Tetrahedron Letters No.51, pp. 3831-3834, 1964. Pergamon Press Ltd.
Printed in Great Britain.

# SOLVOLYTIC CYCLIZATION OF 2-($\Delta^1$-CYCLOPENTENYL)ETHYL BROSYLATE

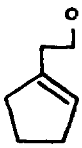
W. D. Closson and George T. Kwiatkowski[1]
Department of Chemistry, Columbia University
New York, New York, 10027

(Received 26 October 1964)

The current interest in the spiro(2.4)heptan-4-yl cation[2] and the recent report on the homoallylic rearrangement of the 2-($\Delta^1$-cyclopentenyl)ethyl system by Hanack and Schneider[3] prompts us to record some of our observations in this area.

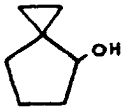
2-($\Delta^1$-Cyclopentenyl)ethanol[4] (Ia) was converted to the corresponding brosylate (Ib) by the usual method. It was an oil at room temperature and liberated 98 percent of the theoretical amount of acid on acetolysis. The first-order rate of acetolysis of Ib at 80° in the presence of a small excess of sodium acetate was found to be $11.0 \times 10^{-5}$ sec.$^{-1}$ ± $0.2 \times 10^{-5}$ sec.$^{-1}$. This is ca. forty times greater than that of 2-($\Delta^2$-cyclopentenyl)ethyl brosylate[5] and about twenty-seven times that of 3-cyclopentylpropyl brosylate,[5] both determined under the same conditions. The acetolysis products of Ib were isolated, reduced with lithium aluminum hydride, and separated by preparative-scale gas chromatography. Olefinic material made up about 13 % of the product and was not investigated further. The hydroxylic products consisted of 4.1% Ia, 9.7% spiro(2.4)heptan-4-ol (II), 18.2% bicyclo(3.2.0)heptan-1-ol

(III), 5.4% 1-bicyclo(3.1.0)hexanemethanol (IV), and 49.4% 3-methylenecyclohexanol (V). The identities of Ia and II were proved by comparison with authentic samples. The structure of V was established from its NMR and infra-red spectrum (strong band at 891 cm$^{-1}$), and its hydrogenation to *cis*-3-methylcyclohexanol. Compound IV was synthesized by reaction of $\Delta^1$-cyclopentenylmethanol[6] with methylene iodide and zinc-copper couple.[7] Both samples of IV had identical NMR spectra (singlets at 5.6 and 6.4 $\tau$, multiplets at 8.3, 8.8, 9.6, and 9.68 $\tau$ ; in $CCl_4$), and infra-red spectra (bands at 3590, 3060, 3020, 2995, and 2940 cm$^{-1}$). The NMR spectrum of III was in agreement with the literature data,[3] as was its melting point (42 - 43°) (literature value[3] 47 - 48°).

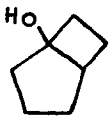


Ia, R = H

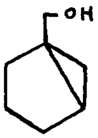
Ib, R = OBs



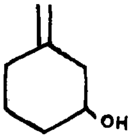
II



III



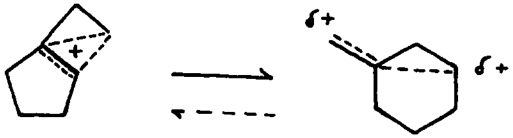
IV



V

The considerable enhancement of the rate of acetolysis of Ib and the almost exclusive formation of rearranged products clearly indicates homoallylic participation by the double bond. Since it was observed that the reaction products were stable under the conditions of formation, one must account for their production in the solvolysis step. An intermediate cation capable of yielding all four rearranged products seems very unlikely.

Hanack and Schneider observed that deamination of 2-($\Delta^1$-cyclopentenyl)ethylamine in aqueous solution and solvolysis of the naphthalenesulfonate of Ia in aqueous acetone yielded III as the major rearrangement product (others were not identified).[3] Under these conditions, unlike solvolysis in acetic acid, it is likely that the initially formed cation is rapidly trapped. Thus, evidence is strong that the initial cation is the bicyclobutonium ion VI. The ion VI could yield the acetates of II and III, and indeed, even that of Ia. The most economical way of accounting for the acetates of IV and V would be the isomerization of VI to ion VII, a "stripped" cholesteryl ion. Many other homoallylic ions could be postulated, and perhaps one or more intervene between VI and VII, but the two illustrated are sufficient (and necessary) to account for all identified products. Considering the high yield of the acetate of V in the reaction it is likely that VII is irreversibly formed from VI.



VI VII

It is interesting that attempts to convert II to the corresponding chloride lead instead to mixtures of two unsaturated chlorides.[2] One was identified as having a structure corresponding to I, while the other was shown to be a methylenecyclohexyl derivative.[2] Considering our observations, we predict that the second chloroalkene is 3-methylenecyclohexyl chloride.

Further work on this interesting system is in progress.

*Acknowledgments.* --- We would like to thank Professor D. E. Applequist of the Chemistry Department, University of Illinois, Urbana, Illinois, for a generous sample of spiro(2.4)heptan-4-yl *p*-nitrobenzoate. Partial support of this work by the Petroleum Research Fund, administered by the American Chemical Society, (Grant No. 1272-A4) is gratefully acknowledged.

## References

1. National Institutes of Health Predoctoral Fellow, 1963-1965.
2. D. E. Applequist and J. E. Landgrebe, *J. Am. Chem. Soc.*, **86**, 1543 (1964).
3. M. Hanack and H.-J. Schneider, *Angew. Chem.*, **76**, 783 (1964).
4. R. T. Arnold, R. W. Amidon, and R. M. Dodson, *J. Am. Chem. Soc.*, **72**, 2871 (1950).
5. W. D. Closson and George T. Kwiatkowski, *ibid.*, **86**, 1887 (1964).
6. A. H. Cook and R. P. Linstead, *J. Chem. Soc.*, 956 (1934).
7. E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).