Solid acid (superacid) catalyzed regioselective adamantylation of substituted benzenes ☆

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Adamantylation of substituted benzenes with 1-bromo-adamantane was catalyzed by solid acids including acidic ion exchange and ionomer resins, HY zeolite, sulfated zirconia and supported superacids on HY zeolite and SiO_2. Adamantylation generally takes place in excellent yield giving predominantly para products without formation of byproducts. The reactions did not require the usual workup of Friedel–Crafts reactions as catalysts were simply filtered of. Cross-linked polystyrene resin sulfonic acid (Amberlyst) was found particularly suitable as besides its high catalytic activity, high regioselectivity was observed with almost exclusive formation of *p*-adamantylated benzenes. AM1, PM3 and MNDO semiempirical calculations of heats of formation showed that of all regioisomers, the para isomer is the most stable. The temperature dependence of adamantylation was also investigated allowing the optimization of *p*-substituted product in high yield and excellent selectivity. Lack of isomerization of 1-*p*-tolyladamantane using solid (Amberlyst, Nafion-H) and liquid acids (neat and modified trifluoromethanesulfonic acid) indicates absence of product isomerization, while the intramolecular rearrangement of the intermediate arenium complex is still possible.

Keywords: regioselective adamantylation; solid acid catalysis; high *p*-selectivity; positional protection

1. Introduction

Homogeneous Friedel–Crafts alkylation of aromatics has been extensively studied [1]. Usually complex formation with the catalyst takes place and longer reaction times result in significant side reactions such as polyalkylation and isomerization. Using solid acid catalysts side reactions and the formation of complex product mixtures can be reduced. Moreover, no usual aqueous basic workup is necessary. The catalyst can be removed by a simple filtration resulting in no loss of catalyst or products in the workup procedure [2]. Advantages of using solid catalysts are that they are generally readily recyclable and non-polluting resulting in environmentally benign processes.

These advantages have also resulted in the increasing use of solid catalyst in synthetic organic chemistry [2,3]. Solid acids have particular importance in electrophilic transformations. One of the most important types of solid acid catalysts is that of sulfonated ion exchange resins or ionomers, which can catalyze, depending on their acidity, a wide range of organic transformations [4]. Cross-linked polystyrene type resins (Dowex, Amberlyst) have moderate acid strength [5], while Nafion-H #1 (a copolymer of perfluorinated alkyl ether and perfluoroalkanesulfonic acid) is of superacidic nature [6]. Other important solid acid catalysts for alkylation of aromatics are zeolites [7] and supported acids [8]. These catalysts and especially Nafion-H [2] are also frequently used in other Friedel–Crafts type reactions, including nitration [9], acylation [10] and alkylation with short chain alkyl halides [11].

Adamantylation of aromatics is not frequently studied, in spite of its potential importance. Since the corresponding olefin (adamantene) is highly unstable only 1-substituted adamantanes are used as adamantylating agents. Testafari and coworkers studied adamantylation of aromatics in a radical reaction with 1-adamantyl radical to describe the effect of substituents on the reactivity and isomer distribution [12]. Newman reported first the $AlCl_3$-catalyzed Friedel–Crafts alkylation of benzene with 1-bromoadamantane, where a complex product mixture was obtained [13]. Later, the adamantylation of reactive aromatics with adamantyl nitrate [14] and a $FeCl_3$-catalyzed reaction were described using excess aromatics [15]. In the case of toluene as substrate exclusive formation of *p*-adamantylated product was reported [15]. The study of Friedel–Crafts adamantylation of benzene and toluene [16] in the presence of boron tris(triflate) was also reported [17] previously by one of us. However, boron tris(triflate), a Lewis superacid, readily generates stable carbocations [18], and catalyzes side reactions such as isomerization of adamantylated aromatics [19]. In the boron tris(triflate) catalyzed isomerization of para-1-adamantyltoluene the extensive

☆ Catalysis by solid superacids, Part 30. For Part 29, see ref. [1a].

