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PREPARATION OF 1-SILYL- AND 1,3-DISILYL-ADAMANTANES

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Summary

1-Dimethylsilyl- and 1,3-bis(dimethylsilyl)adamantane have been prepared in low yield by Wurtz reaction of dimethylchlorosilane with 1-chloroadamantane or 1,3-dichloroadamantane, respectively. On the other hand, reaction of phenyldimethylsilyllithium with 1-bromoadamantane or 1,3-dibromoadamantane gives essentially quantitative yields of 1-phenyldimethylsilyladamantane or 1,3-bis(phenyldimethylsilyl)adamantane, respectively.

The high symmetry and thermodynamic stability of the adamantane polyhedron have stimulated considerable interest in the chemistry of its many derivatives [1]. Surprisingly only a few silyl derivatives of adamantane have been reported [2]. We should like to report two methods which permit the preparation of 1-silyl- and 1,3-disilyl-adamantane derivatives.

Organosilicon compounds are often prepared by the reaction of organometallic reagents with chlorosilanes [3]. The difficulty in preparing silyladamantane derivatives by this approach results from the fact that organometallic derivatives of adamantane are extremely hard to prepare [3–12]. Similarly, Wurtz-type reactions of 1-chloroadamantane (I) are unsuccessful with most chlorosilanes [2,13]. Hydrosilation reactions are frequently used to prepare organosilicon compounds. In this regard, the chloroplatinic acid catalyzed addition of the Si–H bond of trichlorosilane across the strained C–C single bond of 1,3-dehydroadamantane yields 1-trichlorosilyladamantane [14]. Many adamantane derivatives have been prepared by Lewis acid catalyzed rearrangements [15]. While 1-trimethylsilyladamantane (II) has been reported to result from the aluminum bromide catalyzed Wagner–Meerwein rearrangement of 3-trimethylsilyl tricyclo [5.2.1.0^{2,6}] decane [16], we have been unable to repeat this work. Finally the insertion of dichlorosilylene into tertiary C–H bond of adamantane or into a tertiary C–Cl bond of I is reported to yield 1-dichlorosilyladamantane or 1-trichlorosilyladamantane, respectively [17].

Against this background, we find that the success of the Wurtz reaction of I and 1,3-dichloroadamantane (III) with chlorosilanes and sodium is highly dependent on

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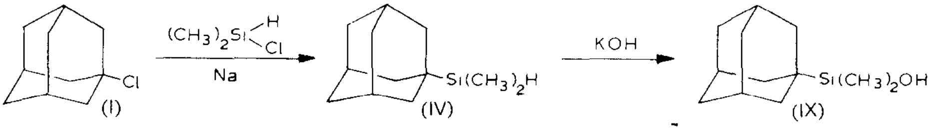
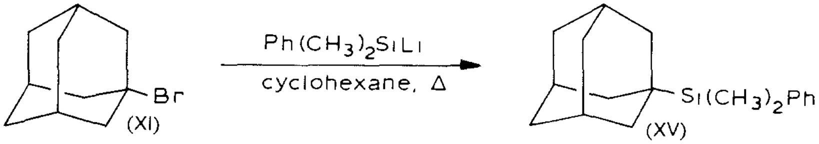
solvent. The reaction fails in ether solvents, resulting in formation of adamantane and 1,1′-biadamantane [7]. On the other hand, in aromatic hydrocarbon solvents low yields of II, 1-dimethylsilyladamantane (IV) and 1,3-bis(dimethylsilyl)adamantane (V) can be obtained. The high stability of the adamantyl free radicals [8–11] is the problem. Thus reaction of III, dimethylchlorosilane (VI), and sodium yields IV as the major product, with only minor amounts of V. Similarly, reaction of 1,3,5-trichloroadamantane (VII) with VI and sodium gives IV and V. None of the expected 1,3,5-tris(dimethylsilyl)adamantane (VIII) was found. The reactive Si–H bond of IV permits the preparation of other 1-adamantyldimethylsilane derivatives. For example, 1-adamantyldimethylsilanol (IX) was prepared by reaction of IV with potassium hydroxide [18].



An alternative route to 1-silyl- and 1,3-disilyl-adamantane derivatives involves the reaction of phenyldimethylsilyllithium (X) [19] with 1-bromo- (XI) or 1,3-dibromoadamantane (XII), respectively. Choice of solvent in this case is also critical. In ether or THF only adamantane and 1,1′-biadamantane are found. On the other hand, in hydrocarbon solvent the reaction proceeds in close to quantitative yield. This is a most unusual example of coupling between a silyllithium reagent and a tertiary alkyl halide.



