

STABILITY OF TRICYCLO[4.1.0.0^{2,7}]HEPTENYL-CATIONS

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In the series of C₇H₇-carbocations the monocyclic ion (1), the bicyclic ions (2)/(3) and the tetracyclic ion (4) are known, but not as yet, the tricyclic ion (5)²⁾



(1)



(2)



(3)



(4)



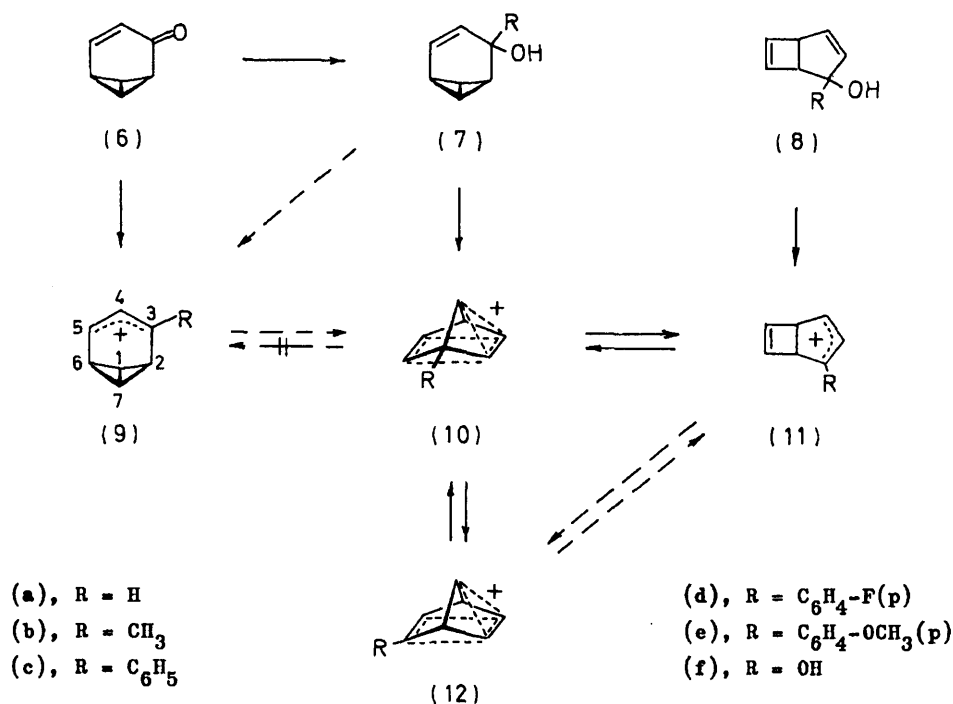
(5)

Considering the relative stabilities and rapid interconversions in this series as well as the high strain in (5) (E_s (bicyclo[1.1.0]butane) = 65 kcal/mole³⁾) the direct identification of (5) is problematic indeed; the more so, as the interaction between allyl- and bicyclobutane fractions of the molecule does not provide appreciable stabilisation: the relationship between LUMO φ_2 of the allyl-cation (C3-C4-C5) with HOMO a_1 of the bicyclo[1.1.0]butane-ring (C1-C2-C6-C7)⁴⁾ is nonbonding, with the "sub-jacent orbital" a_2 bonding, but energetically only slightly rewarding. The interaction φ_2 - a_2 is probably partially responsible for the transformations observed in the tricycloheptene-system. Consequently, under solvolytic conditions, the skeleton (5) remains intact only in strongly nucleophilic environments⁵⁾.

For direct characterisation of (5) and of stabilised derivatives under conditions of "long life"⁶⁾, the precursors (6)⁷⁾ and (7), synthesized recently in the Freiburg and Würzburg laboratories, seemed promising. First results are reported here.

