

# Rearrangement of 1-Azidoadamantane to 3-Aryl-4-azahomoadamantane in the Presence of Aluminum Chloride and Aromatic Substrates<sup>1</sup>

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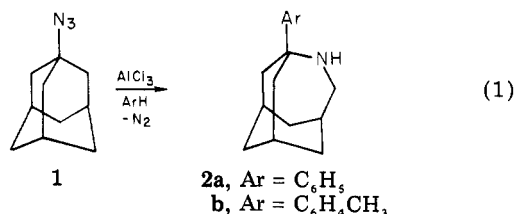
Reaction of 1-azidoadamantane (1) with aromatic substrates in the presence of aluminum chloride at 80 °C for 1.25 h gave the corresponding 3-aryl-4-azahomoadamantane (2) in >90% yield. The reaction of 1 to 2 represents the first report of intermolecular aminoalkylation of aromatics in the benzene series, presumably from an imine intermediate. At 18 °C, only 3-hydroxy-4-azahomoadamantane is obtained. Addition of water to the reaction system at 80 °C yielded 1-phenyladamantane (4) as the major product. Mechanistic features are treated.

The literature contains relatively few reports on the reactions of organic azides in the presence of Lewis acids and aromatic substrates. Whereas aryl,<sup>3-5</sup> acyl,<sup>5,6</sup> sulfonyl,<sup>5</sup>  $\alpha$ -carbonyl,<sup>7</sup> and alkoxy carbonyl<sup>8,9</sup> azides are reported to react primarily with evolution of nitrogen gas, yielding N-substituted anilines, alkyl azides may also undergo elimination of azide ion.<sup>5,10</sup> The resulting products from reactions of the alkyl azides with aluminum chloride in benzene were N-alkylanilines, imines from rearrangement, or alkylbenzenes.<sup>10</sup> The imines apparently did not participate in Friedel-Crafts alkylation. In fact, intermolecular aminoalkylation of aromatic substrates with imines is extremely rare.<sup>11</sup>

In the present study, we report the first reaction of an alkyl azide with aromatic compounds catalyzed by aluminum chloride, resulting in rearrangement followed by aminoalkylation of the aromatic reagents. In addition, we explore the crucial effect of temperature and catalyst on the nature of the product. Mechanistic features are treated.

## Results and Discussion

1-Azidoadamantane (1) was prepared by a modified published procedure.<sup>12</sup> Exposure of 1 at 80 °C for 1.25 h to aluminum chloride in the presence of an aromatic substrate (Table I) resulted in formation of the corresponding 3-aryl-4-azahomoadamantane (2) in >90% yield (eq 1). When the reaction of 1 is carried out in the absence



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Table I. Reaction of 1 with AlCl<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>Y<sup>a</sup>

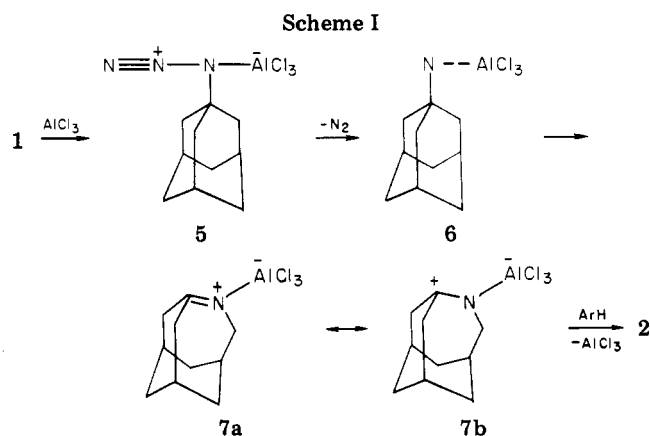
Y	C <sub>6</sub> H <sub>5</sub> Y		1		AlCl <sub>3</sub> , FW × 10 <sup>3</sup>	product % <sup>b</sup>
	mol × 10 <sup>3</sup>	mol × 10 <sup>3</sup>	mol/L × 10 <sup>2</sup>	mol/L × 10 <sup>2</sup>		
H	281	1.70	6.81	15.0	15.0	2a, 98
H	281	1.70	6.81	15.0	15.0	2a, 99 <sup>c</sup>
H	518	2.27	4.93	22.5	22.5	2a, 97
H	844	5.67	7.56	45.0	45.0	2a, 92
CH <sub>3</sub>	235	1.70	6.81	15.0	15.0	2b, 90 <sup>e</sup>
CH <sub>3</sub>	235	1.70	6.81	15.0	15.0	2b, 92 <sup>c</sup>
CH <sub>3</sub>	442	2.27	4.83	22.5	22.5	2b, 91
CH <sub>3</sub>	706	5.67	7.56	45.7	45.7	2b, 94
CH <sub>3</sub>	1442	2.27	1.51	7.5	7.5	2b, 94 <sup>d</sup>