Experimental

^1H NMR spectra were obtained on a IBM-Bruker WP-270-SY spectrometer operating in the FT mode using 5% solution in deuteriochloroform. Chloroform was utilized as the internal standard. ^{13}C NMR spectra were obtained on an IBM-Bruker WP-270-SY spectrometer using 10–15% solutions in deuteriochloroform or on a JEOL-90 FXQ spectrometer using 20% solution in deuteriobenzene. Chloroform and benzene were utilized as internal standards, respectively. ^{13}C spectra were run with broad band proton decoupling. IR spectra were obtained on a Perkin–Elmer 281 spectrometer. Low resolution mass spectra were obtained on a Hewlett–Packard 5985 GC-MS at an ionizing voltage of 70 eV. High resolution mass spectra were obtained on an A.E.I. MS-902 at 70 eV. Exact masses were determined by peak matching against peaks of known mass of perfluoro kerosene. GLPC analysis were performed on a Hewlett-Packard F&M 700 using either a 1/4″ × 18″ 20% polyphenylether on 60–80 mesh Chromosorb W column (A) or a 1/4″ × 10′ 20% carbowax on 60–80 mesh Chromosorb P column (B). Product yields were calculated using octadecane as an internal standard. Elemental analysis were performed by Galbraith Laboratories Knoxville, Tennessee.

Dimethylchlorosilane (VI), trimethylchlorosilane (XIII) and phenyldimethylchlorosilane (XIV) were obtained from Petrarch System Inc. and were redistilled immediately prior to use. Tetrahydrofuran was distilled from sodium/benzophenone ketyl immediately prior to utilization.

1,2-Diphenyltetramethyldisilane was prepared by reaction of XIV with lithium metal in THF [19].

1-Chloroadamantane (I), 1,3-dichloroadamantane (III), and 1,3,5-trichloroadamantane (VII) were prepared by electrophilic chlorination of adamantane by aluminum chloride and carbon tetrachloride [20]. 1-Bromoadamantane (XI) and 1,3-dibromoadamantane (XII) were prepared by bromination of adamantane with bromine and boron tribromide [21].

Wurtz reaction of 1,3-dichloroadamantane (III) and dimethylchlorosilane (VI)

Preparation of 1-dimethylsilyladamantane (IV) and 1,3-bis(dimethylsilyl)adamantane (V)

In a dry 200 ml pressure bottle which has been flushed with purified nitrogen were placed a Teflon covered magnetic stirring bar, III (1.4 g, 6.8 mmol), dry xylene (2 ml), sodium (1.4 g, 61 mmol) and VI (3 ml, 27 mmol). The bottle was sealed with a silicone rubber gasket and the contents stirred at 120–130 °C over a period of 5 h. Sodium chloride was removed by filtration and was thoroughly washed with hexane. Solvents were removed from the combined organic phase by evaporation under reduced pressure. Adamantane (0.67 g, 72%) was isolated by crystallization and was identified by comparison of its spectral properties with an authentic sample. Mp. 268–270 °C (lit. mp. 269.6–270.8 °C) [22].

1-Dimethylsilyladamantane (IV) was formed in 22% yield. It was purified by preparative GLPC column B. It has the following spectral properties: ^{1}H NMR: δ -0.045 (d, J 3.6 Hz, 6H), 1.64 (d, J 2.7 Hz, 6H), 1.75 (d, J 2.7 Hz, 6H), 1.84 (br m, 3H), 3.43 (septet, J 3.6 Hz, 1H). ^{13}C NMR: δ -8.25 (2C), 20.81 (1C), 28.02 (3C), 37.81 (3C), 38.19 (3C); IR: $\bar{\nu}$ 2900, 2090 (Si–H) and 1250 cm^{-1}. MS: m/e (% rel. int.) 194 (56), 149 (37), 135 (100), 107 (13), 93 (26), 91 (32), 79 (78). Exact mass for $SiC_{12}H_{22}$ (M^+) 194.1495, calcd. 194.1491.

1,3-Bis(dimethylsilyl)adamantane (V) was formed in 2% yield. It was purified by preparative GLPC column A. It has the following spectral properties: ^{1}H NMR: δ -0.043 (d, J 3.7 Hz, 12 H), 1.54, 1.64, 1.75 and 1.81 (14 H), 3.42 (septet, J 3.7 Hz, 2H). ^{13}C NMR: δ -8.13 (4C), 19.84 (2C), 27.29 (2C), 37.67 (1C), 37.99 (4C), 38.56 (1C). IR: $\bar{\nu}$ 2900, 2090 (Si–H) and 1250 cm^{-1}. MS: m/e (% rel. int.) 252 (52), 193 (100), 149 (81), 138 (21), 133 (14), 113 (12), 73 (20). Exact mass for $Si_2C_{14}H_{28}$ (M^+) 252.1726, calcd. 252.1729.

Wurtz reaction of 1,3,5-trichloroadamantane (VII) and dimethylchlorosilane (VI)

Reaction of VII (0.3 g, 1.25 mmol), dry xylene (1 ml), sodium (0.4 g, 17 mmol) and VI (0.83 ml, 7.5 ml) as above gave adamantane 24%, IV 59%, and V 9% yield. No VIII was found.

