Substrates. The synthesis of *N*-ethyl-2-azido-3-benzoyl enamines has been described previously.[2] *o*-Hydroxy-*N*-ethylbenzimidoyl azide **6** was prepared by the procedure of Woodward and Kemp[12] and had the following: $\bar{\nu}_{max}$ 2119 and 1610 cm^{-1}; NMR (CCl_4) δ 1.2 (3 H, t), 3.5 (2 H, q), 6.6-7.6 (4 H, m) 9.9 (1 H, s).

p*K*a Determination. The pK_a of *o*-hydroxy-*N*-ethylbenzimidoyl azide **6** was determined spectrophotometrically by using the method previously described[2] for reactive azides. A bell-shaped pH-optical density curve resulted which was treated by adapting the basic empirical equation for a "bell-shaped" pH-rate profile (see eq 3) and fitted to the observed data by using the method outlined in ref 9.

Registry No. 6, 74724-91-7; **9**, 68375-95-1.

Formation of (1-Adamantylcarbinyl)arenes from 3-Azidohomoadamantane-Aluminum Chloride-Aromatic Substrates[1]

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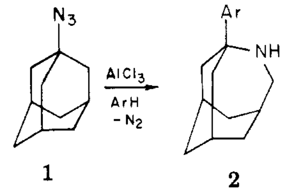
Reaction of 3-azidohomoadamantane with aromatic substrates catalyzed by aluminum chloride at 80 °C gave the corresponding (1-adamantylcarbinyl)arene in >90% yield. The reaction proceeds exclusively with elimination of azide ion. Competitive reaction with toluene (T)-benzene (B) gave an average k_T/k_B of ~14/1. The results indicate that a straightforward primary cation is probably not the actual attacking electrophile. The possible intervention of a bridged ion is discussed.

In a previous paper,[2] we reported that the reaction of 1-azidoadamantane (**1**) with aromatic substrates in the presence of aluminum chloride proceeded exclusively with the loss of nitrogen gas to give the rearranged product, 3-aryl-4-azahomoadamantane (**2**; eq 1). The results were

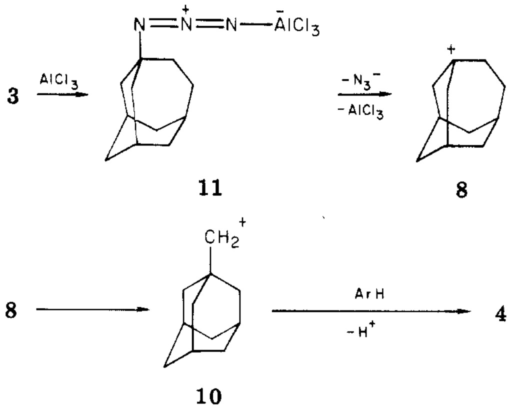


(1)

consistent with those reported for the photolytic[3] or sulfuric acid catalyzed[4] decomposition of **1**, in which a similar rearrangement was observed. In contrast, in the aluminum chloride catalyzed decomposition of primary and secondary alkyl azides in benzene,[5] both azide ion and nitrogen gas are eliminated to give alkylbenzenes and imines from rearrangement. Hence, elimination of azide ion has been observed only with nonbridgehead alkyl azides. Aryl,[6-8] acyl,[6,9] sulfonyl,[6] α-carbonyl,[10] and alkoxycarbonyl[11,12] azides are all reported to react under similar conditions, primarily with evolution of nitrogen gas, to yield N-substituted anilines.

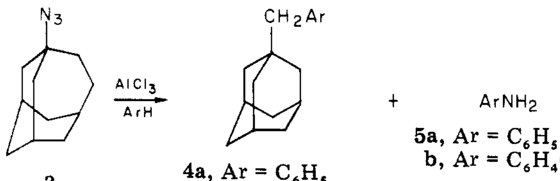
In the present study, we report the reaction of 3-azidohomoadamantane (**3**) with aromatic compounds catalyzed by aluminum chloride, resulting in exclusive elimination of azide ion, followed by rearrangement and alkylation of the aromatic substrate. In addition, we discuss the nature of the cation formed and present data on selectivity in the Friedel-Crafts alkylation.

