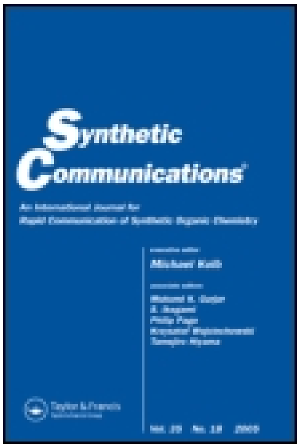

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# Preparation of Diamines of Adamantane and Diamantane from the Diazides

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# Preparation of Diamines of Adamantane and Diamantane from the Diazides

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**Abstract:** A novel synthetic method for preparing diaminodiamondoids from diazidodiamondoids starting from the hydrocarbons is described.

**Keywords:** Adamantane, azidotrimethylsilane, diamantane, diamines, diazides, dibromides

A program to find new high-strength polymeric materials required the three diamines: 1,3-diaminoadamantane (**3**).[1–4] 1,6-diaminodiamantane (**6**),[5] and 4,9-diaminodiamantane (**9**).[6,7] These diamines have been previously prepared by the Ritter reaction on the corresponding dibromides followed by hydrolysis. Although the Ritter reactions proceed to give excellent yields, the subsequent hydrolyses of the amide products required forcing conditions and long reaction times. The yields of the diamines were low in our hands. Therefore, a method was sought that would give these products quickly and in good yield.

A literature survey found the convenient method of Prakash et al.[8] to transform bromoadamantane and bromodiamantanes into the corresponding azides by Lewis acid–mediated exchange with azidotrimethylsilane. Because alkylazides are readily reduced to amines, we imagined then that Prakash et al.'s chemistry[8] on dibromodiamondoids and subsequent reduction would be an alternate route to **3**, **6**, and **9** (see Fig. 1).

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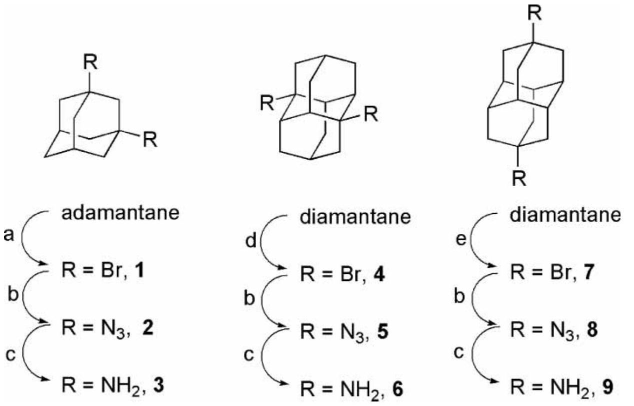

***Figure 1.*** Reagents and conditions: a) $Br_2$, Fe, freon 113, 0 °C to rt; b) $N_3Si(Me)_3$, $CH_2Cl_2$, $SnCl_4$, reflux; c) $H_2$, Pd/C, THF; d) $Br_2$, reflux; and e) $Br_2$ $AlBr_3$.

The dibromides **1**,[9–11] **4**,[12,13] and **7**[12,14,15] were prepared according to literature procedures with slight modifications. Of the two iron-catalyzed methods, Rahkimov et al.'s method[9] was preferred to Likhotvorik et al.'s method[10] to make **1** because it does not require excess bromine. Both these methods were better than Denmark et al.'s more recent two-step process,[11] which uses aluminum bromide and was difficult to control. For **4**, the procedure of Chern and Wang[13] was used, and although the yield was low, the isolation and purification of the product was simple.

In the azide/bromide exchange, the reactions required reflux with an excess of azidotrimethylsilane for completion. Progress was determined by thin-layer chromatography. The three previously unknown diazides **2**, **5**, and **8** were all solids (see Table 1). For reduction of the diazides, catalytic hydrogenation was used, which gave the diamines in high yield and purity. Because **3** is known to react with atmospheric carbon dioxide and water, it was immediately converted to the stable oxalate salt.

In conclusion, a reliable, three-step method to prepare three known diamines of adamantane and diamantane is reported. The key step was transformation of dibromodiamondoids into diazidodiamondoids. Overall yields of **3**, **6**, and **9** from the hydrocarbons were 51%, 39%, and 51%, respectively.