<sup>a</sup> General procedures A, nonhomogeneous. <sup>b</sup> Isolated yield of pure product. <sup>c</sup> Under N<sub>2</sub>. <sup>d</sup> Homogeneous.

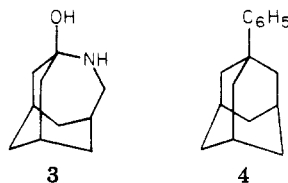
Table II. Effect of Temperature on the Reaction of 1 with AlCl<sub>3</sub> and C<sub>6</sub>H<sub>6</sub><sup>a-d</sup>

temp, °C	% yield		temp, °C	% yield	
	2 <sup>e</sup>	3 <sup>f</sup>		2 <sup>e</sup>	3 <sup>f</sup>
18		94	60	23	74
50	10	79	70	80	16

<sup>a</sup> General procedures A (nonhomogeneous). <sup>b</sup> 1, 2.27 × 10<sup>-3</sup> mol (6.35 × 10<sup>-2</sup> mol/L) for all runs. <sup>c</sup> AlCl<sub>3</sub>, 2.25 × 10<sup>-2</sup> mol. <sup>d</sup> C<sub>6</sub>H<sub>6</sub>, 450 × 10<sup>3</sup> mol; 1.25 h. <sup>e</sup> Isolated yield of pure products. <sup>f</sup> Isolated yield of crude product.

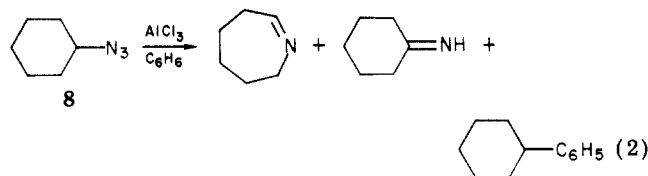


of the Lewis acid catalyst (24 h at 80 °C), approximately 86% 1 is recovered with no 2 present. At room temperature (1.25 h) in the presence of the catalyst, only 3-hydroxy-4-azahomoadamantane (3) was isolated. Table II contains data on the effect of temperature. Alkyl azides are generally considered to be thermally stable at room temperature, but at temperatures in excess of 100 °C nitrogen gas is eliminated in a first-order, homogeneous



process.<sup>13,14</sup> When 1 is treated with aluminum chloride together with added water in benzene at 80 °C, loss of azide ion also occurs and 1-phenyladamantane (4) is obtained as the major product. These results indicate that an anhydrous catalyst is necessary for nitrogen gas elimination and that higher temperatures are required for the aromatic substitution process.

