Friedel–Crafts Alkylation of Aromatics with 1-Chloronorbornane, 3-Halonoradamantane, and Fluorocubane via Their Reactive sp^3-Hybridized Bridgehead Carbocations[1]

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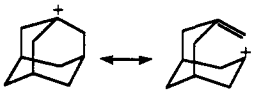
Abstract: 1-Chloronorbornane, 3-chloronoradamantane, and 3-bromonoradamantane, and fluorocubane, in the presence of aluminum chloride or boron trifluoride, respectively, readily alkylate benzene and substituted benzenes at or below room temperature. As back-side S_N2-type displacement at bridgehead positions is not possible, the reported new Friedel–Crafts alkylations must involve strongly polarized bridgehead halide–aluminum chloride (or boron trifluoride) complexes in equilibrium with their energetic, reactive carbocations in which the empty orbital is of sp^3 nature since the strained bridgehead centers can not flatten out. No long-lived 1-norbornyl, 3-noradamantyl, or cubyl cation can be observed in antimony pentafluoride containing superacid systems under stable ion conditions. 1-Halonorbornanes give the rearranged, σ-delocalized 2-norbornyl cation whereas fluorocubane decomposes in the system. The difference between "stable" and "reactive" carbocation intermediates is discussed.

Introduction

There is continued interest in the reactivity of bridgehead organohalides such as 1-halonorbornanes (1-halobicyclo[2.2.1]-heptanes) ever since the preparation of norbornane by Komppa and Beckmann.[2] The derived bridgehead norbornyl radical[3-5] and anion[6] are well known and well studied. However, the 1-norbornyl cation[7] has not been observed in solution. In contrast, the bridgehead adamantyl cation is readily prepared and extensively studied in solution.[8 a–c] An X-ray crystal structure of the 3,5,7-trimethyl-1-adamantyl cation[9] indicates that whereas the ion can not completely flatten out, the deviation from planarity of the sp^2-like carbocation center is only about 2°. The 1-adamantyl cation is stablized by carbon–carbon hyperconjugation (**2**)[10] even though carbon–hydrogen hyperconjugation is not favorable as it would violate Bredt's rule (**4**).[11]



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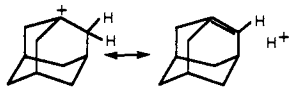

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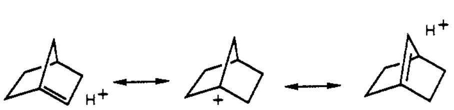
Similarly, the sp^3-hybridized 1-bridgehead norbornyl cation (**6**) can not be stabilized by carbon–hydrogen hyperconjugation (violation of Bredt's rule). However, it is a much more strained system. Maier and Schleyer[12] calculated the strain energies of



5 **6** **7**

olefin precursors of **4**, **5**, and **7**, which could be used to estimate the stability and the reactivity of bridgehead olefins, by using Allinger's MM1 empirical force field program.[13] These strain energies are in excess of 21 kcal/mol, indicating that the bridgehead olefins are too unstable to be observed except probably by low-temperature matrix isolation techniques and could be of diradical nature. White and co-workers[14] reported that the 1-norbornyl cation is involved in the deamination of 1-aminonorbornane. The reactive cation derived from the deamination of 1-aminonorbornane through its *N*-nitrocarbamate and *N*-nitroamide was intercepted by a variety of solvents such as chloroform, benzene, dichloromethane, and carbon tetrachloride. Deamination could also proceed via dediazonation. These studies ruled out free-radical reactions, as norbornane was formed only to the extent of less than 0.5% in dichloromethane and chloroform solvents. However, it is possible that ion **8** or **9** in solution may react with chloroform and benzene before the 1-norbornyl cation is fully formed.

Schleyer and Nicholas[15] reported that the solvolysis of 1-norbornyl bromide proceeded 10^{14} times slower than that of the corresponding *tert*-butyl compounds, 10^{11} times slower than

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(1) (a) Considered as Aromatic Substitution 63. For part 62, see: Olah, G. A.; Hamanaka, S.; Wilkinson, J. A.; Olah, J. A. *Proc. Natl. Acad. Sci. U.S.A.* **1992,** *89,* 915. (b) This work was presented at the 205th ACS National Meeting, Denver, CO, Mar 28–Apr 2, 1993; Organic Division, Paper No. 35.