Scheme I



Results and Discussion

Experimental Results. 3-Azidohomoadamantane (**3**) when exposed at 80 °C for 1.5 h to aluminum chloride and aromatic substrate gave the corresponding (1-adamantylcarbinyl)arene product (**4**) in >90% yield (eq 2). In addition, aminated aromatic product **5** was isolated in minor amounts. When the reaction of **3** is carried out in the absence of the Lewis acid catalyst (24 h at 80 °C),



3

4a, Ar = C_6H_5
b, Ar = $C_6H_4CH_3$

5a, Ar = C_6H_5
b, Ar = $C_6H_4CH_3$

(2)

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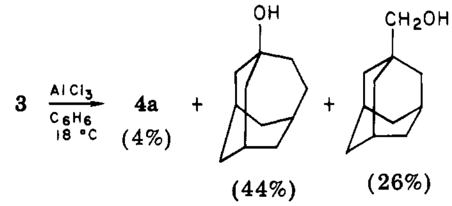
0022-3263/81/1946-1346$01.25/0

Table I. Reactions of 9 or 12 with $AlCl_3$ and C_6H_6

	compd, mol × 10^3	C_6H_6, mol × 10^3	$AlCl_3$, mol × 10^3	4a, %[c]
9	0.50	732	2.26	93[a]
9	1.36	732	2.62	91[a]
9	1.36	1.75	2.25	91[b]
12	1.08	585	1.50	95[a]

[a] Reaction procedure A. [b] In 165 mL of *n*-hexane, reaction procedure B. [c] Isolated yield of pure product.

approximately 94% **3** is recovered with no **4** or **5** present. At room temperature (7.5 h) with the catalyst, three products, 1-benzyladamantane (**4a**), 3-homoadamantanol (**6**), and 1-adamantylcarbinol (**7**), were isolated (eq 3).



(3)

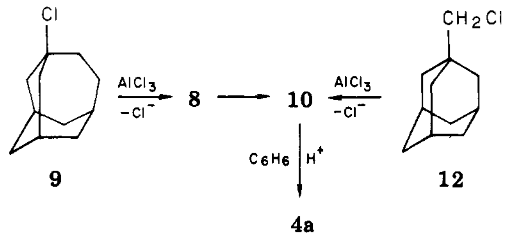
(44%) **6** (26%) **7**

Alkyl azides are generally considered to be thermally stable at room temperature, but above 100 °C nitrogen gas is eliminated in a first-order, homogeneous process.[13,14] When the reaction described in eq 2 is carried out with a 1:1 molar ratio of **3**–benzene in *n*-hexane solvent, 90% of 1-benzyladamantane (**4a**) is obtained, but no aniline (**5a**). These results indicate that the Lewis acid catalyst is necessary for azide ion elimination, that the higher temperatures are required for the aromatic substitution process, and that reaction can proceed in a nonpolar medium.