**Mechanism.** Mechanistically, since nitrogen gas, not azide ion, is generated in the reaction described in eq 1, it is reasonable to propose the intermediacy of an imine complexed with the Lewis acid catalyst (7a, Scheme I). In fact, it has been reported that cyclohexyl azide (8) in the presence of aluminum chloride and benzene at 50 °C gave rearrangement products, namely, the corresponding ring-expanded imine and oxocyclohexanimine, as well as cyclohexylbenzene<sup>10</sup> (eq 2). It was proposed that the imine



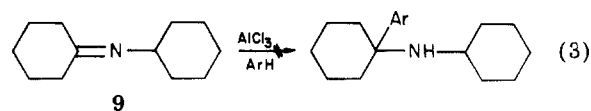
products arose from an intermediate similar to structure 5, in which the Lewis acid catalyst initially coordinated with the  $\alpha$  nitrogen atom. The process, perhaps concerted, may entail participation of a nitrene complexed (nitrenium species) with the Lewis acid catalyst (6). Similarly, acid-catalyzed hydrolysis of azides displays second-order kinetics which also point to a nitrenium ion, rather than a discrete nitrene intermediate.<sup>15</sup>

Formation of the azide-aluminum chloride complex (5) and subsequent elimination of nitrogen gas occurs within 30 s of addition of the Lewis acid (measured by nitrogen gas collection). The rapid formation of the complex (5) is consistent with data reported by Newman and co-workers<sup>6</sup> who measured the rates of Lewis acid catalyzed decomposition of benzoyl azide into phenyl isocyanate and nitrogen gas. In that work, the rate of formation of the complex with aluminum chloride is very rapid, and decomposition of the complex was described as the rate-determining step.

The proposed imine (7a) brings to mind recent publications<sup>16-20</sup> which deal with the effect of heteroatoms (N, O, and S) on the stability of an adjacent bridgehead carbocation in bi- and tricyclic systems. The involvement is most pronounced when nitrogen is situated adjacent to the bridgehead.<sup>16,17</sup> An additional important feature facilitating stabilization of the bridgehead cation (7b) by ni-

trogen is increased flexibility of the C<sub>3</sub>-C<sub>6</sub> bridge. Examination of a model suggests that a very favorable geometry may be achieved for overlap of the empty p orbital with the nitrogen lone pair, providing formal C-N bridgehead double bonding.<sup>20</sup> Formation and trapping of such strained double bonds in azahomoadamantene<sup>21</sup> and homoadamantene<sup>22</sup> have been described previously. Another factor which should affect the ability of adjacent nitrogen to interact with the bridgehead cationic center is the high flexibility of the entire homoadamantyl framework. A relative rate of 0.4:1 in solvolysis of 3-chlorohomoadamantane vs. *tert*-butyl chloride illustrates a comparative lack of bridgehead strain in the 3-homoadamantyl carbonium ion.<sup>23</sup>

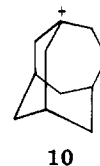
When the imine (9) prepared from cyclohexanone and cyclohexylamine<sup>24</sup> was treated under conditions similar to those for 1, no substitution occurred (eq 3). Similarly, as



indicated in eq 2, cyclohexyl azide gave imine products which did not participate in aromatic aminoalkylation. In addition, lack of Friedel-Crafts alkylation by the imino products is not due to the use of a lower temperature (50 vs. 80 °C in our case). Reaction of 8 at the higher temperature gave results consistent with those reported.<sup>10</sup>

With the exception of the Pictet-Spengler<sup>25,26</sup> and analogous reactions, which are intramolecular processes usually involving highly activated aromatic nuclei, the literature apparently contains no examples of intermolecular Friedel-Crafts substitution in the benzene series by imines. 1-Pyrroline is reported to undergo condensation with pyrrole and indole in the absence of an acidic catalyst.<sup>11</sup> However, the reactivity of this imine is quite limited, as demonstrated by the inertness toward 1-methylpyrrole, carbazole,<sup>11</sup> or 1,3,5-trihydroxybenzene. In contrast, intermolecular aminoalkylation by the Mannich reaction, which requires a highly activated aromatic substrate, is well-known.<sup>27</sup>

