Tetrahedron Letters No. 24, pp 1989 - 1992, 1975. Pergamon Press. Printed in Great Britain.

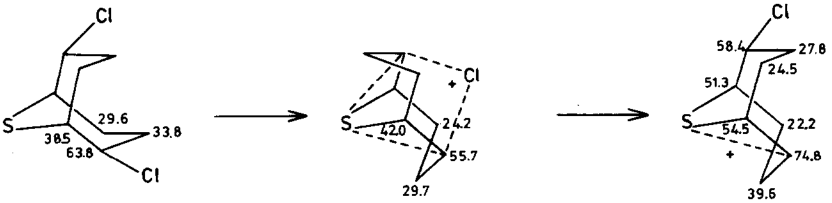
NEIGHBORING GROUP PARTICIPATION OF SULFUR IN CARBONIUM IONS. OBSERVATION OF A SULFURANE-LIKE INTERMEDIATE.

J.A.J.M. Vincent*, P. Schipper, Ae. de Groot and H.M. Buck,
Eindhoven University of Technology, Department of Organic Chemistry,
The Netherlands.

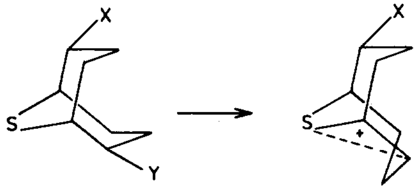
(Received in UK 18 April 1975; accepted for publication 1 May 1975)

The reactivity of 2,6-dichloro-9-thiabicyclo[3.3.1]nonane (I) in nucleofilic substitution reactions is well documented[1]. An intramolecular sulfonium ion has been proposed as an intermediate in these reactions. However, this intermediate does not account for the observed, enhanced reactivity of the first chlorine with respect to the second one. We now report the direct observation of two intermediates in the solvolysis of I which offer an explanation for this phenomenon.

Dissolution of I in a mixture of FSO_3H and liq. SO_2 at -60° C gives rise to species II; at -30° C II isomerizes to III, which is stable even at higher temperatures. The structural assignment is based on the CMR data and the chemical



I II III



IV X = Y = OH VI X = OH , Y = Cl

V X = Y = OCH_3 VII X = OCH_3, Y = Cl

^{13}CMR positions are given in the figure

figure 1

behavior (vide infra). Analogous results were obtained with 2,6-dibromo- and with 2,6-diiodo-9-thiabicyclo[3.3.1]nonane. With the 2,6-dihydroxide (IV), 2,6-dimethoxide (V), 2-chloro-6-hydroxide (VI) and 2-chloro-6-methoxide (VII) only the corresponding type III ions are formed. Ions II and III are also formed in aprotic media (SbF_5/CD_2Cl_2/liq. SO_2 or $AlCl_3/CD_2Cl_2$/liq. SO_2). Upon quenching ion III in water only compounds I (ca 80% by internal return), IV and VI are formed. Identical results are obtained upon quenching ion II. Thus polymerization reactions or skeletal rearrangements are excluded.

The CMR spectrum of II shows 4 absorption signals. This points, a priori, to three possible structures[2].

Complexation of both chlorines with solvent molecules would result in a downfield shift with respect to I of the adjacent C-atoms in the CMR spectrum. Further more, one would expect a temperature and solvent dependent spectrum which is not observed.

Protonation or complexation on sulfur can be eliminated by comparison of the results in different media. The CMR spectra of II in FSO_3H/liq. SO_2 and in the aprotic media SbF_5/CD_2Cl_2/liq. SO_2 or $AlCl_3/CD_2Cl_2$/liq. SO_2 are identical[3].

