and 4-ethynyltoluene (2.03 g, 17.5 mmol) in $CHCl_3$ (60 mL) was allowed to stir for 20 h at room temperature. The resulting solution was diluted with $CHCl_3$ to 90 mL, treated with $MgSO_4$, and concentrated to an oil. Treatment of the oil with CH_2Cl_2 (25 mL) and Et_2O (40 mL) gave phenyl(*p*-tolylethynyl)iodonium tosylate as a white crystalline solid, yield 3.371 g (44%). A portion of the product was recrystallized from CH_2Cl_2/Et_2O for elemental analysis: mp 130–132.5 °C; ^1H NMR δ 2.31 (s, 3 H), 2.37 (s, 3 H), ca. 7.03–8.17 (aromatic m's, 13 H), slight contamination with Et_2O; ^{13}C NMR δ 21.2, 21.6, 37.8, 105.5, 117.05, 118.7, 126.0, 128.6, 129.1, 131.5, 131.6, 132.8, 133.8, 140.0, 141.29, 141.32. Anal. Calcd for $C_{22}H_{19}IO_3S$: C, 53.89; H, 3.91. Found: C, 53.86; H, 3.86.

(Cyclopentylethynyl)phenyliodonium Tosylate. A mixture of [hydroxy(tosyloxy)iodo]benzene (3.922 g, 10.0 mmol) and cyclopentylacetylene (1.12 g, 11.9 mmol) in $CHCl_3$ (80 mL) was allowed to stir for 23 h at room temperature. The resulting solution was washed with H_2O (2 × 25 mL), dried ($MgSO_4$), and concentrated to an oil. Treatment of the oil with a mixture of CH_2Cl_2 (5 mL), Et_2O (25 mL), and pentane (25 mL) followed by filtration gave (cyclopentylethynyl)phenyliodonium tosylate (0.97 g, mp 127–129 °C). A second portion of the iodonium salt (0.308 g, mp 125–128 °C) was isolated from the filtrate: combined yield 1.28 g (27%); ^1H NMR δ 1.45–1.8 (m, 5.1 H), 1.8–2.01 (m, 2.3 H), 2.31 (s, 2.8 H), 2.86 (m, 1 H), ca. 7.05–8.1 (aromatic m's, 9.8 H), relative area of aromatic region ca. 0.8 H high and that of aliphatic region ca. 0.8 H low; ^{13}C NMR δ 21.1, 24.9, 27.1, 31.3, 33.1, 112.5, 118.0, 125.9, 128.5, 131.3, 131.4, 133.5, 139.8, 141.5. Anal. Calcd for $C_{20}H_{21}IO_3S$: C, 51.29; H, 4.52. Found C, 51.11; H, 4.52.

GC Determination of the Yield of Iodobenzene from Phenyl(*p*-tolylethynyl)iodonium Tosylate and Trimethyl Phosphite. Trimethyl phosphite (4.73 g, 38.1 mmol) was added to solid phenyl(*p*-tolylethynyl)iodonium tosylate (1.078 g, 2.198 mmol), and the mixture was heated for 10 min at 95 °C. The resulting solution was allowed to cool to room temperature, *p*-xylene (0.1670 g, 1.57 mmol) was added, and the mixture was diluted volumetrically to 50 mL with CH_2Cl_2 (concentration of *p*-xylene, 3.340 $\mu g/\mu L$). After calibration with a standard solution of *p*-xylene (4.534 $\mu g/\mu L$) and PhI (7.734 $\mu g/\mu L$) in CH_2Cl_2, the yield of iodobenzene from the reaction was determined by GC analysis (three 1-μL injections) to be 92.4%, 92.2%, and 90.6% (average yield, 92%).

GC Determination of the Yields of Iodobenzene and 4d from Phenyl(*sec*-butylethynyl)iodonium Tosylate and Trimethyl Phosphite. Trimethyl phosphite (1.741 g, 14.0 mmol) was added to solid phenyl(*sec*-butylethynyl)iodonium tosylate (0.513 g, 1.12 mmol) at room temperature. Heat was evolved, and a solution resulted within 2 min. After the solution had cooled to room temperature, *p*-xylene (0.1057 g, 0.9956 mmol) was introduced, and the mixture was diluted volumetrically to 25 mL with CH_2Cl_2 (concentration of *p*-xylene, 4.228 $\mu g/\mu L$). After calibrations with standard solutions comprised of *p*-xylene (4.534 $\mu g/\mu L$) and PhI (7.734 $\mu g/\mu L$) in CH_2Cl_2 and *p*-xylene (4.240 $\mu g/\mu L$) and authentic **4d** (3.872 $\mu g/\mu L$) in CH_2Cl_2, the yields of iodobenzene and dimethyl (*sec*-butylethynyl)phosphonate from the reaction were determined by GC analysis (three 1-μL injections): iodobenzene (103.8%, 98.4%, 99.5%), average yield, 101%; **4d** (71.4%, 68.3%, 66.7%), average yield, 69%.

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Boron Tris(triflate) Catalyzed Adamantylation of Benzene and Toluene with 1- and 2-Haloadamantanes and Adamantanoyl Chlorides. Isomerization of Phenyl- and Tolyladamantanes[1]

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Boron tris(triflate) catalyzed adamantylation of benzene and toluene was studied with isomeric 1- and 2-haloadamantanes. The alkylations give 1- and 2-phenyl- and isomeric tolyladamantanes in varying ratios. Interconversion of isomeric 2-phenyl(tolyl)adamantanes into the corresponding 1-phenyl(tolyl)adamantanes was observed through intermolecular isomerization involving adamantyl cations and adamantane, which is formed in significant amount in all the reactions. Decarbonylative alkylation of aromatics with adamantanoyl chlorides was also investigated. Adamantanoylated aromatics were formed only in very low amounts, the major product being adamantylated aromatics in accord with extensive decarbonylation of the adamantanoyl cations. The mechanism of the studies adamantylations was further substantiated by studying the boron tris(triflate) catalyzed isomerization of 1- and 2-aryladamantanes under comparable conditions.