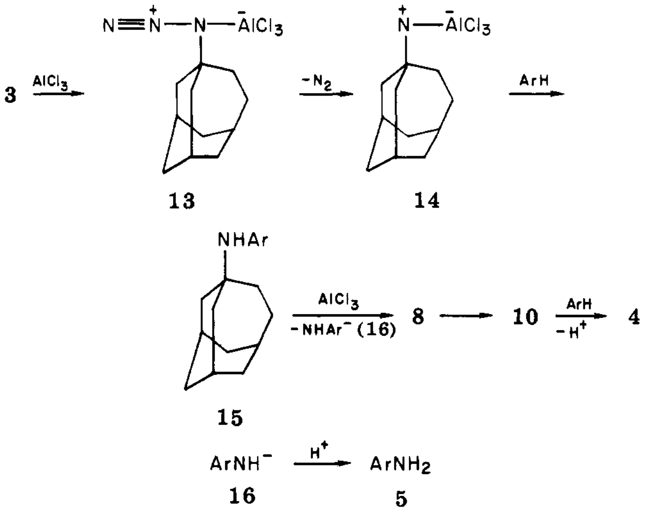
Mechanism. Mechanistically, two routes can be used to rationalize the products formed in the reaction described in eq 2. One involves coordination of the Lewis acid catalyst to the terminal nitrogen of the azido group (**11**), followed by elimination of azide ion, to give the 3-homoadamantyl cation (**8**) (Scheme I). Formation of **8** should be a facile process, since a relative rate of 0.4:1 in solvolysis of 3-chlorohomoadamantane (**9**) vs. *tert*-butyl chloride illustrates a comparative lack of bridgehead strain in **8**.[15] Rearrangement of **8** to the 1-adamantylcarbinyl cation (**10**) accompanied by electrophilic attack on the aromatic substrate yields **4**. Further support for this mechanism comes from studies with **9** or 1-adamantylcarbinyl chloride (**12**). Both chlorides give product **4a** in >90% yield (Table I) under conditions identical with those for reaction of **3** (Scheme II).

Alternatively, the mechanism may involve initial coordination of the Lewis acid catalyst with the α-nitrogen atom (**13**) followed by nitrogen gas elimination and electrophilic attack on the aromatic substrate to give the corresponding *N*-aryl-3-aminohomoadamantane (**15**, Scheme III). The process may either be concerted or may entail participation of a nitrene complexed (nitrenium species) with the Lewis acid catalyst (**14**). Similarly, acid-catalyzed hydrolysis of azides displays second-order kinetics which also point to a nitrenium ion, rather than a discrete nitrene intermediate.[16] Degradation of **15** in the presence of aluminum chloride would give rise to **5** via **16** and **4** via **8** and **10**.

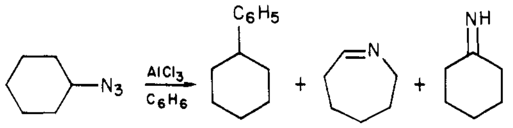
Scheme II



Scheme III



It is reasonable, based on prior work, to consider both mechanistic routes. E.g., reaction of cyclohexyl azide (**17**) with benzene–aluminum chloride at 50 °C gave cyclohexylbenzene (30%), as well as rearrangement products, namely, the corresponding ring-expanded imine (30–40%) and iminocyclohexanone (15%;[5] eq 4). Presumably, cyclohexylbenzene and the imine products arose from intermediates similar to **11** and **13**, respectively.



(4)

17

Formation of aromatic amine **5** can be rationalized by the reaction of hydrazoic acid (generated in situ from eliminated azide ion) with the aromatic substrate, catalyzed by aluminum chloride. Friedel–Crafts amination of aromatic substrates by either hydrazoic acid or organic azides also has literature precedent. Kovacic and coworkers[17] have demonstrated that toluene, and to a lesser extent benzene and chlorobenzene, can be aminated in modest yield by hydrazoic acid and aluminum chloride. Toluene forms *N*-methyltoluidine in low yield with methyl azide under these conditions. Similarly, Borsche and Hahn[8] found that various aromatic substrates are similarly transformed by aromatic azides.

Although there is sufficient precedent to support both of the mechanistic routes discussed, examination of the data provides strong evidence for preference of Scheme I. Scheme III requires that **15** be formed as a common precursor to both products **4** and **5**. As a result, the two should be formed in approximately a 1:1 molar ratio. However, although aminated product is formed in all runs

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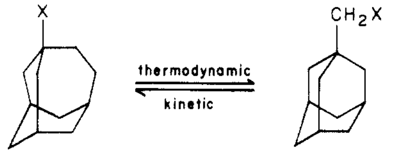
Scheme IV



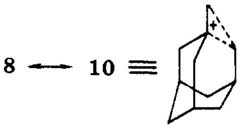
18, X = OTs **21**, X = OTs
19, X = Br **22**, X = Br
20, X = OAc **23**, X = OAc

involving toluene, the yields, which are quite low, are far from the requisite 1:1 molar ratio. Also, little or no **5** is obtained from benzene. In addition, when the reaction is carried out in *n*-hexane (without excess benzene), 90% **4a** but no aniline (**5a**) is isolated. In conclusion, the evidence strongly indicates that elimination of azide ion (Scheme I), rather than nitrogen gas (Scheme III), is preferred.

