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

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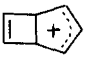
In the series of C_7H_7-carbocations the monocyclic ion (1), the bicyclic ions (2)/(3) and the tetracyclic ion (4) are known, but not as yet, the tricyclic ion (5)2).


(1)


(2)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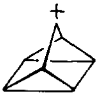
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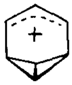
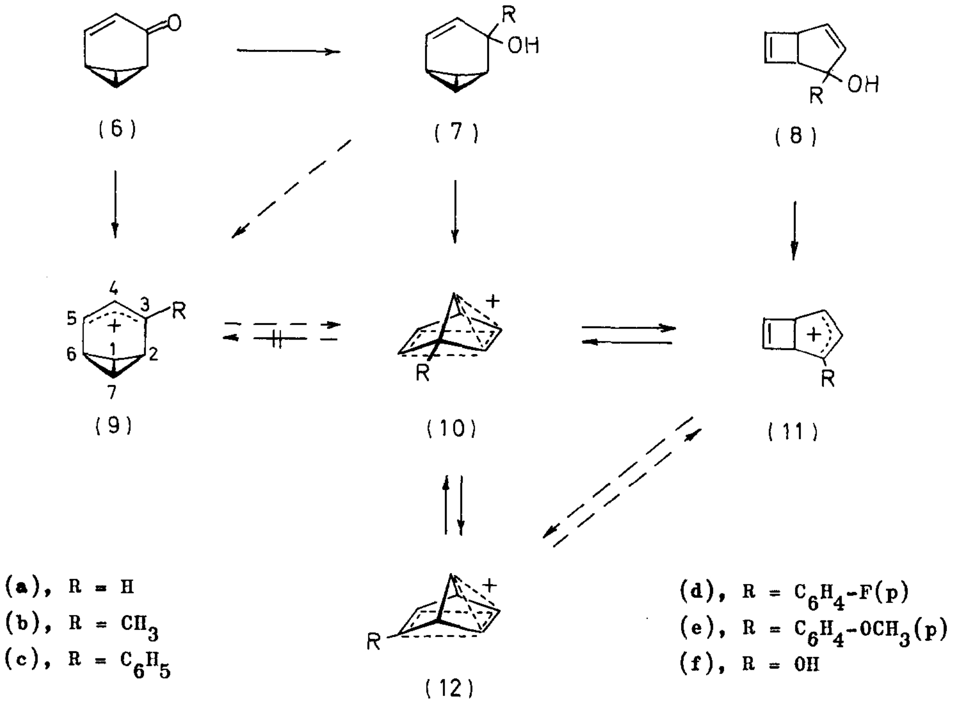

(5)

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/mole 3)) 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 "subjacent 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 FSO_3H-SO_2ClF at -120°C without noticeable decomposition; in the ^{1}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 ^{1}H-nmr-spectroscopically, which -as well known$^{9)}$- between -70° and -50°C rearranges into the isomeric norbornadienyl-cation (12b). The latter is accompanied by



(a), R = H
(b), R = CH_3
(c), R = C_6H_5
(d), R = C_6H_4-F(p)
(e), R = C_6H_4-OCH_3(p)
(f), R = OH

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

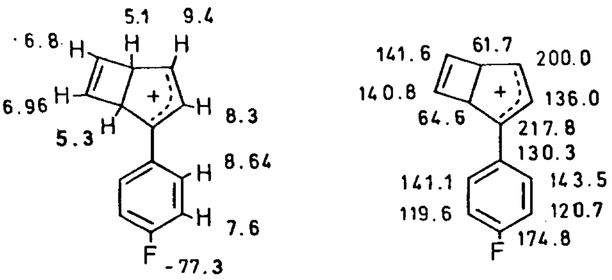
^{1}H-nmr data (δ, ppm) of the cations (10b) and (12b)

(10b)

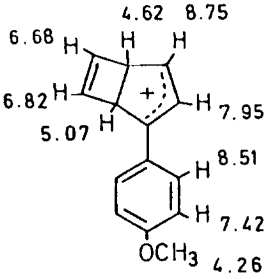
(12b)

The aryl substituents in the carbinols (7c)-(7e) change the situation in a not unexpected way; according to the ^{1}H- 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.

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



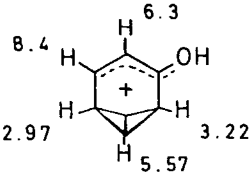
(11d)



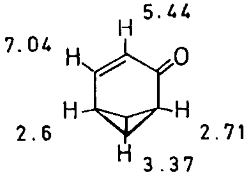
(11e)

With respect to the original goal a pleasing observation results from the protonation of the ketone (6) in FSO_3H-SO_2ClF: between -120^{0} and $-60^{0}C$ a species is formed, which by ^{1}H- 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. (6) and (9f)- and in agreement with the relative shifts in (13)/(6) or (14)/(15) and in (16)/(17) - besides H-5 (Δδ=1.36 ppm) the protons H-1(7) (Δδ=2.2 ppm) are most efficiently deshielded. This is equally pronounced in the ^{13}C-comparison between (6) and (9f) with ΔδC-1(7) = 45.6 ppm.

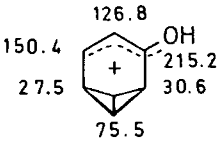
^{1}H-, ^{13}C-nmr data (δ, ppm) of (6) and the cation (9f)



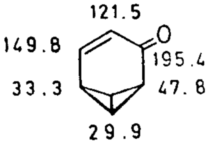
(9f)



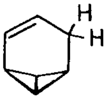
(6)



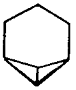
(9f)



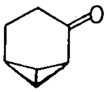
(6)



(13)



(14)



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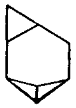

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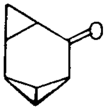

(17)

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 weakend. 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.