Introduction

Friedel–Crafts alkylation of aromatics with diverse alkylating agents[2a] including *tert*-butyl halides[2b] has been extensively investigated.[2] However, the related adamantylation of aromatics remained little explored. Adamantylation of aromatics with 1-adamantyl radical was studied,[3a] and the reactivity of the radical was probed through the effect of substituents on the isomer distribution and relative reactivities. Adamantylation of reactive aromatics using adamantyl nitrate in the presence of H_2SO_4 has also been reported.[3b] $AlCl_3$-catalyzed Friedel–Crafts adamantylation of benzene with 1-bromoadamantane was investigated by Newman.[4] The observation that mixtures of mono, di, and triphenyladamantanes were formed suggested that the $AlCl_3$-catalyzed reaction provides rather harsh conditions for adamantylation. Subsequently adamantylation of benzene and substituted benzenes were carried out in large excess of aromatics using $FeCl_3$ catalyst. In adamantylation of toluene only the para isomer was reported to be formed.[5]

(1) Aromatic Substitution. 58. For part 57, see: Olah, G. A.; Piteau, M.; Laali, K.; Rao, C. B.; Farooq, O. *J. Org. Chem.*, submitted.

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Table I. Boron Triflate Catalyzed Adamantylation of Toluene with 1-Haloadamantanes in CH_2Cl_2 at Room Temperature

adamantyl halide	reaction time, min	adamantane, % yield	tolyladamantanes						
			% yield	% isomer distribution					
				1-*o*	1-*m*	1-*p*	2-*o*	2-*m*	2-*p*
1-ad-Cl	0.25	27	72	–	65	34	–	–	1
	0.5	32	68	–	74	22	–	–	4
	1	33	66	–	72	25	–	–	3
	30	34	56	–	68	27	–	tr	5
	60	34	55	–	61	24	–	2	13
	120	35	54	–	49	29	–	6	16
1-ad-Br	1	17	82	–	66	33	–	–	–
	5	28	71	–	70	29	–	–	–
	12	35	64	–	70	29	–	–	1
	30	32	66	–	67	28	–	–	5

Table II. Boron Triflate Catalyzed Adamantylation of 5:1 (mol:mol) Benzene–Toluene Mixture with 1-Haloadamantane at Room Temperature

adamantyl halides	solvent	reaction time, min	adamantane, % yield	phenyladamantanes			tolyladamantanes						
				% yield	% isomer distrib (norm)		% yield	% isomer distrib (norm)					
					1-Ph	2-Ph		1-*o*	1-*m*	1-*p*	2-*o*	2-*m*	2-*p*
1-ad-F	CH_2Cl_2	1	20	44	99	1	5	–	76	22	–	tr	tr
		5	23	42	98	2	7	–	51	30	–	tr	18
		10	30	41	97	3	5	–	58	28	–	1	13
		15	35	40	98	2	6	–	56	30	–	1	13
		25	42	37	97	3	4	–	57	30	–	1	12
		70	44	36	96	4	4	–	53	31	–	2	14
		120	46	34	94	6	4	–	50	28	–	4	18
1-ad-Cl	CH_2Cl_2	1	37	39	96	4	20	–	59	33	–	–	8
		2	36	36	97	3	25	–	46	35	–	–	19
		5	44	37	98	2	12	–	63	25	–	–	12
		15	50	36	98	2	9	–	61	27	–	–	12
		25	52	35	98	2	10	–	59	27	–	–	14
1-ad-Cl	CH_3NO_2	1	tr	42	100	–	2	–	84	16	–	–	–
		5	1	51	100	–	7	–	74	26	–	–	–
		10	2	53	100	–	8	–	70	30	–	–	–
		15	3	52	100	–	8	–	70	30	–	–	–
		30	2	51	100	–	8	–	68	32	–	–	–

No systematic study of the Friedel–Crafts adamantylation of aromatics such as benzene and toluene was carried out. Nor was adamantylation of aromatics using 2-adamantyl derivatives reported. Further, no study is available concerning the selectivity of such reactions. Isomerization of 2-substituted adamantanes to the 1-substituted bridgehead isomers have also been reported.[6-8] Aluminum trihalide catalyzed isomerization of 2-methyladamantane and 2,2-dihaloadamantanes[8] to the bridgehead isomers has been described, but no isomerization of 2-phenyladamantane or other 2-aryladamantanes was known.

We have recently reported a new class of Friedel–Crafts catalysts[10] based on the trifluoromethanesulfonate (triflate) of group IIIA elements, including boron tris(triflate). We have also reported the activity of this Lewis acid in the generation of stable carbocations,[11] in the isomerization of strained polycyclic hydrocarbons to the adamantanoid cage compounds[12,13] and in the alkylation of aromatics using alkyl an acylic alkyl halides as alkylating agents.[10] We now report our results from the adamantylation of aromatics under Friedel–Crafts conditions using boron tris(triflate) as catalyst and from related studies of isomerization of phenyl- and tolyladamantanes.

Results and Discussion

The adamantylation of benzene and toluene using boron triflate as catalyst with 1-chloro- and 1-bromoadamantanes was carried out in CH_2Cl_2 solution at room temperature. It should be pointed out that whereas $B(OTf)_3$ was used in its pure form, in all reactions inevitably some moisture was present (as no effort was made to assure strictly anhydrous conditions). Under the reaction conditions no hydrolysis to triflic acid was observed to take place, indicating the stability of the hydrate $B(OTf)_3 \cdot H_2O$. In the adamantylation of toluene, tolyladamantanes were obtained in 54–82% yield (Table I) consisting of isomeric 1- and 2-tolyladamantanes. In both reactions isomeric 1-tolyladamantanes were obtained in much higher amounts compared to the 2-tolyladamantanes. 1-*m*-Tolyladamantane predominated over the para isomer, but in case of 2-tolyladamantanes the para isomer was preferentially obtained (Table I).

