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RING-EXPANSION OF A DIHALOGENOCARBENE ADDUCT OF A CYCLOHEPTENE DERIVATIVE AND THE CORRESPONDING RETRO-REACTION

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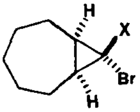
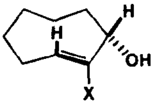
Summary: The dihalogenocyclopropane derivative (8c) was obtained in 41% isolated yield when (9a) was treated with an excess of methanesulphonyl chloride and triethylamine in dichloromethane solution; this transformation may be regarded as the retro-reaction corresponding to the silver(I) perchlorate promoted ring-expansion of (8a) to give (9a).

It was established a number of years ago that, in accordance with the principle of conservation of orbital symmetry[1], *exo*-8-bromobicyclo[5.1.0]octane (1a) undergoes solvolysis in the presence of sodium hydrogen carbonate in boiling aqueous dioxane to give[2] *trans*-cyclo-oct-2-en-1-ol (2a), and that the same transformation can be effected[3] rapidly at room temperature by treating (1a) with a concentrated (>1.0 M) solution of silver(I) perchlorate in acetone-water (9:1 v/v). In the same way, 8,8-dibromobicyclo[5.1.0]octane (1b) readily undergoes silver(I) ions promoted hydrolysis[3] to give (2b), and it is reasonable to conclude that this reaction also proceeds by a concerted mechanism involving heterolytic cleavage of the bond joining the *exo*-bromo substituent to *C*-8.



(1) a; X = H
b; X = Br



(2) a; X = H
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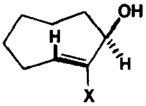
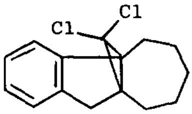
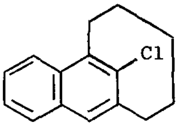


(3) a; X = H
b; X = Br

The above ring-expansion reactions are stereospecific in two respects: first, they lead solely to *trans*-cyclo-octene derivatives and, secondly, only one of the two possible diastereoisomeric alcohols is obtained. Thus no (3a) can be detected[2-4] in the solvolysis products of (1a), and no (3b) can be detected[3] in the solvolysis products of (1b). The conversion of (2a) and (2b) into (1a) and (1b), respectively, requires[5] that the putative *trans*, *trans*-allylic cations, formed by the outward disrotatory ring-opening of the bicyclo[5.1.0]-octane systems, should undergo solvolysis on the same side as that from which the *exo*-bromo group departs.



(4)



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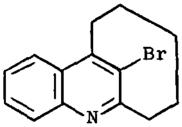
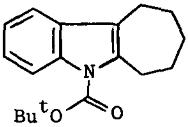
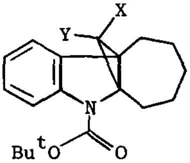


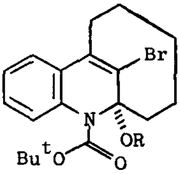
(6)



(7)



(8) a; X = Y = Br
b; X = Y = Cl
c; X = Br, Y = Cl



(9) a; R = H
b; R = Ms

We found[6] that when (4) was treated with silver(I) perchlorate in the presence of 2,6-lutidine in anhydrous tetrahydrofuran solution, the strained [5] metacyclophane derivative (5) was obtained in 55% isolated yield. The present study originated in an attempt to prepare the related [5] (2,4)quinolinophane system (6). Treatment of the protected indole derivative[7] (7) with bromoform and potassium t-butoxide in petroleum ether gives the dibromocarbene adduct (8a) as a crystalline solid, m.p. 131°C, in 83% isolated yield. When (8a) (4.28 mmol) is allowed to react with silver(I) perchlorate (26.0 mmol) in the presence of 2,4,6-collidine (13.0 mmol) in anhydrous tetrahydrofuran (12 ml) at room temperature for 4 hr, with care being taken to exclude both moisture and light, (9a) is obtained and isolated as a crystalline compound, m.p. 118-120°C, in 84% yield. The latter compound (9a) was characterized on the basis of microanalytical, n.m.r. (^{1}H, ^{13}C) and mass spectroscopic evidence, and an X-ray crystal structure analysis (Fig. 1). The corresponding dichlorocarbene adduct (8b) [illegible]