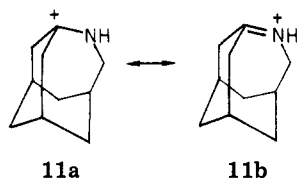
With this background we are now in a position to address the question: why is aminoalkylation effected in the case of 1, but not with the previously described analogues (see above). One point may be less steric hindrance displayed by the imino group which is part of a tricyclic system. However, 1-pyrroline, which is comparatively unhindered, with aluminum chloride and 1,3-dimethoxybenzene gave only polymer product, with no aromatic incorporation. Another factor most likely entails differences in strain energy. The bridgehead 3-homoadamantyl cation (10) is quite similar in ease of formation to the *tert*-butyl



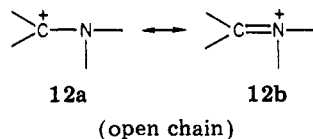
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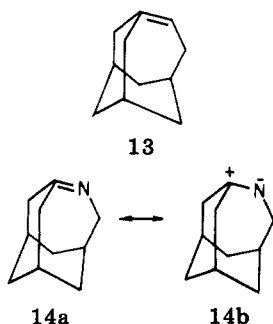
cation (see above). Hence, it is reasonable to predict facile formation of 11a. The crucial aspect would seem to be



associated with the degree of resonance stabilization possible for 11. Since 12b is the main contributor for the



open-chain aliphatic members,<sup>28</sup> reactivity of 12 should be relatively low, in accord with experimental observation for the unstrained systems (9 and eq 2). Although 10 and 11a are comparatively unstrained, this is not the case with the corresponding bridgehead unsaturated species, 3-homoadamantene (13)<sup>22</sup> and 14<sup>21</sup> as evidenced by ease of [2 +



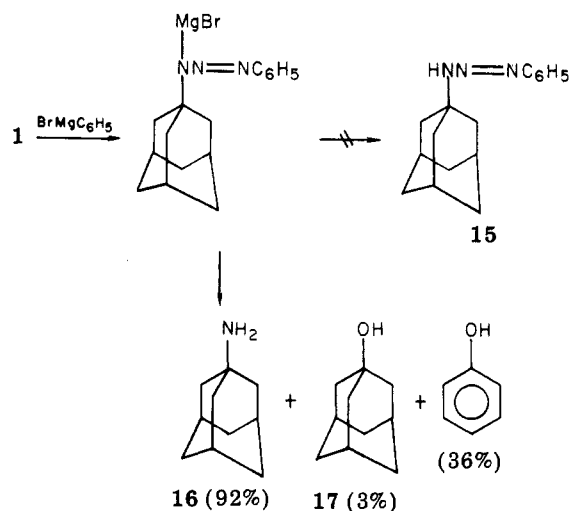
2] cycloaddition. Therefore, 11b would appear not to make as large a contribution as 12b. As a result, the activity of 11 as an electrophile should be enhanced relative to that of the open-chain analogue.

Recently, Kreher<sup>29</sup> has shown that triazene intermediates are not predominantly involved in the reaction of azides with benzene and aluminum chloride. When we attempted to prepare 1-phenyl-3-adamantyl triazene (15) by the method of Dimroth,<sup>30</sup> workup gave 1-aminoadamantane (16), 1-adamantanol (17), and phenol as products (Scheme II). This result suggests that 15, if formed, is extremely labile. Since none of these products was obtained in the reaction of 1 with  $\text{AlCl}_3\text{-ArH}$ , and on the basis of the prior work,<sup>29</sup> it is not reasonable to invoke participation of a triazene intermediate.

In the study of temperature effect, the route giving rise to 3 is intriguing. It may be that the reactive intermediate generated from 1 and  $\text{AlCl}_3$  is not reactive enough at the lower temperature to effect attack on the aromatic nucleus. Introduction of the bridgehead hydroxyl may occur from adventitious moisture or during aqueous workup.

Of final consideration is the reaction of 1 with aluminum chloride exposed to moisture. An aluminum chloride-water complex, or  $\text{Al}(\text{OH})\text{Cl}_2$  from hydrolysis, could be involved.<sup>31</sup> Since one of the products (4) isolated is

Scheme II



analogous to cyclohexylbenzene (eq 2), water cocatalysis ( $\text{H}^+$  as actual catalyst) may promote azide ion elimination, perhaps via a triazene intermediate.

