

Triflic acid-catalyzed adamantylation of aromatics in [BMIM][OTf] ionic liquid; synthetic scope and mechanistic insight†‡

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A mild and efficient process has been developed for the one-pot adamantylation of aromatic substrates employing 1-AdaOH, 1-AdaCl, 1-AdaBr, and 1-Br-3,5,7-trimethyladamantane as adamantylating agents, with triflic acid (TfOH) as promoter and *n*-butylmethylimidazolium triflate [BMIM][OTf] room temperature ionic liquid (IL) as solvent. The influence of reaction temperature, reaction time and the amount of TfOH was gauged in model reactions employing 1-AdaOH, 1-AdaCl and 1-AdaBr with toluene as the substrate. Under optimal conditions, the reactions exhibit high *para* selectivity with little or no adamantane side-product being formed. The synthetic scope of this transformation was tested for representative alkylbenzenes and haloalkylbenzenes. Comparative reactions carried out in 1,2-dichloroethane (DCE) produce increased amounts of the *meta* isomer and substantial amounts of adamantane. Substrate selectivities (K_T/K_B) were measured in competitive experiments in [BMIM][OTf] and in DCE as solvents. Isomerization tests were performed to shed light on the origin of the *meta* isomer. A DFT study was also conducted to compare relative stabilities of the isomeric products, to gauge the relative stabilities of the intermediate isomeric benzenium ions of adamantylation and their charge distribution modes, and to explore the intramolecular process for isomerization in the benzenium ion.

Introduction

There is growing interest in adamantane and its derivatives as building blocks in polymer chemistry for the construction of star polymers, copolymers and dendrimers,^{1–3} and in the field of molecular recognition for the synthesis of adamantyl-appended macrocycles⁴ and adamantylated calixarenes.⁵ Another promising area involving adamantane is the generation of carbocations appended to an adamantane scaffold *via* the bridgehead positions, notably the 1,3,5,7-tetracations and 1,3-dications, and the potential of these systems in self-assembly.⁶

Despite the fact that direct electrophilic adamantylation of aromatics represents a simple and logical route for the synthesis of aryladamantanes,⁷ the scope of Friedel–Crafts type adamantylation of aromatics has not been extensively investigated and mechanistic data are scarce.

Olah and associates used boron (tris)triflate, B(OTf)₃, as a super Lewis acid for adamantylation of benzene and toluene with isomeric 1- and 2-haloadamantanes.⁸ With toluene as the substrate, adamantylation using 1-adamantyl chloride (1-AdaCl) and 1-adamantyl bromide (1-AdaBr) was effected at rt in CH₂Cl₂ solvent, producing a mixture of *meta*- and *para*-tolyladamantanes with the *meta* isomer predominating (the formation of an *ortho* isomer is unfavorable in this transformation on steric grounds). The reaction was accompanied by significant formation of adamantane as a side product. Small amounts of isomeric 2-tolyladamantanes (with preferential formation of

the *para* isomer) were also formed.⁸ These findings indicated that, under these conditions, the formed 1-adamantyl cation (1-Ada⁺) reacts with the arene, and in competition undergoes an intermolecular hydride-shift to form adamantane. The latter is the likely precursor to 2-Ada⁺ which leads to the formation of 2-phenyl- and 2-tolyladamantanes as by-products.⁸ Significant amounts of adamantane were also formed when authentic 1-tolyladamantane was reacted with B(OTf)₃–CH₂Cl₂.⁸ This indicated an intermolecular process. Also, 2-tolyladamantane rapidly isomerized to 1-tolyladamantane in B(OTf)₃–CH₂Cl₂, reflecting the intermolecular nature of 2-Ada⁺ isomerization to 1-Ada⁺.⁸

A solid acid catalyst version for aromatic adamantylation was later reported by Olah and associates,⁹ whereby toluene could be adamantylated with 1-AdaBr in quantitative yields at temperatures above 100 °C over Nafion-H and other solid acids. Under these conditions, little or no adamantane was formed, and the regioselectivity also improved (with the *para* isomer predominating, but some *meta* was also formed).⁹ Furthermore, there was no isomerization of the *para* product to *meta*, which ruled out an intermolecular process (de-adamantylation–re-adamantylation), but did not rule out isomerization within the benzenium ion (adamantyl shift and/or methyl shift).⁹

In a relatively recent study, Prakash *et al.*¹⁰ conducted a survey of various lanthanide triflates and Ga(OTf)₃ as catalysts for adamantylation of toluene using 1-AdaBr. Conversions and isomer distributions were highly variable depending on the choice of the metallic triflate. With Ga(OTf)₃ the reaction could be effected at rt in reasonable yields, but significant amounts of the *meta* isomer were formed. Complete conversion could be effected at 100 °C, but predominant formation of the *meta* isomer was observed, as well as notable amounts of ditolyladamantane.¹⁰

There is tremendous current interest in the utility and application of room temperature ionic liquids (RTILs), especially the imidazolium-based ILs, as “green” solvents and catalysts for a wide variety of organic and organometallic transformations.^{11–13}

In the area of electrophilic aromatic substitution, several studies on alkylation and acylation of aromatics in RTILs have been reported¹⁴ and the efficacy of various metallic triflates as

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‡ Electronic supplementary information (ESI) available: optimized structures for the arenium and benzenium ions; DFT calculations. See <http://www.rsc.org/suppdata/ob/b4/b416997b/>

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catalysts for these reactions has been probed.¹⁵ The halogenation of alkenes and alkynes in RTILs have also been examined.¹⁶

Several recent studies demonstrated that changes in the nature of the imidazolium core or the counterion could bring about notable changes in the reaction mechanism in certain nucleophilic displacement reactions, and that the nucleophilicity order of typical nucleophiles differs in IL solvents as compared to that in regular molecular solvents.^{17,18} A kinetic study on the bromination of alkynes indicated that viscosity and hydrogen bonding effects could also modify the reaction pathway and reactivity in these media as compared to conventional molecular solvents.¹⁹ It has also been reported that in the reaction of toluene and HNO₃, the course of the reaction changes as a function of the IL counterion.²⁰

The interest of this laboratory in the ionic liquid area is mainly focused on electrophilic chemistry and on the synthetic utility of various classes of onium salts as reagents for organic synthesis in these media. To these ends, we have so far reported on aromatic nitration,²¹ transfer-acetylation and deacetylation of aromatics,²² fluorodediazotization,²³ and transfer-fluorination to aromatics using onium dication salts, in particular the SelectfluorTM reagent.²⁴

