

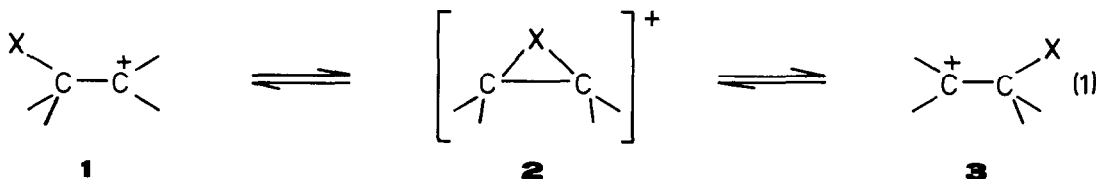
A CARBOCATIONIC 1,3-ALKENYL SHIFT

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Federal Republic of Germany**Summary:** The Lewis acid catalyzed rearrangement **7** \rightarrow **13** is explained by a carbocationic 1,3-alkenyl shift via the cyclobutylcarbanyl cation **10**.

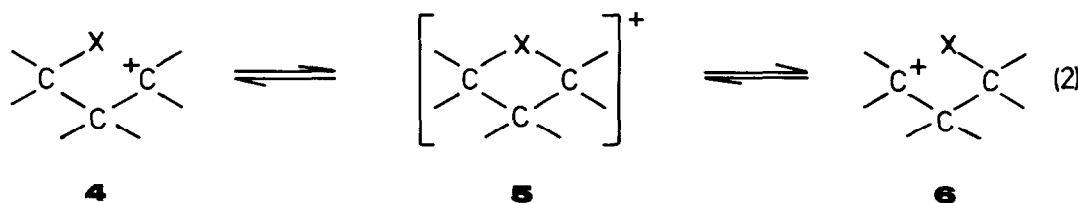
The high tendency to undergo rearrangements is one of the characteristics of carbocations [1]. In acyclic systems, 1,2-H and alkyl migrations usually have small barriers, in many cases below 3-4 kcal/mol (eq. 1). If X corresponds to vinyl or phenyl, the bridged species **2** (cyclopropylcarbanyl cations or phenonium ions) are often more stable than the acyclic isomers **1** and **3**.