The question of the possible participation of triazene intermediates should be addressed. Recently,[18] it was demonstrated in the reaction of azides with benzene and aluminum chloride that triazene intermediates are not involved to any appreciable extent. A similar result was also observed in the case of **1** (eq 1). Analogously, for the reaction of **3**, we conclude that it is not reasonable to invoke participation of triazene intermediates.

The mechanism presented in Scheme I includes the rearrangement of tertiary cation **8** to primary cation **10**. A tertiary cation is generally more stable than a primary one. Rationalization is based on the appreciable net decrease in strain (homoadamantane is estimated to be approximately 12 kcal/mol more strained than adamantane[19]). The conflicting involvement of cation stability (tertiary vs. primary) and ring-strain energy reflects the operation of either kinetic or thermodynamic control in product formation (Scheme IV). For example, acetolysis of tosylate **21** in the absence of a buffer yields unrearranged acetate **23**; in the presence of sodium acetate the product is mainly 3-homoadamantyl acetate (**20**).[20] Similar effects are involved in the reaction of 3-homoadamantanol (**6**) with hydrogen bromide in acetic acid: at 25 °C, 3-homoadamantyl bromide (**19**) is formed; at 125 °C, the product is 1-bromomethyladamantane (**22**).[21] Analogy can be drawn between these results and those presented in eq 2 and 3. At the higher temperature (80 °C) or in a less polar medium (ArH or hexane vs. acetic acid–sodium acetate), the thermodynamic product (**4**) results. At the lower temperature (18 °C), the kinetic pathway leading to **6** predominates.

Based on prior observations,[20,22] the suggestion[20] has been advanced that **8** and **10** exist in equilibrium or that a nonclassical carbonium ion (**24**) exists. Intervention of



24

the bridged ion **24** has also been invoked to rationalize results from acetolysis of a chiral deuterated tosylate, namely, complete retention of configuration.[22]

Table II. Competitive Reactions of **3** with $AlCl_3$ and $C_6H_5CH_3$-C_6H_6[a, b]

3		$C_6H_5CH_3$,	C_6H_6,	
mol × 10^3	mol/L × 10^3	mol × 10^3	mol × 10^3	product ratio, **4b/4a**
1.57	6.58	1223	1223	14.6/1[c]
1.57	6.58	1223	1223	13.6/1[c]
1.57	6.58	1223	1223	14.1/1

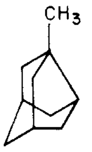
[a] $AlCl_3$ = 3.68 × 10^{-3} mol, homogeneous, 67 °C. [b] General procedure C. [c] Relative yields from GLC analysis (yield >97% for all runs).

Table III. Competitive Reactions of **3** with $AlCl_3$ and $C_6H_5CH_3$-C_6H_6[a, b]

3		$C_6H_5CH_3$,	C_6H_6,	
mol × 10^3	mol/L × 10^3	mol × 10^3	mol × 10^3	product ratio, 4b/4a
1.57	4.28	1880	1880	14.8
1.57	4.51	350	3500	1.39

[a] $AlCl_3$ = 2.25 × 10^{-3} mol, homogeneous, 67 °C. [b] General procedure B. [c] Relative yields from GLC analysis (yield >99% for all runs).

A related system (**25**, **26**, and **27**) has also been studied.



