Tetrahedron Letters No. 22 + 23, pp 1799 - 1802, 1975. Pergamon Press. Printed in Great Britain.

SOLVOLYTIC BEHAVIOUR OF STRAINED SYSTEMS.
THE BENZO[b]BICYCLO[3.1.0]HEX-2-EN-4-YL CATION.

A.C. Răsuş, V. Wertheimer, F. Badea and A.M. Glatz *)

Institute of Organic Chemistry, Spl. Independenţei 202B, Bucharest, Romania

(Received in UK 25 March 1975; accepted for publication 16 April 1975)

The continuous interest in the area of the bicyclo[3.1.0]hex-2-en-4-yl cation[1-4] prompted us to investigate the corresponding benzobicyclo system. This work reports some results on the solvolyses of 4-chloro-benzo[b]bicyclo[3.1.0]hex-2-ene (1-Cl) and the perchloric acid catalyzed isomerisation of the corresponding alcohols (1-OH).

Solvolyses of 1-Cl (mixture of *exo* and *endo*) have been carried out in buffered and unbuffered aqueous dioxane yielding the unrearranged alcohols, *exo*- and *endo*-1-OH as well as the internal return product (1-indenyl)-chloromethane (2-Cl) (see table).

As shown in the unbuffered solvolysis the ratio of 2-Cl increases fivefold.

In acidic aqueous dioxane solution and under mild conditions alcohols 1-OH undergo only *endo* $\rightleftharpoons$ *exo* epimerization. Higher temperatures and prolonged reaction times afford increased amounts of the rearrangement product, (1-indenyl)-methanol (2-OH).

Since all these reactions are accompanied by the formation of small amounts of naphthalene (3), we irradiated *endo*-1-OH in perchloric acid medium and we found markedly increased amounts of naphthalene.

Starting with either 1-Cl or 1-OH in the above mentioned reactions the key intermediate is the benzo[b]bicyclo[3.1.0]hex-2-en-4-yl cation (4) and the epimerization the fastest reaction.

Table.

Product distributions in the rearrangements of **1**.

Run	Substrate	Conditions a)	Products, % moles (vpc)				
			exo-**1**-OH	*endo*-**1**-OH	**2**-Cl	**2**-OH	**3**
1	**1**-Cl b)	66°; 10 hrs; $CaCO_3$	73.1	19.4	3.8	-	<0.5
2		66°; 6 hrs;	53.5	17.8	21.4	1.9	<0.5
3	*endo*-**1**-OH	69°; 28 hrs; $HClO_4$	56.4	18.5	-	21.4	<0.5
4		44°; 10 hrs; $HClO_4$	54.4	45.4	-	traces	<0.5
5		44°; 10 hrs; $HClO_4$; hν	15.7	10.8	-	traces	68.9
6 c)		44°; 10 hrs; hν	5.7	61.1	-	-	19.3 d)

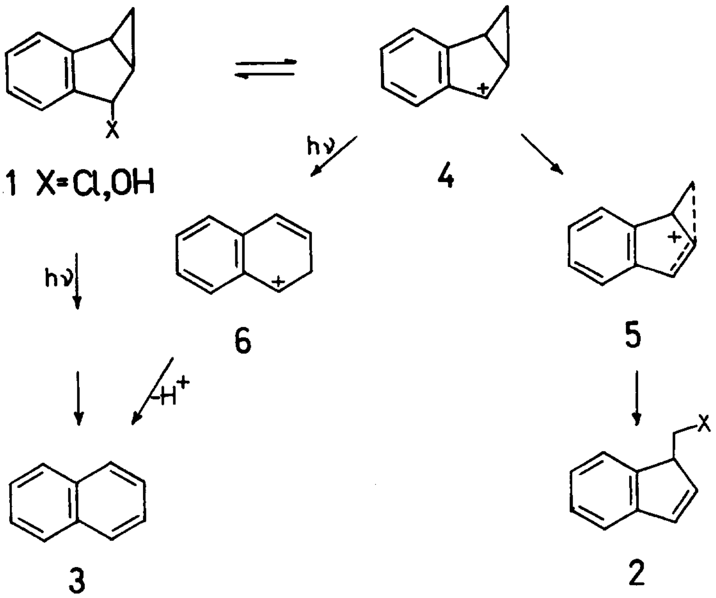
a) In dioxane-water (50% vol.) - run 6 in *n*-hexane. All acid catalysed isomerizations have been performed with 0.3 M $HClO_4$. Irradiations have been carried out under argone with a medium pressure 125 W - mercury lamp.

b) Mixture of 70% *exo*, 30% *endo* (nmr).

c) Some minor unidentified reaction products are also formed.

d) Probably formed from naphthalene precursor during vpc.

