Kurzmitteilung / Short Communication

Solvent-Free [1.1.1]Propellane from 1,3-Diiodobicyclo[1.1.1]pentane

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Received December 18, 1991

Key Words: [1.1.1]Propellane / Iodine, nucleophilic attack at

[1.1.1]Propellane (**1**) could be prepared free of solvent by reaction of 1,3-diiodobicyclo[1.1.1]pentane (**3**) with sodium cyanide in dimethyl sulfoxide (DMSO). Highly pure **1** was obtained in an overall yield of more than 50% related to the propellane precursor 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (**2**).

[1.1.1]Propellane (**1**)[1] is one of the most easily obtained highly strained hydrocarbons and the precursor of choice for the synthesis of 1-substituted and 1,3-disubstituted bicyclo[1.1.1]pentanes[2–5]. Our facile one-pot synthesis of **1**[6] from 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (**2**) and 2.1 equivalents of methyllithium furnishes **1** as a 3% solution in ether. However, for many reactions **1** is required free of solvent or in solvents different from ether. Pure **1** can be obtained by preparative gas chromatography[2]. Modifications of our original procedure using **2** and lithium powder in *n*-decane/triglyme[6] or *n*-butyllithium in tetramethylethylenediamine[7] have afforded **1** in yields of 25–38% (purity 70–75%) and ca. 40%, respectively.

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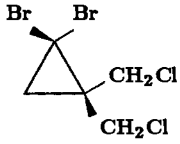

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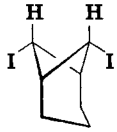

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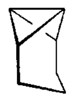

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Na$^+$[I(CN)$_2$]$^-$

6

We have now found a simple method of preparing highly pure **1** in yields exceeding 50% with respect to **2** by reaction of 1,3-diiodobicyclo[1.1.1]pentane (**3**)[2,8] with sodium cyanide in DMSO. Diiodo compound **3** is obtained by reaction of iodine dissolved in pentane with a 3% solution of **1** in ether at −20°C. The best results are recorded when the reaction vessel is irradiated with a 200-W incandescent lamp during addition of the iodine solution. The yield of purified **3** is 61%, it can be stored at −20°C in the dark for several months without noticeable decomposition.

When **3** is treated with 2.0 equivalents of sodium cyanide in [D$_6$]DMSO a yield of 90% of **1** (determined by ^{1}H-NMR integration with an internal standard) is obtained. Compound **1** is distilled from this mixture in vacuo (ca. 10^{-1} Torr) and collected in a nitrogen-cooled flask to afford **1** in yields of 82–88%. Between the reaction flask and the nitrogen-cooled trap an additional trap is placed and kept at −20°C. In this trap volatile parts of the solvent are completely retained. Solid **1** polymerizes spontaneously when melting under nitrogen. This behavior has been observed previously with [1.1.1]propellanes of high purity[9]. In the presence of approximately 0.1% hydroquinone **1** can be kept under nitrogen at room temperature for at least 30 minutes without noticeable polymerization[10]. Propellane **1** is free from impurities according to 400-MHz ^{1}H- and ^{13}C-NMR spectra.

Concerning the mechanism of the formation of **1**, a nucleophilic attack of a cyanide ion at one of the iodine atoms in **3** is most probable, leading to a concerted loss of cyanogen iodide and an iodide ion. A similar type of reaction has been reported by Mazur et al.[11] to occur with 6,7-diiodobicyclo[3.1.1]heptane (**4**) which is converted into tricyclo[4.1.0.0^{2,7}]heptane (**5**) by reaction with sodium cyanide in DMSO. Very recently, Wiberg[12], has observed the formation of **1** from **3** by nucleophilic attack of a hydroxide ion in ethanol. As a pseudohalogen cyanogen iodide is expected to react quickly with **1**. This has been confirmed by an independent experiment in which cyanogen iodide is added to a solution of **1** in [D$_6$]DMSO. ^{1}H-NMR monitoring shows that **1** is completely consumed within minutes. However, when the experiment is conducted with a mixture of cyanogen iodide and 2.0 equivalents of sodium cyanide the intensity of the ^{1}H-NMR signal of **1** at $\delta = 2.05$ remains nearly constant for several hours. An obvious explanation for this result is the complexation of cyanogen iodide with sodium cyanide to give sodium dicyanoiodate(I) (**6**). Indeed, this complex is known from the work of Tebbe et al.[13]. The formation of **1** by the reaction of **3** with 2.0 equivalents of sodium cyanide implies that cyanogen iodide is quickly complexed by the second equivalent of sodium cyanide. A ^{13}C-NMR investigation of independently prepared complex **6** in [D$_6$]DMSO and of our reaction mixture leading to **1** has proved the presence of **6** in this mixture. Additional indirect support for the removal of cyanogen iodide by complexation with a cyanide ion is obtained when **3** is treated with only 1.0 equivalent of sodium cyanide. In this case the yield of **1** drops to 30%[14].