In order to determine the relative reactivities of toluene and benzene toward adamantylation, competitive reactions were carried out. In the competitive adamantylation of benzene–toluene mixtures with 1-haloadamantanes in CH_2Cl_2, isomeric tolyladamantanes were obtained in much

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Table III. Adamantylation of 5:1 (mol:mol) Benzene–Toluene Mixture with 1-Adamantyl Hexafluoroantimonate

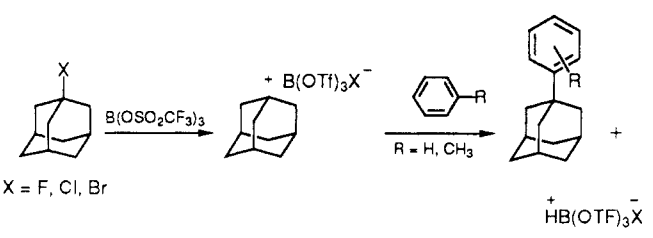
reaction time, min	temp, °C	adamantane, % yield	phenyladamantanes % yield	phenyladamantanes % isomer distrib (norm) 1-Ph	phenyladamantanes % isomer distrib (norm) 2-Ph	tolyladamantanes % yield	tolyladamantanes % isomer distrib (norm) 1-*o*	1-*m*	1-*p*	2-*o*	2-*m*	2-*p*
1	−78	23	35	99	1	17	–	81	19	–	–	–
5	−78	23	41	99	1	26	–	83	16	–	–	0.5
5	−78 to −15	29	36	99	1	15	–	89	10	–	–	1.0
10	−15	31	39	99	1	12	–	76	22	–	–	2
10	−15 to rt	41	39	99	1	7	–	60	34	–	–	6
10	rt	38	44	99	1	8	–	53	37	–	–	10
20	rt	40	42	99	1	7	–	53	38	–	tr	9

lower yield (Table II). In addition isomerization of tertiary and secondary substituted adamantanes, aromatic ring position (positional) isomerization of the adamantylated aromatics was also observed. Consequently the isomer distribution in the tolyladamantane products was rather varied and included isomeric 1- as well as 2-tolyladamantanes (Table II). In the isomeric phenyladamantanes, positional selectivity was highly in favor of 1-phenyladamantane. In the competitive adamantylation reactions low substrate selectivity (k_T/k_B = 0.5–4.8) was observed with higher substrate selectivity observed in case of 1-chloroadamantane than with 1-fluoroadamantane. As in all the adamantylation reactions (Tables I and II) in CH_2Cl_2 (and to a lesser degree in CH_3NO_2) 1–2% of 1-adamantanol and significant amounts of adamantane (up to 30–50%) were formed. The substrate selectivity data obtained in competitive experiments cannot be considered meaningful, as obviously extensive disproportionation affects the results. Observed formation of adamantane indicates significant disproportionation of phenyladamantane (tolyladamantanes) via an intermolecular pathway, which explains the apparent very low substrate reactivities. Consequently no evaluation of competitive rates was attempted.

In all the reactions with 1-haloadamantanes (Table II) 1-adamantanol and isomeric 2-tolyl-2-adamantanols were also identified in the GC and GC–MS in 1–2% and 10–15% yield, respectively. Prolonged reactions also resulted in the formation of 2–6% and 1–2% of ditolyl- and diphenyladamantanes as identified by GC–MS analysis.

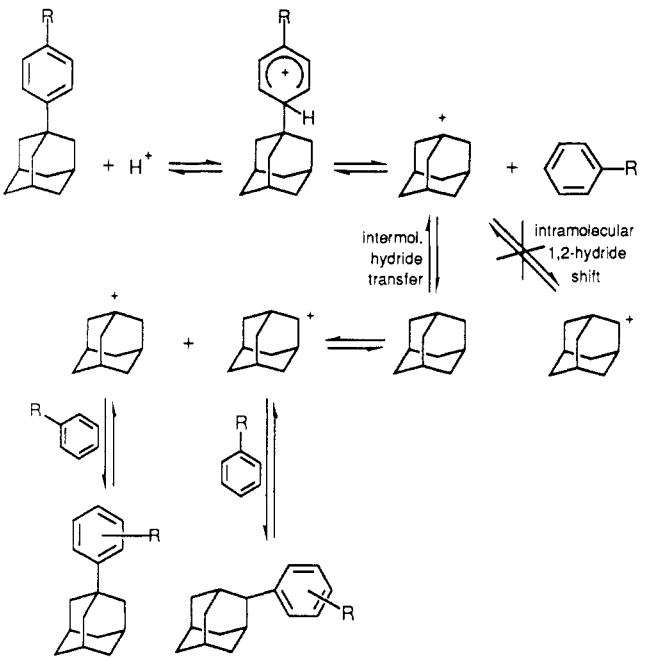
In order to study further the isomer distribution in tolyladamantanes, adamantylation of benzene-toluene mixture with stable, performed 1-adamantyl cation was investigated at temperatures of 25 to −78 °C. The results (Table III) show varying distribution of both isomeric 1-tolyl and 2-tolyladamantanes, with isomeric phenyladamantanes consisting mainly of 1-phenyladamantane (99%). Isomeric adamantanols and 2-tolyl-2-adamantanols were also obtained in 2–3% and 5–10% yield, respectively, together with diphenyl- and ditolyladamantanes in 2–4% yield.

