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TETRACYCLO[5.2.0.$0^{1,6}$.$0^{2,7}$]NONANE, A [2.1.1]PROPELLANE DERIVATIVE AS A REACTION INTERMEDIATE

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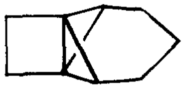
Summary: The reaction of 1-bromo-7-(2-chloroethyl)tricyclo[4.1.0.$0^{2,7}$]heptane (3d) with n-butyllithium (BuLi) in ether led, inter alia, to the formation of the ether 4a as the main product. The deuterated dibromide 10 and BuLi in ether gave rise to a 1:1 mixture of 4b and c, indicating that the title compound 1 was a reaction intermediate.

Whereas [1.1.1]propellanes are now easily accessible,[1] [2.1.1]propellanes have remained quite elusive compounds.[2] We report here on observations made while attempting to synthesize the propellane 1. Furthermore, it is shown that the [3.1.1]propellane 2 can be obtained without difficulty.

As starting material for the intended synthesis of 1, the alcohol 3a[3] was chosen and converted into 3b by two equiv. of BuLi. Subsequently, 3b was transformed to the bromoalcohol 3c by one equiv. of p-toluenesulfonyl bromide (TsBr).[4] The use of two equiv. of TsBr led to a 53% yield of the dibromide 3e (see Scheme 1). 3d was prepared from 3c in 77% yield by refluxing 3c with 1.2 equiv. of triphenylphosphine in CCl_4.[5]

When 3d was treated with BuLi in ether/pentane (1:3) at -40°C, aqueous workup led to 3f. This result indicated that although the bromine lithium exchange between 3d and BuLi had occured, the cyclization affording 1 required higher activation than available at this temperature. Therefore, the reaction was repeated at 20°C, furnishing a 57% yield of the "ether adduct" 4a. By-products were 5 (2%), 6a (2%) and 6b (1%). The compounds were separated by preparative GC (4 m column, 20% Silicon GE SE-30 on kieselguhr); their structures are based on the NMR and mass spectra. The same products were formed, when the dibromide 3e was used instead of 3d. When the reaction of 3d and BuLi was carried out in tetrahydrofuran as solvent, 7 was obtained as the main product in 50% yield.



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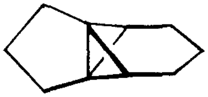

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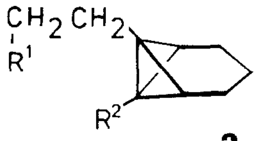

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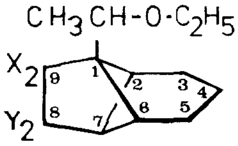

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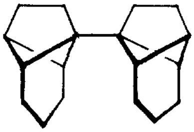
a: X = Y = H

b: X = D, Y = H

c: X = H, Y = D

3	a	b	c	d	e	f
R^1	OH	OLi	OH	Cl	Br	Cl
R^2	H	Li	Br	Br	Br	H



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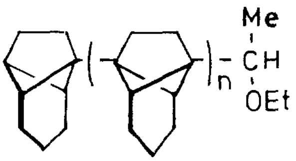

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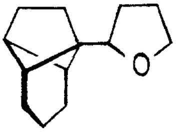
a: n = 1

b: n = 2



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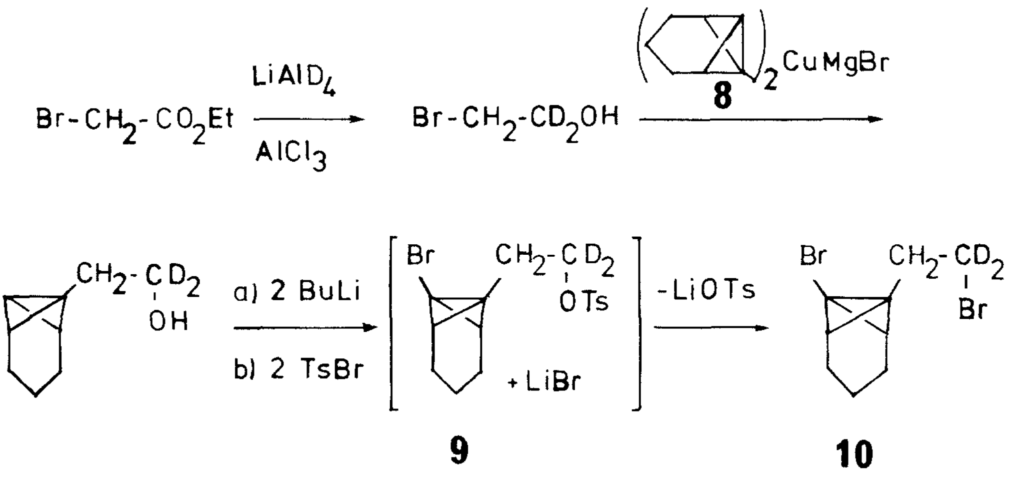
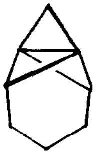
In order to provide further evidence for the intermediacy of 1, the deuterated dibromide 10 was synthesized as shown in Scheme 1. Reagent 8 was prepared from 1-tricyclo[4.1.0.0^{2,7}]-heptylmagnesium bromide and a catalytic amount (2%) of CuBr·SMe$_2$. The bromine atoms of 10 were introduced in one step by using two equiv. of TsBr. The unisolated tosylate intermediate 9 ob-

