164. The Mild Bromination of Adamantane and (Trimethylsilyl)adamantanes

by **Cyril A. Grob*** and **Pawel Sawlewicz**

Institute of Organic Chemistry, University of Basel, St. Johanns-Ring 19, CH–4056 Basel

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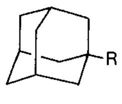
Small amounts of H_2O or MeOH catalyze the reaction of Br_2 with adamantane and its 1-(trimethylsilyl) and 1,3-bis(trimethylsilyl) derivatives.

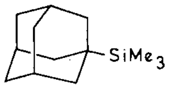
The successful bromination of adamantane **1** to 1-bromoadamantane **2** with Br_2 by *Landa* and *Hála* [1] opened the way to numerous bridgehead-substituted adamantanes [2]. However, the customary procedure of *Stettler et al.* [3] calls for rather drastic conditions, namely heating of **1** with an excess of Br_2 to *ca.* 105° for 4 to 5 h, conditions under which sensitive substituents, such as the Me_3Si group, tend to be destroyed. This also applies to the use of *Lewis* acids, such as $AlBr_3$, $FeBr_3$, and BBr_3, which strongly catalyze the bromination of **1**.

More recently, *Osawa* [4] has claimed that adamantane is more reactive towards Br_2 than hitherto assumed, and that 91% of pure **2** can be obtained from **1** by reaction at room temperature for 2 h, *i.e.* under far milder conditions. Since *Stetter*'s procedure requiring very pure and carefully dried Br_2[1]) could be reproduced in our laboratory [5], it appeared that the discrepancy was due to impurities in the Br_2 used by *Osawa* [4].

In fact, when 0.5 to 1.0 mol of H_2O or 1.5 to 2.0 mol of MeOH per mol of adamantane were added, a vigorous reaction occurred that led to a 93% yield of pure **2** after only 10



1 R=H
2 R=Br



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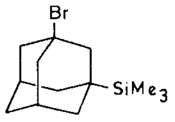

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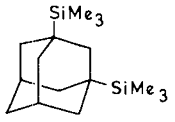

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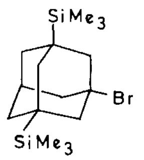

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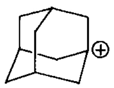

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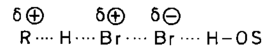

$$\overset{\delta\oplus}{R}\cdots H\cdots\overset{\delta\oplus}{Br}\cdots\overset{\delta\ominus}{Br}\cdots H{-}OS$$

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[1]) The bromine (*Fluka, puriss.*) was dried and distilled over P_2O_5.

min. Likewise, 1-(trimethylsilyl)- and 1,3-bis(trimethylsilyl)adamantane **3** and **5**, respectively, were converted to the corresponding bridgehead bromides **4** and **6**, respectively, in good yields. Attempts to brominate **3** and **5** without addition of H_2O or MeOH, or with the calculated amount of Br_2 in CCl_4, resulted in cleavage of the C–Si bond. Addition of larger amounts of the above protic solvents led to the formation of adamantanols or their methyl ethers by solvolysis of the first-formed bromides. In fact, when **1** was stirred with excess Br_2 and 20 equiv. of H_2O at 0° for 1 min adamant-1-ol **2** (R = OH instead of Br) was obtained in 88% yield²).

While the mechanism of bromination of **1** in the absence of *Lewis* acids is still not entirely clear [7], the ionic pathway proposed by *Stetter* [8] [9] involving a transient adamant-1-yl cation **7** appears to be favored. In fact, it was recently shown [10] that in the bromination of **1** to **2** with iodine bromide (IBr) in CCl_4 the electrophilic I^+ abstracts the hydride ion from **1** and the nucleophilic Br^- subsequently coordinates the cation **7**. This finding suggests that protic solvents assist the initial heterolysis of the Br_2 molecule through H-bonding to the incipient Br^- while Br^+ abstracts a hydride ion from **1**, as in **8**, to form the cation **7**. The latter then abstracts Br^- from the excess Br_2 and liberates further Br^+ in a chain reaction.