The present study focuses on adamantylation of aromatics in *n*-butylmethylimidazolium triflate [BMIM][OTf], as solvent, employing 1-AdaOH, 1-AdaCl, 1-AdaBr, and 1-Br-3,5,7-trimethyladamantane as adamantylating agents, with TfOH as catalyst. Excellent yields, high *para* selectivity, negligible formation of adamantane, mild reaction conditions, and the use of readily available TfOH, are noteworthy features in the IL version of this transformation. The preparative scope of the reaction was tested by using representative substituted benzenes. The origin of the *meta* isomer was evaluated *via* control isomerization experiments. For comparison, and in representative cases, the use of immobilized Sc(OTf)₃ as an adamantylation catalyst was evaluated. In light of the recent mechanistic and kinetic studies showing notable differences in the IL solvents,¹⁹⁻²¹ for competitive experiments, substrate selectivities (K_T/K_B) for adamantylation in [BMIM][OTf] have been compared with those in dichloroethane (DCE). To shed light on relative arenium ion stabilities and relative product stabilities (isomer distributions), and with the aim of better addressing intermolecular rearrangement within the arenium ions, a DFT study was also carried out.

Results and discussion

To determine the effect of temperature, reaction time and AdaX : TfOH ratio on product distribution and conversion,

a series of adamantylation experiments were performed using toluene as substrate, employing 1-AdaOH, 1-AdaCl and 1-AdaBr as adamantylating agents, and with [BMIM][OTf] as solvent (Fig. 1).

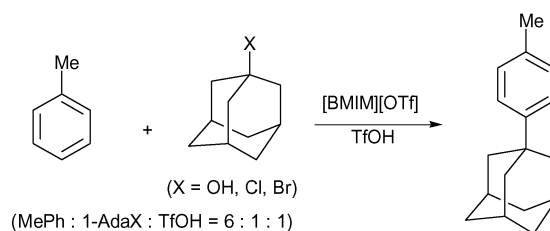


Fig. 1 Adamantylation of toluene.

The toluene to AdaX molar ratio was kept at 6 : 1, and the reactions were performed in small Schlenk tubes. The results are summarized in Table 1.

It can be seen that although reasonable conversions could be obtained in rt reactions, increased conversions are achieved with increasing reaction time and/or by increasing the amount of TfOH. Depending on the choice of adamantylating agent employed, near quantitative conversions could be reached at 60–80 °C after overnight stirring. The reaction exhibits high *para* selectivity with little or no adamantane by-product being formed. These favorable features, in combination with easy separation of the organic phase by addition of ether and the use of ILs in place of CH₂Cl₂ or MeNO₂, make the present system quite attractive. Our survey study also established that the IL solvent could be recycled and reused numerous times without any noticeable drop in conversion.

Control experiments indicated that adamantylation with 1-AdaCl and 1-AdaBr reagents do not proceed under these conditions in the absence of TfOH, *i.e.* AdaX by itself, even in an ionic liquid solvent, was incapable of adamantylation. The observed TfOH-catalyzed process with 1-AdaCl and 1-AdaBr must, therefore, occur by initial halogen protonation forming halonium ions 1-AdaXH⁺ with subsequent loss of HX to generate the bridgehead adamantyl cation as the common electrophile (Fig. 2).

Comparison between adamantylation in [BMIM][OTf] and 1,2-dichloroethane (DCE)

The previous adamantylation studies employed B(OTf)₃, Nafion-H and other solid acids and Ga(OTf)₃.⁸⁻¹⁰ To obtain a meaningful comparison between adamantylation in the ionic liquid solvent *vs.* that in a molecular solvent, it was necessary

Table 1 TfOH-catalyzed adamantylation of toluene with 1-AdaX (6 : 1) in [BMIM][OTf]^a

1-Ada-X	TfOH/eq.	Reaction time/h or d	Temperature/°C	Yield (%)	Composition of reaction mixture		
					Adamantane (%)	<i>m</i> -Tolyladamantane (%)	<i>p</i> -Tolyladamantane (%)
1-AdaOH	0.5	5 d	Rt	44	1	3	40
	0.5	6 d	60	100	1	1	98
	1.2	20 h	60	100	4	2	94
	0.5	20 h	65	100	2	2	96
	0.5	1 h	65	100	—	—	100
1-AdaCl	1.2	20 h	Rt	22	—	—	22
	1.2	4 d	Rt	53	—	4	49
	1.2	6 d	Rt	79	—	2	77
	1.2	20 h	60	96	2	5	89
	2.0	20 h	60	100	—	—	100
	0.6	20 h	60	22	—	—	22
	1.2	20 h	60	16	—	2	14
1-AdaBr	1.2	20 h	80	100	5	5	90
	1.2	20 h	80	100	5	5	90
	2.0	20 h	80	100	5	5	90

^a For each group of reactions, fresh IL was employed in the 1st run and used/recycled IL was utilized in subsequent experiments.

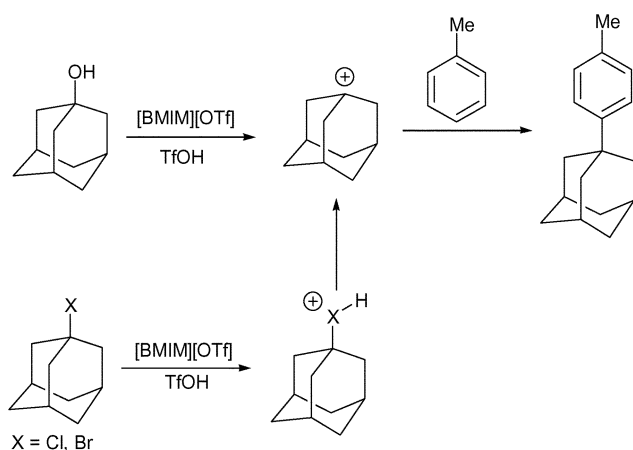


Fig. 2 Proposed reaction mechanism for IL adamantylation.

to conduct the reactions with a common catalyst. Table 2 summarizes the data for TfOH-catalyzed adamantylation with 1-AdOH, 1-AdaCl, and 1-AdaBr in DCE as solvent. Clearly, there are major differences with respect to adamantane formation, as a side reaction and with regard to regioselectivity. The DCE reactions are exemplified by significant formation of adamantane and increased formation of *m*-tolyladamantane, which in most cases exceeds the *p*-tolyladamantane product. It should be noted that the DCE reactions require quenching, acid neutralization and aqueous work-up.