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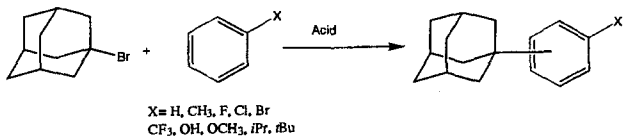
#1 Nafion is a registered trademark of the DuPont Company and commercially available. The active form H-form was generated from potassium salt by treatment with 25% nitric acid washing with water and drying at 105°C for 24 h.

formation of adamantane and 2-adamantylated toluenes was reported [16]. As it is well-known that 1-adamantyl cation is a stable bridge-head cation it can be readily formed from the adamantylated aromatics by protolytic cleavage. This characteristic and its bulky size make the 1-adamantyl group a good candidate for positional protection in aromatic substitution. Tashiro and coworkers have used *t*-butyl group in aromatic substitution as a positional protective group [20]. The *t*-butyl group can not only be easily introduced on to an aromatic ring but also can be removed by solid superacid transalkylation [21,22]. This method was used, for instance in the synthesis of dibenzofurans [23] and other useful substrates.

In the present paper we report a systematic study of solid acid catalyzed Friedel–Crafts adamantylation of aromatics with an aim to achieve high para regioselectivity.

2. Results and discussion

The acid catalyzed adamantylation of substituted benzenes can produce three isomeric products:



It was found, however, previously that in the adamantylation of toluene using superacidic boron tris(triflate) as catalyst only *m*- and *p*-products were formed [16]. Since we were interested in a more selective and convenient route to obtain *p*-adamantylated aromatics our attention turned to solid catalysts. As a model study we first investigated various solid acid catalysts in the adamantylation of toluene and bromobenzene.

2.1. Adamantylation of toluene and bromobenzene over solid acids

To determine the activity and selectivity of the solid acid catalysts the adamantylations of toluene and bromobenzene were carried out at their reflux temperatures. A variety of acids with different acid strengths were used. Dowex and Amberlyst ion exchange resins and HY-zeolite have modest acid strengths. Other catalysts studied were solid superacids such as Nafion-H resin (in different forms, as beads, impregnated on silica catalyst support and supported on silica-nanocomposite), $C_8F_{17}SO_3H$ and $C_{10}F_{21}SO_3H$ perfluoroalkanesulfonic acids supported on HY-zeolite, sulfated zirconia and $H_3[PW_{12}O_{40}]$ heteropolyacid on silica catalyst support (for details, see section 4).

In the case of toluene the catalyst used gave nearly complete reaction after 2 h (100% conversion) except with Nafion-H/SiO_2, sulfated zirconia and Dowex X2-100. Bromobenzene, a less reactive aromatic, showed lower conversion under similar experimental conditions, in spite of its higher boiling point and thus the higher reaction temperature used. The results are summarized in tables 1 and 2.

As can be seen from tables 1 and 2 the formation of only two isomers was observed. The major products were *p*-tolyl-, and *p*-bromophenyladamantane, respectively (as analyzed by GC-MS, ^{1}H- and ^{13}C-NMR). Regioselectivity was found to be strongly dependent on the catalyst used. The best para selectivities were observed with the least active catalyst, such as Nafion-H/SiO_2 (m/p ratio = 8/92 for toluene and 3/97 for bromobenzene) and sulfated zirconia (m/p = 10/90 for toluene and 5/95 for bromobenzene). However, these reactions require prolonged times under reflux.

Using Amberlyst XN-1010 as a catalyst adamantylation was almost complete after 1.5 h with good selectivity for *p*-isomer formation (m/p = 9/91 for both toluene

Table 1
Adamantylation of toluene with 1-bromoadamantane over solid acids

Catalyst	*T* (°C)	*t* (h)	Conversion (%)	Adamantane (%)	*m* (%)	*p* (%)
Nafion-H	111	1.5	100	9	30	70
Nafion-H/SiO_2 [a]	23	48	10	–	30	70
Nafion-H/SiO_2 [a]	111	1.5	100	7	29	71
Nafion-H/SiO_2 [b]	111	1	30	–	8	92
Amberlyst	111	1.5	100	–	9	91
HY	111	1.5	100	–	28	72
$C_{10}F_{21}SO_3H$/HY	111	1.5	100	–	21	79
$C_8F_{17}SO_3H$/HY	111	1	100	–	21	79
$H_3[PW_{12}O_{40}]/SiO_2$	111	1	100	13	48	52
sulfated ZrO_2	111	2	54	–	10	90
DowexX2-100	111	6	10	–	30	70

[a] Silica-nanocomposite.
[b] Impregnated.

