

PREFERRED ENDO-ATTACK ON HEXAMETHYLDEWARBENZENE BY PROTONS

KINETIC VS. THERMODYNAMIC CONTROL

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HexamethylDewarbenzene (1) is attacked by various reagents from the exo side of the molecule.¹ Only recently² has an unambiguous example of endo attack been presented. Another example of endo attack is claimed³, but it is doubtful whether this is correct, because it is possible, as shown in analogous cases^{4,5}, that intermediates of the type 2a and 2b occur, which interconvert rapidly thereby destroying information about the orientation of the initial attack.

We wish to report here the protonation of 1 by HCl under conditions wherein interconversion of the intermediate bicyclic [2.1.1.] ions occurs only for a minor part. The data show that the protonation occurs for at least 80% from the endo side. It will further be shown that the initially formed bicyclic [2.1.1.] addition products of 1 and HCl undergo a number of reactions depending on the experimental conditions, such as temperature and acidity.

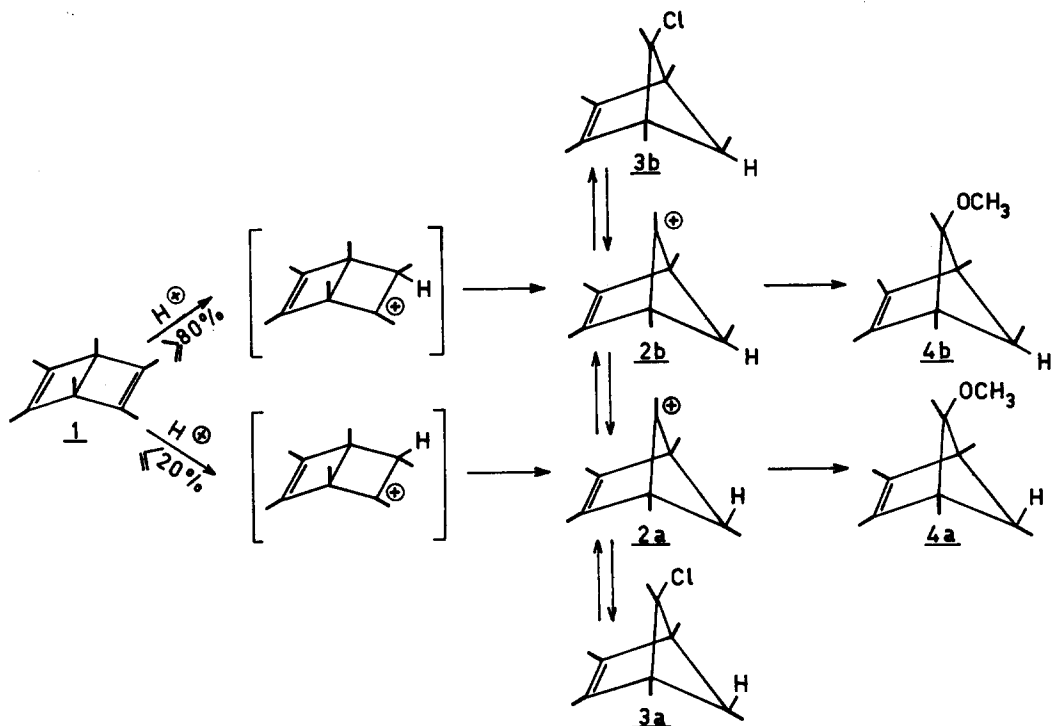
Ions 2a and 2b are formed by dissolving 1 in an excess of an equimolar mixture of HCl and methylene chloride in the temperature range of -50° to -100°C.⁶ The NMR-spectra of the ions were identical (within 0,05 ppm) to those reported in strong acids^{5,7} and the same ratio of the ions 2a:2b = 3:1 was found. When quenched with cold (-60°) sodium methoxide/methanol the ethers 4a and 4b were formed in a ratio of 3:1.⁷

In case the amount of HCl in the methylene chloride solution was decreased to about the same concentration as 1, the NMR-spectra of the ions 2a and 2b and the chloride 3a were observed at -80°. Warming up to -50° resulted in an increase in chloride 3a at the expense of the ions. The reverse reaction was not observed upon cooling to -80°, but this occurred on addition of more HCl. Structure 3a was assigned on the basis of the experiments mentioned above,

the NMR-spectrum and a quenching experiment. The NMR-spectrum in methylene chloride showed peaks at $2,62^{\delta}$ (q, $J=7$ cps, 1H) $1,04$ (d, $J=7$ cps, 1CH_3) ca. $1,03$ (two overlapping s, 3CH_3) and $1,43$ (s, 2CH_3). Pouring out a solution of 3a in sodium methoxide/methanol at -80° gave the ether 4a besides about 5% of 4b. Compound 3a could be isolated by evaporating the solvent after adding LiAlH_4 at -70° to the solution in order to destroy any excess acid. Purification was unsuccessful because 3a completely rearranged to 10 in a couple of hours at room temperature.