## EXPERIMENTAL

Melting points were collected on an electrothermal capillary melting-point apparatus and are not corrected. NMR spectra were obtained on a Bruker AC-200 spectrometer ($^1H$ at 200 MHz, $^{13}C$ at 50 MHz) and are referenced to solvent or tetramethylsilane. Iron powder (325 mesh) was purchased

***Table 1.*** Some physical properties and yields of the bromides, azides, and amines prepared

| Compound | Yield (%) | Mp (°C) | 50 MHz $^{13}$C (CDCl$_3$) *C*-X |
|---|---|---|---|
| **1** | 75 | 100–103 | 62.40 |
| **2** | 74 | 27–28 | 59.89 |
| **3** | 93 | nd | 55.41[a] |
| **4** | 45 | 262–265 | 75.02 |
| **5** | 88 | 87–90 | 62.29 |
| **6** | 99 | 312–315 | 49.99[a] |
| **7** | 57[b] | 320–323 | 63.29 |
| **8** | 92 | 125–127 | 57.48 |
| **9** | 97 | 220–222 | 45.98 |

[a] Solvent $C_6D_6$; nd = not determined.

[b] References 12, 14, and 15; X = Br, $N_3$ or $NH_2$.

from Alfa Products (Andover, MA). MolecularDiamond® diamantane (99%) was provided by MolecularDiamond Technologies, a subsidiary of Chevron Technology Ventures, LLC (Richmond, CA). Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane) and all other reagents and solvents were obtained from Sigma-Aldrich (Milwaukee, WI) and used as received. The preparation of 4,9-dibromodiamantane (**7**)[12,14,15] will be published elsewhere.

## 1,3-Dibromoadamantane (1)

A 250-mL, single-necked, round-bottomed flask was charged with a magnetic stirbar and equipped with a Claisen head and a 50-mL pressure-equalizing addition funnel. The addition funnel and open neck of the Claisen were adapted with tubing to a moderate $N_2$ flow whereby $N_2$ entered the reactor at the addition funnel and exited at the Claisen to a gas scrubbing bottle containing aqueous NaOH. A diagram of a similar setup was published previously.[16] The flask was charged with 20 g of pulverized adamantane (0.147 mol), 800 mg of Fe powder (0.015 mol, 0.1 equiv) and 60 mL of Freon 113 and set to stir at rt. The addition funnel was charged with 16.7 mL of $Br_2$ (0.323 mol, 2.2 equiv). The $Br_2$ was added over 30 min. After 15 min, evolution of HBr began. The internal temperature of the reaction remained at rt throughout. After 3 h, the reaction was partitioned between 200 mL of crushed ice and $H_2O$ and 100 mL of $CHCl_3$. The organic phase was separated and washed once with saturated aqueous $NaHCO_3$ and brine and finally dried over anhydrous $MgSO_4$. The solvent was evaporated, leaving a tan solid. The solid was slurried with 100 mL of MeOH and filtered to obtain 32 g of crude product (75%). The compound crystallized as white leaflets from MeOH. It could also be recrystallized from DMF, DMSO, EtOH, or MeCN. Mp 100–103 °C (lit.[10] 110–111 °C). $\delta_H$ ($CDCl_3$): 2.87 (s, 2H), 2.37–2.2 (m, 10H), 1.70 (m, 2H); $\delta_C$ ($CDCl_3$): 62.40, 59.18, 47.18, 35.21, 33.71. Anal. calcd. for $C_{10}H_{14}Br_2$: C, 40.85; H, 4.8. Found: C, 40.96; H, 4.78.