Where (9a) (1.25 mmol) is allowed to react with methanesulphonyl chloride (12.9 mmol) and triethylamine (12.4 mmol) in dichloromethane (10 ml) at room temperature for 20 min, (8c) is obtained as the main product. The latter compound (8a) was isolated in 41% yield, and was characterized on the basis of its mass spectrum [M^+ at m/z = 411.0597. Calc. for $C_{19}{}^{79}Br^{35}ClH_{23}NO_2$: 411.0600], ^{1}H and ^{13}C n.m.r. spectra[8], and by comparison with authentic material prepared[9] by the addition of bromochlorocarbene to the protected indole derivative (7). Presumably, (9a) reacts with triethylamine and methanesulphonyl chloride to give triethylammonium chloride and the corresponding mesylate derivative (9b). The latter compound (9b), which is derived from a tertiary allylic system with an α-nitrogen substituent readily ionizes to give the *trans,trans*-allylic cation presumed, by analogy with the conversion of (1b) into (2b) (see above), to be involved in the conversion of (8a) into (9a). This cation then undergoes disrotatory ring closure, accompanied by chloride ion solvolysis occurring on the same side[5] as that from which methanesulphonate anion departs from the putative intermediate mesylate (9b). Apart from the fact that chloride ions are involved instead of bromide ions and there is no involvement of silver(I) ions, the conversion of (9a) [*via* (9b)]

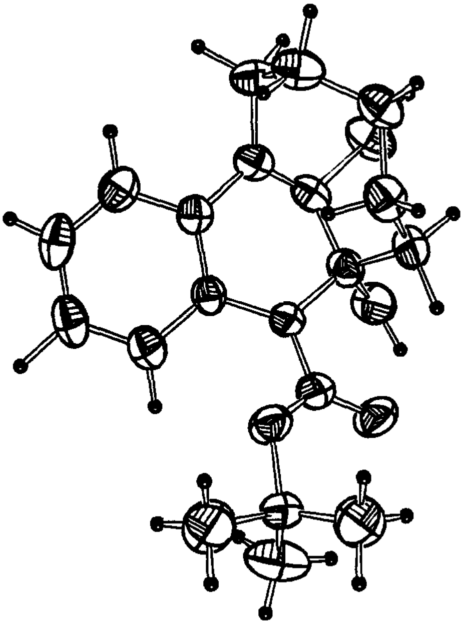


Figure 1

Computer-drawn plot of molecular structure of (9a)

into (8c) is the reverse of the conversion of (8a) into (9a). We are unaware of other examples in the literature in which the transformation of a cyclopropyl into an allylic system and the retro-reaction have both been observed. Presumably, the mild conditions required for the conversion of (9a) into a very strained allylic cation, the presence of a suitable nucleophile [i.e. chloride ions] and the particular stability [as evidenced by its resistance to silver(I) perchlorate promoted solvolysis][9] of the product all contribute to making this retro-ring-expansion reaction particularly favourable.

Acknowledgement. We thank the S.E.R.C. for the award of a Research Studentship.

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[8] The ^{13}C n.m.r. spectrum of (8c) [$\delta_c(CDCl_3$, 62.89 MHz): 26.39, 27.03, 28.21, 30.92, 31.53, 46.53, 61.3, 62.77, 82.10, 115.60, 122.89, 123.77, 128.81, 130.46, 153.05] is closely similar to the corresponding spectra of (8a) [26.50, 27.19, 28.28, 30.66, 31.53, 46.51, 50.79, 61.0, 82.18, 115.61, 122.81, 123.45, 128.90, 132.04, 146.86, 152.72] and (8b) [26.38,