1-Phenyladamantane and isomeric 1-tolyladamantanes are formed by typical electrophilic adamantylation of benzene and toluene, respectively via the tertiary 1-adamantyl cation. 1-Phenyladamantane and isomeric



1-tolyladamantanes can also undergo deadamantylation by the formed conjugate-Brønsted Lewis superacid

Scheme I



through ipso protonation. To account for the observed 2-adamantyl products, isomerization of the 1- and the 2-adamantyl cation must take place. This process cannot take place intramolecularly (because of the orientation of the orbitals). Thus intermolecular hydride abstraction first forms adamantane (observed in significant amounts in all studied reactions), which in turn can form the 2-adamantyl cation (as well as reform the 1-adamantyl cation as the major reaction) as shown in Scheme I. The mechanism is illustrated with only one of the isomeric 1-aryladamantanes shown.

To substantiate the formation of 2-adamantyl cation from adamantane, the latter was treated with boron tris(triflate) in CH_2Cl_2 solution. GC analysis of the reaction products after aqueous workup (ice–bicarbonate) gave 1-adamantanol and 2-adamantanol in the ratio 50:1.

Formation of isomeric 1-tolyl- and 2-tolyladamantanes is due to (1) alkylation of toluene by the corresponding adamantyl cations (with proper orientation) and (2) isomerization of adamantyltoluenes.

Considering alkylations with 1-haloadamantanes in the reaction with 1-fluoroadamantanes, the formed conjugate protic superacid $H^+BF(OTf)_3^-$ (and eventually HBF_4) is stronger than those formed in related chloro or bromo systems and thus causes more extensive isomerization under the reaction conditions. Indeed, in the former reaction more adamantane and isomeric phenyladamantanes (together with some diphenyl- and ditolyladamantanes) are formed than in reactions with 1-chloro- or 1-bromoadamantane. Alkylation with 1-adamantyl hexafluoro-

Table IV. Adamantylation of 5:1 Benzene–Toluene Mixture with 2-Haloadamantanes in CH_2Cl_2 at Room Temperature

adamantyl halide	reaction time, min	% adamantane	phenyladamantanes % yield	phenyladamantanes % isomer distrib 1-Ph	phenyladamantanes % isomer distrib 2-Ph	tolyladamantanes % yield	tolyladamantanes % isomer distrib 1-*o*	1-*m*	1-*p*	2-*o*	2-*m*	2-*p*
2-ad-Cl	0.75	37	20	4	96	36	–	4	tr	–	88	16
	1.5	53	18	63	37	26	–	30	4	–	56	10
	3	54	16	88	12	27	–	50	19	–	19	12
	5	40	16	90	10	31	–	76	7	–	7	10
	15	41	15	93	7	31	–	83	10	–	3	4
	30	40	17	94	6	31	–	70	13	–	3	14
	60	42	15	94	6	34	–	60	10	–	25	5
2-ad-Br	15	42	33	82	18	20	–	29	21	–	9	41

Table V. Adamantylation of 5:1 Benzene–Toluene Mixture with Adamantanoyl Chlorides in CH_2Cl_2 at Room Temperature

adamantanoyl chloride	reaction time, min	adamantane, % yield	phenyladamantanes % yield	phenyladamantanes % isomer distrib 1-Ph	phenyladamantanes % isomer distrib 2-Ph	tolyladamantanes % yield	tolyladamantanes % isomer distrib 1-*o*	1-*m*	1-*p*	2-*o*	2-*m*	2-*p*
1-ad-COCl	1	28	50	100	–	8	–	72	28	–	–	–
	5	28	52	100	tr	7	–	70	30	–	–	–
	10	30	51	99	1	6	–	71	29	–	–	tr
	15	35	48	98	2	7	–	69	31	–	tr	tr
	60	34	48	96	4	6	–	67	33	–	tr	tr
2-ad-COCl	2	3	11	88	12	9	–	–	–	2	30	68
	5	2	10	89	11	7	–	–	–	4	24	72
	10	2	13	85	15	6	–	–	–	3	26	71
	15	3	17	89	11	9	–	–	–	4	15	85
	30	4	23	88	12	14	–	tr	tr	2	9	90
	60	7	23	87	13	12	–	1	tr	1	24	75

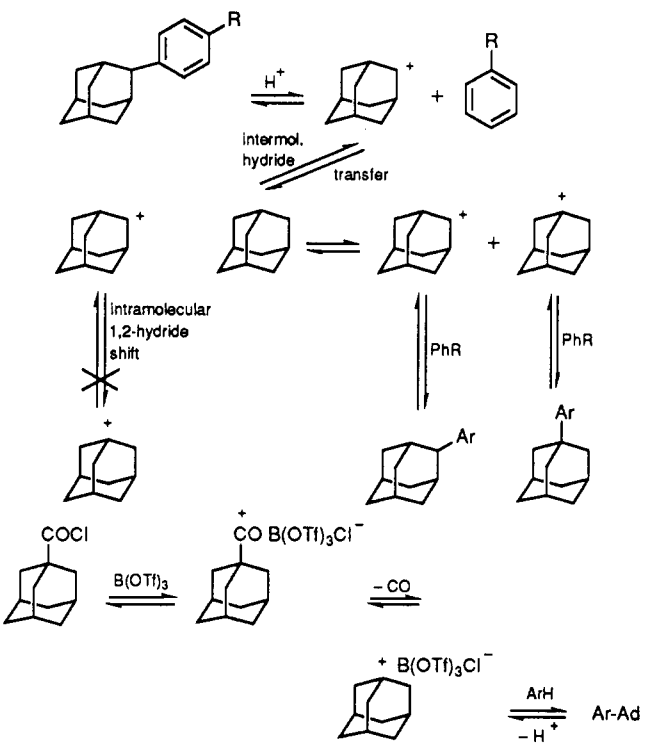
antimonate results in the formation of the even stronger conjugate protic acid $H^+SbF_6^-$, but at the low reaction temperature isomerization is also slower.

