

Concerning the Synthesis of [1.1.1]Propellane

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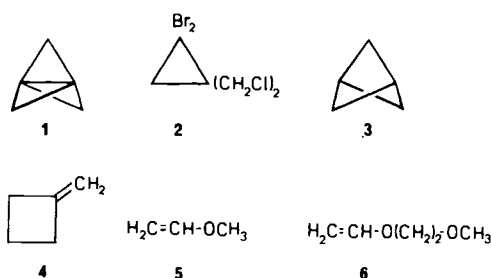
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The reaction of 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (**2**) with methyllithium in ether led to a solution of [1.1.1]-propellane (**1**) in a yield of 70%. **1** could also be prepared free of solvent by reaction of **2** with lithium powder in triglyme/*n*-decane at 73°C.

Our recent report on the facile one-pot synthesis of [1.1.1]-propellane (**1**)^{1,2} from 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (**2**) and two equivalents of *n*-butyllithium or methyllithium in ether has been used by others^{3,4} and by us⁵ as a convenient access to the bicyclo[1.1.1]pentane system. However, our procedure furnished **1** only as a solution in ether. In typical runs, the content of **1** amounted to 3%. Attempts to concentrate **1** by fractional distillation were not successful. Although pure **1** could be obtained by preparative gas chromatography¹, a modification of our original procedure aimed at the synthesis of solvent-free **1** seemed highly desirable, especially in relation to polymerization reactions of [1.1.1]-propellanes discovered recently⁶.

We have now found that **2** is also converted into **1** by reduction with finely dispersed lithium, which contained one percent of sodium. The reaction was carried out at 73°C in vacuo in triglyme/*n*-decane (4:1) under intensive stirring. The volatile material which developed during this reaction was condensed in a dry-ice trap. Besides **1** the trap contained bicyclo[1.1.1]pentane (**3**), methylenecyclobutane (**4**), ethenyl methyl ether (**5**), and some **6** together with *n*-decane, as determined by preparative gas chromatography. NMR spectroscopy, and GC-coupled mass spectrometry. Purification of the condensed liquid was achieved by fractional condensation from a bath kept at -20 to -5°C at 22 Torr. The first fraction contained almost exclusively ethenyl methyl ether and bicyclo[1.1.1]pentane. The second fraction consisted mainly of **1** (70–75%) with **5**⁷ as minor and **3**⁸ and **4**⁹ as major impurities. The total yield of purified **1** based on **2** was 25–38%. The purity of the material was sufficient for most addition reactions to **1**¹⁰.



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Experimental

1. *Starting Materials:* 3-Chloro-2-(chloromethyl)-1-propene was purchased from Aldrich Chemical Co. and used without further purification. Methyllithium was prepared from lithium and bromomethane in ether according to standard procedures.

Preparation of a Lithium Dispersion: In a three-necked 250-ml flask equipped with nitrogen inlet and an Ultra-Turrax stirrer a rod of 16.0 g (2.31 mol) of lithium (99.9%) and 0.500 g (21.7 mmol) of sodium was heated under nitrogen in 60 g of paraffin wax to 200°C. At this temperature the content of the flask was stirred by the Ultra-Turrax stirrer for about 30 s furnishing highly dispersed lithium in paraffin. The material was allowed to cool and was then immediately used for the preparation of [1.1.1]propellane.

2. *1,1-Dibromo-2,2-bis(chloromethyl)cyclopropane (2):* In a three-necked 4-l flask equipped with a dropping funnel, a reflux condenser, and a mechanical stirrer 3-chloro-2-(chloromethyl)-1-propene (400 g, 3.20 mol) in 800 ml of dichloromethane was mixed with bromoform (285 ml, 3.26 mol), trimethylphenylammonium chloride (8.00 g, 46.6 mmol), and ethanol (8.0 ml). To this mixture aqueous NaOH (800 ml, 50% w/w) was added through the dropping funnel within 2 h under vigorous stirring. Stirring was continued for 40 h at room temp., before the reaction mixture was poured into a large beaker containing 4 l of water and 2 l of *tert*-butyl methyl ether. The organic layer was separated, the aqueous layer was washed three times with 500 ml of ether, and the combined organic phases were washed twice with 500 ml of water. The solvent was removed in vacuo, and the remaining dark residue was distilled at 10⁻³ Torr. The forerun consisted mainly of bromoform and 3-chloro-2-(chloromethyl)-1-propene. The main fraction boiling at 52–60°C gave 350 g (37%) of **2** as a pale yellow solid, which was further purified by crystallization from ether affording colorless crystals of m.p. 45–46°C. — ¹H NMR (CDCl₃): δ = 1.80 (s, 2H), 3.91 (s, 4H). — ¹³C NMR (CDCl₃): δ = 32.02 (s), 33.89 (t), 35.20 (s), 47.58 (t). — MS (70 eV): *m/z* (%) = 296, 294 (1) [M⁺], 247 (90), 217 (40), 186 (27), 137, 135 (100), 100 (45), 75 (35), 65 (30), 51 (25).

C₅H₆Br₂Cl₂ (296.8) Calcd. C 20.25 H 2.04
Found C 20.68 H 2.27

In several preparations of **2** at a smaller scale [10.0 g, 80.0 mmol, of 3-chloro-2-(chloromethyl)-1-propene, 20.0 g, 80.0 mmol, of bromoform] the yields of **2** were consistently around 40%.