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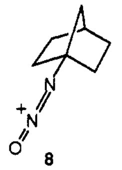

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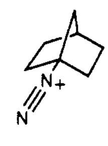

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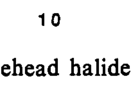
that of 1-adamantyl, and 10^8 times slower than that of 1-bicyclo[2.2.2]octyl bromide. Olah, Schleyer, and co-workers[16] have shown that only the 2-norbornyl cation is observed upon ionization of 1- and 7-chloronorbornanes in an antimony pentafluoride–sulfur dioxide system at low temperatures. They proposed that the intermediately formed 1-norbornyl cation undergoes fast 1,2-hydride shift to give the 2-norbornyl cation. Kropp and co-workers[5] claimed that the cation **6** could be formed by electron transfer from the free radical. Irradiation of 1-iododonorbornane in methanol afforded the nucleophilic substitution product 1-methoxynorbornane accompanied by the reduction product norbornane.

Generally, bridgehead halides are considered to be unreactive toward nucleophiles on the basis of the seminal work by Bartlett and Knox as well as Doering et al.[17] The inertness of the bridgehead halides was explained by considering that neither the S_N2-like displacement of halides (back-side attack) is possible nor the bonds between the bridgehead atom and its neighboring three carbon atoms in a cation can become even close to coplanar (thus allowing no hyperconjugation).[2] Bartlett and Knox reported that 1-chloroapocamphane (1-chloro-7,7-dimethylbicyclo [2.2.1] heptane) does not react under reflux with silver nitrate in water and ethanol.[17]

Beak and co-workers,[18a] however, found that 1-(chloroformyl)-apocamphane reacts with silver fluoroborate or silver hexafluoroantimonate in chlorobenzene at room temperature to give 1-fluoroapocamphane and isomers of 1-(chlorophenyl)apocamphane (*ortho* 40%, *meta* 32%, and *para* 28%). 1-Aminoapocamphane with nitrosyl chloride or nitrosyl hexafluoroantimonate and 1-(chlorosulfinyl)apocamphane with silver fluoroborate in chlorobenzene give the same ratio of isomers as 1-(chlorophenyl)-apocamphane.[18b] However, there have been few reports of the reaction of 1-halonorbornane through the cationic mechanism.[5,14] Doering and co-workers[19] reported that 1-bromonorbornane could be hydrolyzed with aqueous silver nitrate at 150°C.

Noradamantane (tricyclo[3.3.1.$0^{3,7}$]nonane), the lower homolog of adamantane, was synthesized by several groups[20a–c] following Meerwein's synthesis of the first noradamantyl derivative.[21] A mixture of 3-chloronoradamantane and 3-bromonoradamantane was obtained from 3-noradamantanecarboxylic acid[20a] by a Hunsdiecker procedure. So far, the bridgehead 3-noradamantyl cation (**10**) has not been directly observed in solution.



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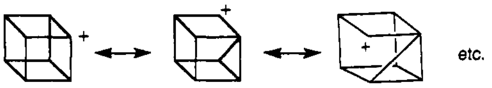
Other interesting bridgehead halide systems are the highly strained cubane derivatives. There is much interest in the possible formation of the cubyl cation (**11**) ever since the synthesis of cubane (pentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane) by Eaton and Cole.[22] Klunder and Zwanenburg[23] have reported that cubane derivatives such as the alcohol, chloride, and acetate can be prepared from the bridgehead diazonium salt. Eaton et al.[24] have found that photolysis of 1,4-diiodocubane in methanol gives 1,4-dimethoxycubane. They believed that the cubyl cation could be formed by electron transfer from the free radical. Fluorocubane[25] was prepared from iodocubane with xenon difluoride through the decomposition of the respective hypervalent cubyl derivatives. Eaton et al.[26a,b] and Moriarty et al.[26c,d] have, respectively, reported that cubyl triflate and its derivatives can be solvolyzed in methanol to give the corresponding methyl ethers. They have shown that cubyl triflate is much more reactive than 1-norbornyl triflate. Hrovat and Borden[27] have applied *ab initio* calculations (6-31G*) to the stability of the cubyl and 1-norbornyl cations relative to that of the *tert*-butyl cation. Their calculations have shown that the cubyl cation is more readily formed than the 1-norbornyl cation. As the cubyl cation might be stabilized by charge delocalization through the carbon–carbon bonds, it was suggested that it might be considered as a nonclassical cyclopropylcarbinyl cation.[26a,b,28]



