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ENDO-5-BROMO-1,2,3,4,5,6-HEXAMETHYLBICYCLO[2.1.1]HEXENYL CATION.

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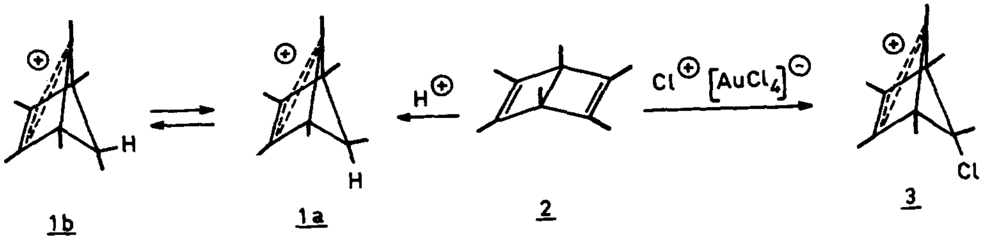
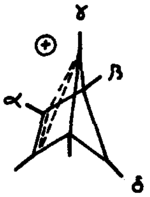
The formation of 1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hexenyl cations (1) by endo-protonation of hexamethylDewarbenzene (2) and their subsequent rearrangement was reported some time ago.[1] Recently the endo-5-chloro analog (3) was reported, which is obtained from reaction of $Cl^{\oplus}[AuCl_4]^{\ominus}$ with 2[2]. Upon addition of other electrophiles products are observed which are presumably derived from similar 1,2,3,4,5,6-hexamethyl-bicyclo[2.1.1]hexenyl cations.[3] However the addition of bromine to the parent Dewarbenzene[4] occurs without skeletal rearrangement, yielding 2,3-dibromobicyclo[2.2.0]hexenes.



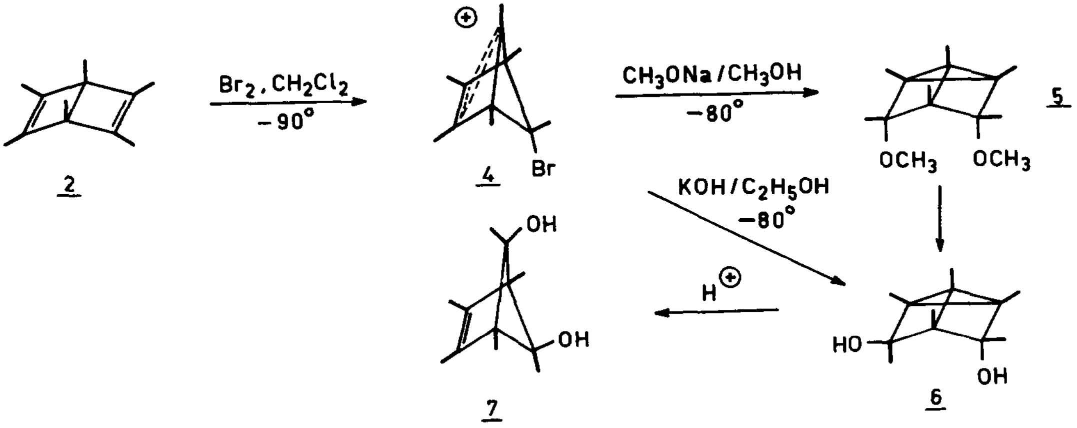
We wish to report here the exclusive formation of endo-5-bromo-1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hexenyl cation (4) from the reaction of a solution of 2 in methylene chloride with one eq. of bromine at -90°. It is assumed that 4 is formed from an endo attack of bromine on 2, as is the case with protons.[1b] Experimental evidence was not found for the alternative pathway, an *exo* attack, followed by rearrangement of the formed *exo*-5-bromo cation. The NMR spectral data of the solution of ion 4 in methylene chloride at -60° are presented in the table. The *endo* position of the bromine atom is assigned on the basis of comparison of the chemical shifts of the methyl groups of 4 with those of the *exo*- and *endo*-ions 1a and 1b as done previously for 3.[2]

	α	β	γ	δ
1b (*endo* CH_3)	2.10	1.68	1.39	0.80
1a (*exo* CH_3)	2.12	1.56	1.43	1.47
3 (*exo* CH_3)	2.27	1.68	1.58	1.95
4 (*exo* CH_3)	2.39	1.70	1.80	2.10