On the synthetic scope

The synthetic scope of adamantylation in the IL solvent with TfOH as catalyst was tested towards a series of substituted benzenes. Table 3 summarizes the outcomes when 1-AdaOH was used as adamantylating agent. The [BMIM][OTf] solvent employed in these reactions was systematically recycled and re-used. High *para* selectivity was observed in reactions with monosubstituted benzenes (PhOMe and EtPh). Also given in Table 3 are isomer distribution and isomer identities. With anisole, increasing the reaction time resulted in the formation of more *meta* isomer (entry 2). The yields decreased with introduction of electron withdrawing substituents (entries for *p*-fluorotoluene and *p*-chlorotoluene) and adamantane started to appear as side products. This was not the case with

p-fluoroanisole. With mesitylene (not included in Table 3) the conversion was quite modest (<20%) and significant amounts of adamantane were formed. Clearly the reactivity of the aromatic substrate and steric factors are both important in this process. Adamantane formation becomes competitive as reaction with the aromatic substrate becomes energetically more demanding.

The synthetic scope of this transformation was also tested by using 1-AdaCl, 1-AdaBr, and 1-Br-3,5,7-trimethyladamantane as adamantylating agents. The results are summarized in Table 4. Isomer distribution and identity are also indicated. Once again, the [BMIM][OTf] used for these reactions was recycled and reused multiple times.

These reactions have similar overall characteristics to those performed with 1-AdaOH. The conversions are quantitative or close to quantitative and there is little or no adamantane present. High *para* selectivity was observed except in the EtPh reaction performed at 85 °C.

Isomerization test

In a control experiment, an isomeric mixture consisting of *ca.* 95% *p*-tolyladamantane and 5% *m*-tolyladamantane was allowed to react with TfOH in [BMIM][OTf] as solvent under the same set of reaction conditions used in the adamantylation reactions. GC analysis of the reaction mixture, following the usual isolation procedure, indicated no noticeable change in the isomeric composition following this treatment. A similar control experiment was performed on an isolated isomeric mixture obtained *via* the EtPh reaction. Once again, GC analysis of the reaction mixture following the above treatment did not indicate any noticeable increase in the *meta* isomer at the expense of *para*. These control experiments seem to rule out an intermolecular process as being responsible for the formation of *meta* isomer and lend support to the idea that isomerization occurs within the arenium ion as was also suggested by Olah *et al.* for adamantylation over Nafion-H and other solid acid catalysts.⁹

Competitive adamantylation in [BMIM][OTf] and in DCE

Competitive adamantylation experiments were carried out with 1-AdOH, 1-AdaCl and 1-AdaBr as adamantylating agents for the 1 : 1 molar mixtures of toluene and benzene in [BMIM][OTf] as solvent. The reactions were subsequently repeated under the same set of conditions in DCE. The results are summarized in

Table 2 TfOH-catalyzed adamantylation of toluene with 1-AdaX (6 : 1) in 1,2-dichloroethane (DCE)

1-Ada-X	TfOH/eq.	Reaction time/h or d	Temperature/°C	Conversion (%)	Composition of reaction mixture		
					Adamantane (%)	<i>m</i> -Tolyl-adamantane (%)	<i>p</i> -Tolyl-adamantane (%)
1-AdOH	0.5	5 d	Rt	100	33	41	26
	0.5	4 h	65	100	26	38	36
1-AdaCl	1.2	6 d	Rt	100	39	36	25
	0.5	1.5 h	65	100	33	44	23
1-AdaBr	0.5	1.5 h	65	100	42	36	22

Table 3 TfOH-catalyzed adamantylation of aromatics with 1-AdaOH in [BMIM][OTf] (arene : 1-AdaOH : TfOH = 6 : 1 : 1)

Arene substrate	Reaction time/h or d	Temperature/°C	Conversion (%)	Adamantane (%)	Aryl-adamantane (%)	Isomer distribution and identity (%)
Anisole ^a	5 h	85	100	—	100	66 (<i>p</i>); 34 (<i>m</i>)
Anisole	1 h	85	99	2	97	99 (<i>p</i>); 1 (<i>m</i>)
Ethylbenzene	2 h	85	100	—	100	95 (<i>p</i>); 5 (<i>m</i>)
<i>p</i> -Cl-toluene ^a	20 h	65	86	39	47	71; 22; 7
<i>p</i> -F-anisole	3 h	70	100	—	100	100 (1,2,4)
<i>p</i> -F-toluene	2 h	70	54	—	54	100 (1,2,4)
<i>m</i> -Xylene	5 d	65	100	5	95	100 (1,3,5)

^a These runs employed fresh IL whereas others were run in used IL.

Table 4 TfOH-catalyzed adamantylation of aromatics in [BMIM][OTf]^a (Arene : 1-AdaX : TfOH = 6 : 1 : 1)

Adamantyl compounds	Benzene derivatives	Reaction time/ h or d	Temperature/ °C	Conversion (%)	Adamantane (%)	Aryl-adamantane (or Me ₃ AdaH) %	Isomer distribution and identity (%)
1-Cl-adamantane	Anisole	20 h	80	100	—	100	100 (<i>p</i>)
	Ethylbenzene	20 h	85	100	6	94	65 (<i>p</i>); 35 (<i>o</i>)
1-Br-adamantane	<i>m</i> -Xylene	4 d	90	100	5	95	100 (1,3,5)
	Anisole	20 h	80	100	—	100	100 (<i>p</i>)
1-Br-3,5,7-trimethyladamantane	<i>m</i> -Xylene	4 d	65	100	5	95	90 (1,3,5)
	Anisole	20 h	85	100	—	100	85 (<i>p</i>); 15 (<i>o</i>)
	Toluene	20 h	80	94	—	94	80 (<i>p</i>); 20 (<i>o</i>)
	<i>p</i> -F-toluene	20 h	65	95	5	90	100 (1,2,4)

^a For each group of reactions fresh IL was employed in the 1st run and used/recycled IL was utilized in subsequent run(s).

Table 5. The K_T/K_B values in the ionic liquid solvent are in the range of 16–17, irrespective of the adamantylating agent. Substrate selectivity in DCE, on the other hand, is close to unity. As mentioned earlier, there are also notable differences in product distribution (significantly more adamantane formation in DCE) and in regioselectivity (substantially higher amounts of *m*-tolyladamantane in DCE).

The substrate selectivity data reflect a comparatively later transition state for adamantylation in the IL solvent (more benzenium ion-like).²⁵ This is compatible with a more complete formation (*i.e.*, increased stability) of the 1-Ada⁺ electrophile in the ionic liquid medium. Formation of adamantane as a major side reaction in DCE solvent using TfOH as catalyst is similar to the results obtained previously by Olah *et al.*⁸ in CH₂Cl₂ solvent using B(OTf)₃ as catalyst, and could stem from disproportionation of aryl-adamantanes, which may also be responsible for the observed high *meta* isomer formation in DCE (*via* de-adamantylated-re-adamantylation) and for the observed K_T/K_B values near unity.