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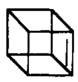
Moriarty et al.,[26c,d] on the other hand, have shown that the rate of solvolysis of 4-methyl-1-cubyl triflate in methanol is slower than that of cubyl triflate, indicating the intermediacy of "classical" cations. Similar results were obtained by Eaton and Zhou;[26b] however, their interpretation involved some hyperconjugative stabilization of the cubyl cation. So far, no cubyl cation has been directly observed in solution under superacidic conditions.[26a,c,e]

Cubene[29] (**12**) and homocub-4(5)-ene (**13**)[30] were generated from their dihalide precusor and trapped with dienes to give Diels–Alder products. However, these strained alkenes may have some diradical character.



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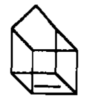

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There is also continued interest in the functionalization of cubane including phenylated cubanes. Octaphenylcubane has been prepared from the thermal decomposition of (4-bromo-1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)dimethyltin bromide[31a,b] and from the irradiation of diphenylacetylene.[31d] Bashir-

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Table I. Aluminum-Chloride-Catalyzed Friedel–Crafts Alkylation of Benzene and Substituted Benzenes with 1-Chloronorbornane at Room Temperature

	product[a] (%)				
arene substrate	*ortho*	*meta*	*para*	rxn time (h)	isolated yield (%)
benzene				2	48
toluene		90.2	9.8	2	60
m-xylene	*ortho,ortho*-2.2	*meta,meta*-94.4	*ortho,para*-3.4[b]	2	44
chlorobenzene	56.2	28.6	15.2[b]	2.5	52
fluorobenzene	54.8	26	19.2[c]	1	55

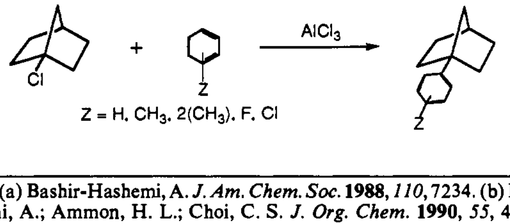
[a] Isomer ratios are determined by GC. [b] Isomer ratio is determined by GC–MS. [c] ^{19}F NMR shows *ortho*:*meta*:*para* = 52.5:27.5:5.20.

Hashemi et al. have prepared bromophenylcubane diamide,[32a,b] diphenylcubane diamide,[32a] and diphenylcubane[32c] from cubane diamide by an orthometalation procedure. The optimized geometry of phenylcubane[33] has been calculated using the *ab initio* SCF MO approach at the STO-5G level. Recently, Della et al.[34] have reported that phenylcubane is formed through a free-radical precursor. However, there has been no report on the isolation or the characterization of phenylcubane.

In continuation of our studies on electrophlic aromatic substitution, we report now that 1-chloronorbornane, 3-chloronoradamantane 3-bromonoradamantane, and fluorocubane readily undergo Friedel–Crafts reactions with benzene, alkylbenzenes, and halobenzenes to give the corresponding bridgehead alkylated derivatives. Mechanistic aspects and consequences of the reactions are discussed.