Formation of isomeric 2-aryladamantanes, although in relatively minor amounts compared to the isomeric 1-aryladamantanes, in the adamantylation of benzene and toluene with 1-haloadamantanes prompted us also to investigate adamantylation at short reaction times with 2-haloadamantanes. As shown in Table IV, isomeric 2-aryladamantanes are formed together with isomeric 1-aryladamantanes in the initial stages of the reaction. Fast isomerization of 2-aryladamantanes to 1-aryladamantanes then gives 1-aryladamantanes as the major isomers. Isomeric 2-aryladamantanes are initially formed by direct adamantylation by the 2-adamantyl cation (or the highly polarized 2-haloadamantane catalyst complex) with appropriate kinetic orientation. Subsequent thermodynamically controlled isomerizations similarly to those discussed previously for isomeric 1-aryladamantanes take over.

Formation of 1-aryladamantanes from the initially formed 2-aryladamantanes must probably involve intermolecular isomerization. The 2-adamantyl cation is relatively unstable[9] and isomerizes rapidly to the more stable 1-adamantyl cation by means of an intermolecular hydride shift (since a 1,2-hydride shift in adamantane is symmetry-forbidden[14]) through the formation of adamantane. 1-Adamantylated products in the reaction with 2-haloadamantanes with aromatics are thus readily explained (see Scheme II). In the adamantylation with 2-haloadamantanes both the proportion of isomeric 2-aryladamantanes formed and their regioselectivity is higher than in reactions with 1-haloadamantanes.

In the course of our studies we have found that not only haloadamantanes lead to the Friedel–Crafts adamantylation of aromatics, such as benzene and toluene, but

Scheme II

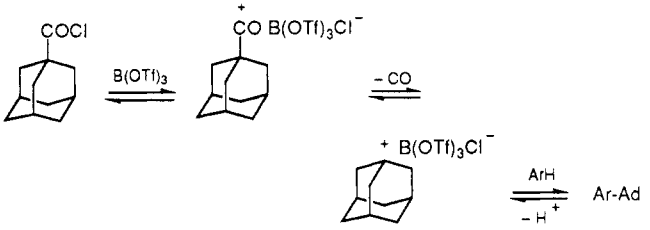


adamantanoyl chlorides also give similar adamantylations. 1-Adamantanoyl chloride readily ionizes with strong Lewis acids, and the formed adamantanoyl cation tends to lose CO forming the corresponding 1-adamantyl cation.

In view of a wide range of isomer distribution obtained in the boron tris(triflate) catalyzed adamantylation of aromatics with both 1- and 2-haloadamantanes, it was of interest to investigate the reaction of aromatics with isomeric adamantanoyl chlorides and boron tris(triflate) under similar reaction conditions. The results of reaction of adamantanoyl chlorides with a benzene-toluene mixture

(14) Schleyer, P. v. R.; Lam, L. K. M.; Raber, D. J.; Fry, J. L.; McKervey, M. A.; Alford, J. R.; Cuddy, B. D.; Keizer, V. G.; Geluk, H. W.; Schlatmann, J. L. M. A. *J. Am. Chem. Soc.* **1970**, *92*, 5246.

presented in Table V show only adamantylated products. Mixtures of isomeric phenyladamantanes and tolyladamantanes obtained were similar to those from the reactions of aromatics with isomeric haloadamantanes. In the reactions with 1-adamantanoyl chloride no adamantanoylated product was obtained nor was any adamantanecarboxylic acid identified upon workup of the reactions. These results show the fast decarbonylation of the 1-adamantanoyl cation to the 1-adamantyl cation, observed previously by NMR spectroscopy under "stable ion" conditions,[16] responsible for the formation of isomeric 1-aryladamantanes by the alkylation mechanism discussed previously.