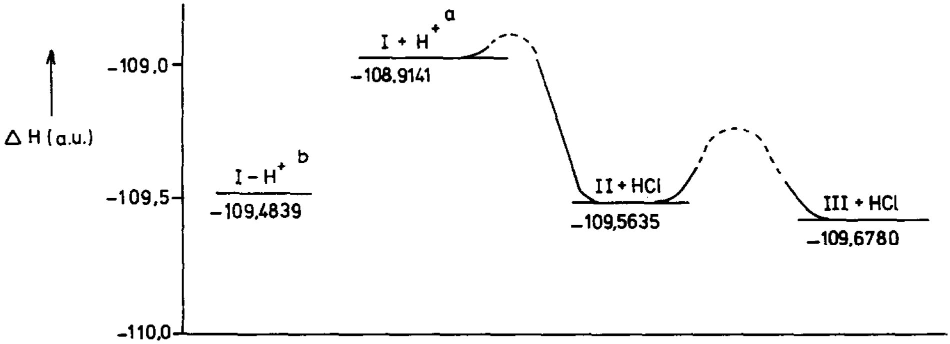
Structure II as depicted in figure 1 offers a good explanation for the CMR spectrum and the chemical behavior. In the CMR spectrum of II C_2 and C_6 show an upfield shift compared with I of 8.1 ppm. This can be explained by an increase of carbon coordination at these positions which offsets the effect of a positive charge induced by chloronium coordination. The small downfield shift for the bridgehead carbons is caused by a partial positive charge on sulfur. The upfield shifts for the other C-atoms might be ascribed to increasing steric interaction. Also the fact that 2-chloro-6-bromo-bicyclo[3.3.1]nonane[4] shows the same spectrum and reactivity in FSO_3H/liq. SO_2 as a mixture of the dichloride and the dibromide is in favor of this structure.

In our opinion, II is best described as a sulfurane, oriented in a square pyramid, in which two positions are coordinated by a chloronium ion.

The occurrence of II in the solvolysis of I in methanol or aqueous dioxane explains the fact that the first chlorine is released much faster than the second one. Presumably, electron donation from sulfur to C_6 enables the adjacent chlorine to assist in the release of the chlorine on C_2. Apparently, hydroxy or methoxy groups cannot participate in solvolysis to the same extent, which is confirmed by the fact that with VI and VII only the corresponding type III ions are formed by the release of a chloride ion.

Ion III is best characterized as a sulfonium ion in which the positive charge is delocalized on sulfur and C_2. This is based on CMR spectra which show a downfield shift for C_2 of ca 42 ppm with respect to 9-thiabicyclo[3.3.1]nonane. The smaller downfield shifts for C_1 (20 ppm) and C_5 (13 ppm), compared with 9-thiabicyclo[3.3.1]nonane and I, respectively, can be explained by an inductive effect from the partially positive sulfur as well as C_2 (for C_1 only).

The charge densities and energies calculated with CNDO/2 agree very well with the observed reactivity. In the dichloride I both chlorines have a higher calculated electron density than sulfur; this implies that a proton or another electrofile will attack on chlorine. The calculated energy profile is given in figure 2[5]. Comparatively, the energy for I protonated on sulfur is also given; this energy appears to be higher than that of the proposed structure II.



[a] The dissociation energy of the acid used is not taken into account.
[b] I-H^+ represents I protonated on sulfur.

figure 2

The reported stereospecificity and reactivity of I in nucleofilic reactions is sufficiently explained by the intermediacy of ions II and III.

Acknowledgement

The authors wish to thank dr. ir. J.W. de Haan for many helpful discussions and ir. J.F.M. Pennings for performing the quantumchemical calculations.

This investigation has been supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization of Advancement of Pure Research (ZWO).

References and Notes

1) a. E.J. Corey, and E. Block, J. Org. Chem., 31, 1663 (1966).
   b. E.D. Weil, K.J. Smith, and R.J. Gruber, J. Org. Chem., 31, 1669 (1966).

2) The fact that both II and III are observed at the same time excludes the possibility that II is structure III rapidly equilibrating between both possible isomers.

3) The CMR spectrum of protonated 9-thiabicyclo[3.3.1]nonane shows 5 absorptions due to the asymmetric positioning of the proton on sulfur, indicating a relatively high energy barrier for proton exchange. If in I sulfur was protonated one would also expect an asymmetric structure. Furthermore, it is highly improbable that only in the dihalides protonation or complexation occurs, whereas in compounds IV, V, VI and VII this would not take place.

4) 2-Chloro-6-bromobicyclo[3.3.1]nonane was prepared by leading HBr through a solution of I in FSO_3H followed by quenching in water. In this manner ca 70% of the mixed halide is formed due to internal return of bromine.

5) Noteworthy is the fact that in the calculations for the corresponding difluoride the stability of the symmetric species is considerably lower with respect to II.