Three ways of cyclopropyl group participation at the cationic center are possible. Participation of the ring fused linkage C_1-C_5 is defavoured because of its great relative stability. This is supported by recent theoretical computations on the equilibrium geometry of the bicyclo[3.1.0]hex-2-en-4-yl cation[4] as well as by nmr investigations of this cation in superacid media[5]. The two homoallylic participations of the bonds C_5-C_6 and C_1-C_6 are not equivalent, the latter requiring the loss of aromaticity in the benzo ring. Therefore only the C_5-C_6 bond is able to homoallylic delocalisation leading thus to products **2** *via* ion **5**. However, owing to the unusual stability of ion 4 the formation of the rearrangement products occurs slowly.



The opening of the C_1-C_5 linkage becomes possible in a concerted disrotatory manner which can be accomplished photochemically. In this way the cationic naphthalene precursor 6 can arise which easily undergoes aromatization. In ion 4, geometrically and electronically closely related to Winstein's cation[2], a conrotatory ring opening is precluded and hence a thermal concerted pathway is impossible.

In order to prove whether the opening of the ring fused linkage occurs only *via* cation 4, *endo*-1-OH has been irradiated without acid in *n*-hexane thus eliminating the possibility of a cationic pathway. The irradiation in these nonpolar, nonionizing conditions yielded 19% naphthalene (or naphthalene precursor). Therefore it may be considered that at least 75% of the naphthalene formed by irradiation in acidic aqueous dioxane arises *via* cation 4. Even with this correction the yield in naphthalene increases more than hundredfold when compared to the nonirradiated reaction.

The small amounts of naphthalene formed in the thermal reaction (even at dark) might arise either by a forbidden disrotatory pathway or by another way (perhaps a diradical one).

The exceedingly high free energy of activation needed for the thermal formation of naphthalene is further proved by the finding that even at 315° **1**-Cl yields 95.3% **2**-Cl and only 4.7% naphthalene. Therefore the cyclopropane ring opening leading to naphthalene requires at least 3.5 kcal/mol more than the opening leading to **2**.

Taking these results into account, ion **4** must be uncomparably more stable than Winstein's bicyclo[3.1.0]hexenyl cation which undergoes forbidden thermal ring opening at a measurable rate at -33.5°.

Kinetics and investigations regarding substituent effects will be fully reported in future papers.

REFERENCES

1. L. Kaplan, J.S. Ritscher and K.E. Wilzbach, *J.Amer.Chem.Soc.*, **88**, 2881 (1966) ; D. Bryce-Smith, A. Gilbert and H.C. Longuet-Higgins, *Chem. Commun.*, **240** (1967).
2. R.F. Childs, M. Sakai and S. Winstein, *J.Amer.Chem.Soc.*, **90**, 7144 (1968) ; R.F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968) ; R.F. Childs, M. Sakai, B.D. Parrington and S. Winstein, *ibid.*, **96**, 6403 (1974) ; R.F. Childs and S. Winstein, *ibid.*, **96**, 6409 (1974).
3. J.A. Berson and N.M. Hasty, Jr., *J.Amer.Chem.Soc.*, **93**, 1549 (1971) ; P. Vogel, M. Saunders, N.M. Hasty, Jr., and J.A. Berson, *ibid.*, **93**, 1551 (1971).
4. W.J. Hehre, *J.Amer.Chem.Soc.*, **96**, 5207 (1974).
5. V.A. Koptyug, V.I. Buraev, I.G. Isaev, A.E. Rezvukin and V.I. Mamatyuk, *Zhur. Org. Khim.*, **10**, 662 (1974).