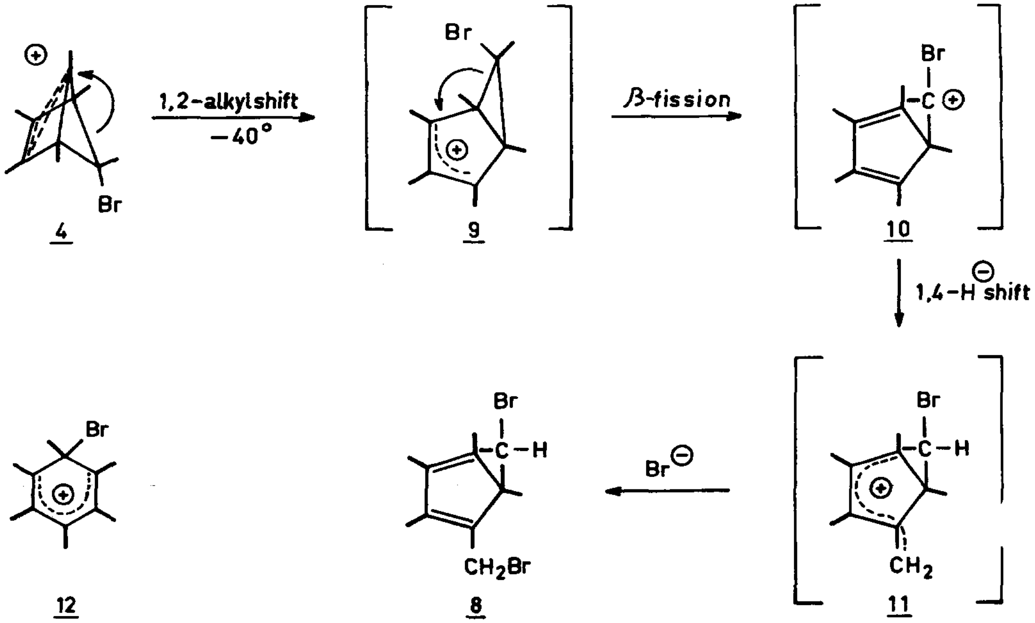


Upon pouring a solution of 4 at -80° in excess sodium methoxide/methanol, compound 5 was formed in 90% yield (determined by NMR). Structure 5[5] was assigned on the basis of the NMR spectrum (CCl_4): 3.12, 1.18, 1.07 (s, each 2 CH_3) 0.99 and 0.95 (s, each 1 CH_3) ppm. The shift enhancement upon addition of Eu(dpm)$_3$[6] is much larger for the peak at 0.99 than for the peak at 0.95 ppm, which can only be explained by assuming an *endo* position of the ether functions.[7] Upon standing in the air at room temperature 5 decomposes, yielding a reaction mixture containing methanol[8], one or more compounds with a terminal methylene group[8] and a major product (60%) for which structure 6 is proposed. This is based on the NMR spectrum (CCl_4) 1.28 (s, 1 CH_3) 1.10 to 1.00 (four partially overlapping s, each 1 CH_3) 0.92 (s, 1 CH_3)[9] ppm, IR spectrum (neat) 3435 cm^{-1} (broad absorption, OH), mass spectrum: strong peak at 178 (196 - H_2O)[10]. In the reaction of 4 with KOH/EtOH of -80°, 6 was formed also (80% yield). In a rapid acid catalysed reaction, which at room temperature even occurs on standing in the air, 6 isomerises to 7, which was identified by comparing the spectra (NMR, IR and mass) with those of authentic material.[11]

When a solution of cation 4 with $Br^\ominus$ as anion in methylene chloride was warmed up, no peaks were observed that could be ascribed to the *exo*-5-bromo isomer of 4. At -40° the spectrum of 4 disappeared and the NMR spectrum showed the presence of 8 (90%), but no intermediates were observed. Structure 8 was assigned on the basis of the following data: mass spectrum: peaks at 320, 322, 324 (1:2:1), IR spectrum: besides absorptions due to C-C and C-H weak absorptions at 1650 and 1620 cm^{-1} (C=C), UV spectrum: $\lambda_{max}^{pentane}$ 278 mμ[12], NMR spectrum (methylene chloride): 4.30 (q, J=7 cps. 1 H) 4.20 (s[13], 2 H) 1.90 (s[13], 2 CH_3) 1.82 (s[13], 1 CH_3) 1.31 (d, J=7 cps. 1 CH_3) 1.14 (s, 1 CH_3) ppm.



A mechanism rationalising the formation of 8 is shown below. In a way analogous to the reaction of the ions 1[1b] 4 conceivably isomerises via an 1,2 alkyl shift to 9, followed by β-fission to give 10. Subsequently 10 may give rise to an 1,4 hydrogen shift, yielding the highly stabilised ion 11, which can react with Br^- to yield 8. The intramolecular nature of the unusual 1,4 hydrogen shift is in agreement with the result of a high dilution experiment[14], in which it was shown that both the product (8) and its rate of formation are independent from the concentration of 4 (10^{-4} mole/l vs. 1 mole/l). From the observed product it is concluded, that 10 shows no effective rearrangement to 12, as in the case of ions 1[1b].



Footnotes and References.

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