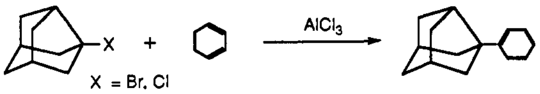
Results and Discussion

1-Chloronorbornane readily reacts with benzene, toluene, *m*-xylene, and halobenzenes, etc., in the presence of anhydrous aluminum trichloride at room temperature. The results are summarized in Table I. The Friedel–Crafts-type alkylation of toluene and *m*-xylene under the reaction conditions preferentially gives the thermodynamically preferred *meta* isomers as the major products. Reaction of halobenzenes gives *ortho*:*meta*:*para* isomers in a 2:1:1 ratio, resembling Beak's results.[18a] Small amounts of dinorbornylated aromatics were also formed in the reactions. No reliable toluene/benzene rate ratios (k_T/k_B ratios vary anywhere from 0.5 to 2.0 at the initial stages of the reaction) could be determined because of apparent rapid isomerization, which can be of intramolecular or intermolecular nature. Relatively small k_T/k_B ratios indicate the high reactivity of the electrophilic species. When 1-phenylnorbornane itself was reacted with excess toluene in the presence of aluminum chloride at room temperature, the starting material was recovered unchanged. This result may, however, not rule out isomerization via the arenium ion intermediates, although phenylnorbornane itself does not isomerize. The course of the Friedel–Crafts alkylation of toluene and fluorobenzene was followed by GC. The *meta*/*para* ratio of 1-tolylnorbornanes increased with time, indicating that the reaction indeed involves isomerization. However, the *meta*/*ortho* and *meta*/*para* ratios of 1-(fluorophenyl)norbornanes remained relatively unchanged. This would support the more facile migratory aptitude of the methyl group but not of the fluorine.

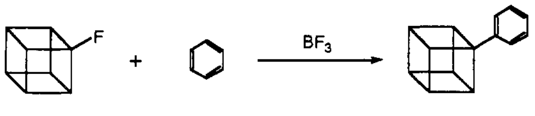


A mixture of 3-chloronoradamantane and 3-bromonoradamantane was obtained from the Hunsdiecker reaction of 3-noradamantanecarboxylic acid in carbon tetrachloride.[17a] Pure 3-bromonoradamantane was, however, obtained when bromotrichloromethane was employed instead of carbon tetrachloride in the Hunsdiecker reaction. 3-Noradamantanecarboxylic acid with *N*-chlorosuccinimide and lead tetraacetate (a modified Hunsdiecker reaction) also gave 3-chloronoradamantane in excellent yield.

3-Chloronoradamantane and 3-bromonoradamantane[20] also undergo Friedel–Crafts alkylation with aromatics. Benzene reacted readily with 3-chloronoradamantane in the presence of aluminum chloride to give 3-phenylnoradamantane in 47% isolated yield.



Fluorocubane was also found to react with benzene and toluene when boron trifluoride was introduced into the reaction mixtures at 10 °C. In the reaction of benzene, after 30 min, phenylcubane was isolated as the sole product (40% yield). Under similar reaction conditions, toluene gave predominantly the thermodynamically most stable *meta* isomer (ortho:*meta*:*para* ratio of 9:21:70). When cubanoyl chloride was reacted with benzene in the presence of aluminum chloride at 10°C for 30 min, only benzoylcubane was detected (based on GC–MS analysis) and no decarbonylative cubylation took place. When the reaction was continued for longer periods of time, benzoylcubane underwent decomposition. We found that the 1-chlorocubane–aluminum trichloride system did not react with either benzene or toluene at room temperature. At elevated temperatures, only decomposition products were observed with no trace of cubylated aromatics.



Why Do the Studied Bridgehead Halides React Readily with Aromatics under Friedel–Crafts Catalysis? Tertiary alkyl cations, such as the *tert*-butyl cation, have planar sp^2-hybridized carbocationic centers with an empty perpendicular p orbital. These ions generally are quite stable and can be readily observed as long-lived species in superacidic media. Their SbF$_6^-$ (or Sb$_2$F$_{11}^-$) salts can even be frequently isolated. Some bridgehead cations such as the 1-adamantyl cation are remarkably stable because of carbon–carbon hyperconjugative stabilization. More strained bridgehead cations such as the 1-norbornyl, 3-noradamantyl and cubyl cations which, due to their rigid framework, can not rehybridize to form planar sp^2 cationic centers will therefore remain relatively unrehybridized with an empty sp^3 like orbital at the carbocationic center. As this orbital can not be adequately conjugatively stabilized, this renders these ions very reactive but at the same time short-lived. Even though these strained bridgehead cations are not directly observable under superacidic