In an effort to shed some light on the nature of the electrophile in IL adamantylation, in a competitive experiment a 1 : 1 mixture of 1-AdaBr and 1-Br-3,5,7-trimethyladamantane was allowed to react with anisole (6 eq.) in the presence of TfOH (1 eq.) at 65 °C for 2 h. The ratio of 1-anisyl-3,5,7-trimethyladamantane to 1-anisyladamantane was 2 : 1 by GC (no adamantane by-product was detected). The finding shows that methyl groups at the 3,5,7-positions increase the reactivity of the electrophile, and this is more compatible with the formation of a 1,3,5-Me₃Ada⁺X⁻ rather than a polarized complex.

On the utility of Sc(OTf)₃ for adamantylation in IL solvent

The efficacy of Sc(OTf)₃ as an immobilized Lewis acid for Friedel–Crafts chemistry has already been realized.¹⁵ In the context of the present study, and for comparison, 1-AdaCl was allowed to react with toluene in the presence of 0.3 eq. of Sc(OTf)₃ immobilized in [BMIM][OTf] at 70 °C. After overnight stirring, 1-tolyladamantane was formed in low yield (*ca.* 5%). Similar observations were made previously by Prakash *et al.*¹⁰ for the toluene–1-AdaBr system using Sc(OTf)₃ (employing excess arene as solvent). The reaction between 1-AdaCl and *p*-methylanisole employing 0.4 eq. of Sc(OTf)₃ in [BMIM][OTf] after 20 h at 65 °C gave a modest 8% conversion to a single isomer (see Experimental section for further details). The conversion was greatly increased (97%) when the reaction was performed at 90 °C for 20 h (Table 6).

The data indicate that Sc(OTf)₃–[BMIM][OTf] system is less efficient as compared to TfOH–[BMIM][OTf] for adamantylation, requiring more reactive arenes, higher temperatures and longer reaction times to reach high conversions. However, both systems offer the advantages of little or no adamantane formation and high regioselectivity.

DFT Study of adamantylation reaction

Relative energies of the benzenium ions for attack at the *ortho*, *meta* and *para* positions of toluene **1** (*o*-1H⁺, *m*-1H⁺, and *p*-1H⁺), ethylbenzene **2** (*o*-2H⁺, *m*-2H⁺, and *p*-2H⁺) and anisole **3** (*o*-3H⁺, *m*-3H⁺, and *p*-3H⁺) were computed by DFT at the B3LYP/6-31G(d) level (see Scheme 1). Relative energies for the resulting neutral isomeric aryladamantane products **1–3** were also computed. In addition, carbocations **4H⁺** and **5H⁺** (and **5aH⁺**) representing transition states for adamantyl shift and ethyl shift in the arenium ion were also calculated (Scheme 1).

The energy data are summarized in Table 7. The NPA-derived overall charges over CH (and oxygen) units in the benzenium ions were also determined and are sketched (along with overall charge delocalization modes) in Fig. 3 and 4.

Optimized geometries and bond-lengths for the benzenium ions and the neutral isomeric products are gathered in the supplementary information.

Table 5 Competitive adamantylation of benzene–toluene (1 : 1) promoted by TfOH (6 : 6 : 1) in [BMIM][OTf] or DCE at 65 °C, for 20 h

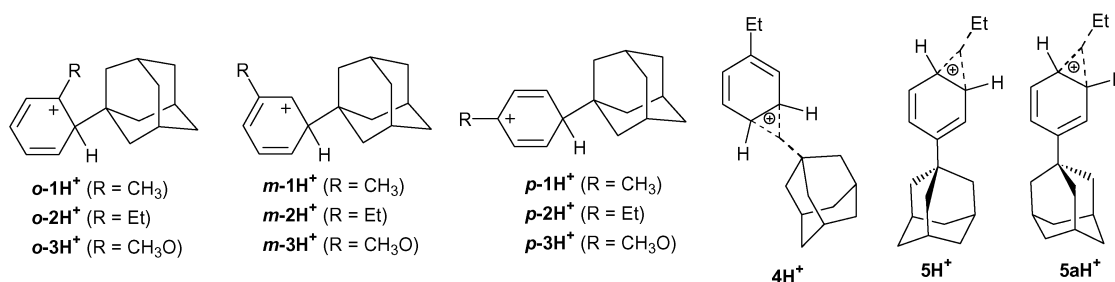
Adamantyl compounds	Solvent	Conversion (%)	Adamantane (%)	Ph-adamantane (%)	Tolyladamantane (%)		Ratio Ph-adamantane : tolyladamantane
					<i>m</i> -%	<i>p</i> -%	
1-AdaOH	[BMIM][OTf] ^a	100	0.13	5.8	94.2		1 : 16.2
1-AdaCl		100	—	6.0	4.9	95.1	1 : 15.6
1-AdaBr		100	0.1	5.6	94.0	93.8	1 : 16.8
1-AdaOH	C ₂ H ₄ Cl ₂	100	18.5	43.9	5.2	94.8	1.17 : 1
1-AdaCl		100	26.0	42.4	37.6	35.0	1.36 : 1
1-AdaBr		100	26.5	45.1	65.0	39.0	1.62 : 1
					31.4		
					61.0		
					28.4		
					63.0	37.0	

^a Fresh IL was employed.**Table 6** Sc(OTf)₃-catalyzed adamantylation of aromatic compounds with 1-AdaX in [BMIM][OTf] (Arene : 1-AdaX : Sc(OTf)₃ = 6 : 1 : 0.4)

Adamantyl compounds	Benzene derivatives	Reaction time/h	Temperature/°C	Conversion (%)	Adamantane (%)	Aryl-adamantane (%)	Isomer distribution and identity (%)
1-AdaCl	<i>p</i> -Me-Anisole	20	65	8	—	100	100 (1,2,4)
	<i>p</i> -Me-Anisole ^a	20	90	97	—	100	100 (1,2,4)

^a Performed in used IL.**Table 7** Energies (*E*), zero point energies (ZPE), Gibbs' free energies (*G*), and relative energies (ΔE and ΔG) for the studied molecules by DFT method at the B3LYP/6-31G(d) level

