,8,9}$), 29.27 ($C_{3,5,7}$), 36.18 ($C_{4,6,10}$); **C(R_1):** 171.71 (CO), 38.53 ($COCH_2$), 58.92 (CH_2OH)
3a	4-MeC_6H_4	MeCO	**C(Ad):** 52.76 (C_1), 46.69 (C_2), 35.39 (C_3), 42.03 ($C_{4,10}$), 29.73 ($C_{5,7}$), 37.79 (C_6), 40.36 ($C_{8,9}$); **C(R):** 146.56 (C_{Ar}), 135.09 (C_{Ar}), 128.72 (CH_{Ar}), 124.59 (C_{Ar}), 20.69 (Me); **C(R_1):** 169.29 (CO), 24.48 (Me)

Table 2. (continued)

Product	R (X for **12**)	R_1	δ, ^{13}C[a]
3b	3,4-$Me_2C_6H_3$	PhCO	**C(Ad):** 53.18 (C_1), 46.75 (C_2), 37.83 (C_3), 42.06 ($C_{4,10}$), 29.84 ($C_{5,7}$), 35.44 (C_6), 40.73 ($C_{8,9}$); **C(R):** 146.84 (C_{Ar}), 135.83 (C_{Ar}), 133.69 (C_{Ar}), 129.18 (CH_{Ar}), 125.92 (CH_{Ar}), 121.92 (C_{Ar}), 19.19 (Me); **C(R_1):** 166.42 (CO), 135.54 (C_{Ar}), 130.81 (CH_{Ar}), 128.16 (CH_{Ar}), 126.44 (CH_{Ar})
3c	4-$MeSO_2C_6H_4$	MeCO	**C(Ad):** 52.29 (C_1), 45.66 (C_2), 35.10 (C_3), 41.48 ($C_{4,10}$), 29.39 ($C_{5,7}$), 38.65 (C_6), 40.69 ($C_{8,9}$); **C(R):** 155.77 (C_{Ar}), 137.53 (C_{Ar}), 126.95 (CH_{Ar}), 125.85 (CH_{Ar}), 44.31 ($MeSO_2$); **C(R_1):** 169.46 (CO), 24.26 (Me)
4	COOH	CF_3COO	**C(Ad):** 41.38 (C_1), 43.99 (C_2), 85.72 (C_3), 39.85 ($C_{4,10}$), 30.19 ($C_{5,7}$), 34.52 (C_6), 37.13 ($C_{8,9}$); **C(R):** 181.96 (COOH); **C(R_1):** 155.64 (CO, J_{CF} = 38.5 Hz), 114.12 (CF_3, J_{CF} = 266 Hz)
5	COOH	$(CH_3)CHCH_2CO$	**C(Ad):** 51.67 (C_1), 42.43 (C_2), 42.09 (C_3), 372.91 ($C_{4,10}$), 29.10 ($C_{5,7}$), 35.37 (C_6), 40.51 ($C_{8,9}$); **C(R):** 177.93 (COOH); **C(R_1):** 171.98 (CO), 46.58 (CH_2), 26.09 (CH), 22.12 (CH_3)
6a[b]	H	NH_2CO	**C(Ad):** 49.27 (C_1), 41.96 ($C_{2,8,9}$), 29.01 ($C_{3,5,7}$), 36.218 ($C_{4,6,10}$); **C(R_1):** 157.89 (CO)
7a[b]	H	NH_2CS	**C(Ad):** 53.21 (C_1), 43.11 ($C_{2,8,9}$), 29.71 ($C_{3,5,7}$), 35.04 ($C_{4,6,10}$); **C(R_1):** 164.59 (CS)
7b[b]	4-$MeSO_2C_6H_4$	NH_2CS	**C(Ad):** 53.87 (C_1), 48.34 (C_2), 36.25 (C_3), 42.28 ($C_{4,10}$), 30.25 ($C_{5,7}$), 34.28 (C_6), 40.48 ($C_{8,9}$); **C(R):** 155.07 (C_{Ar}), 138.67 (C_{Ar}), 127.30 (CH_{Ar}), 126.40 (CH_{Ar}), 43.90 ($MeSO_2$); **C(R_1):** 164.43 (CS)
8a[b]	H	H	**C(Ad):** 52.82 (C_1), 41.46 ($C_{2,8,9}$), 30.42 ($C_{3,5,7}$), 36.46 ($C_{4,6,10}$)
8b	4-$MeSO_2C_6H_4$	H	**C(Ad):** 51.20 (C_1), 48.11 (C_2), 35.05 (C_3), 45.00 ($C_{4,10}$), 29.90 ($C_{5,7}$), 39.14 (C_6), 41.63 ($C_{8,9}$); **C(R):** 156.19 (C_{Ar}), 137.67 (C_{Ar}), 127.18 (CH_{Ar}), 125.90 (CH_{Ar}), 44.35 ($MeSO_2$)