Table 2
Adamantylation of bromobenzene with 1-bromoadamantane over solid acids

Catalyst	T (°C)	t (h)	Conversion (%)	Adamantane (%)	m (%)	p (%)
Nafion-H	156	1	100	16	12	88
Nafion-H/SiO_2 [a]	156	1.5	92	8	11	89
Nafion-H/SiO_2 [b]	156	2	5	–	3	97
Amberlyst	156	1.5	100	17	9	91
HY	156	3	100	13	11	89
$C_{10}F_{21}SO_3H$/HY	156	2	56	21	11	89
$C_8F_{17}SO_3H$/HY	156	1	76	14	16	84
$H_3[PW_{12}O_{40}]/SiO_2$	156	1	100	14	15	85
sulfated ZrO_2	156	3	20	–	5	95

[a] Silica-nanocomposite.
[b] Impregnated.

and bromobenzene). Comparing the adamantylation of toluene to that of bromobenzene, in the latter case the reaction takes place at higher temperature and the formation of adamantane as byproduct becomes more significant. This is caused by increased intermolecular isomerization (disproportionation) and transfer ionic hydrogenation of 1-bromoadamantane.

2.2. *Adamantylation of substituted aromatics with 1-bromoadamantane over Amberlyst XN-1010 and comparison with Nafion-H*

As mentioned earlier our aim was to optimize formation of *p*-adamantylated products in the reaction of substituted benzenes. Amberlyst XN-1010 was selected as a catalyst for adamantylation of a series of compounds such as *t*-butylbenzene, cumene, phenol, anisole, halobenzenes (F-, Cl-), α,α,α-trifluorotoluene and nitrobenzene. For convenience, reactions were again carried out at the reflux temperature of the aromatics. The results showing the adamantylated products and selectivity are tabulated in table 3.

As can be seen in table 3, toluene, anisole, and halogenated benzenes gave the monoadamantylated isomeric products in good yields, while strongly deactivated α,α,α-trifluorotoluene was highly unreactive and nitrobenzene did not give adamantylation under the reaction conditions, only adamantane was obtained. At the reflux temperature of nitrobenzene (210°C) thermal cleavage can occur to provide the hydrogen source for hydrogenation of bromoadamantane. At this temperature Amberlyst itself decomposes to some extent producing SO_3 which can cause further cleavage reactions.

In the acid catalyzed adamantylation of substituted benzenes of the three possible isomers generally only two isomers were formed, whereas in the reaction with anisole, fluorobenzene and phenol only the para isomer was obtained. Product compositions were determined by GC-MS, ^{1}H- and ^{13}C-NMR. The regioselectivity of adamantylation is excellent with anisole, fluorobenzene and phenol and moderate with chloro- and bromobenzene and toluene. α,α,α-trifluorotoluene gave only *one* product and the conversion is very low even after 5 h reflux. The main reaction product was adamantane. Cumene and *t*-butylbenzene were also found to react readily but the reactions gave more complex product mixtures.

For comparison, we also carried out reactions over Nafion-H, a well studied high acidity solid acid catalyst. The results of the Nafion-H catalyzed reactions are summarized in table 4.

Table 3
Adamantylation of substituted benzenes with 1-bromoadamantane over Amberlyst catalyst

X	T (°C)	t (h)	Conversion (%)	Adamantane (%)	m (%)	p (%)
–H	80	2	100	–	–	–
$-CH_3$	111	1	100	–	9	91
$-CH(CH_3)_2$	154	2	61 [a]	–	–	100
$-C(CH_3)_3$	169	2	100 [a]	–	32	68
–OH	182	4	100	–	–	100
$-OCH_3$	154	2	100	–	0	100
$-CF_3$	102	5	40	20	–	100
–F	85	1	40	–	2	98
–Cl	132	1	100	19	4	96
–Br	156	1	100	17	9	91
$-NO_2$	211	6	10	–	30	70

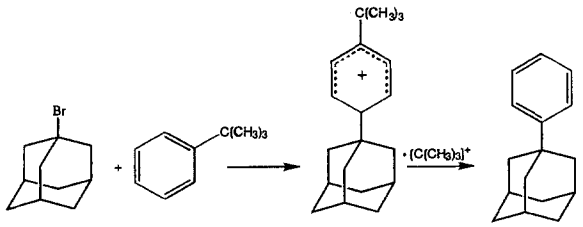
[a] Other byproducts in 70% yield.

Table 4
Adamantylation of substituted benzenes with 1-bromoadamantane over Nafion-H

X	T (°C)	t (h)	Conversion (%)	Adamantane (%)	m (%)	p (%)
-H	80	2	100	1.3	–	–
$-CH_3$	111	1.5	100	0.9	27.7	71.4
$-CH(CH_3)_2$	154	4	100	–	11.2	74.8
$-C(CH_3)_3$	169	2	100[a]	–	–	–
-OH	182	5	100	–	–	100
$-OCH_3$	154	1.5	100	–	–	100
$-CF_3$	102	2	100[b]	10.2	–	89.8
-F	85	5	100	–	–	100
-Cl	132	3	100	–	30.6	69.4
-Br	156	1	100	16	9.8	74.2
$-NO_2$	211	2	0	–	–	–

[a] Only other products.
[b] Other products in 50% yield.