Compound	Molecular point group	<i>E</i> /hartrees	ZPE/hartrees	<i>G</i> /hartrees	ΔE /kcal mol ⁻¹	ΔG /kcal mol ⁻¹
<i>o</i> -1	C ₁	-661.0786857	0.353997	-660.763051	7.4	9.2
<i>m</i> -1	C ₁	-661.0902985	0.353066	-660.777307	0.1	0.3
<i>p</i> -1	C ₁	-661.0904339	0.352887	-660.777711	(0)	(0)
<i>o</i> -1H ⁺	C ₁	-661.4174812	0.361743	-661.099264	0.8 ^a	-2.1 ^a
<i>m</i> -1H ⁺	C ₁	-661.4122067	0.363643	-661.089731	4.1 ^a	3.9 ^a
<i>p</i> -1H ⁺	C ₁	-661.4187558	0.363802	-661.095883	(0) ^a	(0) ^a
	C _s	-661.4187558	0.363803	-661.095871	0.0 ^a	0.0 ^a
<i>o</i> -2	C ₁	-700.3906208	0.382932	-700.047723	8.4	10.3
<i>m</i> -2	C ₁	-700.4038896	0.382089	-700.063411	0.1	0.4
<i>p</i> -2	C ₁	-700.4040042	0.381948	-700.064112	(0)	(0)
<i>o</i> -2H ⁺	C ₁	-700.7313362	0.390686	-700.386369	1.3 ^b	-1.8 ^b
<i>m</i> -2H ⁺	C ₁	-700.7264177	0.392627	-700.376622	4.4 ^b	4.3 ^b
<i>p</i> -2H ⁺	C ₁	-700.7333992	0.392954	-700.383530	(0) ^b	(0) ^b
	C _s	-700.7333992	0.392954	-700.383530	0.0 ^b	0.0 ^b
<i>o</i> -3	C ₁	-736.2912291	0.358537	-735.972773	2.2	3.1
<i>m</i> -3	C ₁	-736.2953468	0.358217	-735.977920	-0.3	-0.2
<i>p</i> -3	C ₁	-736.2948082	0.357988	-735.977660	(0)	(0)
<i>o</i> -3H ⁺	C ₁	-736.6344054	0.369992	-736.305548	3.4 ^c	3.9 ^c
<i>m</i> -3H ⁺	C ₁	-736.6163648	0.368613	-736.289951	14.7 ^c	13.7 ^c
<i>p</i> -3H ⁺	C ₁	-736.6397795	0.369888	-736.311718	(0) ^c	(0) ^c
4H ⁺	C ₁	-700.7312569	0.390487	-700.384628	(0) ^a	(0) ^a
5H ⁺	C ₁	-700.7002111	0.392338	-700.349173	19.5 ^a	22.2 ^a
5aH ⁺	C ₁	-700.6985213	0.392334	-700.347739	20.5 ^a	23.1 ^a

^a Relative energy to that of *p*-1H⁺. ^b Relative energy to that of *p*-2H⁺. ^c Relative energy to that of *p*-3H⁺.

Scheme 1

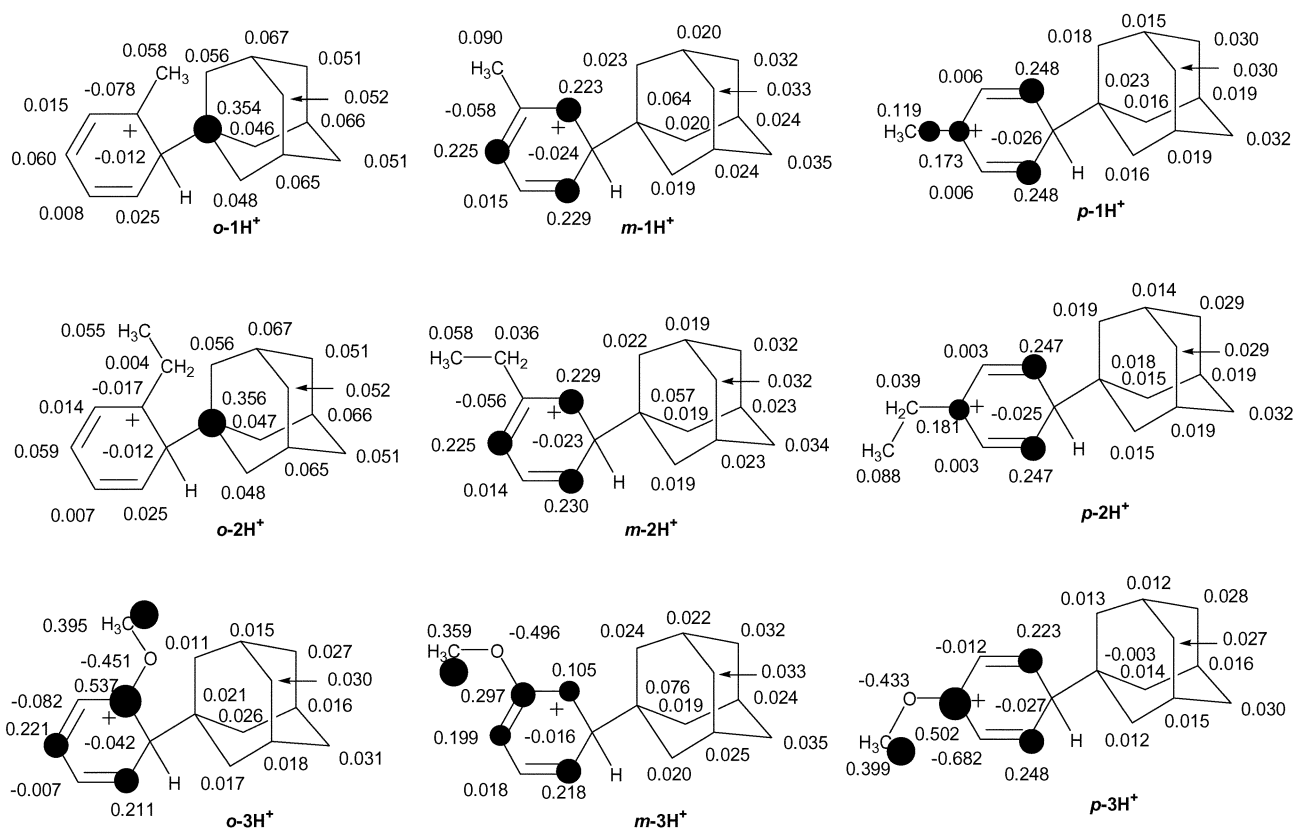


Fig. 3 NPA-derived overall charge over CH and O units for the protonated cations by B3LYP/6-31G(d). Dark circles are roughly proportional to the magnitude of NPA charges; threshold was set to 0.1.

