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SHORT COMMUNICATION

Bridgehead derivatives of bicyclo [1.1.0] butane

The chemistry of bicyclo[1.1.0]butanes is the subject of recent reviews[1,2]. Bridgehead lithium derivatives of some substituted bicyclo[1.1.0]butanes have been prepared[3,4] and the synthesis of 1-lithiobicyclo[1.1.0]butane has been mentioned[5]. We would like to report our results on the synthesis of 1-lithiobicyclo[1.1.0]butane and the corresponding trimethylsilyl derivative. The former was prepared from bicyclo[1.1.0]butane and n-propyllithium in diethyl ether. Subsequent reaction with trimethylchlorosilane produced the latter in good yield. The relative stability of 1-lithiobicyclo[1.1.0]butane in diethyl ether (compared to other tertiary alkyllithium reagents) can be attributed to the high degree of *s*-orbital character at the bridgehead position[1].

Experimental

Bicyclo[1.1.0]butane[1] was manipulated by a vacuum system. Reactions were performed under an atmosphere of prepurified nitrogen. Infrared spectra were obtained on a Perkin Elmer Model 21 spectrophotometer. Gas chromatography was done on an F & M Model 700 chromatograph using a $6\frac{1}{2}' \times \frac{1}{4}''$ column packed with 10% Apiezon L on 60–80 Mesh chromosorb P. The nuclear magnetic resonance spectrum was recorded with a Varian A-60 spectrometer. Elemental microanalysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

1-*Lithiobicyclo*[1.1.0]*butane and* 1-(*trimethylsilyl*)*bicyclo*[1.1.0]*butane*. To a three-necked flask was added 21.3 ml (32 mmole) n-propyllithium[6] in diethyl ether. The flask was cooled by a liquid nitrogen bath and evacuated. Bicyclo[1.1.0]butane (16 mmole) was condensed into the flask. The solution was allowed to warm to 0° and stirred for 16 h at 0–16° and for 7 h at 0°. To the cold solution was added dropwise 3.5 g (32 mmole) trimethylchlorosilane in about 5 ml anhydrous ether. The flask was packed in ice and allowed to warm to room temperature with continued stirring for 3 days. Volatiles were removed by a bulb-to-bulb distillation, then analyzed and fractionated by gas chromatography. The major product (79% based on bicyclo[1.1.0]butane) had n_D^{25} 1.4284. (Found: C, 66.77; H, 11.21; Si, 21.98. $C_7H_{14}Si$ calcd.: C, 66.59; H, 11.18; Si, 22.24%.) The infrared spectrum contained bands at 835 vs, 855 vs, and 1248 s characteristic of the trimethylsilyl group and a band at 3020 w cm^{-1} characteristic of a hydrogen atom bonded to a strained carbon atom. The absence of any band from 1500 to 2800 cm^{-1} indicated the absence of a carbon–carbon double bond. As expected, the compound decolorized iodine in carbon tetrachloride solution.

The proton nuclear magnetic resonance spectrum consisted of four peaks with areas in the ratio 9:2:2:1 at 0 (s), 0.3 (s), 1.2 (~d) and 1.4 (~t) ppm, respectively (up field from tetramethylsilane). The peak at +0.3 ppm is assigned to the two *exo* protons (H_b, Fig. 1) by analogy with the spectrum[7] of tricyclo[$4.1.1.0^{2,7}$]heptane where the protons can be only *exo*. The peak at +1.2 ppm is accordingly assigned to the two *endo* protons (H_a). The peaks at 0 and 1.4 ppm are assigned to the methyl protons and the bridgehead hydrogen atom, respectively.

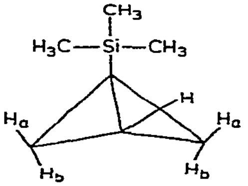

Fig. 1.

1-(Trimethylsilyl)bicyclo[1.1.0]butane was found to undergo no change (infrared spectrum) on storage for 18 months at +10°. No evidence was found for the disubstituted 1,3-bis(trimethylsilyl)bicyclo[1.1.0]butane.

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Norton Exploratory Research Division,
National Research Corporation,
Cambridge, Massachusetts 02142 (U.S.A.)

HARVEY M. COHEN

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