### 1,3-Diazidoadamantane (2)

A mixture of 4 g **1** of (0.014 mol), 12 mL of azidotrimethylsilane (10.44 g, 0.09 mol, 6.5 equiv) and 4 mL of $SnCl_4$ (8.8 g, 0.034 mol, 2 equiv) in 50 mL of $CH_2Cl_2$ was refluxed under $N_2$ for 12 h. After this time, TLC indicated all dibromide and mono-substituted intermediate were consumed. The mixture was poured onto 100 mL of crushed ice and $H_2O$. The mixture was stirred for 30 min and then separated. The organic phase was washed with 50 mL of $H_2O$, 50 mL of saturated aqueous $NaHCO_3$, and finally 50 mL of brine and then dried over anhydrous $MgSO_4$. The solvent was evaporated (10 Torr, rt) to leave a colorless liquid. The liquid was dissolved in 50 mL of hexanes and passed through a short plug of silica gel to remove a tin by-product (which was trapped at the origin). The solvent was evaporated. The crude liquid recrystallized from hexanes at −20 °C, and the crystals were collected on a medium-porosity glass frit at rt. The colorless crystals (2.2 g, 74%) were stored at −20 °C until further use. Mp 27–28 °C. $\delta_H$ ($CDCl_3$): 2.37–2.23 (bs, 2H), 1.76 (s, 2H), 1.73–1.66 (m, 8H), 1.58–1.49 (m, 2H); $\delta_C$ ($CDCl_3$): 59.89, 45.71, 40.31, 34.51, 30.48. Elemental analysis was not performed.

### 1,3-Diaminoadamantane (3) and 1,3-Diaminoadamantane bis-Oxalic Acid Salt

A mixture of 2.2 g of **2** (0.01 mol) and 300 mg of 5% Pd on carbon catalyst in 50 mL of THF (containing 240 ppm of BHT) was hydrogenated (40 psig) in a Parr® apparatus at rt for 22 h. Hexane (25 mL) was added to the mixture before filtering through diatomaceous earth on a coarse glass frit. The addition of hexanes ensured complete removal of the catalyst by a single filtration. Otherwise, a small amount of catalyst was invariably entrained. The solvent was evaporated, leaving 1.56 g of the title compound as a white solid (93%). $\delta_H$ ($C_6D_6$): 1.97 (m, 2H), 1.37–1.24 (m, 10H), 1.20 (s, 2H), 0.73 (bs, 4H); $\delta_C$ ($C_6D_6$): 55.41, 49.19, 45.54, 35.43, 31.07. The crude 1,3-diaminoadamantane was dissolved in 50 mL of $Et_2O$ and magnetically stirred at rt while a solution of 1.58 g of oxalic acid (0.017 mol, 2 equiv) in 50 mL of $Et_2O$ was added dropwise. A white solid precipitated. The solid was collected on a medium glass frit and dried under vacuum (2.8 g, 92%). Mp >300 °C. $\delta_H$ ($D_2O$): 2.47 (m, 2H), 2.08 (s, 2H), 2.03–1.82 (m, 8H), 1.71 (m, 2H). Anal. calcd. for $C_{14}H_{22}N_2O_8$: C, 48.5; H, 6.35; N, 8.08. Found: C, 48.2; H, 6.53; N, 7.88.

### 1,6-Dibromodiamantane (4)

A 1-L, two-neck, round-bottomed flask was charged with 500 g of $Br_2$ and a magnetic stirbar. The flask was equipped with a condenser and screw-feed powder addition funnel. The openings of the apparatus were connected with tubing to a flow of $N_2$ and a gas scrubbing bottle as described in the procedure for **1**. The flask was cooled in an ice bath and magnetically stirred. The addition funnel was charged with 50 g of diamantane (0.26 mol). The solid was added in portions with a screw-feed powder addition funnel (1 h). After stirring 2 h, the cooling bath was removed and the flask was heated to reflux for 12 h. The mixture was cooled, a distillation head was attached to the flask, and the $Br_2$ was distilled at atmospheric pressure. The flask was cooled, and semisolid residue was partitioned between 500 mL of $CHCl_3$ and 500 mL of $H_2O$. Some $NaHSO_3$ was added with stirring to remove the residual $Br_2$, making a light yellow organic solution. The organic phase was separated and washed with 250 mL of $H_2O$, 250 mL of saturated aqueous $NaHCO_3$, and finally 250 mL of brine. The organic phase was dried over anhydrous $MgSO_4$ and evaporated to a solid. The solid was slurried with 200 mL of hexanes and filtered on a coarse-porosity glass frit. The crude, off-white solid was $>90\%$ pure by NMR. The crude product was recrystallized from 1,4-dioxane to give colorless rods (40.5 g, 45%). It can also be recrystallized from DMF, DMSO, toluene, or MeCN. Mp 262–265°C (lit.[13] 272–273 °C). $\delta_H$ ($CDCl_3$): 2.59–2.43 (m, 8H), 2.37 (s, 4H), 1.96 (m, 2H), 1.70 (d, $J = 13.1$ Hz, 4H); $\delta_C$ ($CDCl_3$): 75.02, 52.27, 49.09, 34.34, 30.64. Anal. calcd. for $C_{14}H_{18}Br_2$: C, 48.58; H, 5.24. Found: C, 48.86; H, 5.36.