The literature contains other reports of rearrangement of 1 leading to azahomoadamantanes. For example, 1 on photolysis<sup>21</sup> in the presence of methanol produced the corresponding 3-methoxy-4-azahomoadamantane; in non-hydroxylic media, the dimer of the bridgehead imine resulted. With sulfuric acid, compound 3 is formed.<sup>12</sup> Analogously, 1-(dichloroamino)adamantane on rearrangement with aluminum chloride, followed by treatment with nucleophiles, such as water, alcohol, thiols, or aromatic compounds, gave the corresponding 3-substituted-4-azahomoadamantanes.<sup>32</sup>

Our related work with 3-azidohomoadamantane will be described shortly.<sup>33</sup>

## Experimental Section

**Materials and Analytical Procedures.** Melting points are uncorrected. Spectral data were obtained with the indicated instruments: infrared, Beckman IR8;  $^1\text{H}$  NMR, Varian T60; mass, Hitachi Perkin-Elmer RMU-6E. GLC analyses were done on a Varian Aerograph 90-F instrument (6 ft  $\times$  0.25 in., 30% SE-30 on 80-mesh Chromosorb W column).

1-Adamantanol (17) (99%, Aldrich) and sodium azide (Aldrich, 99% or Baker, 95%) were used directly. Anhydrous aluminum chloride was taken from a freshly opened bottle (Fischer Certified or Aldrich) or sublimed. All solvents were distilled.

Aromatic substrates were purified according to Perrin: benzene<sup>34a</sup> 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<sup>34b</sup> was shaken 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.

All solutions were dried over sodium sulfate. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN (C, H, N), and by Mr. F. Laib, University of Wisconsin—Milwaukee (C, H, N).

**1-Azidoadamantane (1).** The method of Sasaki et al.<sup>12</sup> was used with modifications. When the reported procedure was used, yields of crude product did not exceed 88%. GLC analysis indicated that ~5% of the precursor alcohol (17) was present. Attempts to obtain 1 by recrystallization from aqueous methanol

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increased the quantity of 17 by as much as 50%. Sublimation of the crude product prior to recrystallization provided material that consistently melted at 83–86 °C and contained varying amounts of 17 (1–4%, GLC).<sup>35</sup> By increasing the reaction time (4–4.5 h instead of 3.0 h), the crude yield increased to 97% and GLC analysis indicated that 17 was decreased to ~1%. Purification was then effected by dissolving the product in *n*-hexane (1 g/150 mL), filtering, and removing the solvent at reduced pressure, followed by sublimation (GLC showed no detectable 17): 94% yield (lit.<sup>12</sup> 96% crude yield); mp 78.5–79 °C (lit.<sup>36</sup> mp 80–81 °C); IR (KBr) 2920, 2860, 2100 (N<sub>3</sub>), 1440, 1340, 1250, 1100, 1080, 1045 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.4–2.15 (m), 2.1–1.85 (m).

**Reaction of 1 with ArH–AlCl<sub>3</sub>. General Procedure A.** Anhydrous aluminum chloride (2.00 g, 1.13 × 10<sup>-2</sup> mol) was quickly added to a solution of 1 (0.30 g, 1.70 × 10<sup>-3</sup> mol) dissolved in ArH (ca. 25 mL) which had been preheated to 42 °C. The temperature was quickly raised to 80 °C and maintained there for 1.25 h with the exclusion of moisture. Reactions run under nitrogen gave identical results.