We thank the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for support of this work.

Experimental

1. *1,3-Diiodobicyclo[1.1.1]pentane* (**3**)[2]: To a magnetically stirred solution of **1** (7.67 g, 0.116 mmol) in ether, prepared from 49.2 g (0.166 mol) of **2** and 300 ml of 1.16 M methyllithium[6], was added dropwise a solution of 29.4 g (0.116 mol) of iodine in 1.2 l of pentane/ether (5:1) at −20°C. During the addition of iodine the reaction flask was irradiated with a 200-W incandescent bulb. After warming to room temperature, the solution was washed with aqueous sodium thiosulfate and dried with $MgSO_4$. The solvent was removed in vacuo, and the remaining crude **3** (35.8 g, 67% related to **2**) was purified by washing with 100 ml of cold pentane affording 32.3 g (61%) of **3**, the ^{1}H-NMR spectrum of which was free from any signals of impurities. – ^{1}H NMR ($CDCl_3$): $\delta = 2.65$ (s).

2. *Solvent-Free [1.1.1]Propellane* (**1**): Under nitrogen 4.80 g (15.0 mmol) of **3** was added to 1.62 g (33.1 mmol) of sodium cyanide in 50 ml of DMSO (dried by distillation from CaH_2), and the mixture was stirred for 30 min. The flask was connected with a cooling trap (−20°C) and a Schlenk flask, cooled with liquid nitrogen and charged with 1.5 mg (0.014 mmol) of hydroquinone[15]. Distillation of the volatile material was maintained for 45 min at room temperature and at ca. 10^{-1} Torr affording 0.81–0.83 g (82–84%) of a colorless liquid which was pure **1** according to ^{1}H- and ^{13}C-NMR spectroscopy. In a further experiment using 20.0 g (62.5 mmol) of **3** and 9.21 g (188 mmol) of sodium cyanide, **1** was obtained in a yield of 3.63 g (88%). – ^{1}H NMR (C_6D_6): $\delta = 1.77$ (s). – ^{13}C NMR (C_6D_6): $\delta = 1.23$ (s), 73.91 (t).

3. *^{13}C-NMR Experiments on Sodium Dicyanoiodate(1)* (**6**): The ^{13}C-NMR spectrum of independently prepared **6**[13a] in $[D_6]$DMSO showed a sharp singlet at $\delta = 100.2$. Addition of sodium iodide caused a broadening of this signal. A mixture obtained by the reaction of **3** with 2.2 equivalents of sodium cyanide in $[D_6]$DMSO showed (besides the signals of **1**) a broadened singlet at $\delta = 98.5$. A mixture of the two solutions gave one broadened singlet at $\delta = 104.9$.

RAS Registry Numbers

1: 35634-10-7 / **3**: 105542-98-1

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[14] The formation of **1** from **3** can also be affected by use of other nucleophiles. So far, sodium thiophenolate and triphenylphosphane led to yields of **1** inferior to those obtained with sodium cyanide.

[15] An even coverage of the flask walls with hydroquinone was achieved by charging the flask with 0.7 ml of a 0.019 M solution of hydroquinone in ether and removing the solvent in a nitrogen stream.

[488/91]