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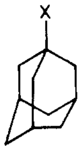
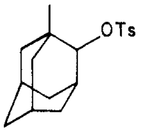


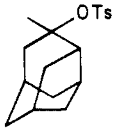
26

27

A relative solvolysis rate of 2.5-4:1.7 × 10^4 for the neopentyl precursors (**21**:**25**) in producing bridgehead carbonium ions was observed.[23] By analogy to **24**, bridged ion **27** may be involved. Also in the adamantane–protoadamantane series, attention has been given to **28**, **29**, and **30**. The result from solvolysis of optically active **28**, 90% retention of configuration, is reported to be consistent with participation of a weakly bridged ion **30** and the modest magnitude of rate enhancement produced by the methyl substituent.[24]



28



29

30

Additional insight concerning the nature of the alkylating entity in our system can be gained from relative rate data (k_T/k_B) which are presented in Tables II and III. Product ratios were determined by either GLC analysis or direct isolation. Consistent results were obtained within and between the two procedures used. An average k_T/k_B value of 14.3 was obtained for a 1:1 molar ratio. When the competitive reaction was carried out with a 1:10 (T:B) ratio, the result was k_T/k_B = 13.9 (adjusted) which is within experimental error of the figure from the 1:1 run.

Difficulties arise in attempts to correlate our relative rate data with pertinent literature reports,[25-28] due to differ-

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ences in conditions and the nature of the precursor for the cation, as well as lack of knowledge concerning catalyst–cocatalyst effects and the rate-determining step. Our k_T/k_B of ~14/1 is greater than those reported for either a primary (ethyl) or secondary (isopropyl) bromide. This factor indicates that in our system a straightforward primary cation would not satisfactorily rationalize the results. In contrast, there is close correspondence from comparison with data reported for tert-butylation: isobutylene–aluminum chloride (or ferric chloride) (k_T/k_B = ~15.3/1)[28] or *tert*-butyl bromide–stannic chloride (k_T/k_B = 16.6/1).[28] Although there are also examples of tert-butylation characterized by different results (k_T/k_B = 1.17–1.90),[25,28] the figures indicate that a more active electrophile is involved in these cases. It is pertinent that, as presented in Scheme II, **4** can be experimentally approached from either the tertiary **9** or primary **12** chloride. Both chlorides **9** and **12** must involve a common intermediate (**24**). As in the case for optically active **28**, a weakly bridged ion may be involved.

Finally, the reaction described in eq 3 will be treated. The hydroxyl products **6** and **7** may arise from the presence of adventitious moisture in the system or during aqueous workup. This result is similar to that obtained from the reaction of **1** with benzene–aluminum chloride at 18 °C. In that case only 3-hydroxy-4-azahomoadamantane (**31**; 94%), with no **2a**, was obtained.[2] Although either moisture in the system or from the workup could also explain the result, **31** was believed to arise from workup since direct addition of water gave 1-phenyladamantane (50%) and **2a** (28%) but no **31**.

Experimental Section

Materials and Analytical Procedures. Melting points are uncorrected. Spectral data were obtained with the indicated instruments: infrared, Beckman IR8, Perkin-Elmer 735B, 710A, and 137; ^1H NMR, Varian T60; mass, Hitachi Perkin-Elmer RMU-6E. GLC analyses were done on a Varian Aerograph 90-P or 1800 instrument (20 ft × 0.25 in., 15% Carbowax 20M).

1-Adamantanecarboxylic acid (**32**, 99%, Aldrich), 1-adamantanemethanol (**7**; 99%, Aldrich), thionyl chloride (97%, Aldrich), lithium tetrahydroaluminate (95%, Alfa), and sodium azide (99%, Aldrich) were used directly. Anhydrous aluminum chloride was taken from a freshly opened bottle (Fischer Certified or Aldrich) or sublimed. *n*-Hexane was stirred over concentrated sulfuric acid, then washed successively with water, aqueous 10% sodium carbonate, and water (twice), dried, and distilled from sodium hydride. Nitromethane was dried over calcium chloride, then distilled, stored over calcium sulfate, and redistilled prior to use. All other solvents were distilled.

