J. Chem. Research (S),
1997, 132–133
J. Chem. Research (M),
1997, 0880–0894

Synthesis of an Areno-anellated [3.3.1]Propellane

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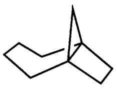
The reactivity of a highly strained [3.3.1]propellane **6** is exemplified by the addition of formic acid to the central C–C single bond.

Propellanes have stimulated a multitude of syntheses and investigations of their chemical and physical properties because of their fascinating topology. Small-ring propellanes are especially of interest with regard to their structure and reactivity, as they allow the study of effects of high ring strain and in some cases inverted carbon geometries.[1] Despite steric hindrance, the central C–C single bond of small-ring propellanes is, in practice, an available reaction site.

Addition of carboxylic acids is a typical method used to determine the reactivity of these single bonds: the [4.2.1]propellane **1** adds acetic acid with a half life of 1.6 h at 50 °C,[2] whereas the [3.3.1]propellane **2**[3] and the [3.2.1]propellane **3**[4] react rapidly at room temperature. The reactivity of other [3.3.1]propellanes[5–7] was only examined marginally. Here we report the facile synthesis and structure of an areno-anellated [3.3.1]propellane.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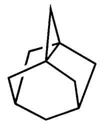
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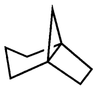
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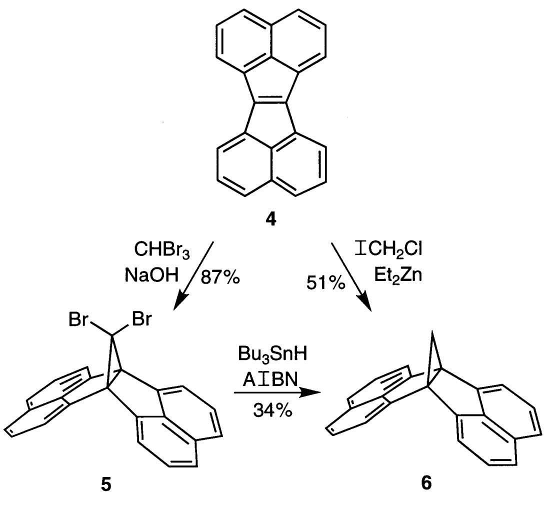
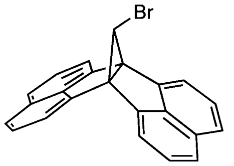
We tested two independent pathways to the [3.3.1]propellane **6** starting from the pentalene system **4**.[8,9] The reaction of **4** with dibromocarbene, generated *in situ* from tribromomethane and sodium hydroxide by phase-transfer catalysis, led to the formation of a poorly soluble powder in 87% yield, the mass spectrum of which was in accord with cycloadduct **5**. The transformation into hydrocarbon **6**, and at the same time the chemical proof of structure **5**, took place *via* radical hydrodebromination with tributyltin hydride. The partially dehalogenated compound **7** was isolated as a by-product.

Compared to this two-step procedure, the alternative one-step approach to **6** involving a Simmons–Smith reaction[10] proved to be superior because it gave a higher overall yield, although in this case the major by-product, the isopropyl-substituted hydrocarbon **8**, was formed in a side reaction, since the propellane **6** itself is stable under Simmons–Smith conditions. The mechanism for the formation of **8** is still unknown, but one can speculate that the isopropyl group is presumably formed *via* a methylene transfer involving C–H insertion into the ethylzinc group.

X-Ray crystal structure analysis[11] of the small-ring propellane **6** revealed an elongation of the central single bond C-6b–C-12b with a bond length of 155.4(2) pm compared to that in cyclopropane (152 pm). The geometry at the bridgehead carbon atoms is on the verge of being inverted; a slight pyramidalization was still observed: the carbon atom C-6b is only 6.0 pm out of the plane defined by the neighbouring carbon atoms C-6a, C-6c and C-13.



Scheme 1



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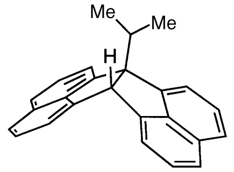

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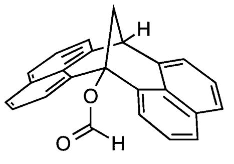

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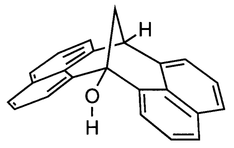

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Because of the distorted geometry at the bridgehead positions a pronounced reactivity was anticipated. In fact, the propellane **6** reacted slowly with formic acid at 95 °C (24 h reaction time). The formate **9** and the tertiary alcohol **10** were isolated as products of the addition reaction. Obviously, **10** is formed by hydrolysis of **9**, as the product ratio is shifted in favour of **10** with increasing reaction time.

From this result it is clear that **6** is somewhat less reactive towards the addition of carboxylic acids than the small-ring propellanes **1**, **2** and **3**.

Crystal data for **6**. $C_{23}H_{14}$, triclinic, space group $P\bar{1}$, $a = 770.38(12)$, $b = 881.9(2)$, $c = 1147.9(2)$ pm, $\alpha = 101.492(9)°$, $\beta = 107.875(9)°$, $\gamma = 93.999(11)°$, $V = 0.7201$ nm^3, $Z = 2$, $D_x = 1.339$ mg m^{-3}, λ(Mo-Kα) = 71.073 pm, $\mu = 0.08$ mm^{-1}, $T = -130$ °C.

Data collection and reduction. A colourless tablet $0.8 \times 0.7 \times 0.3$ mm was mounted in inert oil. Data were collected to $2\theta_{max}$ 50° with a Stoe SDADI-4 diffractometer. Of 2817 measured data, 2549 were unique.

Structure solution and refinement. The structure was solved by direct methods and refined anisotropically on F^2 by using

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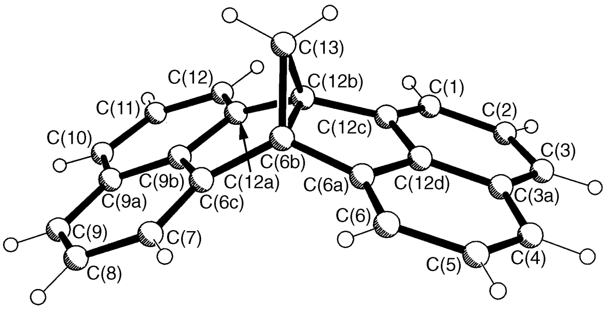

Fig. 1 Molecular structure of **6**

all reflections (program SHELXL-93, G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included by using a riding model. The final $wR(F^2)$ was 0.104 for 209 parameters, conventional $R(F)$ 0.038. $S = 1.04$; max. $\Delta/\sigma < 0.001$; max. $\Delta/\rho = 227$ e nm^{-3}.

Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Techniques used: IR, UV–VIS, ^{1}H and ^{13}C NMR, EI-MS, elemental analysis, X-ray analysis

Schemes: 1

Tables: 3

Figure: 1

Received, 23rd December 1996; Accepted, 10th January 1997
Paper E/6/08573C

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