On further decreasing the amount of HCl in the methylene chloride solution to about half the concentration of 1 and carrying out the reaction at lower temperature (-95° , part of the solution became solid) the NMR-spectrum at -80° showed besides 1 the presence of 3a and the isomeric chloride 3b, whereas ions 2a and 2b were absent. The ratios 3a and 3b varied between 3:10 and 4:10. Repeating this experiment in vinyl chloride at -115° and measuring the spectrum at -80° gave a ratio of 2,5:10 to 3:10. Warming up the solution to -30° gave an increase in 3a at the expense of 3b. Addition of HCl resulted in the formation of ions 2a and 2b in a ratio 3:1 from any mixture of 3a and 3b. Structure 3b was assigned on the basis of the experiments mentioned above, the NMR-spectra and a quenching experiment. The NMR-spectrum of 3b showed peaks at $3,22^{\delta}$ (q, $J=6$ cps, 1H) $0,72$ (d, $J=6$ cps, 1CH_3) $1,67$ and $0,95$ (s, 2CH_3 each) $1,39$ (s, 1CH_3). Pouring out mixtures of 1, 3a and 3b, prepared at -115° to -60° , in sodium methoxide/methanol of -90° gave besides 1, the ethers 4a and 4b in ratios varying from 10:1 to 10:7.

From the literature^{5a} the kinetics of the interconversion of 2a and 2b are known. At temperatures of about -90° the half-life for the interconversion is about half an hour. Ions formed at this or lower temperature will partially conserve their configuration, when the reaction with a negative ion is faster than the interconversion. This is the case in the reaction of HCl with excess 1 at very low temperature, described above. In an NMR-spectrum, recorded within half an hour after preparation, no ions were observed demonstrating that the reaction of the ions with chloride ion is faster than the interconversion of the ions at these temperatures. Hence the stereochemistry of the chlorides observed gives information about the stereochemistry of the ions initially formed. From the observation that 3b is formed predominantly we conclude that the proton attacks 1 for at least 80% from the endo side. The observed amount of 3a can be explained either by an exo attack or by partial isomerization of the ion 2b.



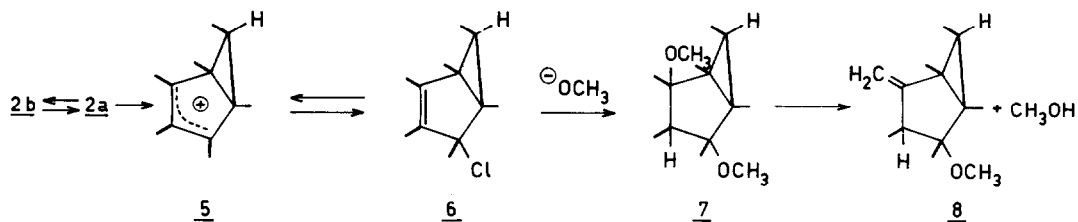
The experiments described above show that increasing the reaction temperature gives the same effect as increasing the HCl concentration, namely an increase of compound **3a**. At higher temperature the interconversion of **2a** and **2b** is faster and at a higher HCl concentration the concentration of the ions is larger and thus the rate of interconversion of **2a** and **2b** is larger. These conditions allow equilibrium to be established and as a result only chloride **3a** is observed. Chloride **3b** is presumed to be thermodynamically less favoured, due to steric hindrance between the *exo* CH_3 group and the chlorine atom in this compound.⁸

Also during the quenching of chlorides **3a** and **3b** to form the ethers **4a** and **4b**, interconversion of the intermediate ions **2a** and **2b** is likely to change the ratio of *endo* and *exo* compounds.

When the reaction between **1** and one equivalent HCl was performed at temperatures of -60° to 0° , a new bicyclic[3.1.0]chloride **6** was formed; at the lowest temperature compound **3a** was observed also. Warming up the reaction mixture gave more **6** at the expense of **3a** and at -30° about 90% of **6** was formed. This reaction was enhanced by increasing the HCl concentration.