Aromatic substrates were purified according to Perrin:[29] benzene[29a] was washed with concentrated sulfuric acid, then aqueous 5% sodium bicarbonate, and water, followed by drying with Davidson 4A molecular sieves, and then distilled; toluene[29b] was stirred twice with cold concentrated sulfuric acid, once with water, and once with aqueous 5% sodium bicarbonate and then dried successively with calcium sulfate and phosphorus pentoxide, with final distillation from phosphorus pentoxide.

Ether solutions were dried over magnesium sulfate, all others over sodium sulfate. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN, and by Mr. F. Laib, University of Wisconsin—Milwaukee.

3-Homoadamantanol (6). The procedure of Nordlander et al.[20] was used to prepare **6** from **32** (three steps) or **7** (two steps): 88% yield; mp 274–276 °C (lit. mp 274–276 °C,[20] 274–275.5 °C[21]); IR (KBr) 3280, 2910, 2855, 1440, 1360, 1170, 1150, 1070, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) broad peaks at δ 2.0, 1.85, and 1.55 (relative intensities ~1:3:1), sharp singlet at δ 1.35 (OH, one proton); mass spectrum, *m/e* (relative intensity) 166 (17), 141 (10), 135 (4), 124 (12), 123 (15), 110 (23), 109 (58), 108 (23), 107 (10), 106 (12), 97 (12), 96 (25), 95 (100), 94 (20), 93 (16), 91 (15), 82 (14), 81 (21), 74 (25), 71 (17), 67 (22).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.57; H, 10.90.

3-Azidohomoadamantane (3). The method of Sasaki et al.[4] was used with a modification in the workup stage. The crude product was recrystallized by dissolving it in methanol and then cooling in a dry ice–acetone bath. Sublimation afforded pure **3**: 72% yield; mp 97–98 °C (lit.[4] mp 97–98 °C); IR (KBr) 2910, 2855, 2095, 1450, 1250, 1150, 1070, 1045, 985, 960, 690; ^1H NMR ($CDCl_3$) broad peaks at δ 2.0, 1.85, and 1.55.

Anal. Calcd for $C_{11}H_{17}N_3$: C, 69.08; H, 8.96; N, 21.96. Found: C, 68.89; H, 9.01; N, 22.01.

3-Chlorohomoadamantane (9) was prepared according to a previously published method[21] except that the reflux time was increased from 3 h to 4 h: 90.5% yield; mp 157.5–158.5 °C (lit.[21] mp 160–161 °C).

1-(Chloromethyl)adamantane (12) was prepared by a modification of the method used to prepare **9**. Thionyl chloride (20 mL) was added to **7** (0.80 g, 4.80 × 10^{-3} mol) in a 25-mL flask with cooling in an ice bath. After 1 h of reflux, 10 mL of solution was distilled and then both the residue and distillate were worked up separately as follows. Each was poured over a 1:1 mixture of 100 mL of ice–methylene chloride solution. After basification in the cold with a saturated solution of NaOH, the phases were promptly separated. The aqueous phase was then extracted with three 45-mL portions of methylene chloride and the organic portions were combined. Solvent was removed from the dried solution at reduced pressure with no heating. Sublimation [18 °C (60 mmHg)] afforded pure product: 76% yield; mp 29–30 °C (lit.[21] mp 27 °C).

Reaction of 3 with ArH–$AlCl_3$. General Procedure A. Anhydrous aluminum chloride (0.32 g, 2.4 × 10^{-3} mol) was quickly added to a solution of **3** (0.40 g, 2.09 × 10^{-3} mol) dissolved in ArH (ca. 180 mL), in a flask protected by a drying tube, at 40 °C. The temperature was quickly raised to 80 °C and maintained there for 1.25 h. Reactions run with slight variations in the quantities mentioned or under nitrogen gave identical results.