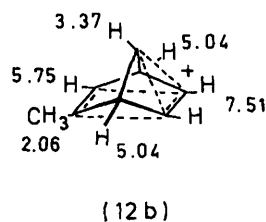
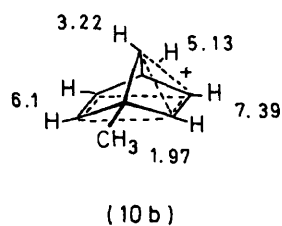
The carbinol (7a)^{5,7)} is dissolved in $\text{FSO}_3\text{H-SO}_2\text{ClF}$ at -120°C without noticeable decomposition; in the $^1\text{H-NMR}$ -spectrum recorded promptly, only the typical signals of the norbornadienyl-cation (10a)²⁾ are present. Because of the clear separation of some signals (cp. (9f)) even very small proportions of (9a) would have been detected. Under identical conditions with (7b)⁸⁾ first the 1-methyl-norbornadienyl-cation (10b) is

observed ^1H -nmr-spectroscopically, which—as well known⁹)—between -70° and -50°C rearranges into the isomeric norbornadienyl-cation (12b). The latter is accompanied by

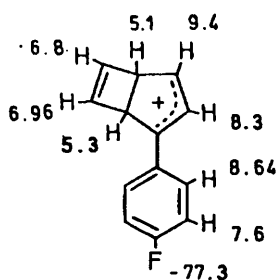


very small equilibrium concentrations of the bicyclo[3.2.0]heptadienyl-cation (11b). ^1H -nmr-spectra for the solution of the bicyclic carbinol (8b), prepared between -78° and -50°C and under identical conditions, indicate an analogous composition.

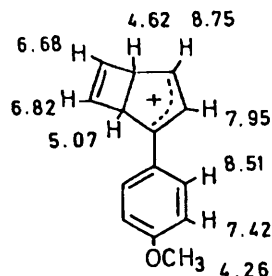
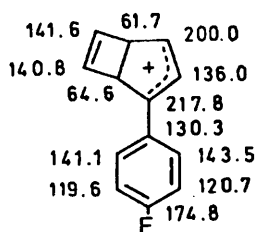
^1H -nmr data (δ , ppm) of the cations (10b) and (12b)



The aryl substituents in the carbinols (7c)-(7e) change the situation in a not unexpected way; according to the ^1H - and ^{13}C -nmr-spectra, measured between -120° and -20°C , the cations (11c)-(11e) are present exclusively. Only in the case of (7e) are there indications in favour of a precursor, which, however, is not (9e). The ions (11c)-(11e) are stable up to -20°C .

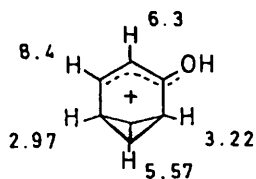
^1H -, ^{19}F -, ^{13}C -nmr data (δ , ppm) of the cations (11d) and (11e)

(11d)

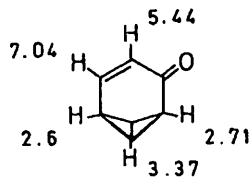


(11e)

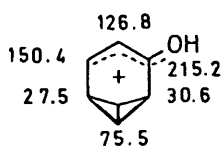
With respect to the original goal a pleasing observation results from the protonation of the ketone (6) in $\text{FSO}_3\text{H-SO}_2\text{ClF}$: between -120° and -60°C a species is formed, which by ^1H - and ^{13}C -analysis is clearly identified as the 3-hydroxytricyclo[4.1.0.0^{2,7}]heptenyl-cation (9f). As a consequence of the appreciable charge delocalisation -cp.

 ^1H -, ^{13}C -nmr data (δ , ppm) of (6) and the cation (9f)

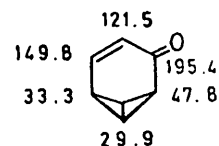
(9f)



(6)

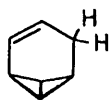


(9f)



(6)

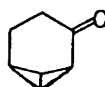
(6) and (9f)- and in agreement with the relative shifts in (13)/(6) or (14)/(15) and in (16)/(17) - besides H-5 ($\Delta\delta=1.36$ ppm) the protons H-1(7) ($\Delta\delta=2.2$ ppm) are most efficiently deshielded. This is equally pronounced in the ^{13}C -comparison between (6) and (9f) with $\Delta\delta\text{C-1(7)} = 45.6$ ppm.



(13)



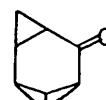
(14)



(15)



(16)



(17)

The substituent effects upon the stability of (5) as manifested in the examples (9) - (12) is qualitatively in line with the earlier observations with (4) ¹⁰. Only after massive diminution of the electron deficit by donor-substituents at C-3 - admittedly changing drastically the character of the ion (5) - is the driving force for rearrangements sufficiently weakened. No information is available yet concerning the detailed mechanisms of the transformations leading to the ions (10) and (11) ¹¹.

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- 11) Mechanistic studies are being undertaken.