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A CARBOCATIONIC 1,3-ALKENYL SHIFT

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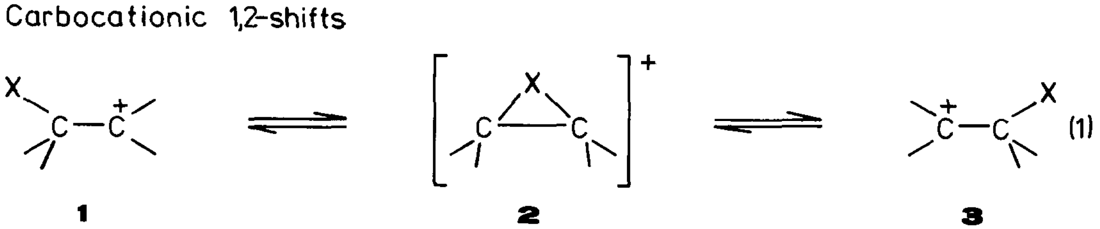
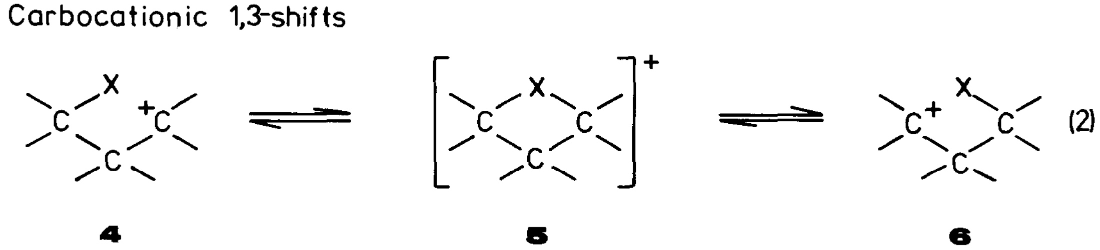
Summary: The Lewis acid catalyzed rearrangement **7** ⟶ **13** is explained by a carbocationic 1,3-alkenyl shift via the cyclobutylcarbinyl cation **10**.

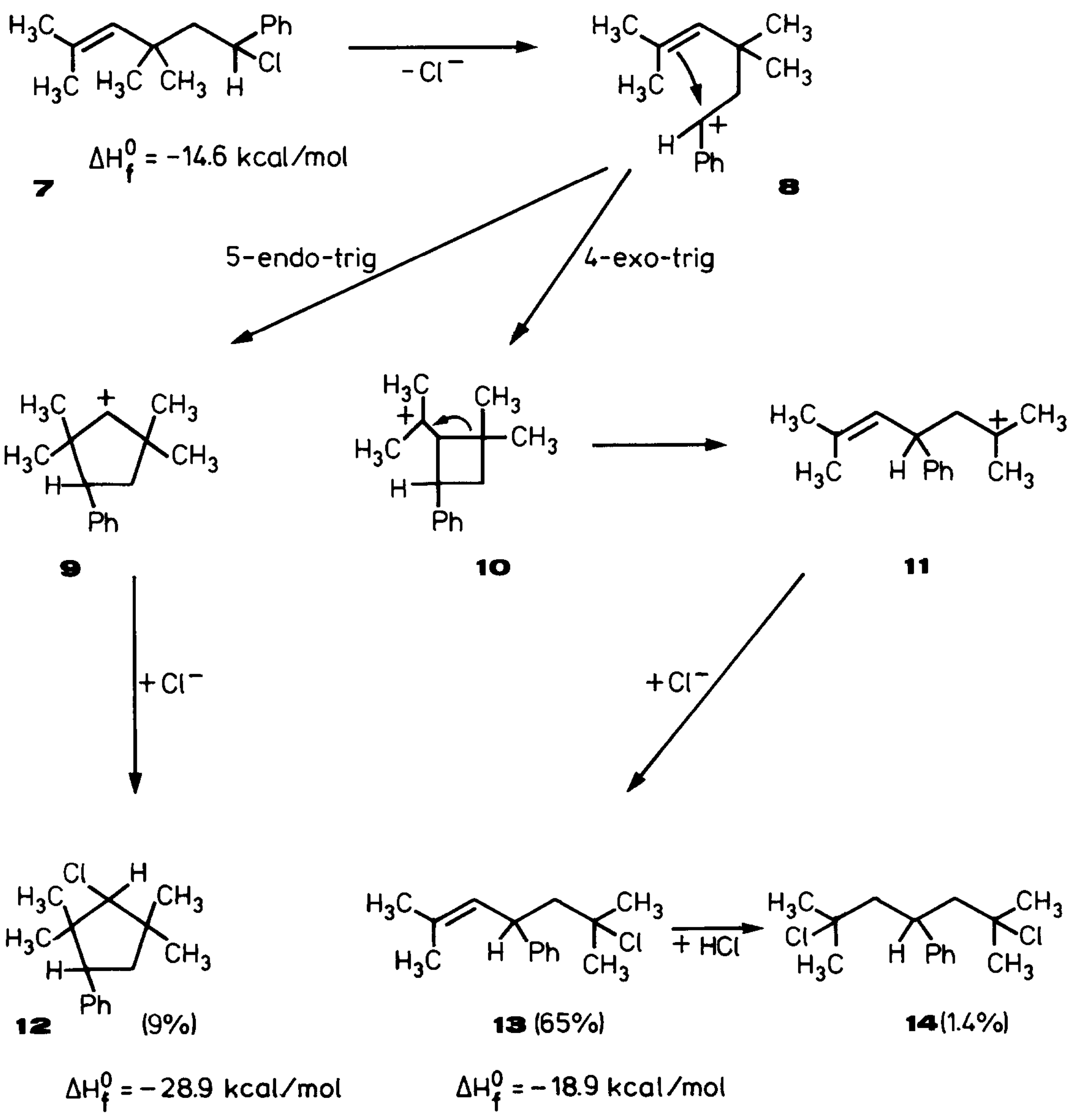
The high tendency to undergo rearrangements is one of the characteristics of carbocations [1]. In acyclic systems, 1,2-H and alkyl migrations usually have small barriers, in many cases below 3-4 kcal/mol (eq. 1). If X corresponds to vinyl or phenyl, the bridged species **2** (cyclopropylcarbinyl cations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



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.



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 (ΔH_f^o = -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** ---> **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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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°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_{gem} = 13.1 Hz, J_{trans} = 6.9 Hz, 1 H, 4-H), 2.21 (t, J_{gem} = J_{cis} = 13.2 Hz, 1 H, 4-H), 2.80 (dd, J_{cis} = 13.2 Hz, J_{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, C_o,C_m,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. - ^{1}H 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, $(\underline{C}H_3)_2C=$), 32.9, 33.4 (2 q, $(\underline{C}H_3)_2CCl$), 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. - ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.37, 1.45 (2 s, 12 H, 4 CH_3), 2.19, 2.25, 3.31 (A_2B_2X-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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