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SILVER ION PROMOTED SOLVOLYSIS OF 7,7-DIBROMOBICYCLO[4,1,0]HEPTANE

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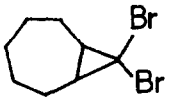
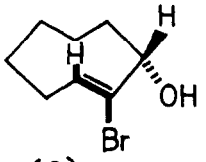
We recently found[1] that when 8,8-dibromobicyclo[5,1,0]octane (1) was treated with an excess of silver perchlorate in aqueous acetone solution at 20°, it was quantitatively converted into trans-2-bromocyclo-octen-3-ol (2) within 5 min. 6,6-Dibromobicyclo[3,1,0]hexane (3) also reacts rapidly under the same conditions to give 2-bromocyclohexen-3-ol (4) as the only product. We now report that 7,7-dibromobicyclo[4,1,0]heptane (5a) undergoes Ag^+-promoted solvolysis much more slowly than either (1) or (3). Thus, after 21 hr. at 20°, (5a) was incompletely (ca. 75%) converted into a mixture of 2-bromocyclohepten-3-ol (6, 40%) and cyclohexene-1-carboxaldehyde (7a, 11%).

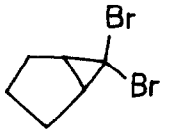
The major product (6) was that expected[2,3] for a reaction involving an inward disrotatory mode of ring opening; however, as the mechanism of the formation of the minor product (7a) required further elucidation, the solvolysis of 1-deuterio-7,7-dibromobicyclo[4,1,0]heptane[4] (5b) was examined. The latter compound reacted under the same conditions as (5a) to give monodeuterio-derivatives of (6) (52%) and (7a) (11%). N.m.r. spectroscopy revealed that, within experimental error, the deuterium atom in d_1-2-bromocyclohepten-3-ol was equally distributed between the 1- and 3-positions and that the deuterium atom in d_1-cyclohexene-1-carboxaldehyde was equally distributed between the formyl



(1)



(2)



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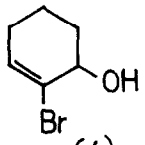
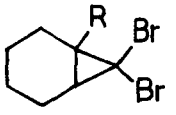
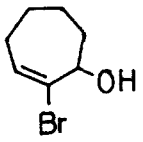


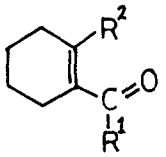
(4)



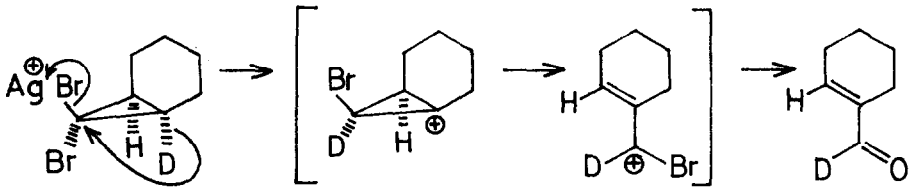
(5) a; R=H
b; R=D



(6)

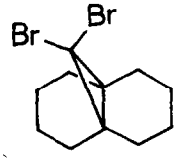


(7) a; $R^1 = R^2 = H$
b; $R^1 = D, R^2 = H$
c; $R^1 = H, R^2 = D$

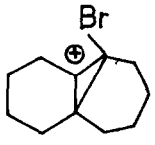


(5b) (8) (9) (7b)

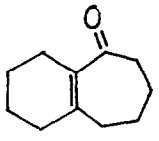
Scheme



(10)



(11)



(12)

group and the 2-position. The solvolysis of (5b) was not significantly affected by the presence of a slight excess of pyridine, which was added to limit the acidity of the reaction medium.

