1,2-Methanoadamantane: A Molecule with a Twist Bent σ Bond†

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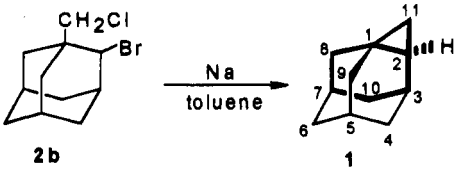
Summary: The reaction of 1-(chloromethyl)-2-bromoadamantane with sodium leads to ring closure to the hitherto unknown 1,2-methanoadamantane (**1**). Reactivity studies of **1** provide strong evidence for the existence of a twist bent σ bond.

Over 20 years ago, Gassman suggested that the *trans* fusion of cyclopropane to a sufficiently small ring should result in the formation of a twist bent σ bond that would impart unusual physical and chemical properties to the molecule in which it is contained.[1] Since then, numerous attempts have been made to fuse the cyclopropyl moiety with other small rings in the *trans* configuration.[2–5]

The chemical and thermal reactivity of derivatives of *trans*-bicyclo[4.1.0]hept-3-ene has been shown to be dramatically different from that of the corresponding derivatives of *cis*-bicyclo[4.1.0]hept-3-ene.[4] These major changes in reactivity have been attributed to the increased strain energy which results from the *trans*-ring fusion and formation of a twist bent σ bond. Theoretical calculations have provided substantial evidence for the existence of a twist bent σ bond.[6] Several examples of molecules which contain the *trans*-bicyclo[4.1.0]heptane unit as part of a more complex structure have been reported in the literature.[5]

In this paper we report on the synthesis, properties, and chemical reactivity of the hitherto unknown 1,2-methanoadamantane (**1**), tetracyclo[4.3.1.1^{3,8}.0^{3,5}]undecane, a molecule possessing a twist bent σ bond.



We chose 1-(chloromethyl)-2-bromoadamantane (**2b**) as the precursor of **1**. As shown in Scheme 1, the synthesis of **2b** started with 4-protoadamantanone (**3**).[7] Epoxidation with dimethylsulfonium methylide afforded a mixture of 4-*exo*- and 4-*endo*-epoxymethyleneprotoadamantane (**4**) in a 3:2 ratio, respectively.[8] On treatment with 33% of HBr in acetic acid the oxirane **4** gave the rearranged products, bromoacetates **5a** and **5b** in the ratio 4:1. Alkaline hydrolysis of the acetates gave the alcohols **6** which were separated on silica gel using (0 → 100%) CH_2Cl_2 in pentane as eluent. Treatment of **6b** with carbon tetrachloride and triphenylphosphine gave **2b** in 80% yield.[9] 1-(Chloromethyl)-2-bromoadamantane (**2b**) reacted readily with sodium to give a mixture of three products. The reaction was carried out in toluene at 105 °C under intensive stirring for 30 min. The reaction mixture was cooled, and products were transferred to the flask *via* canula. The mixture of products contained **1**, 1-methyladamantane, and 4-methyleneprotoadamantane in the ratio 18:15:1.[10a] Purification of products was achieved by vacuum transfer.[10b] The total yield of purified **1** based on **2b** was 37%.

The structure proof of **1** is based on the mass spectrum *m/z* 148 (M^+),[11a] the IR spectrum (ν 3050 cm^{-1}),[11b] as well as the ^1H and ^{13}C NMR spectra.[11c] On the basis of selective decoupled and COSY NMR spectra we found that the triplet at δ −0.03 and the multiplet at δ 1.08–1.22 are in interaction and therefore correspond to the cyclopropyl methyne proton at C_2 and cyclopropyl meth-

† Dedicated to the memory of Professor Paul G. Gassman, deceased on April 21, 1993.

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(9) The structure of 1-(chloromethyl)-2-bromoadamantane (**2b**) was confirmed by spectroscopic means. ^1H NMR ($CDCl_3$) δ: 4.61 (br s, 1H), 3.57 (d, 1H, J = 10.7 Hz), 3.20 (d, 1H, J = 10.7 Hz), 2.35–2.20 (m, 2H), 2.05–1.25 (m, 11H). ^{13}C NMR ($CDCl_3$) δ: 64.8 (d), 55.0 (t), 39.8 (t), 38.5 (s), 37.8 (t), 37.0 (t), 36.8 (d), 34.9 (t), 31,3 (t), 27.7 (d), 27.4 (d). IR (KBr): 2920 (s), 2850 (m), 1450 (m), 1290 (m), 750 (s), 710 (m) cm^{-1}. MS *m/z* (rel intensity): 264 (M^{2+}, 8), 262 (M^+, 6), 185 (38), 183 (92), 147 (100), 119 (36), 105 (64), 91 (65). HRMS: calcd for $C_{11}H_{16}$BrCl 262.0118, found 262.0147.