As can be seen from table 4, Nafion-H produces similar yields and isomer distributions as previously used catalysts; however, some significant differences can also be noticed. Nitrobenzene gave no adamantylated product, but no adamantane was formed either. *t*-butylbenzene gave many side reactions resulting from cleavage reactions. In comparison about 30% adamantylated product was obtained with the Amberlyst catalyst. The differences can be explained by the higher acidity of Nafion-H and lower stability of Amberlyst. Nafion-H, a solid superacid, can readily cleave the aromatic–tertiary carbon bond and can thus result in *t*-butyl- and adamantyl cation interchange. 1-phenyladamantane is the only adamantylated reaction product. This indicates that adamantyl–*t*-butyl cation exchange takes place as indicated. It is worth mentioning that the formation of 1-phenyladamantane is also observed over Amberlyst catalyst, but to a lower extent (15%).



To avoid adamantane formation by reductive dehalogenation of 1-bromoadamantane acid catalyzed adamantylations were also carried out at lower temperatures. Indeed, adamantane formation decreased and at the same time para regioselectivity increased.

In order to obtain some information on the possible effect of isomerization semiempirical quantum chemical calculations were carried out to determine the heat of formation of isomeric products indicative of their thermodynamic stability. The heats of formation data of all possible isomers were calculated by three methods (AM1, PM3 and MNDO) and data are shown in table 5.

Although the calculated heats of formation vastly differ from method to method, the trends in individual sets of data clearly indicate the stability of p-isomers over o-isomers in each case.

The significant differences in the stability of *o*- and *p*-isomers can be explained by the strong steric interaction between the ortho substituent and the bulky adamantyl group. The stability of *m*- and *p*-isomers hardly differs. The obtained experimental results of adamantylation indicate that the reactions studied were affected in part by thermodynamic control. Thus appropriate selection of reaction temperature can modify the selectivity and regioselectivity.

Consequently, temperature dependence studies were carried out with toluene, bromo- and chlorobenzene. Anisole gave only *p*-isomer even at reflux temperature (154°C). The experimental results show that the reaction rates decrease significantly in parallel with the decrease in reaction temperature. The adamantylation reaction

Table 5
Heat of formation of isomeric adamantylated benzenes calculated by semiempirical methods

X	Isomer	$\Delta H_{f,298K}$ (kcal mol^{-1})		
		AM1	PM3	MNDO
-F	*o*	−53.493	−44.247	−27.257
	m	−55.989	−48.852	−31.126
	p	−55.989	−47.489	−32.126
-Cl	*o*	−10.692	−5.886	15.192
	m	−17.861	−11.951	6.736
	p	−17.945	−10.634	6.593
-Br	*o*	3.253	8.586	26.151
	m	−5.909	2.354	17.140
	p	−6.071	2.434	16.022
$-CH_3$	*o*	−11.417	−9.882	18.123
	m	−18.121	−13.093	6.922
	p	−18.216	−14.432	6.483
$-OCH_3$	*o*	−45.244	−37.032	−17.278
	m	−48.338	−43.077	−24.697
	p	−48.381	−42.995	−25.061

does not take place at room temperature and the conversion is generally very low up to 80–90°C. The results are summarized in table 6.

As expected, the lower reaction temperature promotes more selective formation of the *p*-adamantylated products. At the same time, at these temperatures formation of adamantane also decreased. In the case of toluene, for example, no adamantane formation was observed. The formation of *m*-isomers clearly is affected by isomerization (vide infra).

2.3. Isomerization of p-adamantylated substituted benzenes

In accordance with the directing effect of primary substituents, the formation of *o*- and *p*-products is expected in the adamantylation reactions [26]. It is also, however, known that 1-*p*-tolyladamantane can isomerize to its *m*-derivative in the presence of acid catalysts such as boron tris(triflate) [16]. With the same catalyst the *m*-isomer is also formed in high extent in the adamantylation reaction of toluene. In the light of these observations we carried out a study of the isomerization of *p*-adamantylated toluene with different acid catalyst in order to gain insights into the formation of *m*-isomer in the studied adamantylations. The results of isomerization experiments are collected in table 7.

