Tetrahedron Letters Vol. 21, pp 5025 - 5026
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0040-4039/80/1222-5025$02.00/0

# SOLVOLYSIS OF BRIDGEHEAD CHLORIDES WITH STRAINED BRIDGEHEAD DOUBLE BOND.

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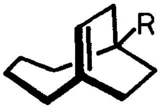
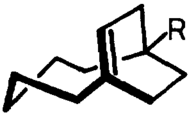
Summary: Product study and kinetic data of the solvolysis of the bridgehead chlorides (1c) and (2c) indicate the neighboring group participation of the strained bridgehead double bonds.

Although the homoallylic participation of carbon-carbon double bond with carbonium ion center in solvolysis reactions are extensively studied,[1] little is known for that of strained bridgehead double bond.[2] Recently, we have explored the synthetic route to bicyclo[n.2.2]bridgehead alkenes (1a)-(3a) having an acetoxyl group at the opposite bridgehead position based on the oxidative decarboxylation of [n.2.2]propellane carboxylic acids and the solvolytic rearrangement of the resulting tricyclic acetates (4a) and (5a).[3] In this connection, we wish to report here the neighboring group participation of the strained bridgehead double bond and the effect of the ring size (n) of the bicyclo[n.2.2] framework on the above interaction in the solvolysis of the bridgehead chlorides (1c)-(3c) derived from 1a-3a.

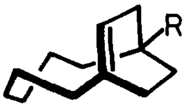
The chlorides 1c-3c[4] were prepared by the reaction of thionyl chloride or phosphorous oxychloride with the bridgehead alcohols (1b)-(3b)[4] which were obtained by the reduction of 1a-3a with lithium aluminum hydride. The solvolysis of the chlorides 1c-3c were carried out in 80 % (v/v) acetone-water buffered with 2,6-lutidine. Whereas the solvolysis of 3c gave only the unrearranged alcohol 3b, 1c afforded the rearranged cyclopropylcarbinyl type tricyclic alcohol (4b)[4,5] as a sole product, and 2c gave 87 % of the rearranged alcohol



1a-c

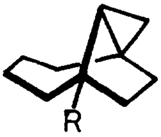


2a-c

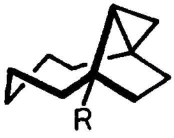


3a-c

a, R=OAc
b, R=OH
c, R=Cl



4a-b



5a-b

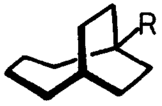


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Table I. Kinetic Data for the Ethanolysis of the Chlorides 1c-3c and 6.

| Chloride | Temp(°C)[a] | $k(sec^{-1})$[b] | $k_{rel}$ | $\Delta H^{\ddagger}$(kcal/mol) | $\Delta S^{\ddagger}$(eu) |
|---|---|---|---|---|---|
| 1c | 25.0 | $1.52 \times 10^{-4}$ | 214 | 23.9 | -1.8 |
| | 20.0 | $7.50 \times 10^{-5}$ | | | |
| 2c | 33.0 | $1.96 \times 10^{-4}$ | | | |
| | 25.0 | $7.44 \times 10^{-5}$ | 105 | 21.4 | -5.9 |
| 3c | 33.0 | $3.00 \times 10^{-5}$ | | | |
| | 25.0 | $1.07 \times 10^{-5}$ | 15.1 | 22.8 | -5.0 |
| 6 | 55.0 | $4.27 \times 10^{-5}$ | | | |
| | 40.0 | $6.07 \times 10^{-6}$ | | 25.9 | +4.5 |
| | 25.0[c] | $7.10 \times 10^{-7}$ | 1.0 | | |

a, ±0.1°C. b, Determined by GLC and the deviations are within 6 %. c, Extrapolated value.

(5b)[4,5] and 13 % of the unrearranged one 2b. These results indicate clearly the presence of the participation of the strained double bond in the solvolysis of 1c and 2c. Moreover, this was supported by the kinetic study of the solvolysis of 1c-3c in ethanol[6] containing 10 % (v/v) of 2,6-lutidine[7] (Table I) For comparison, the ethanolysis rates of the saturated chloride (6)[4,8] were also measured. As shown in Table I, 1c was most reactive and it solvolyzed at a rate 214 times faster than the corresponding saturated chloride 6. The solvolysis rate of 2c was about a half of that of 1c but was considerably greater than those of 3c and 6.[9]

In conclusion, the strained bridgehead double bonds of bicyclo[4.2.2]octene and bicyclo[5.2.2]nonene systems showed remarkable neighboring group participation with the carbonium ion center at the opposite bridgehead position, and the degree of the participation was greatest in the former system because more favorable geometry can be attained for the homoallylic interaction between the developing p orbital and the bridgehead double bond with decrease in the size (n) of the bicyclo[n.2.2] framework.

## References and Notes

(1) P.R.Story and B.C.Clark,Jr., "Carbonium Ions", Vol. IV, G.A.Olah and P.v.R. Schleyer, Ed., Wiley-Interscience, New York, 1972, Chapter 23.

(2) For the only one example; P.G.Gassman, G.M.Lein,Jr., and R.Yamaguchi, Tetrahedron Lett., 3113(1976).

(3) (a) Y.Sakai, S.Toyotani, Y.Tobe, and Y.Odaira, Tetrahedron Lett., 3855 (1979). (b) Y.Sakai, Y.Tobe, and Y.Odaira, Chem.Lett., 691(1980).

(4) All new compounds gave satisfactory analytical and spectral data.

(5) Identified by comparison with the authentic materials prepared by the lithium aluminum hydride reduction of the acetates 4a and 5a.

(6) Since, unfortunately, the hydrolysis rates of 1c-3c were too rapid, the solvolysis rates were measured in ethanol.

(7) Because the unsaturated bridgehead chlorides, especially 1c, were unstable in acidic media, the ethanolysis rate measurements were carried out in the presence of large excess of 2,6-lutidine.

(8) 6 was prepared by the diimide reduction of 1b followed by the reaction with thionyl chloride.

(9) In addition to the transition state stabilization by the double bond participation, relief of large strain in the ground state of 1c and 2c may also contribute to the observed rate acceleration.

(Received in Japan 28 August 1980)