Carbocationic 1,2-shifts

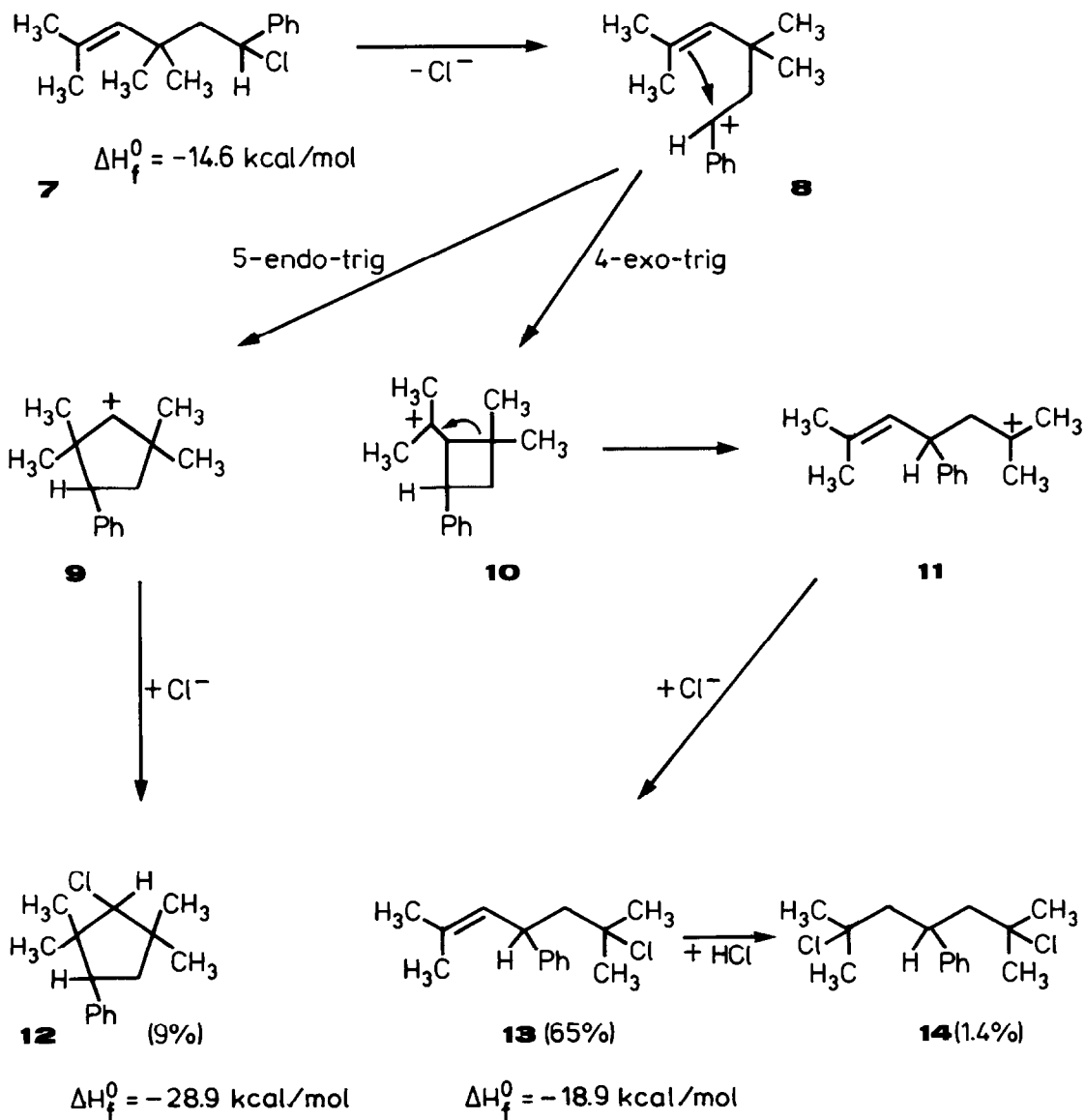


In contrast to the innumerable examples of 1,2-migrations, only few cases of 1,3-hydride shifts have been observed [2]. We report now on a carbocationic 1,3-alkenyl migration, to our knowledge the first example of this type of rearrangement.

Carbocationic 1,3-shifts



When **7**, the addition product of tetramethylallyl chloride with styrene [3], was treated with SnCl_4 at -90°C for 1 h, 9% of the cyclopentane derivative **12** were obtained besides the rearranged acyclic product **13** (65%) and a trace of **14** [4,5]. Compound **13** was inert under the reaction conditions, and all attempts to convert **13** into **12** by treatment with Lewis acids at elevated temperature led to polymeric material.



The reaction is suggested to proceed via cations **8** - **11**. The initially generated benzyl cation **8** can undergo a 5-endo-trig or 4-exo-trig cyclization [6] to give the cyclic carbenium ions **9** or **10**. Alternatively, the cyclopentyl cation **9**, which can be estimated to be thermodynamically more stable than **10** [3], may be formed via ring enlargement of **10**. The failure to detect five membered ring compounds different from **12** is explained by ion pairing effects, which inhibit 1,2-methyl shifts in **9**. Ring cleavage of the cyclobutylcarbinyl cation **10** may either regenerate the cation **8** or give the carbenium ion **11**, the precursor of the 1,3-migration products **13** and **14**.

Heats of formation of the isomers **7**, **12**, and **13** have been obtained by force field calculations [7]. The calculated enthalpy differences are large enough that a change of the stability order $12 > 13 > 7$ by entropy contributions can be excluded. The lower ground state enthalpy of **13** compared with **7** can account for the fact that **13**, once formed, cannot be converted into the thermodynamically most stable isomer **12**. The tertiary chloride derived from cation **10** was calculated to be less stable ($\Delta H_f^\circ = -12.2$ kcal/mol) than the isomeric compounds **7**, **12** and **13** in accord with the failure to detect derivatives of **10**.

The extremely mild conditions (-90°C), under which the cationic 1,3-migration $7 \rightarrow 13$ took place, indicate this type of rearrangement to have a very low barrier if the intermediate cyclobutylcarbinyl cation is of comparable stability as its acyclic precursor.