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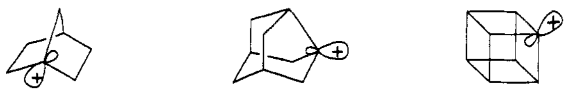
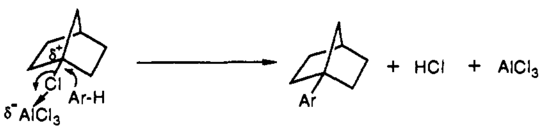
stable-ion conditions (*vide supra*), they can be formed as energetic, short-lived species.



1-norbornyl cation 3-noradamantyl cation cubyl cation
sp^3 hybridized carbocationic center, empty sp^3 orbital

Friedel–Crafts alkylation with 1-chloronorbornane, 3-chloronoradamantane or 3-bromonoradamantane, and fluorocubane mechanistically can occur by two pathways. The first would involve the previously discussed reactive bridgehead carbocationic intermediates in an S_N1-type reaction. The second would proceed by S_N2-like displacement of polarized donor–acceptor complexes. This, however, could take place only by an unprecedented front-side displacement reaction. In the case of chloro and bromo derivatives, the donor–acceptor complexes could also be in equilibrium with the corresponding halonium ion species.[35a]

Front-side S_N2-like displacement would involve a crowded interaction with the aromatic moiety and leaving group in close proximity, leading to strong repulsion. As a matter of fact, *no bona fide* front-side S_N2 displacement of any kind was so far proven.[36] Thus, it is more likely that the highly reactive bridgehead carbocations are involved in the Friedel–Crafts alkylation process. In the case of the 1-norbornyl system, for example, the 1-norbornyl cation formed in low concentration could be in equilibrium with the polarized 1-chloronorbornane–aluminum chloride complex and the 1,1′-dinorbornylchloronium ion (neither of which in its own right will effect alkylation). However, it is difficult to predict the life time of the reactive bridgehead ions or the ion-pair complexes.

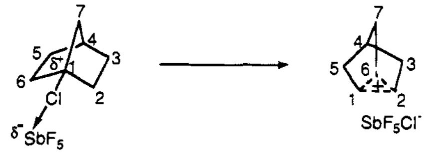


1-Chloronorbornane when reacted with cyclohexane in the presence of aluminum chloride gave a complex reaction mixture including norbornane, again indicative of the intermediacy of the reactive norbornyl cation in the hydride-abstraction process (ionic hydrogenation).

We have also carried out Koch–Haaf carbonylation of 1-chloronorbornane with carbon monoxide gas in an antimony pentafluoride–sulfur dioxide solution of 1-chloronorbornane at −78 °C. Only 2-*exo*-norbornanecarboxylic acid was obtained. However, in sulfuryl chloride fluoride (an even less nucleophlic solvent), a 3:7 mixture of 1-norbornanecarboxylic acid and 2-*exo*-norbornanecarboxylic acid was obtained.

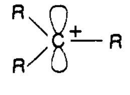
Attempts were made to observe the 1-norbornyl cation in low-temperature NMR studies. When 1-chloronorbornane was dissolved in antimony pentafluoride–sulfuryl chloride fluoride at −78 °C, only the corresponding 1-chloronorbornane–antimony pentafluoride donor–acceptor complex **14** was initially observed and no 1,1′-dinorbornylhalonium ion could be detected. It showed ^{13}C absorptions at δ 106.1 (C1), 34.3 (C2,6), 29.6 (C3,5), 30.7 (C4) and 43.6 (C7). Upon warming to −55 °C, the donor–acceptor complex slowly rearranges to the nonclassical 2-norbornyl cation **15**.