9[b]	H		**C(Ad):** 37.88 (C_1), 39.93 ($C_{2,8,9}$), 28.33 ($C_{3,5,7}$), 35.99 ($C_{4,6,10}$); **C (barbituric acid):** 168.65 (2CO), 151.56 (CO), 61.42 (CH)
11	Et	$PhCH_2CO$	**C(Ad):** 52.65 (C_1), 45.60 (C_2), 34.33 (C_3), 40.95 ($C_{4,10}$),* 29.47 ($C_{5,7}$), 35.67 (C_6), 40.56 ($C_{8,9}$);* **C(R):** 35.79 (CH_2), 6.90 (Me); **C(R_1):** 169.93 (CO), 44.83 (CH_2), 135.38 (CH_{Ar}), 129.16 (CH_{Ar}), 128.73 (CH_{Ar}), 126.95 (CH_{Ar})
12a	Me (H)	$ClCH_2CO$	**C(Ad):** 35.66 (C_1), 38.19 ($C_{3,5,7}$), 36.84 ($C_{4,6,10}$); **C(CHR):** 53.46 (CH), 14.19 (Me); **C(R_1):** 164.86 (CO), 42.84 (CH_2Cl)
12b	Me (H)	3-pyridylCO	**C(Ad):** 37.75 (C_1), 39.75 ($C_{2,8,9}$),* 29.92 ($C_{3,5,7}$), 38.21 ($C_{4,6,10}$);* **C(CHR):** 55.23 (CH), 14.26 (Me); **C(R_1):** 167.59 (CO), 152.05 (CH_{Py}), 148.70 (CH_{Py}), 137.58 (CH_{Py}), 132.92 (C_{Py}), 125.31 (CH_{Py})
12c	Me (H)	$ClC_6H_4CH_2CO$	**C(Ad):** 35.61 (C_1), 38.09 ($C_{2,8,9}$), 28.00 ($C_{3,5,7}$), 38.09 ($C_{4,6,10}$); **C(CHR):** 52.82 (CH), 14.13 (Me); **C(R_1):** 169.43 (CO), 42.99 (CH_2), 133.73 (C_{Ar}), 132.81 (C_{Ar}), 130.41 (CH_{Ar}), 128.68 (CH_{Ar})
12d	Et (H)	MeCO	**C(Ad):** 36.18 (C_1), 38.56 ($C_{2,8,9}$), 28.28 ($C_{3,5,7}$), 37.02 ($C_{4,6,10}$); **C(CHR):** 59.39 (CH), 21.19 (CH_2), 11.26 (Me); **C(R_1):** 170.06 (CO), 23.40 (Me)
12e	Et (H)	$ClCH_2CO$	**C(Ad):** 36.23 (C_1), 38.46 ($C_{2,8,9}$), 28.16 ($C_{3,5,7}$), 36.88 ($C_{4,6,10}$); **C(CHR):** 60.01 (CH), 20.96 (CH_2), 11.14 (Me); **C(R_1):** 165.71 (CO), 42.73 (CH_2Cl)
12f	Et (4-MeC_6H_4)	MeCO	**C(Ad):** 36.40 (C_1), 44.34 (C_2), 35.11 (C_3), 42.53 ($C_{4,10}$), 28.91 ($C_{5,7}$), 37.34 (C_6), 37.91 ($C_{8,9}$); **C(CHR):** 59.22 (CH), 21.40 (CH_2), 11.23 (Me); **C(R_1):** 170.07 (CO), 23.39 (Me); **C(X):** 147.56 (C_{Ar}), 135.09 (C_{Ar}), 128.78 (CH_{Ar}), 124.59 (CH_{Ar}), 20.75 (Me)
14a	Me	HCO	**C(Ad):** 38.19 (C_1), 36.49 ($C_{2,8,9}$),* 28.17 ($C_{3,5,7}$), 35.77 ($C_{4,6,10}$);* **C(CR, Me):** 57.63 (C), 22.51 (Me); **C(R_1):** 163.49 (CO)
14b	Me	NH_2COCH_2CO	**C(Ad):** 38.75 (C_1), 36.47 ($C_{2,8,9}$), 27.96 ($C_{3,5,7}$), 35.45 ($C_{4,6,10}$);* **C(CR, Me):** 58.28 (C), 20.96 (Me); **C(R_1):** 165.70 (CO), 170.50 (CO), 43.41 (CH_2)