In the presence of studied solid acids (Amberlyst, Nafion-H) no isomerization was observed. This suggests that isomerization of the *p*-product as an explanation for the *m*-isomer formation can be excluded over solid acids. Such para to meta isomerization, however, can readily take place in the presence of strong liquid acids. The formation of the *o*-isomer is thermodynamically very unfavorable in all studied systems. Using trifluoromethanesulfonic acid for isomerization at room temperature, only adamantane was obtained, indicative of the intermolecular nature of the reaction resulting in reductive cleavage.

Product isomerization as a possible cause for the formation of meta isomers in the present adamantylation reactions can be excluded. One must, however, consider intermolecular isomerization within the *p*-adamantylated arenium ion intermediate as the cause for the formation of meta isomer. These rearrangements involve intramolecular migration of adamantyl and methyl groups, which results in the formation of a *m*-(1-adamantyl)toluenium cation. The para-to-ortho or meta-to-ortho rearrangements can be excluded because these conversions are thermodynamically more unfavorable. At higher acidity or at higher temperature the isomerization reaction of the intermediate arenium cation seemingly can occur more readily, while at lower temperature and acidity, the directing effect of the substituents determines the final product distribution (according to kinetic control). The proposed mechanism of the adamantylation reaction is shown in scheme 1.

3. Conclusions

In conclusion, the solid acid catalyzed Friedel–Crafts adamantylation reaction of substituted benzenes was found to be a convenient method for the preparation of adamantylated aromatics with generally high para regioselectivity. Amberlyst XN-1010 was found to be a catalyst of choice because of high sulfonation content, high surface area, porosity and low cost.

Table 6
Influence of the temperature on the reactivity and regioselectivity of the Friedel–Crafts adamantylation of substituted benzenes with 1-bromoadamantane over Amberlyst catalyst

X	*T* (°C)	*t* (h)	Conversion (%)	Adamantane (%)	*m* (%)	*p* (%)	*m*/*p* ratio
$-CH_3$	23	48	0	–	–	–	–
	70	18	2	–	–	2	0/100
	75	5	30	–	1.5	27.5	5/95
	75	15	46	–	2.3	41.7	5/95
	80	5	73	–	4.7	68.4	6.5/93.5
	90	5	100	–	8.0	92.0	8/92
	110	1.5	100	–	9.3	90.7	9.3/90.7
	250	0.3	100	traces	14.3	85.6	14.3/85.6
–F	23	48	0	–	–	–	–
	82	1	40	1	1	99	1/99
–Cl	90	3	0	–	–	–	–
	100	3.5	81	8.0	–	74.0	0/100
	115	4	100	8.5	3.0	88.5	3/97
	132	1.5	100	19.0	3.6	77.4	4.5/95.5
–Br	100	7	0	–	–	–	–
	115	4	70	15.0	traces	55.0	1/99
	130	7	77	50.5	traces	17.3	1/99
	156	1	100	17.7	7.3	75.0	9/91
	156	14	100	1.6	1.6	96.8	

