134. The Adamantane Rearrangement of 1,2*endo*-Trimethylenenorbornane

Preliminary Communication

by **Alfred Michael Klester, Franz Josef Jäggi** and **Camille Ganter**

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule,
Universitätstrasse 16, CH-8092 Zürich

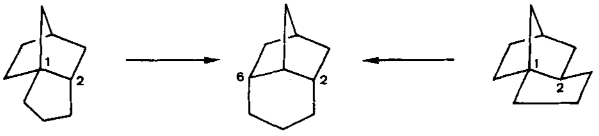
(4.VI.80)

Summary

1,2*endo*-Trimethylenenorbornane (**1**) in the presence of aluminium bromide in carbon disulfide at −60° isomerizes at a much higher rate than its 2*exo*-isomer **2** to 2*endo*,6*endo*-trimethylenenorbornane (**3**) as the sole product. By consequence, the hydrocarbon **2** being the next intermediate in the sequence of the adamantane rearrangement of **1** seems to be very unlikely.

In 1968 *Whitlock & Siefken* [1] described a map of interconversions of tricyclodecanes that contain all 10 carbon atoms within rings (no alkyl groups) and no three- and four-membered rings. Including stereoisomers, the 'adamantane-land' is composed of a set of 19 isomeric $C_{10}H_{16}$ hydrocarbons. On the basis of molecular mechanics (empirical force field calculations) on these tricyclodecanes and presumed cationic intermediates, *Schleyer et al.* [2] made predictions of the most likely pathways[1] leading from each isomer to adamantane. For the rearrangement of 1,2*endo*-trimethylenenorbornane (**1**)[2] its stereoisomer 1,2*exo*-trimethylenenorbornane (**2**)[3] was proposed as the next intermediate in the sequence.

Scheme



1 **3** **2**

---

[1] Darkened lines and arrows in the *Figure* (tricyclodecane graph) in [2].

[2] *endo*-**8** in the *Figure* (tricyclodecane graph) in [2]. For the synthesis of the novel hydrocarbon **1** see [3].

[3] *exo*-**8** in the *Figure* (tricyclodecane graph) in [2]. The *Lewis*-acid-catalyzed isomerization of **2** has already been studied by *Schleyer et al.* [2] and by *Farcasiu et al.* [4].

0018-019X/80/5/1294-02$01.00/0

Table. *$AlBr_3$-catalyzed rearrangements of* **1** *and* **2**

Run	Starting material	Temperature [°C]	Reaction time [Min]	Composition (%)[a]		
				1	**2**	**3**
1	**1**	−60	1	20	-	80
2	**2**	−60	1	-	≥95	≤ 5
3	**1**	−60	5	≤1	-	≥99
4	**2**	−60	5	-	≥95	≤ 5
5	**2**	−60	30	-	90	10

[a] Determined by VPC.

In the present communication we describe our preliminary results on the adamantane rearrangement of the *endo*-isomer **1**.

Treatment of **1** with aluminum bromide as catalyst (molar ratio approx. 2:1) in carbon disulfide at −60° yielded 2*endo*,6*endo*-trimethylenenorbornane (**3**)[4]) as the sole product. For comparison the *exo*-isomer **2** was treated under the same reaction conditions. The results are summarized in the *Table.*

The *endo*-isomer **1** rearranges at a much higher rate than **2** and in no experiment (runs 1 and 3) the *exo*-isomer **2** was found as a product. By consequence, **2** being the next intermediate in the sequence of the adamantane rearrangement of **1**, as proposed in [2], seems to be very unlikely. Mechanistic studies concerning the isomerization of **1** are under further investigation using also specifically labeled analogs of **1**.

Financial support by the *Swiss National Science Foundation* and *Ciba-Geigy AG,* Basel, is gratefully acknowledged.

REFERENCES

[1] *H. W. Whitlock, Jr. & M. W. Siefken,* J. Am. Chem. Soc. *90,* 4929 (1968).
[2] *E.M. Engler, M. Farcasiu, A. Sevin, J.M. Cense & P.v.R. Schleyer,* J. Am. Chem. Soc. *95,* 5769 (1973).
[3] *F.J. Jäggi & C. Ganter,* Helv. *63,* 866 (1980).
[4] *M. Farcasiu, E.W. Hagaman, E. Wenkert & P.v.R. Schleyer,* Abstract ORGN 187, 173rd ACS Meeting, New Orleans, La. (1977).
[5] *J.G. Henkel & L.A. Spurlock,* J. Am. Chem. Soc. *95,* 8339 (1973).
[6] *N. Takaishi, Y. Fujikura, Y. Inamoto & K. Agami,* J. Org. Chem. *42,* 1737 (1977).
[7] *Z. Majerski & J. Janjatović,* Tetrahedron Lett. *1979,* 3977.

---

[4]) Tricyclo[5.2.1.$0^{3,8}$]decane, 4-homobrendane [2] [5-7].