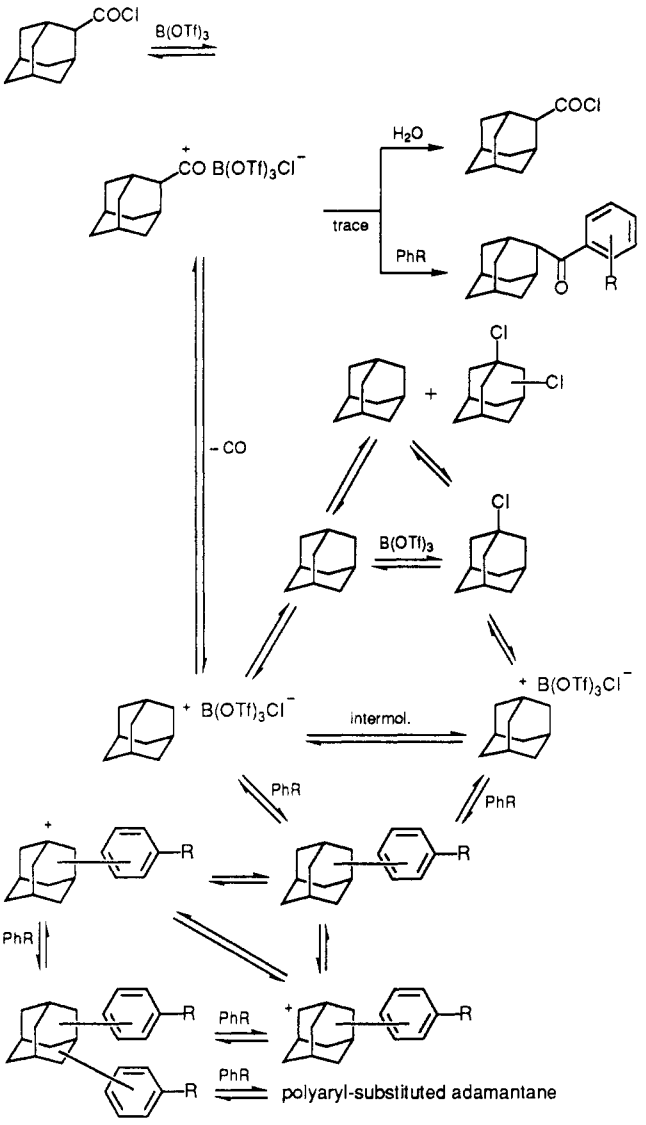


Hoogeveen[15] studied carbonylation–decarbonylation equilibria of carbocationic systems and remarked the decarbonylation of 1-adamantanoyl cation to be a fast process. We have reported the preparation of the 1-adamantanoyl cation in SbF_5–SO_2ClF solution[16] and have also observed formation of the stable 1-adamantyl cation via decarbonylation. Fast decarbonylation of 1-adamantanoyl cation was also indicated through its reaction with benzene, yielding predominantly 1-phenyladamantane. Our present investigation not only further proves this decarbonylation process but also that 1-adamantanoyl chloride can be used as an efficient Friedel–Crafts adamantylating agent.

In the reaction with 2-adamantanoyl chloride, on the other hand, besides 10–20% of adamantylated products, 2-adamantanecarboxylic acid was obtained upon workup as the major product (30–70%), together with 2–3% of (isomeric) 2-adamantanoyltoluenes identified by GC–MS (Scheme III). These results clearly show the much higher stability of the secondary 2-adamantanoyl cation (even at room temperature), which at the same time is a electrophile for acylation of aromatics. In addition to those previously mentioned products, about 5–15% of isomeric diphenyladamantanes were identified (GC–MS) from the reaction mixture, which were formed by the reaction of the phenyl-substituted adamantyl cation with benzene during the course of reaction (Scheme III). In the reaction with 2-adamantanoyl chloride, 7–16% of isomeric 1- and 2-chloroadamantanes were also identified by GC–MS. 2-Chloroadamantane was presumably formed from the decarbonylation of the 2-adamantanylation to the 2-adamantyl cation as well as from possibly intermolecular isomerization of 1-chloroadamantane.

As seen from data in Table V, the isomerization of isomeric 2-tolyladamantanes to isomeric 1-tolyladamantanes is limited. This is attributed to the formation of the more stable 2-adamantanoyl ion or polarized 2-adamantanoyl chloride–boron tris(triflate) complex, and less boron tris(triflate), therefore, is available to promote the isomerization. The high yield (52%) of 2-adamantanecarboxylic acid obtained in the reaction together withe the low yield of adamantane and phenyladamantanes (Table V) further substantiates this suggestion. The isomeric adamantanoyl chlorides, as seen in Table V, thus act as adamantylating rather than adamantanoylating agents.

Scheme III



In the isomer distribution of tolyladamantanes obtained in the studied reactions, no 1-*o*-tolyladamantane has been observed. This is attributed to the high steric hindrence with the tertiary bridgehead system and possible fast isomerization. On the other hand, 2-*o*-tolyladamantane was identified, albeit in very low amount, in the very early stage (~15 s) in reaction of toluene with 2-chloroadamantane. 2-*o*-Tolyladamantane (2–4%) was found in the reaction with 2-adamantanoyl chloride (Table V) where as discussed limited availability of free catalyst-promoting isomerization makes this isomer more accessible.

In order to probe the isomerization of phenyl- and tolyladamantanes, we have extended our studies of the adamantylation of aromatics to the isomerization of 1- and 2-phenyladamantane, as well as isomeric tolyladamantanes with boron tris(triflate) (activated by some water, as again no precautions were used to exclude moisture from the system).

The isomerization of 2-phenyladamantane gave 1-phenyladamantane (Table VI) with substantial amounts of adamantane, as well as 1,3-di and 1,3,5-triphenyl- and some 1-biphenylyladamantane (Scheme IV). 1,3,5,7-Tetraphenyladamantane and diadamantylbenzenes were

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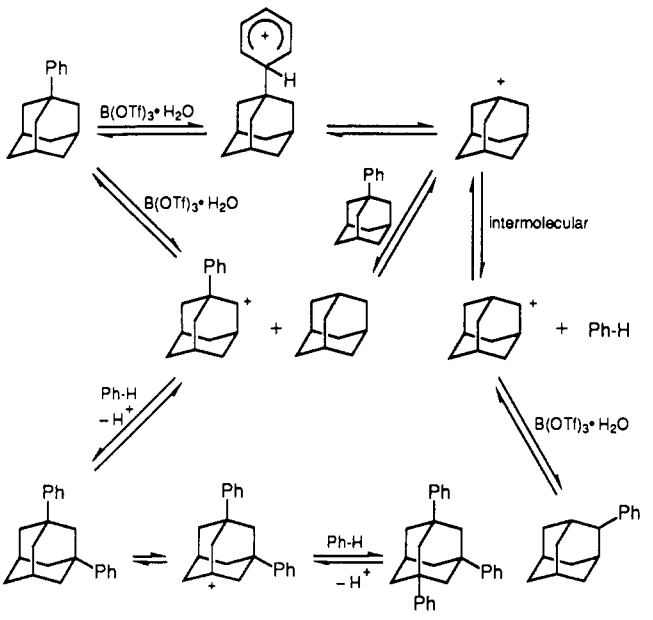
Table VI. Isomerization of 1- and 2-Phenyladamantane with Boron Tris(triflate) in CH_2Cl_2 Solution at Room Temperature

time, min	2-phenyladamantane	1-phenyladamantane	adamantane	1,3-diphenyl-, 1,3,5-triphenyl-, and 1-biphenylyladamantane
0	100	0	0	0
1	49	4.6	45	1.4
15	35.4	6.8	55	2
120	22.5	13.6	54	10
(24 h)	20.3	23.6	45	8
time, min	1-phenyladamantane	2-phenyladamantane	adamantane	other products
0	100	0	0	0
1	95	0	4	1
(24 h)	49	0	41	9