(10) (a) The ratio of products was determined on capillary GC (DB-210, 3 min 90 °C and then 90–180 °C, 10 °C/min) connected to the mass spectrometer. (b) The separation of products by preparative GC or by column chromatography on silica gel or Al_2O_3 was unsuccessful because of the high reactivity of **1**. Therefore, the identification of **1** as well as the reactivity studies were performed in a mixture with 1-methyladamantane.

(11) (a) MS *m/z* (rel intensity): 148 (M^+, 25), 133 (16), 119 (18), 105 (58), 91 (97), 79 (100). HRMS: calcd for $C_{11}H_{16}$ 148.124651, found 148.124635. (b) IR (KBr, film): 3050 (w), 2980 (w), 2900 (s), 2840 (m), 1440 (w) cm^{-1}. (c) ^1H NMR ($CDCl_3$): 2.75 (br s, 1H), 2.30 (d, 1H), 2.14–1.48 (m, 10H), 1.22–1.08 (m, 2H), 1.02–0.95 (m, 1H), −0.03 (t, 1H). ^{13}C NMR ($CDCl_3$) δ: 44.8 (t, J_{CH} = 128 Hz), 44.4 (t, J_{CH} = 128 Hz), 42.9 (t, J_{CH} = 127 Hz), 38.0 (t, J_{CH} = 128 Hz), 33.4 (d, J_{CH} = 129 Hz), 32.8 (t, J_{CH} = 133 Hz), 31.7 (d, J_{CH} = 133 Hz), 29.6 (t, J_{CH} = 157 Hz), 27.1 (d, J_{CH} = 133 Hz), 25.3 (d, J_{CH} = 143 Hz), 12.2 (s).

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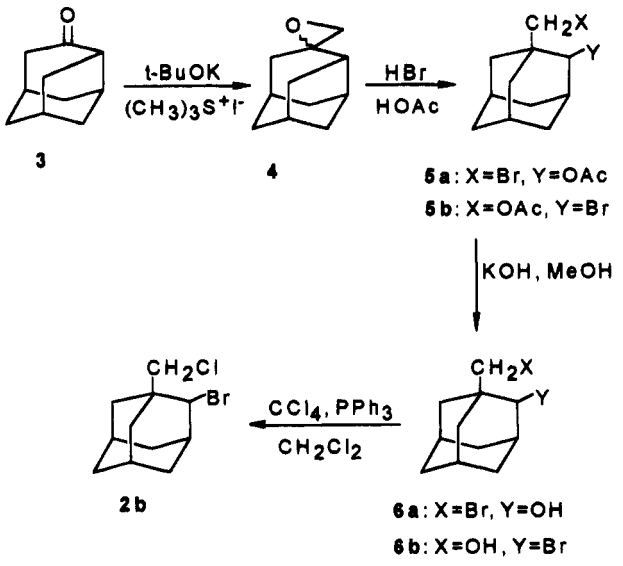
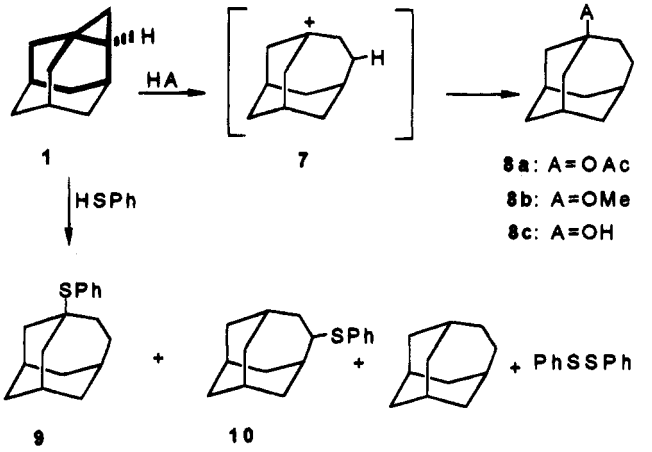
Scheme 1



Scheme 2



ylene protons at C_{11}, respectively. The chemical shift of cyclopropyl methyne proton upfield from trimethylsilane is in accord with the change in cyclopropane ring anisotropy due to *trans* ring fusion.[4] Also, the C—H coupling constants of the ^{13}C NMR signals, triplet at δ 29.1 (157Hz) and doublet at δ 25.3 (143 Hz), are typical for cyclopropane carbon atoms,[12] which provides additional evidence for the structure of **1**.