3. *Preparation of [1.1.1]Propellane (1) from 2 and Methyllithium:* A solution of methyllithium (14.22 mmol) in 8 ml of ether was added dropwise to a solution of 2.01 g (6.77 mmol) of **2** in 14 ml of ether, which was kept at -30°C under stirring. The mixture was stirred for 1 h at room temp., then the formation of a white precipitate was complete. The solvent and the volatile products were distilled at 14 Torr from a 20°C bath into a Schlenk flask which was kept at -78°C. ¹H-NMR analysis of the condensate showed besides

ether the signals of bromomethane and **1**. The yield of **1** was determined to be 70% (by ¹H-NMR integration of the methylene proton signals at $\delta = 2.57$ with added benzene as an integration standard).

The reaction of **2** with methyllithium was performed several times with **2** ranging from 2.00 to 40.0 g in concentrations up to three times higher than described above, affording essentially the same yields of **1** in all experiments.

If the same procedure was carried out with *n*-butyllithium instead of methyllithium, the ether solution of **1** contained 1-bromobutane, which could be removed by repeated bulb-to-bulb distillation of the volatile material from a 0°C bath at 14 Torr. After three cycles the condensate was essentially free of 1-bromobutane. The yield of **1** was 50%.

4. Preparation of 1 from 2 and Lithium: 16.0 g (2.31 mol) of dispersed lithium and 0.500 g (21.7 mmol) of sodium, prepared as described above, were transferred under nitrogen using 90 ml of *n*-decane into a 2-l three-necked flask, equipped with nitrogen inlet, dropping funnel, and reflux condenser, the top of which was connected by a dry ice trap to an aspirator. The flask was charged with 80 ml of triglyme and 20 ml of *n*-decane. At 14 Torr the mixture was heated to reflux (73°C) under vigorous magnetic stirring, and a solution of **2** (50.0 g, 168 mmol) in 60 ml of triglyme and 20 ml of *n*-decane was added dropwise within 1 h. Vacuum was maintained for additional 30 min. During the process, 8–10 g of a colorless, partially solidified product was condensed in the dry ice trap.

Purification of the condensed material was achieved by fractional distillation at 22 Torr over a short column equipped with a cooling jacket. At a bath temp. of –20°C and a temp. of the cooling jacket of –30°C a forerun of 2.0–3.0 g of a colorless liquid was collected, which consisted mainly of ethenyl methyl ether (**5**) and bicyclo-[1.1.1]pentane (**3**). The main fraction (4.0–6.0 g, bath temp. –5°C, jacket temp. –15°C) consisted mainly (according to ¹H-NMR spectroscopy, 70–75%) of **1**, which was a solid at –78°C and melted above –20°C. The total yield of **1** in the main fraction was

25–38%. Besides a small portion of **1** the residue contained methylenecyclobutane (**4**), *n*-decane, and some ethenyl 2-methoxyethyl ether (**6**). In order to determine the nature of the impurities in the main product, the mixture was separated by preparative GC (Varian Aerograph 1400, 6 m × 1 cm column, packed with 20% of Carbowax 20 M on Kieselghur) and the fractions were investigated by ¹H- and ¹³C-NMR spectroscopy. In addition, the mixture was analyzed by GC-coupled mass spectrometry. The main impurities were determined as **3** and methylenecyclobutane (**4**) (ratio 1:3); traces of **5** were also present.

CAS Registry Numbers

1: 35634-10-7 / **2:** 98577-44-7 / **3:** 311-75-1 / **4:** 1120-56-5 / **5:** 107-25-5 / **6:** 1663-35-0 / 3-chloro-2-(chloromethyl)-1-propene: 1871-57-4

- ¹⁾ First synthesis of **1**: ^{1a)} K. B. Wiberg, F. H. Walker, *J. Am. Chem. Soc.* **104** (1982) 5239. — ^{1b)} K. B. Wiberg, W. P. Dailey, F. H. Walker, S. T. Waddell, L. S. Crocker, M. Newton, *J. Am. Chem. Soc.* **107** (1985) 7247.
- ²⁾ K. Semmler, G. Szeimies, J. Belzner, *J. Am. Chem. Soc.* **107** (1985) 6410.
- ³⁾ K. B. Wiberg, S. T. Waddell, K. Laidig, *Tetrahedron Lett.* **1986**, 1553.
- ⁴⁾ P. Kaszynski, J. Michl, *J. Am. Chem. Soc.* **110** (1988) 5225.
- ⁵⁾ U. Bunz, K. Polborn, H.-U. Wagner, G. Szeimies, *Chem. Ber.* **121** (1988) 1785.
- ^{6a)} A.-D. Schlüter, *Macromolecules* **21** (1988) 1208. — ^{6b)} H. Bothe, A.-D. Schlüter, *Makromol. Chem., Rapid Commun.* **9** (1988) 529. — ^{6c)} A.-D. Schlüter, *Polymer Commun.*, in press.
- ^{7a)} C. N. Banwell, N. Sheppard, *Mol. Phys.* **3** (1960) 351. — ^{7b)} A. C. Rojas, J. K. Crandall, *J. Org. Chem.* **40** (1975) 2225.
- ⁸⁾ K. B. Wiberg, D. S. Conner, *J. Am. Chem. Soc.* **88** (1966) 4437.
- ^{9a)} *High Resolution NMR Spectra Catalogue*, Varian Associates, Palo Alto 1962. — ^{9b)} S. H. Grover, J. B. Stothers, *Can. J. Chem.* **53** (1975) 589.
- ¹⁰⁾ Professor J. Michl, University of Texas at Austin, has informed us that he has also prepared solvent-free **1** by reaction of **2** with *n*-butyllithium in tetramethylethylenediamine.

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