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References and Spectral Data

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- 2) a) Okazawa, N.E.; Sorensen, T.S., *Can. J. Chem.*, **1982**, 60, 2180. b) Saba, J.A.; Fry, J.L., *J. Am. Chem. Soc.*, **1983**, 105, 533. c) Proudfoot, J.R.; Djerassi, C., *J. Am. Chem. Soc.*, **1984**, 106, 5613.
- 3) Mayr, H.; Klein, H.; Kolberg, G., *Chem. Ber.*, **1984**, 117, 2555.
- 4) As described in ref. 3, rearrangements of **8** during the preparation of **7** can be avoided, when the life time of **8** is reduced by adding a tetraalkylammonium chloride to the reaction mixture.
- 5) 1-Chloro-2,2,5,5-tetramethyl-3-phenyl-cyclopentane **12**: mp $40 - 42^\circ\text{C}$ (pentane). - ^1H NMR (CDCl_3 , 200 MHz): δ 0.73 (s, 3 H), 0.97 (s, 3 H), 1.17 (s, 3 H), 1.21 (s, 3 H), 1.83 (dd, $J_{\text{gem}} = 13.1$ Hz, $J_{\text{trans}} = 6.9$ Hz, 1 H, 4-H), 2.21 (t, $J_{\text{gem}} = J_{\text{cis}} = 13.2$ Hz, 1 H, 4-H), 2.80 (dd, $J_{\text{cis}} = 13.2$ Hz, $J_{\text{trans}} = 6.9$ Hz, 1 H, 3-H), 3.77 (s, 1 H), 7.1 -

7.4 (m, 5 H). - ^{13}C NMR (CDCl_3): δ 16.5, 26.7, 28.3, 31.6 (4 q, CH_3), 38.5 (s, C-5), 43.4 (t, C-4), 48.0 (s, C-2), 51.3 (d, C-3), 81.0 (d, C-1), 126.6, 127.9, 128.8 (3 d, $\text{C}_o, \text{C}_m, \text{C}_p$), 139.3 (s, C_i). - 6-Chloro-2,6-dimethyl-4-phenyl-2-heptene **13**: bp 55 - 62°C (bath)/0.025 mbar. - ^1H NMR (CDCl_3 , 200 MHz): δ 1.48 (s, 3 H), 1.53 (s, 3 H), 1.67 (d, $J = 1.3$ Hz, 3 H), 1.70 (d, $J = 1.4$ Hz, 3 H), 2.14, 2.24, 3.88 (ABX-system of 5- H_2 and 4-H with $J_{AB} = 14.4$ Hz, $J_{AX} = 7.3$ Hz, $J_{BX} = 5.3$ Hz, and $J_{X,3} = 9.6$ Hz), 5.32 (br. d, $J = 9.6$ Hz, 1 H, 3-H), 7.1 - 7.4 (m, 5 H). - ^{13}C NMR (CDCl_3): δ 18.1, 25.8 (2 q, $(\underline{\text{CH}}_3)_2\text{C}=\text{C}$), 32.9, 33.4 (2 q, $(\underline{\text{CH}}_3)_2\text{CCl}$), 41.8 (d, C-4), 52.9 (t, C-5), 71.4 (s, C-6), 125.8 (d, C-3), 127.2, 128.5 (2 d, C_o, C_m), 129.6 (d, C_p), 130.7 (s, C-2), 146.4 (s, C_i). - 2,6-Dichloro-2,6-dimethyl-4-phenyl-heptane **14**: bp 50 - 56°C (bath)/0.004 mbar. - ^1H NMR (CDCl_3 , 200 MHz): δ 1.37, 1.45 (2 s, 12 H, 4 CH_3), 2.19, 2.25, 3.31 ($\text{A}_2\text{B}_2\text{X}$ -system of 3- H_2 , 5- H_2 and 4-H with $J_{AB} = 14.5$ Hz, $J_{AX} = 8.7$ Hz, $J_{BX} = 3.6$ Hz), 7.27 (mc, 5 H).

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