Table 7
Isomerization of 1-*p*-tolyladamantane with different acids

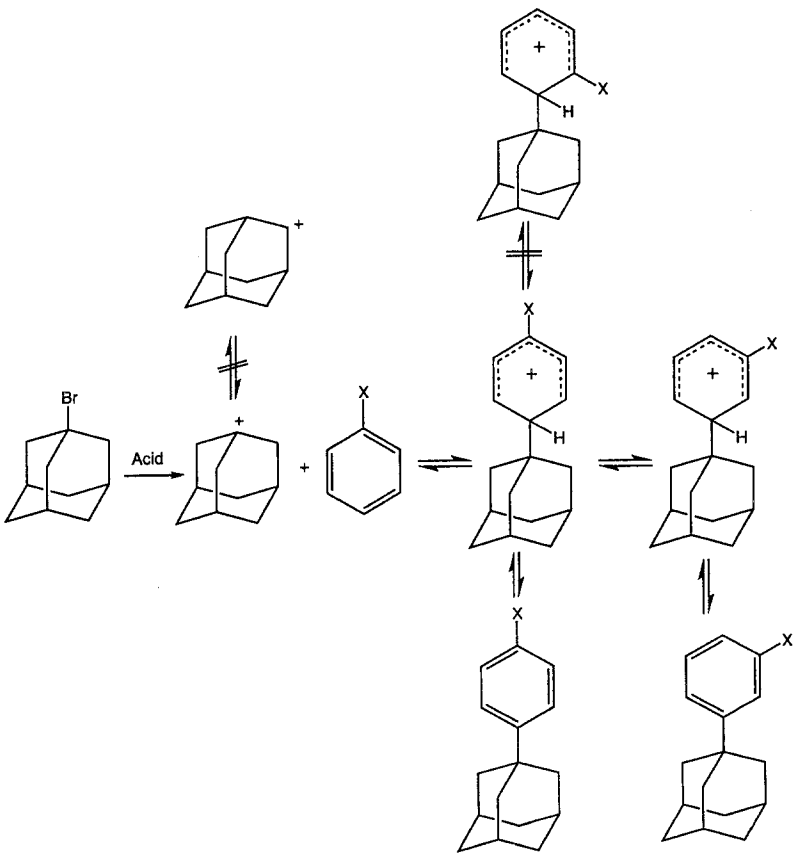
Acid	*T* (°C)	*t* (min)	Conversion (%)	Adamantane (%)	*m* (%)	*p* (%)
Amberlyst	111	300	0	–	–	–
Nafion-H	111	300	0	–	–	–
TFSA [a]	23	4	100	100	–	–
TFSA [a]	0	2	95	56.9	18.5	5.1
TFSA/TFA [b]	0	2	92	22.4	31.2	9.55
TFSA/H_2O [c]	0	2	12	5	traces	88.7

[a] Trifluoromethanesulfonic acid, $H_0 = -14.1$.
[b] Trifluoromethanesulfonic acid trifluoroacetic acid mixture, $H_0 = -11.2$, for preparation see ref. [23].
[c] Trifluoromethanesulfonic acid distilled water mixture, $H_0 = -11.2$, for preparation see ref. [23].

4. Experimental

Materials: 1-bromoadamantane, toluene, cumene, *t*-butylbenzene, phenol, anisole, halogenated (F-, Br- and Cl-) benzenes, α,α,α-trifluorotoluene and nitrobenzene were available from Aldrich (minimum purity > 99%). Trifluoromethanesulfonic acid was purchased from 3M and was purified by distillation under dry nitrogen stream before use.

Catalysts: Ion exchange resins Amberlyst XN-1010 (high surface area macroreticular resin suitable for non-aqueous applications, 50–100 mesh) and Dowex X2-100 were commercially available from Aldrich, while sulfated zirconia was purchased from Strem, and were used as received. Nafion as a potassium salt was obtained from the DuPont Company. The acidic form (Nafion-H) was prepared by acid treatment according to the literature [2,6]. HY zeolite was prepared by a heat treatment of NH_4Y form at 450°C under dynamic vacuum. $C_8F_{17}SO_3H$/HY and $C_{10}F_{21}SO_3H$/HY were made by impregnation of HY with the corresponding perfluoroalkanesulfonic acid. $C_8F_{17}SO_3H$ and $C_{10}F_{21}SO_3H$



Scheme 1.

were available from PCR as potassium salts. $H_3[PW_{12}O_{40}]$, 5% Nafion-H solution, and SiO_2 catalyst support were purchased from Aldrich and were used for the preparation of SiO_2 supported acids by impregnation. Nafion-H/silica-nanocomposite catalyst was synthesized from Nafion-H solution and $Si(OCH_3)_4$ (Aldrich) by the sol–gel method according to a recently published procedure [24].

Analysis: Gas chromatographic analyses were performed with an HP-5890 GC coupled with an HP-5971 mass spectrometer and a 30 m DB-5 capillary column, with helium as carrier gas. The ^{1}H- and ^{13}C-NMR measurements were carried out on a Varian VXR 300 MHz NMR spectrometer in $CDCl_3$ as a solvent with tetramethylsilane standard. The chemical shifts are reported in ppm. The products were identified via their ^{1}H-, ^{13}C-NMR, MS-spectra.

Theoretical calculations: Theoretical calculation of the heat of formation data was carried out by AM1, MNDO and PM3 semiempirical quantum chemical methods using SPARTAN (Version 2.0) program package [25].

General procedure for the adamantylation of benzenes over solid acid catalysts

The reactions were carried out in a 10 ml round-bottomed flask equipped with a reflux condenser and magnetic stirrer. A mixture of 200 mg (0.93 mmol) 1-bromoadamantane and 200 mg of catalyst was introduced into the flask, then 2.5 ml substituted aromatic compound was added as a reactant as well as a solvent. The reaction mixture was heated up to a desired temperature and stirred at that temperature for the corresponding time and a sample was withdrawn and used after filtration for GC-analysis. The exact conditions related to individual reactions are given in the tables.