14c	Et	MeCO	**C(Ad):** 40.86 (C_1), 36.72 ($C_{2,8,9}$), 28.59 ($C_{3,5,7}$), 36.99 ($C_{4,6,10}$); **C(CR, Me):** 62.62 (C), 25.65 (CH_2), 8.66 ($CH_2\mathit{CH}_3$), 18.15 (Me); **C(R_1):** 169.52 (CO), 25.00 (Me)
15a	*i*-Pr	$C_6H_5CH_2COO$	**C(Ad):** 52.75 (C_1), 43.17 (C_2), 36.57 (C_3), 37.81 ($C_{4,10}$), 29.41 ($C_{5,7}$), 35.90 (C_6), 41.02 ($C_{8,9}$); **C(R):** 37.01 (CH), 16.28 (Me); **C(R_1):** 169.80 (CO), 44.80 (CH_2), 135.38 (C_{Ar}), 129.11 (2CH_{Ar}), 128.87 (2CH_{Ar}), 126.88 (CH_{Ar})
15b	*i*-Pr	MeCO	**C(Ad):** 52.67 (C_1), 43.32 (C_2), 36.64 (C_3), 37.87 ($C_{4,10}$), 29.44 ($C_{5,7}$), 35.95 (C_6), 41.14 ($C_{8,9}$); **C(R):** 37.04 (CH), 16.28 (Me); **C(R_1):** 169.14 (CO), 24.53 (Me)
15c	*i*-Pr	$ClCH_2CO$	**C(Ad):** 53.30 (C_1), 43.07 (C_2), 36.71 (C_3), 37.83 ($C_{4,10}$), 29.46 ($C_{5,7}$), 35.86 (C_6), 40.84 ($C_{8,9}$); **C(R):** 37.07 (CH), 16.32 (Me); **C(R_1):** 164.45 (CO), 42.81 (CH_2Cl)
15d	*i*-Pr	$ClCH_2CO$	**C(Ad):** 53.75 (C_1), 42.72 (C_2), 36.72 (C_3), 37.71 ($C_{4,10}$), 29.36 ($C_{5,7}$), 35.72 (C_6), 40.48 ($C_{8,9}$); **C(R):** 37.01 (CH), 16.30 (Me); **C(R_1):** 162.86 (CO), 67.00 ($CHCl_2$)
15e	*i*-Pr	$CH_2=CHCO$	**C(Ad):** 52.89 (C_1), 43.19 (C_2), 36.56 (C_3), 37.86 ($C_{4,10}$), 29.43 ($C_{5,7}$), 35.93 (C_6), 41.10 ($C_{8,9}$); **C(R):** 37.04 (CH), 16.28 (Me); **C(R_1):** 164.41 (CO), 132.04 (CH=), 125.26 (=CH_2)
15f	*i*-Pr	$HOCH_2CH_2CO$	**C(Ad):** 52.98 (C_1), 43.39 (C_2), 36.61 (C_3), 37.86 ($C_{4,10}$), 29.44 ($C_{5,7}$), 35.92 (C_6), 41.20 ($C_{8,9}$); **C(R):** 37.06 (CH), 16.32 (Me); **C(R_1):** 165 (CO, brs), 38.53 ($CO\mathit{CH}_2$), 58.87 (CH_2OH)
16[c]	*i*-Pr	NH_2CO	**C(Ad):** 51.95 (C_1), 44.74 (C_2), 37.43 (C_3), 39.02 ($C_{4,10}$), 30.71 ($C_{5,7}$), 37.03 (C_6), 42.60 ($C_{8,9}$); **C(R):** 38.16 (CH), 16.75 (Me); **C(R_1):** 160.56 (CO)
17[d]	*i*-Pr	MeCO	**C(Ad):** 40.03 (C_1), 43.21 (C_2), 36.43 (C_3), 40.62 ($C_{4,10}$), 30.01 ($C_{5,7}$), 36.72 (C_6), 38.54 ($C_{8,9}$); **C(R):** 38.23 (CH), 16.59 (Me); **C (barbituric acid):** 168.85 (2CO), 151.51 (CO), 62.53 (CH)
19	*t*-Bu	$C_6H_5CH_2CO$	**C(*t*-Bu):** 51.08 (C), 28.52 (Me); **C(R_1):** 170.17 (CO), 44.68 (CH_2), 135.32 (C_{Ar}), 129.10 (2CH_{Ar}), 128.72 (2CH_{Ar}), 127.20 (CH_{Ar})
21	PhCH	MeCO	**C[$(Ph)_2CH$]:** 141.40 (C_{Ar}), 128.48 (2CH_{Ar}), 127.28 (4CH_{Ar}), 56.83 (CH); **C(R_1):** 169.09 (CO), 23.09 (Me)