According to MM2 calculations,[13] the estimated strain energy of **1** is 47 kcal/mol greater than that of adamantane itself, implying a high reactivity of this system. 1,2-Methanoadamantane (**1**) is a highly reactive species indeed. It reacts with acetic acid, methanol, and water to give corresponding 3-homoadamantane derivatives **8**.[14] However, in the reaction of **1** with thiophenol a mixture of 3-(phenylthio)homoadamantane (**9**), 4-(phenylthio)-homoadamantane (**10**), homoadamantane, and diphenyl disulfide was obtained.[15]

The formation of products **8a—c** could be explained by the attack of a proton, as a strong electrophile, on the central bond of the cyclopropane ring and formation of cation **7** which then reacts with the nucleophile (AcOH, CH_3OH, H_2O) to give 3-homoadamantane derivatives. However, the formation of **9** and **10** probably proceed *via* radical addition of thiophenol to the central bond of the cyclopropane ring in **1**.

1,2-Methanoadamantane is thermally stable and inert to bases such as diethylamine and alkyllithium. Hydrogenolysis of **1** with Pd/C in toluene solution at room temperature gave 1-methyladamantane as the sole product. Interestingly, the central bond (C_1—C_2) in **1** is not cleaved (this would lead to homoadamantane[16]).

The reactivity of **1** is consistent with the bond distortion of the central cyclopropane bond in the *trans*-fused bicyclo[4.1.0]heptane unit,[4,6,17] the HOMO being associated with the C_1—C_2 bond, and provides strong evidence for the existence of a twist bent σ bond.

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Supplementary Material Available: Experimental procedure and copies of ^1H and ^{13}C NMR spectra of **1** and ^1H NMR spectra of **9** and **10** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(13) Molecular mechanics calculations were performed using the computer program PC MODEL 386 version 4.0.

(14) The products **8a—c** were identified by comparing its ^1H and ^{13}C NMR spectra with those of the authentic samples.

(15) The products were separated by column chromatography on Al_2O_3 activity 1 using 0 → 5% ether in pentane as eluent. **9.** MS *m/z* (rel intensity): 258 (M^+, 10), 149 (100), 109 (25), 93 (32), 79 (28). ^1H NMR ($CDCl_3$): 7.55—7.15 (m, 5H), 2.18—1.21 (m, 17H). ^{13}C NMR ($CDCl_3$) δ: 137.5 (d), 132.7 (s), 128.5 (d), 128.2 (d), 52.7 (s), 44.7 (t), 40.2 (t), 37.4 (t), 35.3 (t), 32.9 (t), 31.2 (d), 28.6 (d). HRMS: calcd for $C_{17}H_{22}S$ 258.1467, found 258.1452. **10.** MS *m/z* (rel intensity): 258 (M^+, 37), 149 (100), 110 (72), 93 (38), 79 (60). IR (KBr, film): 3050 (w), 2900 (s), 2840 (s), 1580 (m), 1475 (m), 1435 (m), 730 (m), 680 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.40—7.10 (m, 5H), 3.55 (t, 1H), 2.48—2.34 (m, 1H), 2.20—1.43 (m, 15H). ^{13}C NMR ($CDCl_3$) δ: 137.1 (s), 130.7 (d), 128.8 (d), 126.1 (d), 52.5 (d), 41.4 (t), 41.0 (t), 40.5 (t), 36.4 (t), 36.1 (d), 34.6 (t), 31.0 (d), 29.8 (t), 27.1 (d), 26.9 (d). HRMS: calcd for $C_{17}H_{22}S$ 258.1467, found 258.1436.

(16) An attempt to reduce the C_1—C_2 bond of **1** with lithium in diethylamine was unsuccessful; **1** was unchanged after 3 h at room temperature. For electron transfer reduction of strained rings see: Moore, R. W.; Hall, S. S.; Largman, C. *Tetrahedron Lett.* **1969**, 4353. Mlinarić-Majerski, K.; Majerski, Z. *J. Am. Chem. Soc.* **1983**, *105*, 7389.

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