19. 1,7-Trimethylenenorbornane. A Novel Member of the 'Adamantaneland'

Preliminary communication

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Dedicated to Professor Dr. *Edgardo Giovannini* on the occasion of his seventieth birthday

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Summary

A synthesis of the novel $C_{10}H_{16}$ hydrocarbon 1,7-trimethylenenorbornane (**13**), one of the 19 members of the adamantane family, is described.

1,7-Trimethylenenorbornane (**13**)[1]) is a member of the 'adamantaneland' [1], a set of 19 isomeric tricyclic $C_{10}H_{16}$ compounds. In the present communication we describe a synthesis of this hithertho unknown member[2])[3]). The dihydropentalene **2**, readily available by the reaction of 8,8-dibromobicyclo[5.1.0]octa-2,4-diene (**1**) with methyl lithium according to *Baird & Reese* [3], was chosen as suitable starting material. An obvious approach to construct the 1,7-trimethylenenorbornane skeleton is by a [4+2] cycloaddition of **2** and a ketene equivalent [4]. Addition of α-acetoxyacrylonitrile to the reaction mixture of **1** and methyl lithium in diethyl ether at -40 to 0° yielded with full regio- and stereoselectivity in a 9:1 ratio **6**[4]) (an adduct of **2**) and **4** (an adduct of the isomerized triene **3** [3])[5]). Hydrogenation

[1]) Tricyclo[4.2.2.0^{1,5}]decane or 1,3a-Ethanoperhydropentalene.

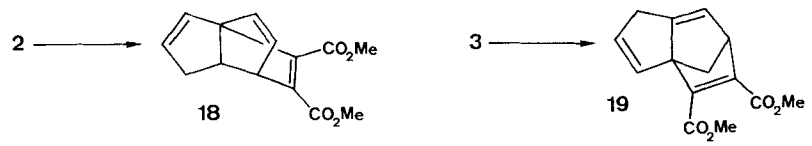
[2]) An analogous synthesis of **13** by *L. Skattebøl et al.* (University of Oslo) as well as studies on the *Lewis* acid catalyzed rearrangement of **13** by *Schleyer et al.* (University of Erlangen-Nürnberg) will be described by these authors elsewhere. We thank them for discussing results prior to publication.

[3]) For a recent synthesis of two other representatives see *e.g.* [2].

[4]) **6** can be separated from the reaction mixture of **6** and **4** by filtration on silicagel, subsequent recrystallisation and sublimation.

[5]) Addition of dimethylacetylenedicarboxylate to the dihydropentalenes **2** and **3** yielding the [4+2] cycloaddition products **18** and **19**, respectively, was already reported by *Baird & Reese* [3]. However no further transformations were described.

Scheme 2



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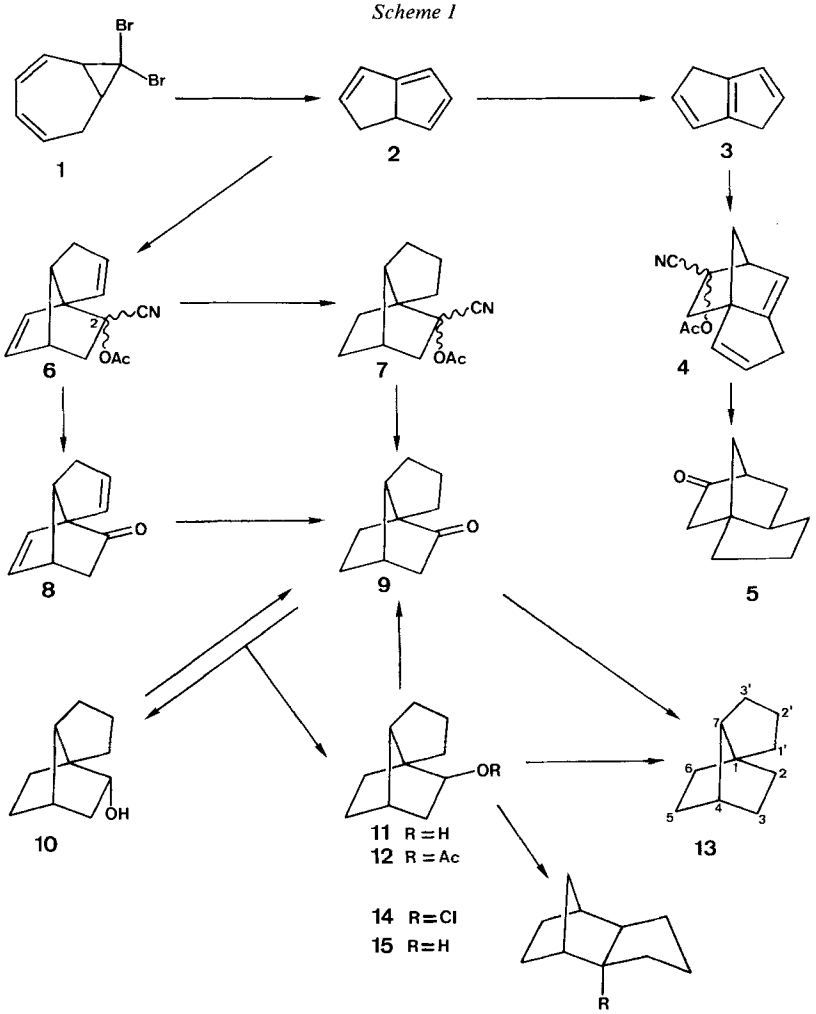
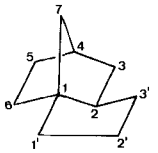
Scheme 1