Scheme 1



viously reacted with LiBr affording a 47% yield of 10. When 10 was treated with BuLi in ether, a 1:1 mixture of 4b and c was formed as the major product. The deuterium distribution followed from the ^{13}C NMR spectrum of 4b/c, in which the intensities of the signals of C-8 and C-9 at δ = 25.69 and 26.44 were reduced to half of those of the corresponding signals of 4a. Further, the C-8 and C-9 signals of the 4b/c mixtures were accompanied by low intensity quintets.

The formation of 4a, of 7 and of the equimolar mixture of 4b/c support the assumption that the [2.1.1]propellane 1 is generated by the reaction of BuLi with 3d. In contrast to the [3.1.1]propellane 2 and the [1.1.1]propellane 11,[1] 1 is too reactive to be isolated.[6] A probable mechanism for the formation of 4a might be a radical chain process with the radicals 12 and 13 as chain carriers. It would also explain the formation of 6a and 6b, not, however, of 5.



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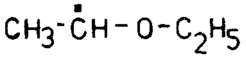
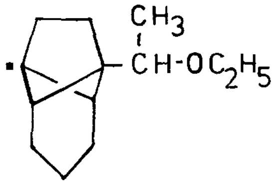


$CH_3\text{-}\dot{C}H\text{-}O\text{-}C_2H_5$

12



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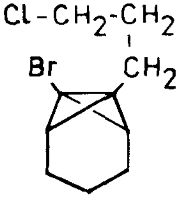
The synthesis of 2 was achieved in 52% yield by reacting 14 with BuLi in ether. The alcohol 15, the precursor of 14, was obtained in 58% yield from 8 and 3-bromopropanol. 15 was converted into 14 in two steps in analogy to the synthesis of 3d from 3a. The spectroscopic data of 2 are in accord with the propellane structure. 2 proved to be highly sensitive towards traces of electrophilic catalysts. When kept in C_6D_6 in an NMR tube, 2 slowly isomerized to the 1,3-diene 16.[7] We have previously encountered this type of [3.1.1]propellane isomerization.[8]



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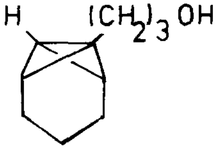

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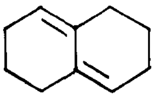

16

Table 1. Selected NMR Data of **4a**, **5**, **6a**, **6b**, **7**, **2**, and **16**

4a: ^{1}H NMR (CDCl$_3$) δ = 1.07 (t, J = 6.7 Hz, 3 H), 1.15 (t, J = 6.1 Hz, 3 H), 1.41-1.92 (m, 12 H), 2.28 (s, 1 H), 3.23-3.63 (m, 2 H), 3.69 (q, J = 6.1 Hz, 1 H).
^{13}C NMR (C$_6$D$_6$) δ = 14.35, 16.12 (2 q), 16.42, 21.69, 21.84, 25.69, 26.44 (5 t), 40.59, 47.20, 47.89 (3 d), 55.61 (s), 64.06 (t), 71.36 (d).

5 ^{13}C NMR (C$_6$D$_6$) δ = 16.99, 25.17 (4 C), 25.72, 31.69 (4 t), 49.19, 51.13 (4 C) (2 d), 53.04 (s).

6a: ^{1}H NMR (CDCl$_3$) δ = 0.71-2.17 (m, 30 H), 2.28 (s, 1 H), 3.14-3.93 (m, 3 H).

6b: ^{1}H NMR (CCl$_4$) δ = 0.99 (t, J = 7 Hz, 3 H), 1.08 (t, J = 7 Hz, 3 H), 1.29-2.16 (m, 36 H), 2.28 (s, 1 H), 3.00-3.69 (m, 3 H).

7: ^{1}H NMR (C$_6$D$_6$) δ = 1.17-2.06 (m, 16 H), 2.23 (s, 1 H), 3.63-3.86 (m, 2 H), 3.97 (t, J = 7.4 Hz, 1 H).
^{13}C NMR (C$_6$D$_6$) δ = 16.39, 21.66, 22.14, 25.78, 26.17, 26.56, 26.99 (7 t), 40.86, 47.19, 48.07 (3 d), 54.10 (s), 68.12 (t), 75.90 (d).

2: ^{1}H NMR (C$_6$D$_6$) δ = 1.07-2.25 (m, 12 H), 2.99 (broadened s, 2 H).
^{13}C NMR (C$_6$D$_6$) δ = 21.11, 22.84 (2 C), 31.83 (2 C) (3 t), 35.04 (s), 41.50 (t), 63.30 (d).

16: ^{13}C NMR (C$_6$D$_6$) δ = 23.84, 26.32, 31.59 (3 t), 122.58 (d), 134.54 (s).

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