All attempts to observe the cubyl cation under superacidic conditions were unsuccessful.[26a,c,e] Attempts to decarbonylate 3-noradamantanoyl chloride to the bridgehead 3-noradamantyl cation were also not successful and led only to decomposition products.[35b]

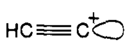


14 **15**

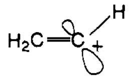
Trivalent alkyl cations with planar sp^2 centers are generally stable and observable as long-lived ions in superacidic solutions. Vinyl and aryl cations, in contrast, are usually only transient and highly reactive intermediates, although examples of the former have been recently observed under long-lived stable-ion conditions by Siehl.[37] In these ions, conjugative (hyperconjugative) stablization is not effective as the carbocationic centers contain an empty sp^2 and not an empty p orbital. Similarly, in the ethynyl cation, an empty sp orbital is involved. The presently studied systems involve energetic bridgehead cations with empty sp^3-like orbitals.



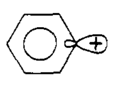
alkyl cations
sp^2 hybridized carbocation center
empty p orbital



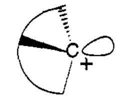
ethynyl cation
sp hybridized carbocation center
empty sp orbital



vinyl cation
sp^2 hybridized carbocation center
empty sp^2 orbital



phenyl cation
sp^2 hybridized carbocation center
empty sp^2 orbital



strained bridgehead cation
sp^3 hybridized carbocation center
empty sp^3 orbital

Sorensen was the first to propose a sp^3-hybridized carbocationic center in the case of the 1-methyl-1-cyclobutyl cation.[38] It was, however, later shown that this ion is indeed a nonclassical bicyclobutonium ion.[39] The presently studied Friedel–Crafts systems thus seem to involve the first examples of reactive bridgehead carbocations with empty sp^3 orbitals, although only as reactive, short-lived intermediates.

Conclusion

1-Chloronorbornane, 3-chloronoradamantane, 3-bromonoradamantane, and fluorocubane under typical Friedel–Crafts conditions readily alkylate benzene and substituted benzenes even at or below room temperature. As back-side S_N2-type displacement at bridgehead positions is not possible, the reported new Friedel–Crafts alkylations involve strongly polarized bridgehead halide–aluminum chloride (or boron trifluoride) complexes in equilibrium with their energetic carbocations. Since the strained bridgehead cationic centers can not completely flatten out, the empty orbital must be of sp^3 nature. Attempts to generate the corresponding long-lived 1-norbornyl, 3-noradamantyl, and cubyl cations under superacidic conditions were unsuccessful.

Experimental Section

Benzene and pentane were distilled from sodium before use. 2-Norbornanone, phosphorus pentachloride, 3-noradamantanecarboxylic acid, lead tetraacetate and *N*-chlorosuccinimide were obtained from Aldrich.

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Phosphorus trichloride was from J. T. Baker, aluminum chloride from EM Science, and boron trifluoride from Matheson. GC analysis of the reaction mixtures was conducted on a Varian 3740 gas chromatograh equipped with a J & W Scientific DB-WAX fused silica capillary column (30 m, 0.25 μm). GC–MS analyses were performed on a Finnigan-Mat/Incos-50 mass spectrometer equipped with a Varian 3400 gas chromatograph or on a Hewlett-Packard 5971 mass spectrometer equipped with a Hewlett-Packard 5890 gas chromatograph. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Varian VXR-200 or Unity 300 spectrometers.

1-Chloronorbornane, fluorocubane, and cubanoyl chloride were prepared by known literature procedures.[40 a,b,25]

3-Bromonoradamantane. A 25-mL 3-necked round-bottom flask, equipped with a magnetic stirrer, a reflux condenser, and a dropping funnel, was charged with red mercuric oxide (0.43 g, 2 mmol) and 3-noradamantanecarboxylic acid (0.5 g, 3 mmol) in 1 mL of bromotrichloromethane. Bromine (0.18 mL, 3.5 mol) in 3 mL of bromotrichloromethane was slowly added through a dropping funnel in the dark under continuous stirring. The reaction mixture was then refluxed in the dark for 20 h. The mixture was cooled to room temperature and filtered to remove mercuric salts. The filtrate was washed with saturated sodium thiosulfate and extracted with dichloromethane (3 × 10 mL). The combined dichloromethane layers were washed with saturated sodium bicarbonate, dried over magnesium sulfate, and filtered, and the solvents were carefully rotary evaporated. The residue was purified by column chromatograhy on silica gel, using dichloromethane–pentane mixtures, to give 3-bromonoradamantane (0.06 g, 10%).[20] Mp 101.6°C. MS: (*m/z*) 79 (37), 77 (13), 80 (17), 93 (17), 121 (100). ^{1}H NMR (in chloroform-*d*): δ 1.54, 2.0, 2.24 (12H), 2.64 (1H, t). ^{13}C NMR (in chloroform-*d*): δ 66.2 (C3), 55.4 (C2,4), 48.7 (C7), 43.3 (C6,8), 38.5 (C1,5), 33.3 (C9).