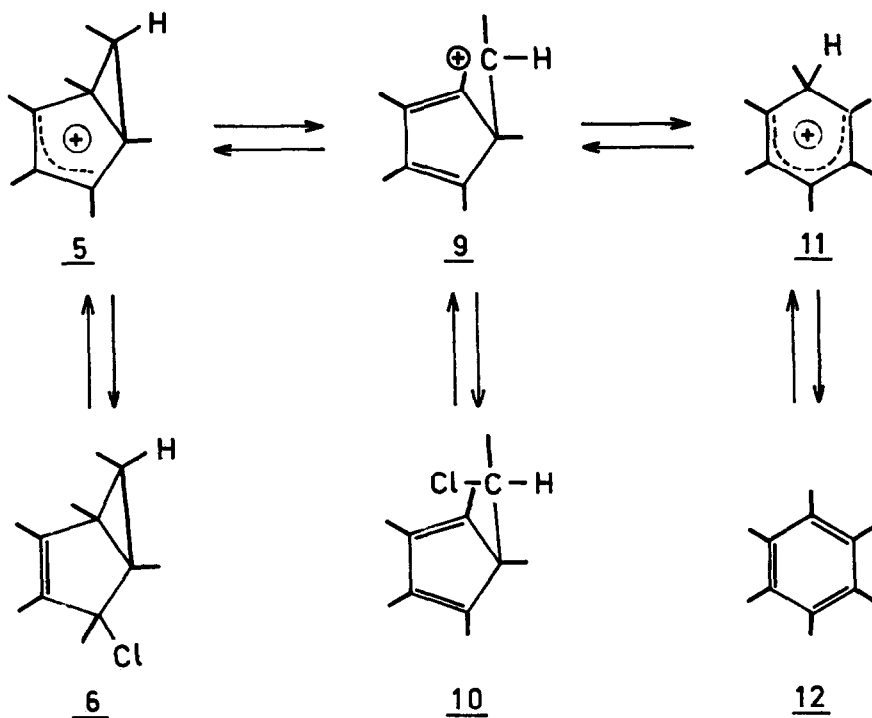
Isolation of 6 was possible by adding LiAlH_4 to these mixtures, so that any excess acid was destroyed. Washing with water and evaporating the solvent gave the crude product. Structure 6 was assigned on the basis of the experiments mentioned above, the NMR-spectrum and a quenching experiment. The NMR-spectrum in methylene chloride showed peaks at 2.18 (q, $J = 6.5$ cps, 1H), 1.10 (d, $J = 6.5$ cps, 1CH_3), 1.54, 1.45, 1.11, 1.04, 1.01 (s, each 1CH_3). From the value of the chemical shift of the doublet and the quartet the conclusion can be made that the methyl group is oriented endo.⁹ This is confirmed by the fact that 6 rearranges at 0° .¹⁰

Pouring out a solution containing 6 in sodium methoxide/methanol afforded compound 7 in nearly quantitative yield. Structure 7 was supported by the following data: the NMR-spectrum showed peaks at 1.02 (d, $J = 7$ cps, 1CH_3), 0.78 (d, $J = 7$ cps, 1CH_3), 3.14, 1.00 and 0.88 (s, each 2CH_3). This is consistent with structure 7 with the methoxy groups arranged cis. On standing at room temperature 7 decomposed in a week's time into one equivalent methanol and one equivalent 8. 8 was characterised by its NMR, IR and Mass spectra.^{5a}



On standing at 0° or at room temperature 6 completely isomerised to 10 within a week. Identification of 10 was possible by comparing spectra of the isomerisation product with spectra of authentic material.¹¹ The rate of isomerisation increased upon adding acid and prolonged contact with acid resulted in the formation of hexamethylbenzene (12).

That 12 can be obtained from [3.1.0.] structures is well known. Hogeveen and Volger⁵ proposed a [3.1.0.] ion as an intermediate in the formation of 11 from 2a and 2b. Childs and Winstein¹² observed the isomerisation of 5 (the structure was established later as endo CH_3 ¹⁰) to the hexamethylbenzeniumion (11) at -34° , the half-life being about 10 minutes. This observation suggests a mechanism in which 9 is an intermediate:



The possibility of a rearrangement of 5 and 9 is proposed by Schäfer and Hellmann¹³ and the observed rearrangement 6 to 10 obviously occurred via 5 and 9. It remained to be shown that in strong acids 10 can be converted into 11. Abstraction of Cl^- by SbF_5 in SO_2 gave 11 only, within 8 minutes at -60° . The half-life of 9 therefore certainly is less than 1 minute at -60° . This makes clear why Childs and Winstein did not observe this intermediate in their experiment, performed at -34° . It is likely therefore, that in contrast to the symmetry-allowed, concerted photochemical ring closure of 11 into 5¹², the reverse thermal reaction is a stepwise reaction rather than a symmetry-forbidden concerted reaction.

FOOTNOTES AND REFERENCES

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b. ibid. 87, 1042 (1968).
6. The ions 2a and 2b are much more stable than the tert.-butyl cation, which is not formed at all from tert.-butyl alcohol in these circumstances.
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8. The big Cl atom near the exo CH₂ group causes an extra steric strain in the molecule 3b. This is thought to be the reason for the relative instability compared with 3a and perhaps it is also the reason for the inverse positions of the quartets in the NMR-spectra of 3a and 3b compared with 2a and 2b.
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