[a] ^{13}C NMR spectra (75.4 MHz) were recorded in $CDCl_3$ using tetramethylsilane as internal standard. [b] DMSO-d_6. [c] C_2D_5OD. [d] Acetone-d_6. * May be interchanged pairwise.

Adamantylation of Amides, Nitriles and Ureas with 3-(*R*)-1-Adamantanols and 1-Adamantylalkanols in TFA. General Procedure:
A solution of alcohol **1a–e**, **10a–d**, **13a,b**, **18**, **20** (2 mmol) and corresponding amides, nitriles or ureas in TFA (indicated in Table 1) was kept under conditions indicated in Table 1. In the cases specially noted in Table 1, $LiClO_4$ (0.1 mmol) or trifluoromethanesulfonic acid (0.09 mL, 1 mmol) was added as well. After the reaction was completed (TLC control), the mixture was poured into ice-cool H_2O (20 mL), the product was filtered off, washed with H_2O and pentane (3 × 5 mL) or extracted with $CHCl_3$ (3 × 20 mL). The organic phase was washed with H_2O, dried ($MgSO_4$) and concentrated under vacuum. Purification was performed by recrystallization **(2a–g, 2j, 9, 14a, 14c, 15a, 17)** or column chromatography on silica gel **(2h, 2i, 2k–m, 3a–c, 5, 11, 12a–f, 14b, 15b–f)** using hexane/$CHCl_3$ (1:1), $CHCl_3$ and $CHCl_3$/acetone (20:1) as eluent. Compounds **(4, 6a, 7a,b, 16, 19, 21)** were isolated from the reaction mixture in analytically pure form without additional purification by recrystallization or by chromatography. The main characteristics of synthesized compounds are presented in Table 1.

1-Adamantylamine trifluoroacetate (8a):
A solution of 1-adamantanol (0.304 g, 2 mmol), and urea (0.24 g, 4 mmol) in TFA (1.54 mL, 20 mmol) was heated at 115–120 °C for 7 h. After the reaction was complete the mixture was kept at r.t. overnight. Then acetone (2 mL) was added to the precipitate that formed, the crude product was filtered after cooling, washed with pentane and was dried to give **8a** (yield 0.43 g, 83 %; mp 350 °C dec).

3-(4-Methylsulfonylphenyl)-1-adamantylamine (8b):
A solution of 3-(4-methylsulfonylphenyl)-1-adamantanol (0.61 g, 2 mmol), and urea (0.18 g, 3 mmol) in TFA (2.25 mL, 30 mmol) was heated at 115–120 °C in presence of $LiClO_4$ for 7 h. The excess of TFA was removed under vacuum and the residue was dissolved in H_2O (15 mL). The aqueous solution was extracted with Et_2O (2 × 15 mL) and was neutralized with 1 M NaOH solution, and the precipitate that formed was removed by suction filtration. The product was dried under vacuum to give **8b** (yield 0.19 g, 31 %; mp 162–165 °C).

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