### 1,6-Diazidodiamantane (5)

Procedure similar to **2** using 9 g of **4** (0.026 mol), 22 mL of azidotrimethylsilane (19.6 g, 0.17 mol, 6.5 equiv), and 6.1 mL of $SnCl_4$ (13.5 g, 0.05 mol, 2 equiv). The compound crystallized as colorless leaflets from MeCN (6.34 g, 88%). Mp 87–90 °C. $\delta_H$ ($CDCl_3$): 2.18–2.03 (m, 6H), 1.91 (s, 4H), 1.87–1.81 (m, 4H), 1.46 (d, $J = 11.9$ Hz, 4H); $\delta_C$ ($CDCl_3$): 62.29, 41.35, 41.25, 31.69, 27.83. Anal. calcd. for $C_{14}H_{18}N_6$: C, 62.2; H, 6.71. Found: C, 62.38; H, 6.59.

### 1,6-Diaminodiamantane (6)

A mixture of 6.34 g of **5** (0.023 mol) and 700 mg of 5% Pd on carbon catalyst in 50 mL of THF (containing 240 ppm of BHT) was hydrogenated (40 psig) at rt for 22 h. Hexanes (50 mL) were added to the mixture before filtering through diatomaceous earth on a coarse glass frit. The addition of hexanes ensured complete removal of the catalyst by a single filtration. Otherwise, a small amount of the catalyst was invariably entrained. The solvent was evaporated, leaving a crude, white solid (5.0 g, 99%) that was pure by NMR. The material crystallized as colorless leaflets from MeCN. Mp 312–315 °C (lit.[5] 324 °C). $\delta_H$ ($C_6D_6$): 2.11 (d, $J = 13.0$ Hz, 4H), 1.79 (pentet, $J = 2.5$ Hz, 2H), 1.41–1.32 (m, 8H), 1.26 (d, $J = 13.0$ Hz, 4H), 0.77 (bs, 4H); $\delta_C$ ($C_6D_6$): 49.99, 48.34, 45.21, 32.56, 29.47. Anal. calcd. for $C_{14}H_{22}N_2$: C, 77.01; H, 10.16. Found: C, 76.91; H, 10.13.

### 4,9-Diazidodiamantane (8)

The procedure is similar to that used for **2**, using 3.9 g of **7** (0.011 mol), 9.5 mL of azidotrimethylsilane (8.2 g, 0.07 mol, 6.5 equiv), and 2.36 mL of $SnCl_4$ (5.2 g, 0.02 mol, 2 equiv). The compound crystallized as colorless leaflets from MeCN (2.78 g, 92%). Mp 125–127 °C. $\delta_H$ ($CDCl_3$): 1.97 (s, 6H), 1.83 (s, 12H); $\delta_C$ ($CDCl_3$): 57.48, 41.08, 37.73. Anal. calcd. for $C_{14}H_{18}N_6$: C, 62.2; H, 6.71. Found: C, 61.55; H, 6.32.

### 4,9-Diaminodiamantane (9)

A procedure similar to that used for **6**, using 2.78 g of **8** (0.01 mol), gave a quantitative yield of crude product. The material crystallized as colorless microcrystals from MeCN (2.2 g, 97%). Mp 220–222 °C (lit.[6] 238–240°C). $\delta_H$ ($CDCl_3$): 1.81 (s, 6H), 1.60 (s, 12H), 1.25 (bs, 4H); $\delta_C$ ($CDCl_3$): 45.98, 45.81, 38.04. Anal. calcd. for $C_{14}H_{22}N_2$: C, 77.01; H, 10.16. Found: C, 76.41; H, 10.03.

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