The synthesis of 1-(trimethylsilyl)adamantane (**3**) from 1,3-dichloroadamantane and Me_3SiCl *via* 1,3-dehydroadamantane was recently described by *Sasaki et al.* [11]. However, reaction of the bromide **2** with Me_3SiLi proved to be more suitable, because the method could also be applied to the preparation of **5** from the bromide **4**.

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Experimental Part

1-Bromoadamantane (**2**). In an ice-cooled flask equipped with an efficient condenser (connected to a HBr absorber), 100 g (0.74 mol) of adamantane were added in one portion to a well-stirred mixture of 733 g (4.6 mol) Br_2 (dried over P_2O_5) and 6.5 ml (0.36 mol) dist. H_2O, the inside temp. being kept below 30°. After 10 min, the homogenous mixture was worked up as described in [3]. The crude bromide **2** was sublimed at 110°/20 Torr. Yield: 146 g (93%). M.p. 118–120° ([3]: 119–120°).

1-Bromo-3-(trimethylsilyl)adamantane (**4**). To 14.65 g (183 mmol) of dry Br_2 were added 0.8 ml (19.2 mmol) of MeOH and 3.5 g (16.8 mmol) of **3** with stirring and cooling to 0°. The inside temp. rose temporarily to 25° and then dropped to 15° as the cooling bath was removed. After further 8 min, the mixture was diluted with 50 ml of CCl_4 and poured onto ice. Solid $Na_2S_2O_5$ was added to remove excess Br_2. The org. layer was separated, washed with H_2O, dried (Na_2SO_4), and evaporated. The crude product was purified by reversed-phase flash chromatography on octadecyl-modified phase (15–40 m [12]) with acetone/H_2O 9:1. Distillation in a bulb tube at 130°/0.05 Torr gave 3.86 g (80%) of pure bromide **4**. M.p. 36–37° (subl.). ^{1}H-NMR ($CDCl_3$): –0.085 (*s*, Me_3Si); 1.55–1.82 (*m*, 6 ring H); 2.13–2.6 (*m*, 8 ring H). ^{13}C-NMR ($CDCl_3$): –5.36 (*q*, Si–C); 28.04, 32.91, 35.38, 35.67, 49.12, 49.48, and 68.06 (*s*, *d*, *t*, *t*, *t*, *t*, and *s*, resp., ring C). MS: 286 ($M^{+\cdot}$, 1 Br). Anal. calc. for $C_{16}H_{31}BrSi_2$ (359.51): C 53.46, H 8.69; found: C 53.36, H 8.88.

1-(Trimethylsilyl)adamantane (**3**). Me_3SiLi was prepared from 25 ml (125 mmol) of hexamethyldisilane according to *Still* [13], but without addition of THF. The resulting deep red soln. was chilled to –78°, and a soln. of 16 g (74.4 mmol) of 1-bromoadamantane in 100 ml of Et_2O was then added during 1 min, when the inside temp. rose to 10°. Workup as described in [13] gave 8.5 g of a low-melting solid. From MeOH: 4.65 g (30%) of **3**. M.p.

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²) Similar reactions of **2** with nucleophiles in liquid Br_2 have been reported recently [6].

49–50° ([11]: 48–49°). The IR and ^{1}H-NMR spectra were identical with the published data [11]. MS: 208. Anal. calc. for $C_{13}H_{24}Si$ (208.42): C 74.92, H 11.60; found: C 74.94, H 11.88.

1,3-Bis(trimethylsilyl)adamantane (**5**) was prepared from 8.6 g (29.9 mmol) of **4** as described for **3**. After chromatography on an octadecyl-modified phase (15–40 m) with acetone/H_2O 97:8, the crude **5** was distilled in a bulb tube at 110°/20 Torr. Yield: 2.52 g (30%). M.p. 50–51.5°. ^{1}H-NMR ($CDCl_3$): −0.1 (*s*, 2 Me_3Si); 1.51–1.78 (*m*, 14 ring H). ^{13}C-NMR ($CDCl_3$): −5.49 (*q*, Si–C); 20.04, 27.22, 36.52, 37.26, and 37.88 (*s*, *d*, *t*, *t*, and *t*, resp., ring C). MS: 280. Anal. calc. for $C_{16}H_{32}Si_2$ (280.60): C 68.49, H 11.50; found: C 68.20, H 11.32.

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