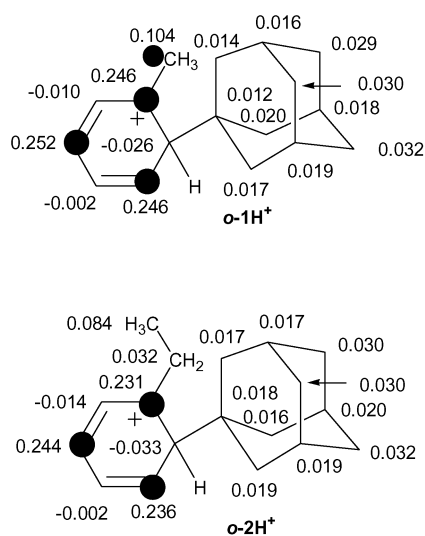


Fig. 4 NPA-derived overall charge over CH units for the benzenium ions by B3LYP/6-31G(d)//HF/6-31G(d). Dark circles are roughly proportional to the magnitude of NPA charges; threshold was set to 0.1.

For isomeric **1** and **2**, relative product stability order is *para* > *meta* > *ortho*, but the *meta* isomer lies only <1 kcal mol⁻¹ above *ortho*. With **3**, differences in energies between isomers are small, with the *meta* isomer being very slightly favored over *para* (*meta* > *para* > *ortho*). Focusing on the benzenium ions, where for **3** the stability order *p*-3H⁺ > *o*-3H⁺ > *m*-3H⁺ is derived, for **1** and **2** the *ortho* isomer was computed to be lower in energy than *para*! A closer look at the NPA-derived charges and charge delocalization maps (Fig. 3) revealed that *o*-1H⁺ and *o*-2H⁺ cations have the characteristics of oriented π -complexes of arene-1-Ada⁺ which are also reflected in their optimized geometries showing very long Ar-Ada⁺ distances (2.83–2.84 Å). Charge delocalization and optimized geometries for the *para* and

meta isomeric carbocations are consistent with benzenium ions. The charge delocalization maps show that the positive charge resides *ortho/para* to the site of attack. With **3**, contribution by mesomeric oxonium ions are revealed by positive charge localization on the methoxy methyl. The stability order *p*-3H⁺ > *o*-3H⁺ > *m*-3H⁺ seems to reflect a balance of steric and electronic effects of the –OMe substituent.

The carbonium ions **4**H⁺, **5**H⁺ and **5a**H⁺ were found to be transition states at the B3LYP/6-31G(d) level. Their optimized geometries are included in the supplementary information. Consideration of their relative energies at this level (Table 7), leads to the conclusion that ~Ada shift is more facile than ~Et shift as an intramolecular process within the arenium ion.

To examine the effect of the basis set on relative benzenium ion energies for *ortho* attack, isomeric carbocations *o*-1H⁺, *m*-1H⁺, and *p*-1H⁺ as well as *o*-2H⁺, *m*-2H⁺, and *p*-2H⁺ were subsequently computed at the B3LYP/6-31G(d)//HF/6-31G(d) level. The data (summarized in Table 8) show that at this level of theory, relative arenium ion stabilities for both substrates follow the sequence *para* > *meta* > *ortho*, showing that the HF/6-31G(d) level affords better geometries.

Comparative discussion and summary

The system [BMIM][OTf]-TfOH is an efficient medium for the adamantylation of arenes employing 1-AdaOH, 1-AdaCl, 1-AdaBr and 1-Br-3,5,7-Me₃-Ada as adamantylating agents. Since adamantylation with 1-adamantyl halides does not proceed without TfOH under the reaction conditions employed, an activation step involving halonium ion formation 1-AdaXH⁺ is presumed with subsequent formation of Ada⁺ and HX. Adamantylation can be effected under mild conditions, in high yields, high chemoselectivity (little or no adamantane) and high *para* regioselectivity. Reactions carried out in DCE as solvent exhibit increased formation of adamantane and low regioselectivity (mixtures of *para* and *meta* isomers with *meta*

Table 8 Energies (E), zero point energies (ZPE), Gibbs' free energies (G), and relative energies (ΔE and ΔG) for the studied carbocations at the HF/6-31G(d) level (rows at the B3LYP/6-31G(d)//HF/6-31G(d) level in parentheses)

Compound	Molecular point group	E/hartree	ZPE/hartree	G/hartree	$\Delta E/\text{kcal mol}^{-1}$	$\Delta G/\text{kcal mol}^{-1}$
<i>o</i> -1H ⁺	C ₁	-656.9238588	0.390083	-656.572793	7.6 ^a	9.3 ^a
	(C ₁)	-661.4059522			5.6 ^a)	
<i>m</i> -1H ⁺	C ₁	-656.9259046	0.389168	-656.576907	6.3 ^a	6.7 ^a
	(C ₁)	-661.4073465			4.5 ^a)	
<i>p</i> -1H ⁺	C _s	-656.9359873	0.389125	-656.587618	(0.0) ^a	(0.0) ^a
	(C _s)	-661.4146831			(0.0) ^a)	
<i>o</i> -2H ⁺	C ₁	-695.9581842	0.420788	-695.578356	8.6 ^b	9.6 ^b
	(C ₁)	-700.720307			5.6 ^b)	
<i>m</i> -2H ⁺	C ₁	-695.9611839	0.419913	-695.583396	6.7 ^b	6.5 ^b
	(C ₁)	-700.7220399			4.5 ^b)	
<i>p</i> -2H ⁺	C ₁	-695.9718343	0.420338	-695.593674	(0.0) ^b	(0.0) ^b
	(C ₁)	-700.7292251			(0.0) ^b)	

^a Relative energy to that of *p*-1H⁺. ^b Relative energy to that of *p*-2H⁺.

often exceeding *para*). The synthetic scope of this reaction was tested for representative alkylbenzenes and haloalkylbenzenes, and the results are compared. Decreasing the reactivity of the arene nucleophile or increasing the steric crowding on the nucleophile reduces the conversions and leads to increased formation of adamantane.

Substrate selectivities (K_T/K_B) measured in [BMIM][OTf] are higher than those obtained in DCE. The data imply a comparatively later, more benzenium-ion like TS in the IL solvent involving a more selective electrophile. A competitive experiment with a 1 : 1 mixture of 1-AdaBr and Br-3,5,7-Me₃Ada gave a product ratio of 1 : 2, indicative of inductive stabilization of the adamantyl electrophile by the methyl groups located at other bridgehead positions.