**General Isolation Procedure A.** The cooled reaction mixture was poured over 80 mL of 18% hydrochloric acid. The reaction vessel was then washed with 20 mL of additional acid solution, 25 mL of water, and 40 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 40-mL portions of *n*-pentane and combined with the organic layer (Ib). The solid obtained from addition of 50% sodium hydroxide to acidic solution (final pH ~11, temperature controlled by cooling) was extracted with five 65-mL portions of methylene chloride. Evaporation of the combined, dried, methylene chloride extracts under reduced pressure yielded a brown oil which solidified (IIa) upon standing for ~1 week. Cooling or placing the crude product under vacuum or nitrogen did not reduce the time of solidification.

The combined organic portion (Ib) was washed with 5% sodium bicarbonate and water (each 40 mL) and then dried. Removal of the solvent under reduced pressure afforded a brown liquid which was washed with 40 mL of 18% hydrochloric acid. Workup of this acidic solution (vide supra) yielded a brown oil which solidified (IIb) after standing. Vacuum sublimation of the crude products, IIa and IIb, provided white solid and clear liquid on the cold finger. The latter solidified upon standing or by seeding and scratching. In order to realize the reported yields, it was necessary to rework the residues from the sublimations with 18% hydrochloric acid, followed by the subsequent, standard steps. Final yields: (a) 90–92%; (b) 3–6%. (For runs in which 1 > 0.30 g, all isolation solutions and solvents were increased proportionately.)

**2a:** mp 49.5–51.5 °C; IR (KBr) 3350 (NH), 3045, 2920, 2860, 1650, 1460, 1440, 1150, 740, 680 (monosubstituted aromatic) cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>) δ 7.5–7.18 (m, 5), 3.15 (d, NHCH<sub>2</sub>, 2), 2.35–1.45 (m, 14, one exchangeable proton); mass spectrum, *m/e* (relative intensity) 227 (100), 226 (58), 225 (62), 170 (100), 156 (49), 143 (81), 131 (54), 102 (30), 91 (39), 77 (32).

Anal. Calcd for C<sub>16</sub>H<sub>21</sub>N: C, 84.46; H, 9.23; N, 6.16. Found: C, 84.54; H, 9.30; N, 6.06.

**Separation of 2b Isomers.** To a stirred mixture of 18% hydrochloric acid and methylene chloride (20 mL each) was added 0.25 g of 2b. After stirring was continued for 0.67 h, the phases were then separated. Workup of the acidic solution (procedure A) yielded an off-white solid (para). Drying and removal of solvent by reducing pressure (methylene chloride phase) similarly gave an off-white solid (ortho–meta). Vacuum sublimation provided the pure para and an apparent mixture of ortho–meta isomers; recovery: 93% for 2b (47% for para).

**2b (ortho–meta):** mp 42–44 °C; IR (KBr) 3350 (NH), 3045, 2920, 2860, 1650, 1460, 1440, 1150, 675, 735 cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>) δ 7.6–7.0 (m, 4), 3.15 (d, NHCH<sub>2</sub>, 2), 2.6 (s, NH, 1), 2.30 (d, ArCH<sub>3</sub>, 3), 2.2–1.5 (m, 13).

**2b (para):** mp 57.5–59 °C; IR (KBr) 3350 (NH), 3045, 2920, 2860, 1650, 1460, 1440, 1150, 850 (para) cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>) δ

7.65–7.0 (m, 4), 3.15 (d, NHCH<sub>2</sub>, 2), 2.6 (s, NH, 1), 2.30 (s, ArCH<sub>3</sub>, 3), 2.2–1.5 (m, 13); mass spectrum, *m/e* (relative intensity) 241 (84), 240 (65), 239 (90), 226 (35), 198 (84), 184 (78), 170 (57), 169 (55), 158 (100), 146 (53), 132 (29).

Anal. Calcd for C<sub>17</sub>H<sub>23</sub>N: C, 84.52; H, 9.53; N, 5.80. Found (ortho–meta): C, 84.62; H, 9.23; N, 5.85. Found (para): C, 84.64; H, 9.27; N, 5.77.

