Tetrahedron Letters No. 52, pp 5361 - 5364, 1972. **Pergamon Press. Printed in Great Britain.**

DOUBLE BOND VS. CYCLOPROPANE RING REACTIVITY IN 1,2,4,5,6-PENTAMETHYL-3-METHYLENETRICYCLO[2.2.0.0^{2,6}]HEXANE TOWARDS DIFFERENT ACIDS

H. Hogeveen and P.W. Kwant

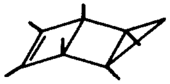
Department of Organic Chemistry, The University,
Zernikelaan, Groningen, The Netherlands.

(Received in UK 8 November 1972; accepted for publication 30 November 1972)

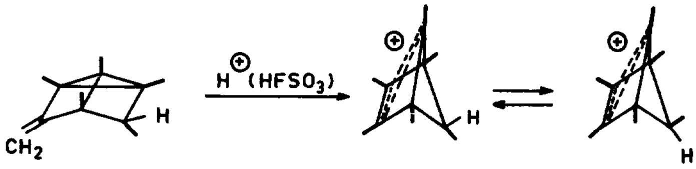
Usually HCl attacks a molecule at the same site as stronger acids. It was reported[1] recently that (1),containing a double bond and a cyclopropane ring,was attacked at the cyclopropane ring by HCl/CH_2Cl_2, but superacids as $FHSO_3$-SO_2ClF, $FHSO_3$-SbF_5-SO_2F_2 and HF-BF_3 did not give the product expected upon attack on the cyclopropane ring. Perhaps protonation of the double bond occurred as the first step under the latter conditions.

1,2,4,5,6-Pentamethyl-3-methylenetricyclo[2.2.0.0^{2,6}]hexane (2)[2] is reported here to give reaction at the double bond with $HFSO_3$ and at the cyclopropane ring with HCl/CH_2Cl_2.

When compound 2 was dissolved in $HFSO_3$ at -80° (0.5 mole/l), the NMR spectrum of the solution showed only the peaks of the ions 3a and 3b in a ratio of 3:1.[3] This result can readily be explained by a protonation of the double bond, as usual at the least substituted carbon atom.