in the presence of 5% $Pd/CaCO_3$ as a catalyst and subsequent hydrolysis in KOH/CH_3OH led to the saturated ketones **9** and the already known isomer **5** [5], which were easily separated by chromatography on silicagel. The ketone **9** was also obtained by inverting the reaction sequence, *i.e.* by first hydrolyzing **6** to the unsaturated ketone **8** and subsequently hydrogenating the latter. Conversion of ketone **9** to the title hydrocarbon **13** was achieved either by *Wolff-Kishner* reduction (approximately 30% overall yield relative to the starting material **1**) or by photochemical reduction of the acetate **12** in hexamethylphosphoric triamide (HMPT)/water 95:5 according to a procedure described by *Pète et al.* [6]. Reduction of ketone **9** with sodium borohydride in ethanol gave the *endo*- and the *exo*-alcohols **10** and **11** in a ratio of 1:4. Both were reconverted to ketone **9** on oxidation with pyridinium chlorochromate. The acetate **12** was formed from the alcohol **11** by standard treatment with acetic anhydride in pyridine.

The ^{13}C-NMR.-spectrum of **13** shows 10 signals: 7 triplets, 2 doublets and 1 singlet[6]). Only two other members of the adamantane family are also consistent with this multiplicity. As **13** they are trimethylenenorbornanes, the 1,2*exo*-hydrocarbon **16** [1b][7]) and its 1,2*endo*-isomer **17**[8]). Further evidence for the 1,7-trimethylene-

Scheme 3



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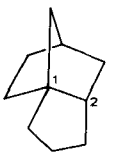

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norbornane skeleton of the compounds **6**–**13** is given by the ^{1}H- and ^{13}C-NMR.-spectra of the primary cycloaddition product **6**[9]) indicating 4 olefinic C-atoms each bearing one H-atom in contrast to the spectral data of adduct **4**[10]).

The orientation of the trimethylene bridge towards C(2) is deduced from the result of reducing ketone **9**, where a preferred attack of sodium borohydride from below was observed (**10**/**11** 1:4)[11]) and the ease of the quantitative rearrangement of the *exo*-alcohol **11** in thionylchloride at room temperature to **14**, which on reduction with magnesium and subsequent hydrolysis yielded the well known 2*exo*, 3*exo*-trimethylenenorbornane (**15**). On the other hand, the *endo*-alcohol **10** reacted much slower under analogous reaction conditions and gave a mixture (approx. 10:1) of the same chloride **14** and some not further identified chlorides.

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6) ^{13}C-NMR. ($CDCl_3$) of **13**: 21.51, 28.77, 29.04, 30.32, 32.30, 32.84 and 37.56 (7*t*, C(2), C(3), C(5), C(6), C(1'), C(2') and C(3')); 36.87 (*d*, C(4)); 60.47 (*d*, C(7)); 58.66 (*s*, C(1)).

7) ^{13}C-NMR. ($CDCl_3$) of **16**: 26.58, 28.76, 29.61, 33.74, 33.74, 40.04 and 41.13 (7*t*, C(3), C(5), C(6), C(7), C(1'), C(2') and C(3')); 39.29 (*d*, C(4)); 48.14 (*d*, C(2)); 56.49 (*s*, C(1)).

8) The synthesis of **17** will be described in a separate communication by *F.J. Jäggi & C. Ganter*, in preparation. ^{13}C-NMR. ($CDCl_3$): 23.26, 27.54, 27.68, 28.23, 29.87, 32.26 and 40.41 (7*t*, C(3), C(5), C(6), C(7), C(1'), C(2') and C(3')); 43.48 (*d*, C(4)); 53.62 (*d*, C(2)); 55.86 (*s*, C(1)).

9) ^{13}C-NMR. ($CDCl_3$) of **6**: 131.91, 133.45, 137.47 and 144.23 (4 *d*).

10) ^{13}C-NMR. ($CDCl_3$) of **4**: 112.12, 124.01 and 144.93 (3*d*); 164.06 (*s*).

11) In an unhindered case a ratio of approximately 9:1 in favour of an *endo*-alcohol would be expected; see *e.g.* [7].