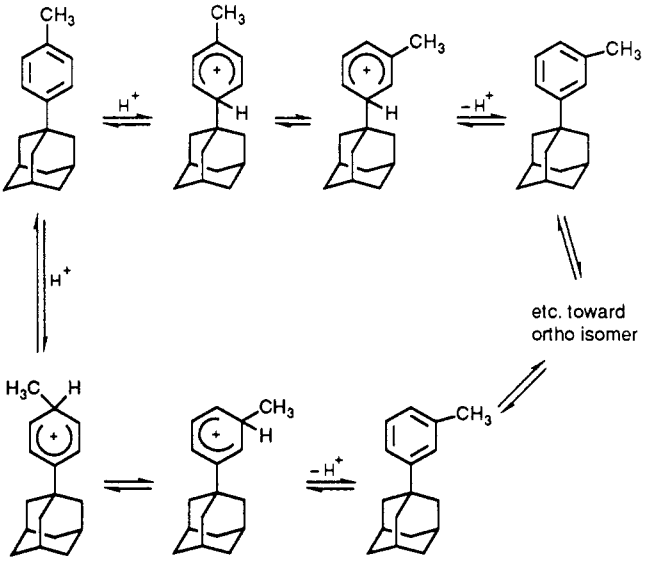
Table VII. Boron Triflate Catalyzed Isomerization of Isomeric 1-Tolyladamantanes in CH_2Cl_2 at Room Temperature

tolyladamantanes	reaction time, min	% adamantane	tolymadamantanes % isomer distrib (norm) 1-*o*	1-*m*	1-*p*	2-*o*	2-*m*	2-*p*
1-ad-C_6H_4-CH_3	1	42	tr	76	24	–	–	–
(isomeric)	3	48	tr	65	32	–	–	tr
(o, m, p:	5	47	–	68	31	–	–	1
59 15 26)	7	41	–	69	31	–	tr	2
	20	44	–	67	32	–	1	7
	30	45	–	68	31	–	2	12
1-ad-C_6H_4-CH_3	0	–	–	–	100	–	–	–
(para isomer)	0.5	14	–	83	17	–	–	tr
	1	21	–	67	33	–	–	tr
	10	62	–	71	29	–	–	tr
	20	60	–	63	32	–	2	10
	30	59	–	–	–	–	4	19

Scheme IV



Scheme V



indicated only in traces (GC–MS). In the attempted isomerization of 1-phenyladamantane, primarily products of disproportionation, adamantane, 1,3-di and 1,3,5-triphenyladamantanes were observed, but not 2-phenyladamantane.

The results of isomerization of isomeric 1- and 2-tolyladamantanes are summarized in Tables VII and VIII, respectively. In all the isomerization reactions adamantane was found to be formed in significant amount indicative of the intermolecular nature of the reactions. Formation of isomeric 2-tolyladamantanes in the isomerization of isomeric 1-tolyladamantanes (Table VII) is extremely limited (if any). On the other hand, facile isomerization of isomeric 2-tolyladamantanes to 1-tolyladamantanes reflects the intermolecular nature of the isomerization of the 2- to 1-adamantyl cation (Table VIII).

While isomerization of 2- and 1-tolyladamantanes involves the intermolecular isomerization of the corresponding adamantyl cations (via hydride transfer involving adamantane), the 1- and 2-isomerization and isomerization within each group of isomers may involve intramolecular migration of adamantyl and methyl groups as illustrated in the intraconversion of *p*- and *m*-tolyl-1-adamantane isomers (Scheme V).

Similar further paths are suggested for the formation of isomeric 2-tolyladamantanes (Table VIII).

In conclusion, boron tris(triflate) catalyzed Friedel–Crafts adamantylation of aromatics, such as benzene or toluene, is a most convenient way to prepare aryladamantanes. The mechanism of the reaction involves carbocationic processes.

Experimental Section

Boron tris(triflate) was prepared according to our reported method.[10] 1-Chloroadamantane, 1- and 2-bromoadamantanes,

Table VIII. Boron Triflate Catalyzed Isomerization of 2-Tolyladamantanes in CH_2Cl_2 at Room Temperature

adamantyltoluenes	reaction time, min	% adamantane	tolyladamantanes % isomer distrib (norm)					
			1-*o*	1-*m*	1-*p*	2-*o*	2-*m*	2-*p*
4-(2′-adamantyl)toluene	0.5	38	–	tr	tr	–	17	83
	0.75	39	–	6	2	–	10	82
	2	47	–	8	3	–	7	82
	5	61	–	12	6	–	6	76
	15	52	–	17	5	–	7	71
	30	55	–	28	13	–	8	42
	60	58	–	44	22	–	8	26
3-(2′-adamantyl)toluene	0.5	28	–	tr	tr	–	32	68
	1	46	–	10	6	–	13	71
	7	47	–	17	11	–	9	57
	15	50	–	28	14	–	8	50
	30	51	–	42	21	–	5	32
	60	50	–	34	17	–	4	45
2-(2′-adamantyl)toluene	0.5	24	–	2	4	–	15	79
	1	30	–	2	1	–	10	87
	3	25	–	4	2	–	5	89
	8	42	–	5	4	–	7	84
	23	34	–	8	3	–	7	82
	75	23	–	17	14	–	5	64

1-adamantanoyl chloride, benzene, toluene, dihalobenzenes, and halotoluenes were available from Aldrich (>99%). 1-Fluoroadamantane,[17] 2-chloroadamantane,[17] and 1-phenyladamantane[18] were prepared according to literature procedure. 2-Phenyladamantane and isomeric 2-tolyladamantanes were prepared according to our reported procedure.[19] Other reference compounds were prepared as described.

GC analysis was carried out on a Varian Associates Model 3700 gas–liquid chromatograph using a 30-m quartz silica column coated with DB-1.