Isomerization of 1-p-tolyladamantane

(a) Isomerization over solid acids: To a solution of 15 mg (0.07 mmol) of 1-p-tolyladamantane in 1 ml toluene 15 mg catalyst was added and stirred at reflux temperature. Under stirring and reflux, samples were taken periodically and analyzed by GC after filtration.

(b) Isomerization with neat and modified trifluoromethanesulfonic acid: 1-*p*-tolyladamantane, 15 mg (0.07 mmol) was dissolved in 1 ml dichloromethane and maintained at a desired temperature with a thermostat, 0.1 ml catalyst (neat or modified trifluoro-methanesulfonic acid) #2 was added and under stirring and reflux, samples were withdrawn periodically and analyzed by GC after the usual workup.

Preparation of authentic 1-o-tolyladamantane [16]

A solution of 1-bromoadamantane (0.5 g, 0.23 mmol), magnesium metal (0.2 g, 8.2 mmol) and dry diethyl ether (1 ml) was introduced into a pressure tube and *o*-bromotoluene (0.36 g, 0.23 mmol) was added dropwise with stirring at 0°C under nitrogen atmosphere during a 10 min period. After the addition, the tube was sealed and heated slowly to 100°C by an external oil bath for 2 h then cooled to −78°C in a dry ice–acetone bath and carefully opened. The reaction mixture was transferred to a separatory funnel filled with 20 g of ice and extracted with ether (3 × 20 ml). The combined ethereal extracts were dried over anhydrous magnesium sulfate and evaporated in vacuum. A crude 1-*o*-tolyladamantane was used for GC-MS analysis as reference sample directly.

1-phenyladamantane: From the reaction of 1-bromoadamantane (2.0 g, 9.3 mmol) and 20 ml benzene in the presence of 1.5 g Amberlyst XN-1010 ion exchange resin 1-phenyladamantane was obtained in 81% yield, m.p. 68–70°C. MS (*m/z*, %, 70 eV, EI): 212 (M^+, 37.3), 155 (100), 115 (44.5), 77 (29.3); ^{1}H-NMR: 1.76 (t), 1.92 (d), 2.09 (s), 7.33 (m); ^{13}C-NMR: 29.59, 35.91, 36.38, 43.21, 124.80, 128.07, 148.32, 151.26.

1-o-tolyladamantane: MS (*m/z*, %, 70 eV, EI): 226 9 (M^+, 46.3), 169 (74.0), 115 (100), 91 (80.1).

1-m-tolyladamantane: MS (*m/z*, %, 70 eV, EI): 226 (50.0), 169 (93.9), 115 (100), 91 (96.9); ^{13}C-NMR: 21.71, 29.66, 36.07, 42.44, 121.84, 125.63, 127.97, 137.39, 151.31.

1-p-tolyladamantane: From the reaction of 1-bromoadamantane (2.0 g, 9.3 mmol) and 20 ml toluene in the presence of 1.5 g Amberlyst XN-1010 ion exchange resin 1-*p*-tolyladamantane was obtained in 85% yield, m.p. 81–82°C, MS (*m/z*, 70 eV, EI): 226 (M^+, 33.3), 169 (100), 115 (65.9), 91 (56.6); ^{1}H-NMR: 1.76 (t), 1.9 (d), 2.08 (s), 2.31 (s), 7.14 (d); ^{13}C-NMR: 20.87, 29.01, 35.83, 36.86, 43.22, 124.70, 128.79, 134.86, 148.44.

1-m-anisoyladamantane: MS (*m/z*, %, 70 eV, EI): 242 (M^+, 98.4), 185 (100), 135 (7.1), 115 (15.3).

1-p-anisoyladamantane: From the reaction of 1-bromoadamantane (2.0 g, 9.3 mmol) and 20 ml anisole in the presence of 1.5 g Amberlyst XN-1010 ion exchange resin 1-*p*-anisoyladamantane was obtained in quantitative (100%) yield, m.p. 74–76°C, MS (*m/z*, %, 70 eV, EI): 242 (M^+, 79.6), 185 (100), 135 (4.2), 115 (10.3); ^{1}H-NMR: 1.75 (t), 1.88 (d), 2.08 (s), 3.78 (s), 6.86 (d); ^{13}C-NMR: 29.01, 35.55, 36.82, 43.40, 55.18, 113.39, 125.75, 143.70, 157.32.