Selected control experiments ruled out an intermolecular process for the isomerization (formation of *meta* product) in [BMIM][OTf], pointing to an intermolecular process within the benzenium ion.

Based on DFT calculations \sim Ada shift is considerably more facile than \sim Et shift in the benzenium ion of *para* attack for adamantylation of ethylbenzene. DFT also provided insight as to charge delocalization modes in the benzenium ions and their relative stabilities, and regarding relative energies of the neutral isomeric products. Computation at the B3LYP/6-31G(d)//HF/6-31G(d) level did a better job in predicting the benzenium ion stability order as *para* > *meta* > *ortho*. Optimized geometries and the NPA-derived charges for the benzenium ions of *ortho* attack in adamantylation of PhMe and PhEt at the B3LYP/6-31G(d) level have the appearance of 1-Ada⁺-Arene oriented π -complexes which may be responsible for the computed lower energy of the *ortho* "benzenium ions". Based on limited studies performed with Sc(OTf)₃ as catalyst in the present study, it may be concluded that [BMIM][OTf]-TfOH system is superior to [BMIM][OTf]-Sc(OTf)₃, as higher temperatures and more reactive arenes are needed to achieve high conversions in the latter system, but both systems exhibit high *para* regioselectivity with little or no adamantane by-product formation.

Experimental

General

All items of glassware were oven-dried at 120 °C and flushed with nitrogen prior to use. Adamantylation reactions were performed in small Schlenk tubes under nitrogen with magnetic stirring. Reagents were transferred and manipulated under a stream of dry nitrogen. The adamantane derivatives (1-AdaOH, 1-AdaCl, 1-AdaBr and 1-Br-3,5,7-trimethyladamantane) were high purity commercial samples (Aldrich) which were used without further purification. The [BMIM][OTf] ionic liquid was purchased from ACROS and from Merck and used without any

pre-treatment. The aromatic compounds were highest purity commercial samples, their purity checked by GC prior to use. Triflic acid (Aldrich) was distilled under nitrogen and stored in a Nalgene bottle in a freezer.

Et₂O used for extraction was dried over sodium and distilled. 1,2-Dichloroethane (DCE) used for the comparative study was distilled prior to use.

Sc(OTf)₃ was purchased from Aldrich and was handled under nitrogen.

Typical optimized procedure

The [BMIM][OTf] ionic liquid (1.15 g, 4.43 mmol) was charged into a Schlenk tube and 1-AdaCl (0.171, 1 mmol) was added under nitrogen. The closed Schlenk tube was placed in an ultrasonic bath at rt for several minutes (typically 10–15 min) to increase solubility. After addition of toluene (0.552, 6.0 mmol) under nitrogen and magnetic stirring at rt for 10 min. the Schlenk tube was cooled to 0 °C and TfOH (0.1 mL, 1 mmol) was added under nitrogen *via* a micropipette. The Schlenk tube was re-sealed and placed in a thermostatic bath at 60 °C under magnetic stirring for 20 h. Typical work-up procedure involved addition of dry Et₂O (4 mL \times 5) and neutralization of combined extracts (as a precaution for subsequent GC and GC-MS analysis) by washing with water (4 mL \times 2), with 5% NaHCO₃ (4 mL \times 2) and water (4 mL \times 2) respectively, followed by separation of the organic phase, drying (MgSO₄) and simple filtration. The procedure was similar for 1-AdaOH reactions and for 1-AdaBr. In the latter case, the reactions were carried out at 80 °C. In competitive experiments great care was taken to prepare and transfer the benzene-toluene equimolar mixtures as carefully as possible for both the IL and the DCE reactions. Reactions in DCE solvent (either single substrate or competitive) were performed at 65 °C in small round-bottom flasks under a blanket of nitrogen. These reactions required TfOH neutralization and standard aqueous work-up (5% NaHCO₃, extraction with ether, drying over MgSO₄ and filtration). For Sc(OTf)₃-catalyzed reactions, the Lewis acid catalyst was immobilized in the IL by sonication. Following the general procedure outlined above, the reactions were conducted at 90 °C to increase conversion.

Reaction mixtures were first analyzed by capillary-GC (on a fused silica column) followed by GC-MS (ion-trap instrument). Conversions were determined by GC and are based on the amount of 1-AdaX reacted. The minor *meta* isomers typically had shorter retention times than *para*. Subsequent vacuum drying of the reaction mixtures left behind the aryl-adamantanes, which were rechecked by GC and GC-MS analysis. Since several attempts to remove minor isomers from the isomeric mixtures by crystallization techniques proved unsuccessful, they were directly assayed by NMR (300 MHz). In several cases, the aryl-adamantane products had previously been reported⁹ and/or

were commercially available (Aldrich, TCI-America *etc.*). The *para* isomers were readily recognizable in the ^1H NMR as they gave rise to a pair of doublets in the aromatic region (typically with $J = 8\text{--}9$ Hz). With *m*-xylene, the product was C-5 adamantylated; this was readily apparent in the NMR [2 aromatic proton resonances (in 2 : 1 ratio) and 4 aromatic carbons]. Substitution patterns for the *p*-disubstituted substrates followed the expected directive effects.

1-*p*-Tolyladamantane. MS ($m/z\%$, 70 eV, EI mode) 226 (100, M^+); 183 (22), 169 (80), 115 (20), 91 (30); ^1H NMR (CDCl_3): 7.26 (d), 7.12 (d), 2.32 (Me), 2.08 (Ada), 1.76 (Ada), 1.89 (Ada).

1-(*p*-Ethylphenyl)adamantane. MS ($m/z\%$, 70 eV, EI mode) 240 (80, M^+), 197 (40), 183 (80), 155 (100), 91 (38); ^1H NMR (CDCl_3) 7.25 (d), 7.15 (d), 2.63 (Et), 2.08 (Ada), 1.90 (Ada), 1.77 (Ada), 1.23 (Et); ^{13}C NMR (CDCl_3) 148.8 (Ar, C), 141.4 (Ar, C), 127.7 (Ar, CH), 124.9 (Ar, CH), 43.4 (Ada), 37.0 (Ada), 36.0 (Ada), 29.2 (Ada), 28.5 (Et), 15.7 (Et).

1-*p*-Anisyladamantane. MS ($m/z\%$, 70 eV, EI mode) 242 (100, M^+), 185 (83), 148 (32), 77 (15); ^1H NMR (CDCl_3) 7.27 (d), 6.85 (d), 3.79 (OMe), 2.08 (Ada), 1.76 (Ada), 1.89 (Ada); ^{13}C NMR (CDCl_3) 157.5 (Ar, C), 143.9 (Ar, C), 125.9 (Ar, CH), 113.5 (Ar, CH), 55.4 (OMe), 43.5 (Ada), 36.9 (Ada), 35.7 (Ada), 29.2 (Ada).