^{13}C and ^1H NMR measurements were carried out on a Varian VXR 200 superconducting spectrometer equipped with a variable-temperature probe.

General Method of Adamantylation of Aromatics. To a well-stirred solution of 16.2 mmol of toluene, 81.0 mmol (1:5 ratio) of benzene and 16.2 mmol of haloadamantane in methylene chloride was added 4.05 mmol of boron tris(triflate) in CH_2Cl_2 under dry nitrogen atmosphere. While the reaction was continuing, aliquots were taken at different time intervals and were subjected to GC/analysis after usual workup.

Competitive reactions with isomeric adamantanoyl chlorides were carried out similarly.

Isomerization of Phenyl(tolyl)adamantanes. To a solution of 0.7 mmol of 1- or 2-phenyladamantane in dichloromethane at room temperature was added 0.07 mmol of boron tris(triflate). While stirring, samples were taken periodically and analyzed by GC after usual workup.

Preparation of Authentic 1-Tolyladamantanes: General Procedure. To a pressure tube charged with a solution of 1-bromoadamantane (3.23 g, 15.0 mmol), magnesium metal (1.08 g; 45 mmol), and dried ether (7.5 mL) was added dropwise bromotoluene (para, meta, or ortho, 7.70 g; 45 mmol) with constant stirring at 0 °C (using an external ice bath) under nitrogen atmosphere during a period of 10 min. After the addition of bromotoluene had been completed, the reaction tube was sealed and heated slowly to 100 °C by an external oil bath for additional 2 h then cooled to ambient temperature. The sealed tube was carefully opened, and the reaction mixture was poured into a separatory funnel charged with ice (50 g) and then extracted with ether (50 mL × 3). The combined ethereal layers were dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuo to leave crude 1-tolyladamantane. The analytical sample was obtained by column chromatography on silica gel (hexane eluent).

1-*o*-Tolyladamantane. From the reaction of 1-bromoadamantane (3.23 g; 15 mmol), magnesium (1.08 g; 45 mmol), and *o*-bromotoluene (7.70 g; 45 mmol) was obtained the corresponding 1-*o*-tolyladamantane (2.26 g; 10.0 mmol; 67% yield from 1-bromoadamantanes) as colorless microcrystals, mp 77–79 °C. ^{13}C NMR (50 MHz; $CDCl_3$): δ 23.35 (q), 29.16 (d), 35.75 (s), 36.90 (t), 41.28 (t), 121.80 (d), 125.60 (d), 125.90 (d), 133.04 (d), 136.04 (s), 147.20 (s). GC/MS (70 eV): *m/e* 226 (M^+; 2.9), 211 (0.6), 135 (100.0) 91 (74.3). Anal. Calcd for $C_{17}H_{22}$: C, 90.27; H, 9.73. Found: C, 90.41; H, 9.52.

1-*m*-Tolyladamantane. From the reaction of 1-bromoadamantane (3.23 g; 15 mmol), magnesium (1.08 g; 45 mmol), and *m*-bromotoluene (7.70 g; 45 mmol) was obtained the corresponding 1-*m*-tolyladamantane (2.49 g; 11.0 mmol; 73.3% yield from 1-bromoadamantanes) as colorless microcrystals, mp 76–77 °C. ^{13}C NMR (50 MHz; $CDCl_3$): δ 20.56 (q), 27.88 (d), 34.92 (s), 35.72 (t), 42.07 (t), 120.69 (d), 124.48 (d), 125.09 (d), 126.83 (d), 136.24 (s), 147.15 (s). GC/MS (70 eV): *m/e* 226 (M^+; 3.9), 135 (100.0), 91 (185.2). Anal. Calcd for $C_{17}H_{22}$: C, 90.27; H, 9.73. Found: C, 90.50; H, 9.40.

1-*p*-Tolyladamantane. From the reaction of 1-bromoadamantane (3.23 g; 15 mmol), magnesium (1.08 g; 45 mmol), and *p*-bromotoluene (7.70 g; 45 mmol) was obtained the corresponding 1-*p*-tolyladamantane (2.73 g; 12.1 mmol; 80.7% yield from 1-bromoadamantanes) as colorless microcrystals, mp 81–82 °C. ^{13}C NMR (50 MHz; $CDCl_3$): δ 19.70 (q), 27.83 (d), 35.43 (s), 35.67 (t), 42.10 (t), 123.53 (d), 127.61 (d), 133.68 (s), 147.26 (s). GC/MS (70 eV): *m/e* 226 (M^+; 5.2), 211 (3.2), 135 (100.0), 91 (69.3). Anal. Calcd for $C_{17}H_{22}$: C, 90.27; H, 9.73. Found: C, 90.39; H, 9.72.

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Registry No. 1-ad-Cl, 935-56-8; 2-ad-Cl, 7346-41-0; 1-ad-Br, 768-90-1; 2-ad-Br, 7314-85-4; 1-ad-F, 768-92-3; 1-ad-COCl, 2094-72-6; 2-ad-COCl, 40079-92-3; 1-ad-Ph, 780-68-7; 2-ad-Ph, 19066-24-1; $B(OTf)_3$, 64371-01-3; toluene, 108-88-3; benzene, 71-43-2; 1-*m*-tolyladamantane, 1974-86-3; 1-*p*-tolyladamantane, 1459-55-8; 2-*m*-tolyladamantane, 19214-04-1; 2-*p*-tolyladamantane, 19066-25-2; adamantane, 281-23-2; *o*-bromotoluene, 95-46-5; *m*-bromotoluene, 591-17-3; *p*-bromotoluene, 106-38-7; 1-*o*-tolyladamantane, 61051-34-1; 2-*o*-tolyladamantane, 115942-81-9; 1-adamantyl hexafluoroantimonate, 2062-52-4.

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