While the observed distribution of deuterium in d_1-2-bromocyclohepten-3-ol is in accord with a mechanism involving an intermediate allylic cation, the distribution of deuterium in d_1-cyclohexene-1-carboxaldehyde suggests a process involving a 1,2-deuteride or hydride shift. A possible mechanism for the conversion of (5b) into (7b) is indicated in the Scheme: a 1,2-deuteride shift concerted with the Ag^+-promoted ionization of the endo-bromine leads to a cyclopropyl cation (8) which collapses to an allylic cation (9). Solvolysis of (9) gives the product (7b). It is not necessary to invoke the cyclopropyl cation (8) as an actual intermediate as both steps (5b)→(8)→(9) may be concerted. A similar process involving a 1,2-hydride shift would lead to (7c). It is apparent from the deuterium distribution that the reaction does not exhibit a measurable deuterium isotope effect.

Compound (5a) occupies a special position in the series of dibromocarbene adducts of cycloalkenes. The outward disrotatory mode of ring opening is favourable in the Ag^+-promoted solvolysis of higher homologues (e.g. 1) and the inward disrotatory mode is favourable in the solvolysis of lower homologues (e.g. 3). In the case of (5a), neither mode is particularly favourable: outward disrotation leads to the highly strained trans,trans-cycloheptenyl cation and inward disrotation leads to the cis,cis-cycloheptenyl cation, which is subject[5] to torsional and possibly also to transannular strain. This would appear to suggest an explanation for the observations that the Ag^+-promoted solvolysis of (5a) is slow and that a process involving a 1,2-hydride shift competes with the normal ring expansion reaction. The slow reaction of (5a) correlates with reported data[6] on the acetolysis of the toluene-p-sulphonate esters of exo- and endo-bicyclo[4,1,0]-heptan-7-ols.

Finally, the solvolysis of (10)[7] was examined. When (10) was treated with silver perchlorate in aqueous acetone solution at 20°, a rapid reaction ensued. Examination (t.l.c.) of the products after 30 min. revealed

one major component: the latter was isolated by distillation as a colourless liquid, b.p. 86°/0.2 mm, in 62% yield; it was identified as (12)[8] on the basis of its n.m.r. [CCl_4 solution: τ7.4-8.0 (m), 8H; 8.2-8.6 (m), 8H], i.r. [ν_{max}^{film} 1660, 1630 cm^{-1}], u.v. [95% ethanol: λmax 248, 360 (ε 8,000, 360), λ min 220 nm (ε 950)] and high resolution mass [Found: M^+ at m/e = 164.1203. Calc. for $C_{11}H_{16}O$: 164.1201] spectra; its analytically pure 2,4-dinitrophenylhydrazone had m.p. 204-205.5° (lit.[9] 203-205°). The only possible disrotatory mode of ring opening of (10) is very unfavourable as it leads to a highly-strained transition state. It seems likely that the mechanism of the formation of (12) is similar to that of (7a) except that a 1,2-carbon shift (via a species such as (11)) rather than a 1,2-hydride shift is involved.

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References and Footnotes

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2. R. B. Woodward and R. Hoffmann, J. Amer. Chem. Soc. 87, 395 (1965); H. C. Longuet-Higgins and E. W. Abrahamson, ibid. 87, 2045 (1965).

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4. 1-Deuterio-7,7-dibromobicyclo[4,1,0]heptane (6b) was prepared from 1-deuteriocyclohexene (> 95% d_1, obtained by quenching 1-lithiocyclohexene [E. A. Braude and J. A. Coles, J. Chem. Soc., 2014 (1950)] with D_2O), bromoform and potassium tert-butoxide by the usual procedure [W. von E. Doering and A. K. Hoffmann, J. Amer. Chem. Soc., 76, 6162 (1954)]; its mass spectrum revealed that it was 96% $C_7H_9DBr_2$.

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8. Since this work was completed, Ledlie [D. B. Ledlie, J. Org. Chem. 37, 1439 (1972)] has identified (12) as one of the products obtained by treating (10) with silver nitrate in methanol solution.

9. R. K. Hill and R. T. Conley, J. Amer. Chem. Soc. 82, 645 (1960).