3-Chloronoradamantane. A 25-mL 3-necked round-bottomed flask, equipped with a magnetic stirrer and a reflux condenser, was charged with *N*-chlorosuccinimide (2.28 g, 16.7 mmol) and 3-noradamantanecarboxylic acid (0.5 g, 2.9 mmol) in 9 mL of dimethylformamide and 2 mL of glacial acetic acid. The solution was freed of oxygen by repeated evacuation under an argon atmosphere. Lead tetraacetate (1.35 g, 2.9 mmol) was added, and the reaction mixture was degassed. The reaction was continued for 2 h at 72 °C. The solution was extracted with pentane and filtered to remove unreacted lead tetraacetate. The pentane solution was washed with 20% perchloric acid and saturated sodium bicarbonate, dried over magnesium sulfate, and filtered, and the pentane was carefully evaporated under reduced pressure to give 3-chloronoradamantane (0.24 g, 53%).[20,41] Mp 121 °C. MS: (*m/z*) 39 (13), 77 (26), 78 (12), 79 (59), 80 (100), 81 (26), 91 (12), 93 (17), 112.95 (22), 121 (27), 156 (23). ^{1}H NMR (in chloroform-*d*): δ 1.54, 2.11 (10H), 2.27 (2H), 2.52 (1H, t). ^{13}C NMR (in chloroform-*d*): δ 73.8 (C3), 53.9 (C2,4), 47.6 (C7), 43.3 (C6,8), 38.3 (C1,5), 33.5 (C9).

3-Phenylnoradamantane. 3-Chloronoradamantane (0.12 g, 0.76 mmol) was reacted with excess benzene (5 mL) in the presence of aluminum chloride (0.1 g, 0.76 mmol) at 0°C and slowly warmed to room temperature. The reaction was continued for 1 h. After the reaction was quenched with ice water, the solution was extracted with pentane, dried over magnesium sulfate, and filtered and the solvent was rotary evaporated. The residue was purified by column chromatography on silica gel, using dichloromethane–pentane mixtures, to give 3-phenylnoradamantane (0.07 g, 47%). Bp 92 °C, 2mmHg.

MS: (*m/z*) 77 (14), 80 (14), 91 (21), 128 (17), 129 (13), 141 (14), 142 (13), 155 (100), 156 (20), 198 (66), 199 (11). ^{1}H NMR (in chloroform-*d*): δ 1.67, 1.72, 1.96 (10H), 2.35 (2H), 2.53 (1H), 7.29, 7.31 (5H). ^{13}C NMR (in chloroform-*d*): δ 52.9 (C3), 51 (C2,4), 47.6 (C7), 44.8 (C7), 44.8 (C6,8), 38 (C1,5), 34.9 (C9), 150.1 (C1′), 128 (C2′,6′), 126 (C3′,5′), 125 (C4′).

Phenylcubane. Boron trifluoride was bubbled into fluorocubane (20 mg, 0.16 mmol) in benzene (2 mL, 22 mmol) at 10°C for 30 min. The reaction was quenched with water and the mixture extracted with pentane. The pentane solution was dried over magnesium sulfate and filtered, and the pentane carefully evaporated under reduced pressure to give a residue which upon chromatography on silica gel, using pentane–dichlormethane mixtures, gave phenylcubane as an oily residue (11 mg, 40% yield). MS: (*m/z*) 76 (19), 89 (18), 102 (32), 115 (13), 152 (21), 153 (11), 165 (65), 176 (10), 178 (71), 179 (100), 180 (81), 181 (10). ^{1}H NMR (in chloroform-*d*): δ 4.02, 4.18 (7H), 7.19, 7.3 (5H). ^{13}C NMR (in chloroform-*d*): δ 50.9 (C1), 51.2 (C2,6,8), 44.1 (C3,5,7), 48.6 (C4), 143.4 (C1), 128.4* (C2,6), 124.7* (C3,5), 125.6 (C4) (asterisk, assignment interchangeable).