Trimethylsilyladamantane (II) was prepared in an analogous reaction of XIII and I in 12% yield. It was purified by preparative GLPC column B. M.p. 36.5 °C (lit. mp. 35 °C) [2]. It has the following spectral properties: ^{1}H NMR: δ -0.14 (s, 9H), 1.61 (d, J 2.3 Hz, 6H), 1.73 (d, J 2.3 Hz, 6H), 1.82 (br, 3H). ^{13}C NMR: δ -5.48 (3C), 21.33 (1C), 28.10 (3C), 37.37 (3C), 37.97 (3C). IR: $\bar{\nu}$ 2900 and 1250 cm^{-1}. MS: m/e

(% rel. int.) 208 (28), 193 (14), 165 (13), 135 (17). 73 (100). Exact mass for $SiC_{13}H_{24}$ (M^+) 208.1650, calcd. 208.1647.

Preparation of 1-adamantyldimethylsilanol (IX)

1-Dimethylsilyladamantane (IV) (0.085 g, 0.44 mmol) and powdered KOH (~ 10% H_2O) (0.3 g, 5.3 mmol) were stirred in xylene (1 ml) at 120 °C for 5 h [18]. The reaction mixture was cooled, poured into 2 *N* HCl (10 ml) and extracted with hexane. The organic solvents were dried, filtered and removed by evaporation under reduced pressure to yield IX as white needles in 87%. An analytic sample was purified by preparative GLPC column A. M.p. 91–92 °C. It has the following spectral properties: ^{1}H NMR: δ 0.024 (s, 6H), 1.45 (br, 1H), 1.68 (d, J 2.8 Hz, 6H), 1.75 (d, J 2.6 Hz, 6H), 1.86 (br, 3H). ^{13}C NMR: δ −4.46 (2C), 22.86 (1C), 27.58 (3C), 36.59 (3C), 37.66 (3C). IR: $\bar{\nu}$ 3640 cm^{-1} (s) (Si–O–H) [23], 2880 and 1250 cm^{-1}. MS: *m/e* (% rel. int.) 210 (49), 195 (15), 167 (14), 149 (19), 135 (27), 79 (16), 46 (100). Exact mass for $SiC_{12}H_{22}O$ (M^+) 210.1446, calcd. 210.1440.

Preparation of 1-dimethylphenylsilyladamantane (XV)

A 10 mol aliquot of a THF solution of dimethylphenylsilyllithium (X) (prepared by reaction of 5.0 g of 1,2-diphenyltetramethyldisilane and 0.7 g of lithium in 75 ml of THF over 10 h [19]) was placed in a pressure bottle. The THF was removed by evaporation under high vacuum. The dark-brown residue was dissolved in 3 ml of cyclohexane. To the above solution was added a solution of 178 mg of XI in 2 ml of cyclohexane. The reaction mixture was heated in a sealed pressure bottle at 100 °C for 3 h, cooled to room temperature. The reaction was quenched with H_2O. XV was obtained in 93% yield. It has the following spectral properties: ^{1}H NMR: δ 0.205 (s, 6H); 1.49–1.80 (m, 15H); 7.31–7.47 (m, 5H). ^{13}C NMR: δ −7.28 (2C); 21.67 (1C); 27.78 (3C); 37.30 (3C); 37.59 (3C); 127.36 (2C); 128.65 (1C); 134.63 (2C); 137.29 (1C). IR ($CDCl_3$): $\bar{\nu}$ 3140w, 2970s, 1470m, 1490m, 1280s, 1140s cm^{-1}. MS: *m/e* (rel. int.) 270 (3.4) M^+; 255 (0.5) $M^+ - 15$; 135 (100) $M^+ - 135$. Anal. Found: C, 79.72; H, 9.82. $SiC_{18}H_{26}$ calcd.: C, 79.92; H, 9.68%.

Preparation of 1,3-bis(dimethylphenylsilyl)adamantane (XVI)

A 15 ml aliquot of a THF solution of X (as above) was placed in a pressure bottle. The THF was removed and the residue was dissolved in 5 ml cyclohexane. To the above solution was added a solution of 250 mg of XII in 3 ml of cyclohexane. The reaction mixture was heated in a sealed pressure bottle to 100 °C for 6 h. The reaction was cooled to room temperature and quenched with H_2O. XVI was obtained in 95% yield. It has the following spectral properties: ^{1}H NMR: δ 0.40 (s, 12H); 1.78–1.95 (m, 14H); 7.51–7.65 (m, 10H). ^{13}C NMR: δ −7.27 (4C); 20.60 (2C); 27.13 (2C); 37.03 (1C); 37.23 (4C); 37.48 (1C); 127.38 (4C); 128.67 (2C); 134.58 (4C); 137.215 (2C). IR ($CDCl_3$): $\bar{\nu}$ 3050w, 2980s, 1430w, 1260s, 1150s, cm^{-1}. MS: *m/e* (rel. int.) 404 (5.8) M^+; 389 (1.0) $M^+ - 15$; 269 (7.8) $M^+ - 135$; 135 (100) $M^+ - 269$. Anal. Found: C, 76.80; H, 9.08. $Si_2C_{26}H_{36}$ calcd.: C, 77.15; H, 8.97%.

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