1-m-fluorophenyladamantane: MS (*m/z*, 70 eV, EI): 230 (M^+, 92.3), 173 (100), 153 (41.9), 146 (18.1), 109 (44.9).

1-p-fluorophenyladamantane: From the reaction of

#2 The Hammett acidity constant of the neat trifluoromethanesulfonic acid (TFSA) was found to be $H_0 = -14.1$ by Saito et al. [27a] and the acidic strength of TFSA was modified by addition of water and trifluoroacetic acid according to refs. [27b] and [27a].

1-bromoadamantane (2.0 g, 9.3 mmol) and 20 ml fluorobenzene in the presence of 1.5 g Amberlyst XN-1010 ion exchange resin 1-*p*-fluorophenyladamantane was obtained in 92% yield, m.p. 47–49°C. MS (*m/z*, %, 70 eV, EI): 230 (M^+, 98.1), 173 (100), 153 (45.6), 146 (21.4), 109 (36); ^{1}H-NMR: 1.77 (t), 1.87 (d), 2.08 (s), 6.99 (m); ^{13}C-NMR: 27.14, 34.91, 39.34, 41.53, 112.70 (d), 124.51, 145.21, 160.65.

1-m-chlorophenyladamantane: MS (*m/z*, %, 70 eV, EI): 246 (M^+, 73.6), 189 (100), 153 (50.5), 125 (23.3).

1-p-chlorophenyladamantane: From the reaction of 1-bromoadamantane (2.0 g, 9.3 mmol) and 20 ml chlorobenzene in the presence of 1.5 g Amberlyst XN-1010 ion exchange resin 1-*p*-chlorophenyladamantane was obtained in 96% yield, m.p. 56–58°C. MS (*m/z*, %, 70 eV, EI): 246 (M^+, 79.6), 203 (15.9), 189 (100), 153 (49.7), 125 (27.0); ^{1}H-NMR: 1.75 (t), 1.87 (d), 2.08 (s), 7.28 (m); ^{13}C-NMR: 28.84, 36.65, 42.08, 43.08, 126.33, 128.09, 129.66, 149.77.

1-m-bromophenyladamantane: MS (*m/z*, %, 70 eV, EI): 292 (M^+, 59.8), 290 (66.0), 154 (100), 128 (70.1), 115 (90.4).

1-p-bromophenyladamantane: From the reaction of 1-bromoadamantane (2.0 g, 9.3 mmol) and 20 ml bromobenzene in the presence of 1.5 g Amberlyst XN-1010 ion exchange resin 1-*p*-chlorophenyladamantane was obtained in 97% yield, m.p. 65–67°C. MS (*m/z*, %, 70 eV, EI): 292 (M^+, 68.3), 290 (72.7), 154 (100), 128 (58.0), 115 (74.5); ^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 1.75 (t), 1.87 (d), 2.08 (s), 7.23 (m); ^{13}C-NMR (300 MHz, $CDCl_3$, ppm): 28.82, 36.64, 41.99, 43.01, 126.77, 131.04, 131.19, 150.27.

1-p-(α,α,α-trifluoromethyltolyl)-adamantane: MS (*m/z*, %, 70 eV, EI): 280 (M^+, 100), 223 (76.7), 183 (54.9), 159 (28.6).

1-m-t-butylphenyladamantane: MS (*m/z*, %, 70 eV, EI): 268 (M^+, 20.3), 253 (100), 128 (15.8), 115 (16.1).

1-p-t-butylphenyladamantane: MS (*m/z*, %, 70 eV, EI): 268 (M^+, 16.5), 253 (100), 115 (8.3).

1-m-cumyladamantane: MS (*m/z*, %, 70 eV, EI): 254 (M^+, 78.6), 239 (63.1), 155 (100), 128 (91.3), 115 (86.2), 91 (74.4).

1-p-cumyladamantane: MS (*m/z*, %, 70 eV, EI): 254 (M^+, 77.7), 239 (100), 155 (45.5), 128 (27.4), 115 (26.4), 91 (23.50).

1-p-hydroxyphenyladamantane: From the reaction of 1-bromoadamantane (200 mg, 0.93 mmol) and 2.0 ml phenol in the presence of 1.5 g Nafion-H ion exchange resin 1-*p*-hydroxyphenyladamantane was obtained in 100% conversion. MS (*m/z*, %, 70 eV, EI): 228 (M^+, 61.8), 171 (100), 134 (23.4), 107 (15.8).

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