1-Phenylnorbornane. 1-Chloronorbornane (1.3 g, 0.01 mol) was reacted with excess benzene (8.94 mL, 0.1 mol) in the presence of aluminum chloride (1.33 g, 0.01 mol) at 0°C and slowly warmed to room temperature. The reaction was continued for 2 h. After the reaction was quenched with ice water, the solution was extracted with pentane, dried over magnesium sulfate, and filtered and the solvent rotary evaporated. The residue was distilled in vacuum to give 1-phenylnorbornane (0.84 g,- 48%). Bp 65–70°C, 6mmHg; lit.[42,43] bp 124–128 °C, 16mmHg. MS: (*m/z*) 91 (11), 115 (16), 128 (25), 129 (15), 143 (100), 144 (14), 172 (28). ^{1}H NMR (in chloroform-*d*): δ 1.4, 1.59, 1.65 (10H), 2.28 (1H), 7.23, 7.24 (5H). ^{13}C NMR (in chloroform-*d*): δ 51.5 (C1), 37.3 (C2,6), 31.1 (C3,5), 37.5 (C4), 43.0 (C7), 146.5 (C1′), 126.3 (C2′,6′), 127.9 (C3′,5′), 125.5 (C4′).

Similar reactions were carried out with other aromatic compounds, and the analyses were carried out by GC. The NMR data of major isomers where possible are given below.

1-(3-Methylphenyl)norbornane. ^{13}C NMR (in chloroform-*d*): δ 51.4 (C1), 37.3 (C2,6), 31.0 (C3,5), 37.4 (C4), 43.0 (C7), 137 (C1′), 146 (C3′), 21.6 (methyl), 126.4, 127.2, 128.0, 123.5 (four other aromatic carbons).

1-(3,5-Dimethylphenyl)norbornane. ^{13}C NMR (in chloroform-*d*): δ 51.2 (C1), 37.3 (C2,6), 30.9 (C3,5), 37.4 (C4), 42.9 (C7), 146.6 (C1′), 124 (C2′,6′), 137.4 (C3′,5′), 21.4 (methyl), 127.3 (C4′).

1-(2-Chlorophenyl)norbornane. ^{13}C NMR (in chloroform-*d*): δ 48 (C1), 33.8 (C2,6), 30.8 (C3,5), 36.0 (C4), 43.3 (C7), 134.2 (C1′), 144 (C3′).

1-(2-Fluorophenyl)norbornane. ^{13}C NMR (in chloroform-*d*): δ 49.3 (C1), 35.4 (C2,6), 30.6 (C3,5), 36.8 (C4), 42.5 (C7), 133 (C1′), 164 (C3′). ^{19}F NMR (in chloroform-*d*, internal standard trichlorofluoromethane): δ –112.4 (br s).

1-(4-Fluorophenyl)norbornane. ^{19}F NMR (in chloroform-*d*, internal standard trichlorofluoromethane): δ –114.43 (sextet, *J* = 4.0 Hz).

1-(3-Fluorophenyl)norbornane. ^{19}F NMR (in chloroform-*d*, internal standard trichlorofluoromethane): δ –118.59 (psuedoseptet).

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Supplementary Material Available: ^{13}C NMR spectra of 3-phenylnoradamantane (Figure 1), 1-phenylcubane (Figure 2), 1-(3-methylphenyl)norbornane (Figure 3), 1-(3,5-dimethylphenyl)norbornane (Figure 4), isomeric 1-(chlorophenyl)norbornanes (Figure 5), and isomeric 1-(fluorophenyl)norbornanes (Figure 6), ^{19}F NMR spectrum of isomeric 1-(fluorophenyl)norbornanes, and additional graphs and tables for these compounds (30 pages). Ordering information is given on any current masthead page.

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