General Procedure B. Anhydrous aluminum chloride (0.22 g, 1.75 × 10^{-3} mol) was quickly added to a solution of **3** (0.30 g, 1.57 × 10^{-3} mol) dissolved in benzene (0.16 mL, 0.14 g, 1.80 × 10^{-3} mol) and 165 mL of *n*-hexane at 40 °C in a flask protected by a drying tube. The temperature was quickly raised to 68 °C and maintained there for 6 h (heterogeneous system).

General Isolation Procedure. The cooled reaction mixture was poured over 100 mL of 18% hydrochloric acid. The reaction vessel was then washed with 45 mL of additional acid solution, 45 mL of water, and 70 mL of *n*-pentane. The washes were combined and added to the reaction mixture–acid solution (I).

The aqueous layer (Ia) from separation was extracted with three 60-mL portions of *n*-pentane and combined with the organic layer (Ib). Basification of the remaining aqueous layer with 50% sodium hydroxide (final pH ~11, temperature controlled by cooling) produced a slightly cloudly solution which was extracted with five 70-mL portions of methylene chloride. Evaporation of the combined dried methylene chloride extracts under reduced pressure yielded a brown liquid (IIa), crude yield 0–17%.

The combined organic portion (Ib) was washed with 5% sodium bicarbonate and water (each 175 mL) and then dried. Removal of solvent under reduced pressure afforded a yellow-brown oil (IIb), crude yield 96–99%.

Column chromatography (alumina adsorption, Fisher, column packed dry) was carried out on the separate crude products (IIa, IIb); e.g., IIb was dissolved in a minimal amount of methylene chloride and added to the column. Elution was carried out with the following solvents in the indicated order: 260 mL of *n*-pentane; 140 mL each of a 3:1, 1:1, and 1:3 mixture of *n*-pentane–methylene chloride solution; 100 mL of methylene chloride; 140 mL each of a 4:1, 2:1, and 1:2 mixture of methylene chloride–methanol solution; 260 mL of methanol (all ratios for eluant mixtures are

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by volume and smaller proportionate quantities were used for crude product IIa). Products were obtained only from the *n*-pentane (first) and methanol (last) eluants. Final yields: aromatic adamantanecarbinyl products (**4a**,**b**), IIa, 0%, IIb, 96–97%; aminated aromatic products (**5a**,**b**), IIa, 0–9%, IIb, 0–3%. Aniline and *p*-toluidine were identified by comparison to authentic materials.

Characterization of 4a: mp 42–43 °C (lit. mp 43–44°C,[30] mp 42–44 °C[31]); IR (melt) 3050, 2920, 2850, 1600, 1500, 1455, 1355, 1350, 1320, 1310, 1235, 780, 705, 615; NMR ($CDCl_3$) δ 7.3–7.0 (m, 5), 2.4 (s, 2), 2.0–1.6 (m, 15); mass spectrum, *m/e* (relative intensity) 226 (8), 211 (3), 167 (4), 155 (6), 141 (6), 135 (100), 115 (6), 107 (8), 93 (16), 91 (20), 79 (19), 67 (10), 55 (8), 44 (14), 41 (17).

Anal. Calcd for $C_{17}H_{22}$: C, 90.20; H, 9.80. Found: C, 89.90; H, 10.10.

The NMR spectrum was essentially identical with that of authentic material.[32]

Characterization of 4b: NMR ($CDCl_3$) δ 7.2–6.8 (4), 2.3–2.1 (5), 2.1–0.8 (15); mass spectrum, *m/e* (relative intensity) 240 (8), 225 (6), 181 (6), 169 (7), 135 (100), 115 (6), 107 (9), 93 (9), 90 (14), 81 (8), 79 (8), 77 (12), 69 (8), 67 (11), 57 (9), 55 (13), 44 (22), 41 (23).

Anal. Calcd for $C_{18}H_{24}$: C, 89.92; H, 10.08. Found: C, 89.93; H, 10.05.

