

182. The Aluminum-Bromide-Catalyzed Adamantane Rearrangement of *syn*- and *anti*-Tricyclo[4.2.1.1^{2,5}]decane

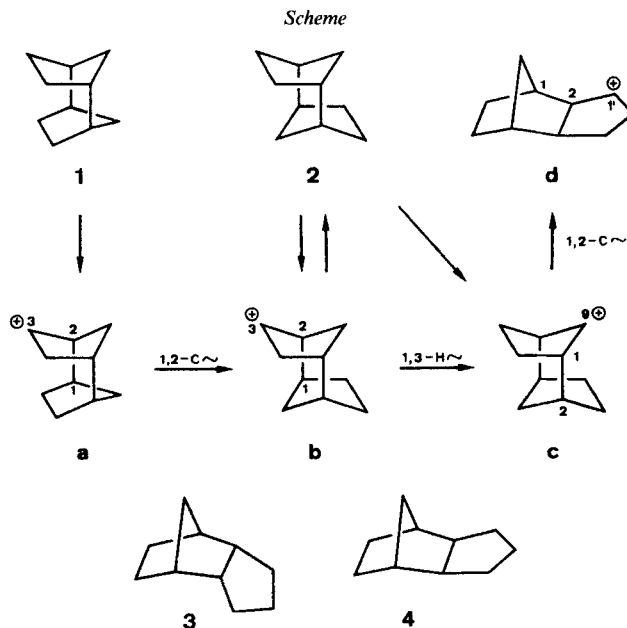
by **Marco Brossi**¹⁾ and **Camille Ganter**^{*}

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

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In the presence of AlBr_3 in CS_2 at temperatures below 0° , *syn*-tricyclo[4.2.1.1^{2,5}]decane (**1**) isomerizes exclusively to *anti*-tricyclo[4.2.1.1^{2,5}]decane (**2**) at a higher rate than the latter rearranges to 2-*exo*,3-*exo*-trimethylene-8,9,10-trinorbornane (**4**). However, at temperatures above 0° , the *anti*-isomer **2** isomerizes to **4** faster than **1** to **2** and **4**. As a consequence, hydride abstraction occurs at C(3) (\rightarrow carbocation **a**, which rearranges to carbocation **b** (*anti*-skeleton)) in the *syn*-isomer **1** and more readily at C(9) (\rightarrow carbocation **c**) than at C(3) (\rightarrow carbocation **b**) in the *anti*-isomer **2**.

Of the 19 isomeric $C_{10}H_{16}$ hydrocarbons of the adamantaneland [1-3], *syn*-tricyclo[4.2.1.1^{2,5}]decane (**1**) with two five-membered rings connected face-to-face at their 1- and 3-positions holds an extraordinary position. On the basis of empirical force-field calculations by *Schleyer et al.* [4], **1** is the member highest in energy (calc. $\Delta H_f^\circ = +0.96$



¹⁾ Present address: *Ciba-Geigy AG*, CH-4002 Basel.

kcal/mol²). It is closely related to *anti*-tricyclo[4.2.1.1^{2,5}]decane (**2**) (calc. $\Delta H_f^\circ = -8.76$ kcal/mol²) with two cyclopentane rings fused head-to-tail at their 1- and 3-positions. Both diastereoisomers **1** and **2** are synthetically accessible by different routes elaborated by ourselves [5] as well as by *Paquette et al.* [6] and *Eaton and Patterson* [7].

In view of the mechanistic interest, the behaviour of the *syn*-hydrocarbon **1** under *Lewis*-acid catalysis was already once the subject of a detailed investigation by *Paquette* and coworkers [8] who reported: 'No reaction was observed with AlBr₃ in CS₂ at 0°; heating solutions of **1** in CH₂Cl₂ with AlCl₃ for prolonged periods left the hydrocarbon unchanged'. On the basis of their results, the authors came to the following conclusion: 'The inability of the *syn*-tricyclo[4.2.1.1^{2,5}]decane ring system to undergo facile skeletal isomerization to thermodynamically less strained isomers appears to be unprecedented in 'adamantaneland'.'

From the fact that all other adamantane isomers so far studied undergo *Lewis*-acid catalyzed rearrangements, it seemed very unlikely that exclusively the *syn*-hydrocarbon **1**, indeed the most highly strained one, should not be able to rearrange to a thermodynamically more stable isomer. We, therefore, reinvestigated the behaviour of the *syn*-compound **1** on treatment with AlBr₃ in CS₂ (weight ratio 1:11) at various temperatures (–30 to +18°) and for different reaction times (5 to 60 min). Included in the studies were the corresponding *anti*-isomer **2** as well as for further informations the two 2,3-trimethylene-8,9,10-trinorbornanes **3** (2-*endo*,3-*endo*) and **4** (2-*exo*,3-*exo*). The results are listed in the *Table*. All four hydrocarbons **1–4** remained unchanged within 60 min at –78° (*Runs 1–4*), the *exo*-isomer **4** even at 18° (*Run 51*).

At –30°, the *syn*-isomer **1** slowly rearranged to the corresponding *anti*-isomer **2** (2% after 30 min and 4% after 60 min, respectively (*Runs 13* and *17*)), whereas the latter still remained unchanged under the same reaction conditions (*Runs 14* and *18*). However, faster than the isomerization **1**→**2** was the rearrangement **3**→**4**³⁾ (*Runs 7, 11, 15, and 19*).