**General Procedure B. Reaction of 1 with AlCl<sub>3</sub>–H<sub>2</sub>O.<sup>37</sup>** Reaction and isolation procedures were identical with procedures A except that aluminum chloride was exposed to moisture and benzene was used. The majority of the product was isolated from the organic phase (Ib) and was identified as 1-phenyladamantane (4): mp 87–88 °C (lit. mp 87–89 °C,<sup>38</sup> 82 °C<sup>39</sup>); IR (KBr) 3050, 2920, 2860, 1560, 1465, 1420, 1360, 1010, 740, 685 (monosubstituted aromatic) cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>) δ 7.4–7.2 (m, 5), 2.15–1.65 (m, 15, no exchangeable proton). The yield of 4 varied, increasing with increased exposure to moisture, but typically was greater than 50%. Compound 2a (<20% yield) and an unidentified oil were isolated from the aqueous phase (Ia).

**Control Reactions of 1.** Procedure A was used. In the noncatalyst experiment, no aluminum chloride was added. Conditions and quantities for the temperature control runs are presented in Table II. When product 2 was subjected to procedure A, no change was observed.

**Reactions of 9 with AlCl<sub>3</sub>–ArH.** Anhydrous aluminum chloride (4.5 g, 3.38 × 10<sup>-2</sup> mol) was quickly added to a solution of 9 (0.6 g, 3.35 × 10<sup>-3</sup> mol) dissolved in ArH (ca. 40 mL) which had been preheated 40 °C. The temperature was quickly raised to 80 °C and maintained there for 1.25–6.5 h (ArH = C<sub>6</sub>H<sub>6</sub>) or 86 h (ArH = C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>) with the exclusion of moisture. Workup was identical with that of procedure A. A dark brown oil was obtained whose <sup>1</sup>H NMR spectrum exhibited no aromatic absorption.

**Reactions of 8 with AlCl<sub>3</sub>–ArH.** The procedure was identical with that for the corresponding reaction of 9. Workup yielded no aminoalkylated product.

**Nitrogen Gas Collection.** The nitrogen gas evolved was collected over mercury in a gas buret; the volumes were corrected for the vapor pressure of solvent and converted to milliliters of nitrogen at 760 mm and 0 °C.

**1-Phenyl-3-adamantyltriazenes (15) (Attempted Preparation).** Reaction of 1 with the Grignard reagent prepared from bromobenzene followed the procedure of Dimroth.<sup>30</sup> Workup provided only 16 (92%), 17 (3%), and phenol (36%) which were identified by comparison with authentic materials.

**Reactions of 1-Pyrroline.** (a) 1-Pyrroline was prepared and treated with 1,3,5-trihydroxybenzene according to the procedures of Fuhlhage and VanderWerf.<sup>11</sup> No aminoalkylated aromatic product was obtained. (b) 1-Pyrroline (0.2 g, 2.94 × 10<sup>-3</sup> mol), 40 mL of toluene, and anhydrous aluminum chloride (0.8 g, 6.0 × 10<sup>-3</sup> mol) were mixed and heated at 80 °C for 1.5 h under N<sub>2</sub>. Workup was identical with procedure A. The NMR spectrum of the isolated product showed an absence of aromatic proton absorption.

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**Registry No.** 1, 24886-73-5; 2a, 76036-39-0; o-2b, 75470-71-2; m-2b, 76036-40-3; p-2b, 75470-72-3; 4, 780-68-7; 8, 19573-22-9; 9, 10468-40-3; 16, 768-94-5; 17, 768-95-6; phenol, 108-95-2; 1-pyrroline, 5724-81-2; AlCl<sub>3</sub>, 7446-70-0; C<sub>6</sub>H<sub>6</sub>, 71-43-2; C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, 108-88-3.

(37) Water, 0.15–0.30 mL, was added to 4.45 g, 3.33 × 10<sup>-3</sup> mol, of freshly sublimed AlCl<sub>3</sub> at –30 °C with stirring. After the solid was warmed to 15 °C, approximately 0.75 g was used. The experiment was done under N<sub>2</sub>.

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