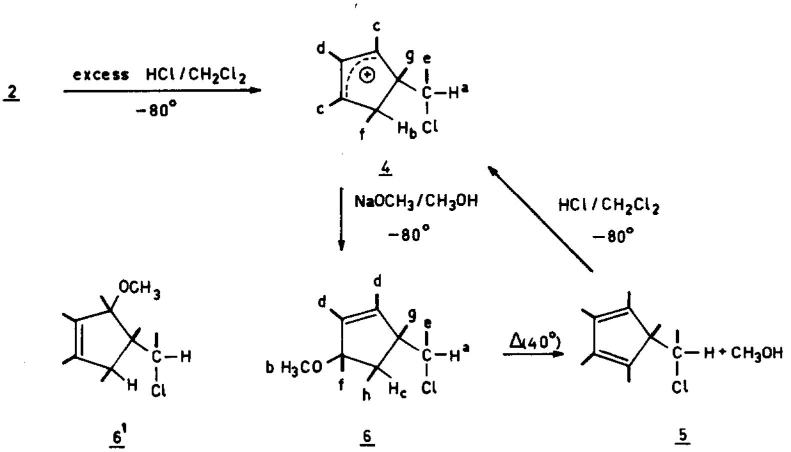


1



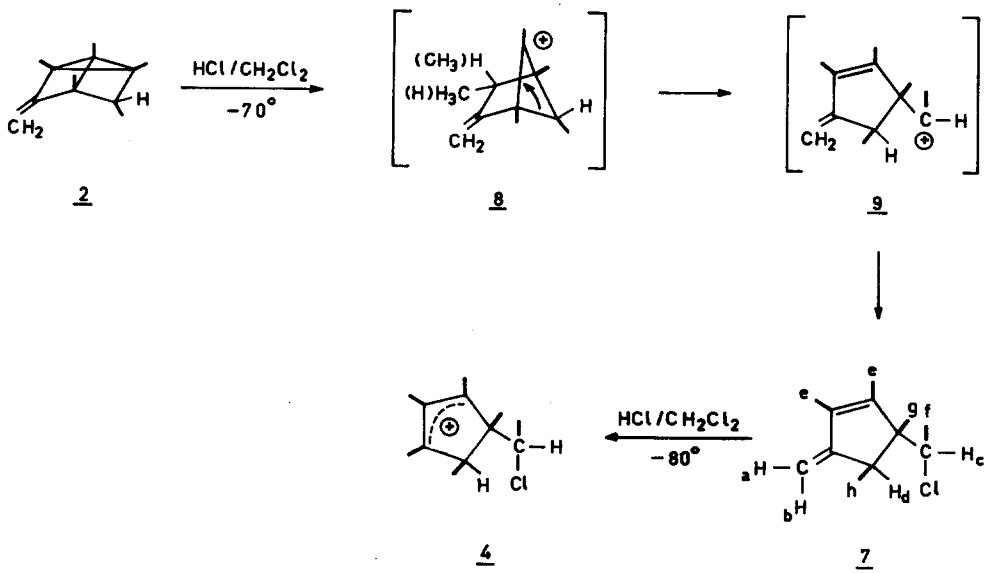
2 3a 3b

When compound 2 was dissolved (0.5 mole/l) in a mixture of CH_2Cl_2 and liquid HCl (2 : 3 v/v) at -80°, the NMR spectrum of the yellow liquid at -80° was identical to the NMR spectrum of 5[4] under the same conditions. This spectrum was ascribed to the cyclopentenyl-cation 4, showing peaks at $\delta = 4.52$ (quartet, J = 7 cps., 1H, a), 3.52 (multiplet, 1H, b), 3.00 (multiplet, $2CH_3$, c), 2.27 (multiplet, $1CH_3$, d), 1.77 (doublet, J = 7 cps., $1CH_3$, e), 1.53 (doublet, J = 7 cps., $1CH_3$, f)[5], 1.38 (singlet, $1CH_3$, g). This structure was confirmed by quenching a solution of 4 in excess of sodium methoxide/methanol at -80°, which after evaporating of the solvent, gave compound 6 as a crude product (80% yield, determined by NMR). Assignment of structure 6 is based on the following data: molecular weight: 230 (determined mass spectrometrically) and NMR spectrum (CCl_4): peaks at $\delta = 4.05$ (quartet, J = 7 cps., 1H, a[6]), 3.01 (singlet, $1CH_3$, b), 2.12 (quartet, J = 7 cps., 1H, c[6]), 1.59 (two overlapping singlets, $2CH_3$, d), 1.44 (doublet, J = 7 cps., $1CH_3$, e[6]), 1.21 (singlet, $1CH_3$, f), 1.01 (singlet, $1CH_3$, g), 0.96 (doublet, J = 7 cps., $1CH_3$, h[6]). The observation that the product decomposed into 5 and methanol upon standing at 40° for several hours indicates that 6 is the correct structure rather than 6'.

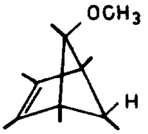


When a solution of 2 (0.5 mole/l) in CH_2Cl_2 was treated at -70° with ca. 0.7 eq. of dry HCl gas, compound 7 was formed with the following NMR spectrum $\delta = 4.77$ (multiplet, 1H, a), 4.67 (multiplet, 1H, b), 4.29 (quartet, J = 7 cps., 1H, c), 2.77 (multiplet, 1H, d), 1.72 (two broad overlapping singlets, $2CH_3$, e), 1.54 (doublet, J = 7 cps., $1CH_3$, f), 1.06 (singlet, $1CH_3$, g), 1.02 (doublet, J = 7 cps., $1CH_3$, h). Upon heating to 40° 7 isomerized quantitatively to 5. Addition of excess of liquid HCl to a solution of 7 in methylene chloride at -80° resulted in the formation of 4. Pouring a solution of 7 in methylene chloride of -70° into a mixture of sodium methoxide and methanol of -70° did not give rise to ether formation, in accordance with the assigned structure.[7]

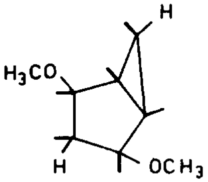
From these experiments the conclusion can be drawn that HCl in methylene chloride attacks 2 at the cyclopropane ring at temperatures of -70° to -80°. This attack opens the ring presumably in such a manner that intermediate 8 is formed; this rearranges to 9 by a β fission and 9 subsequently reacts with Cl^- ion providing 7. Another molecule of HCl can attack 7 to yield 4. Mechanisms involving initial proton addition at another carbon atom of the cyclopropane ring, would either lead to other products or would involve more steps.



When the reaction of 2 with excess HCl (2 to 100 fold) was carried out at temperatures above -60° followed by quenching with sodium methoxide and methanol at the same temperature, the products were found to be not only 5, 6 and hexamethylbenzene, but also 10 (max. 5%) and 11 (max. 25%). The latter compounds have been obtained before from 3a and 3b[8], so that it is possible that at temperatures above -60° HCl attacks the double bond as well as the cyclopropane ring.



10



11

The difference between the reaction of $HFSO_3$ and HCl/CH_2Cl_2 at -80° can be explained by the fact that in the latter case hardly any ions are present.[9] The attacking reagent is not a solvated proton[10], as in the strong acid (as $HFSO_3$), but rather a polar H-Cl molecule, which obviously can change the reaction pattern dramatically.

REFERENCES.

1. H. Hogeveen, C.F. Roobeek and H.C. Volger, *Tetrahedron Letters*, **1972**, 221.
2. H. Hogeveen and P.W. Kwant, accompanying paper.
3. H. Hogeveen and H.C. Volger, *Rec. Trav. Chim.*, **88**, 353 (1969).
4. L.A. Paquette and G.R. Krow, *Tetrahedron Letters*, **1968**, 2139.
5. The peaks of doublet f show additional structure, due to coupling with CH_3 groups of the ring.
6. These assignments were confirmed by double resonance measurements.
7. The chloroethyl groups of compounds 5 and 6 are not converted into the corresponding ethers under these conditions either.
8. H. Hogeveen and P.W. Kwant, *Tetrahedron Letters*, **1972**, 3197.
9. N.G. Dorofeeva and O.K. Kudra, *Ukrain. Khim. Zhur*. **27**, 306 (1961), C.A. **56**, 5455 (1962).
10. Compare the reactivity of liquid HCl towards a double bond, M.E. Peach and T.C. Waddington, *J. Chem. Soc.*, **1962**, 600.