The experiments at 0° and the ones at 18° unambiguously demonstrated that both, the *syn*-hydrocarbon **1** (in contrast to *Paquette*'s results [8]) as well as the *anti*-isomer **2**, indeed undergo well defined AlBr₃-catalyzed rearrangements, **1**→**2** (*Runs 25, 29, 32 and 36, 40, 44, 48, respectively*) being remarkably slower than **2**→**4** (*Runs 26, 33 and 37, 41, 45, 49, respectively*).

On the basis of the above results, especially the fact that the *syn*-hydrocarbon **1** rearranges already below 0° and exclusively to the *anti*-isomer **2** as well as the observation that the latter isomerizes only above 0° and in addition at a much higher rate under formation of the *exo*-hydrocarbon **4**, the following conclusion has to be drawn concerning the mechanistic pathways: the carbocation **b** with an *anti*-isomer skeleton obtained from the *syn*-compound **1** by hydride abstraction (→**a**) and subsequent rearrangement obviously differs from the one (**c**) formed directly from the *anti*-isomer **2**, i.e. both 1,2-C-bond migrations, **a**→**b** as well as **c**→**d**, have to proceed relatively fast in

²⁾ For comparison: the calc. ΔH_f° for adamantane is –32.50 kcal/mol [4].

³⁾ The isomerization of **3** (calc. $\Delta H_f^\circ = -12.31$ kcal/mol [4], –14.36 kcal/mol [9]; exp. $\Delta H_f^\circ = -14.38$ kcal/mol [10], –63.4 kJ/mol [11]) into **4** (calc. $\Delta H_f^\circ = -16.77$ kcal/mol [4]) with aluminum halides in a solvent was first studied by *Schleyer and Donaldson* [12]: 'In methylcyclohexane at the boiling point, compound **3** was isomerized by AlCl₃ to a mixture of 99.1% **4** and 0.9% **3**. Adamantane was not formed'.

Table. $AlBr_3$ -Catalyzed Rearrangements of 1–4

Run	Reactant	Temperature [°C]	Reaction time [min]	Composition [%] ^{a)}			
				1	2	3	4
1	1	– 78	60	100	–	–	–
2	2			–	100	–	–
3	3			–	–	100	–
4	4			–	–	–	100
5	1	– 30	5	100	–	–	–
6	2			–	100	–	–
7	3			–	–	98	2
8	4			–	–	–	100
9	1	– 30	15	100	–	–	–
10	2			–	100	–	–
11	3			–	–	97	3
12	4			–	–	–	100
13	1	– 30	30	98	2	–	–
14	2			–	100	–	–
15	3			–	–	95	5
16	4			–	–	–	100
17	1	– 30	60	96	4	–	–
18	2			–	100	–	–
19	3			–	–	89	11
20	4			–	–	–	100
21	1	0	5	100	–	–	–
22	2			–	100	–	–
23	3			–	–	72	28
24	4			–	–	–	100
25	1	0	15	97	3	–	–
26	2			–	99	–	1
27	3			–	–	48	52
28	4			–	–	–	100
29	1	0	30	89	11	–	–
30	3			–	–	–	100
31	4			–	–	–	100
32	1	0	60	77	21	–	2
33	2			–	67	–	33
34	3			–	–	–	100
35	4			–	–	–	100
36	1	18	5	93	5	–	2
37	2			–	33	–	67
38	3			–	–	11	89
39	4			–	–	–	100
40	1	18	15	84	13	–	3
41	2			–	12	–	88
42	3			–	–	1	99
43	4			–	–	–	100
44	1	18	30	83	15	–	2
45	2			–	2	–	98
46	3			–	–	–	100
47	4			–	–	–	100
48	1	18	60	71	25	–	4
49	2			–	–	–	100
50	3			–	–	–	100
51	4			–	–	–	100

^{a)} Yields ($\geq 90\%$) and compositions were determined by capillary GLC (SE 52). Some experiments were also carried out on a preparative scale (see *Exper. Part*).

comparison to a possible 1,3-H shift **b**→**c** and/or a hydride addition **b**→**2**. Hence, **b** is the most stable of the three carbocations **a**, **b**, and **c**⁴).

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Experimental Part

General. See [15].

General Procedures for Rearrangements with AlBr₃ in CS₂. a) *Analytical Scale.* Under Ar, to 30 µl of an AlBr₃ soln. (prepared from 100 mg of freshly sublimed AlBr₃ and 0.9 ml of CS₂) and 1.5 mg of decane (*Fluka puriss.*, reference substance for GLC) as internal standard, precooled to the appropriate temperature, a soln. of 3 mg of reactant in 30 µl of CS₂ (also precooled to the same temp.) was added under stirring. The reactions were quenched by adding 5 ml of Et₂O and 2 ml of pyridine (precooled to ca. – 100°) and subsequently 1 ml of H₂O. For workup, the solns. were washed with 2N HCl (2 ×), sat. Na₂CO₃ (1 ×), and sat. NaCl soln. (1 ×), dried (MgSO₄), and filtered through *Celite*. Yields: ≥ 90% (determined by cap. GLC (*SE 52*) according the ratio of reactant and/or products to internal standard). The compositions are given in the *Table*.

b) *Preparative Scale.* Procedure as above with ≥ 100 mg of reactant. After workup, the org. solvents were carefully removed by distillation through a *Vigreux* column, and the residue was distilled (Kugelrohr, 90°/15 Torr). The compounds were separated by prep. GLC (5% *SE-30*) and identified by MS, ¹H- and ¹³C-NMR.

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⁴) Carbocations on a C₁ bridge as in **c** are known to be relatively unstable [13] [14].