Competitive Alkylations of Aromatic Substrates by 3–AlCl$_3$. Anhydrous aluminum chloride (0.49 g, 3.68 × 10^{-3} mol) was quickly added to a solution of **3** (0.30 g, 1.57 × 10^{-3} mol) dissolved in a 1:1 mixture of toluene–benzene, 1.233 mol each) preheated to 45 °C with exclusion of moisture. The temperature was quickly raised to 80 °C and maintained there for 1.5 h. The general isolation procedure was followed. Yield ratios were determined by GLC analysis (Table II).

Alternatively, **3** dissolved in an appropriate mixture of toluene–benzene (for 1:1, 0.513 mol each; for 1:10, 0.10:1.00 mol, respectively) was added during 1.5 h to a homogeneous solution of anhydrous aluminum chloride (0.72 g, 2.25 × 10^{-3} mol) in a mixture of toluene–benzene (for 1:1, 1.37 mol each; for 1:10, 0.25:2.50 mol, respectively) preheated to 67 °C. Moisture was excluded. The temperature was quickly raised to 80 °C and then maintained there for 1.5 h. The general isolation procedure was followed. Yield ratios were determined by GLC analysis (Table III).

Reactions similar to those described for **3** were also run with either **9** or **12**. The appropriate procedure and data are presented in Table I.

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Registry No. 3, 63534-35-0; **4a**, 7131-11-5; **4b**, 76429-91-9; **5a**, 62-53-3; **5b**, 106-49-0; **6**, 14504-80-4; **7**, 768-95-6; **9**, 27011-47-8; **12**, 770-70-7; **32**, 828-51-3; AlCl$_3$, 7446-70-0.

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Isotopic Perturbation of the Carbon-13 Nuclear Magnetic Resonance Spectrum of a Pyramidal Dication

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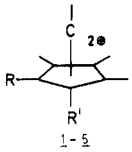
The recently developed method of deuterium-induced perturbation of ^{13}C NMR chemical shifts, which allows distinction between classical and nonclassical cations, has been applied to a pyramidal dication (**1**). The results obtained are in agreement with a symmetrical structure for this species.

We recently reported the synthesis and chemical behavior of $(CCH_3)_6{}^{2+}$ (**1**)[1] as well as of some derivatives of this class of ions with general formulas $[(CCH_3)_5CR]^{2+}$ (**2**, **3**) and $[(CCH_3)_4C_2R_2]^{2+}$ (**4**, **5**).[2,3]

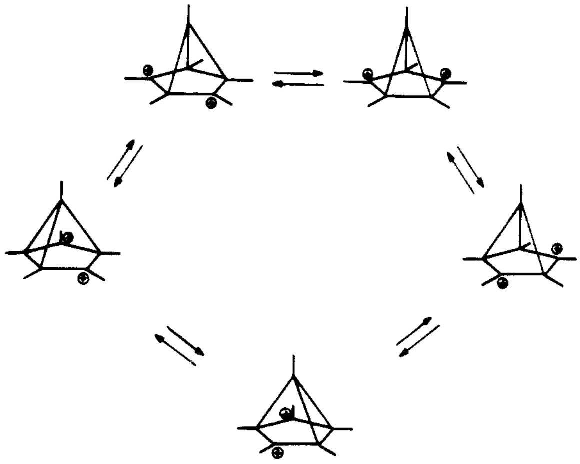


1-5

— ≡ CH_3
1 $R = R' = CH_3$
2 $R = CH_3, R' = C_2H_5$
3 $R = CH_3, R' = i\text{-}C_3H_7$
4 $R = R' = C_2H_5$
5 $R = R' = i\text{-}C_3H_7$

There are several indications that dication **1** has a nonclassical structure (a single energy minimum), and these include the inconsistency of the values of the ^{13}C NMR chemical shifts calculated by using Olah's rule[4,5] with

Scheme I



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[3] For reasons of simplicity we have used a representation of the pyramidal dications in the way indicated (the similarity with organometallic chemistry is clear). The positions of the substituents may be indicated as basal (at the five-membered ring) and apical (at the top).

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