1-(*m*-Fluoro-*o*-anisyl)adamantane. MS ($m/z\%$, 70 eV, EI mode) 260 (100, M^+), 217 (20), 203 (45), 166 (20), 91 (10), 77 (8); ^1H NMR (CDCl_3) 6.93 (dd), 6.86–6.74 (m), 3.80 (OMe), 2.05 (Ada), 1.76 (Ada); ^{13}C NMR (CDCl_3) 157.4 (d, $J_{\text{CF}} = 237$ Hz), 155.0, 140.6 (d, $J_{\text{CF}} = 6$ Hz), 114.0 (d, $J_{\text{CF}} = 24$ Hz), 112.5 (d, $J_{\text{CF}} = 9$ Hz), 112.3 (d, $J_{\text{CF}} = 22$ Hz), 55.7 (OMe), 40.5 (Ada), 37.2 (Ada), 29.1 (Ada); ^{19}F NMR (CDCl_3 , CFCl_3) –124.4 ppm.

1-*m*-Xylyladamantane. MS ($m/z\%$, 70 eV, EI mode) 240 (100, M^+), 197 (20), 183 (62), 91 (20); ^1H NMR (CDCl_3) 6.98 (d, poorly resolved; 2H), 6.83 (broad singlet appearance; 1H), 2.32 (Me), 2.08 (br-s; Ada), 1.91 (d, Ada), 1.76 (t, Ada); ^{13}C NMR (CDCl_3) 151.6, 137.5, 127.4, 122.9, 43.4 (Ada), 37.0 (Ada), 36.1 (Ada), 29.2 (Ada), 21.8 (Me).

1-*p*-Tolyl-1,5,7-trimethyladamantane. MS ($m/z\%$, 70 eV, EI mode) 268 (100, M^+), 253 (53), 197 (100), 121 (47), 105 (35), 91 (25); ^1H NMR (CDCl_3) 7.24 (d), 7.11 (d), 2.30 (Me), 1.44 (Ada), 1.12 (Ada), 0.88 (Me).

1-*p*-Anisyl-3,5,7-trimethyladamantane. MS ($m/z\%$, 70 eV, EI mode) 284 (100, M^+), 269 (33), 213 (61), 121 (58), 91 (28); ^1H NMR (CDCl_3) 7.27 (d), 6.85 (d), 3.79 (OMe), 1.43 (Ada), 1.12 (Ada), 0.88 (Me).

1-(*m*-Methyl-*o*-anisyl)adamantane. MS ($m/z\%$, 70 eV, EI mode) 256 (100, M^+), 213 (15), 199 (40), 91 (10); ^1H NMR (CDCl_3) 7.15 (d, 2 Hz), 6.97 (dd), 6.77 (d, 8 Hz), 3.80 (OMe), 2.28 (Me), 2.08 (Ada), 2.05 (Ada), 1.77 (Ada); ^{13}C NMR (CDCl_3) 158.0 (Ar, C), 137.8 (Ar, C), 131.1 (Ar, CH), 127.5 (Ar, CH), 127.1 (Ar, CH), 111.9 (Ar, CH), 55.3 (OMe), 40.7 (Ada), 37.3 (Ada), 36.9 (Ada), 29.8 (Ada), 21.0 (Me).

1-(*m*-Fluoro-*o*-tolyl)-1,3,5-trimethyladamantane. MS ($m/z\%$, 70 eV, EI mode) 286 (83, M^+), 271 (100), 215 (50), 121(40); ^1H NMR (CDCl_3) 7.03 (dd, 1H), 6.96–6.81 (2H), 2.30(Me), 1.57 (Ada), 1.15 (Ada), 0.88 (Me).

1-(*m*-chloro-*o*-tolyl)adamantane (mixture of 3 isomers all with M^+ at m/z 260); for major isomer: MS ($m/z\%$, 70 eV, EI mode) 260 (55, M^+), 203 (33), 135 (44), 91 (22), 53 (100).

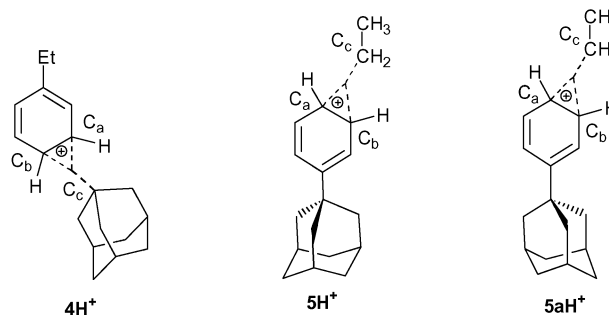
Recycling and reuse of the ionic liquid

Following the removal of organics from the IL phase by Et_2O extraction, the used IL was heated in the same Schlenk tube under high vacuum at 100 °C for several hours or overnight to remove any residual organics. Recovered [BMIM][OTf] was then used

in the subsequent run and the cycle was repeated several times without compromising the efficiency of the adamantylation reactions (as can be seen in the reported conversions summarized in Tables 1–4).

DFT calculations

Structures for *o*-1, *m*-1, *p*-1, *o*-2, *m*-2, *p*-2, *o*-3, *p*-3, *m*-3, and their protonated carbocations were optimized using molecular point groups shown in the supplementary information by the density functional theory (DFT) method at B3LYP/6-31G(d) or by the Hartree–Fock method at HF/6-31G(d) level using the Gaussian 03 package.²⁶ Transition structures, 4H^+ and 5H^+ , and 5aH^+ , for adamantyl shift and ethyl shift were located by changing the bond angles for $\text{C}_a\text{--C}_b\text{--C}_c$ in 4H^+ , 5H^+ , and 5aH^+ (see Scheme 2). Computed geometries were verified by frequency calculations. Furthermore, global minima were checked by manually changing the initial geometries and by comparing the resulting optimized structures and their energies. The supplementary information summarizes the total energies (E), relative energies (ΔE), zero point energies (ZPE), Gibbs' free energies (G), relative Gibbs' free energies (ΔG), by B3LYP/6-31G(d), HF/6-31G(d) and by B3LYP/6-31G(d)//HF/6-31G(d) levels. Gibbs' free energies were evaluated by frequency calculations at 298 K under 1 atm pressure which is the default for Gaussian 03 program.



Scheme 2

Acknowledgements

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