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SILVER ION ASSISTED SOLVOLYSIS OF 11-BROMO-11-FLUOROTRICYCLO[4.4.1.0^{1,6}]UNDECANE

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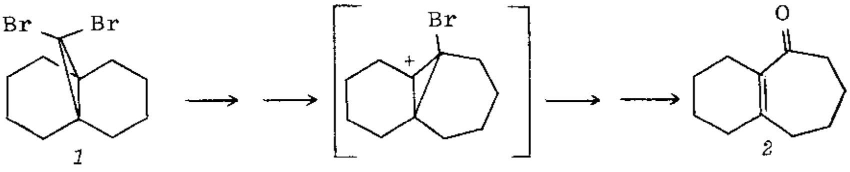
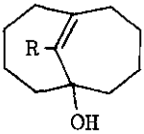
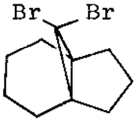
We previously reported[1] that 11,11-dibromotricyclo[4.4.1.0^{1,6}]-undecane *(1)* reacted rapidly with silver perchlorate in aqueous acetone solution to give *2* as the major product. Like Ledlie[2], who independently obtained *2* as a product of the silver ion-assisted solvolysis of *1*, we favoured, in the absence of any experimental evidence to the contrary, a reaction pathway involving a 1,2-alkyl shift in an initially formed cyclopropyl cation (Scheme 1) over a pathway involving disrotatory ring-opening to give a bridged *trans*-cycloheptene intermediate *(3a)*. Nevertheless we found[3] that the silver perchlorate-promoted solvolysis of 10,10-dibromotricyclo[4.3.1.0^{1,6}]-decane *(4)* gave *5* as the major product and we proposed[3] that the latter compound resulted from the fragmentation of an intermediate bridged *trans*-cycloheptene derivative *(6)*, corresponding to *3a*. Subsequent studies by Warner and Lu[4] on the solvolysis of ^{13}C-labelled 11,11-dichlorotricyclo[4.4.1.0^{1,6}]undecane (the dichloro-analogue of *1*) have suggested that the mechanism outlined in Scheme 1 for the conversion of *1* into *2* is incorrect and that the latter compound *(2)* is obtained exclusively from *3a* *via* the rearrangement of its hydration product *(7)* (see below). We now report what we believe to be convincing evidence in support of Warner and Lu's mechanism.[4]

Scheme 1





3a; R = Br
b; R = F



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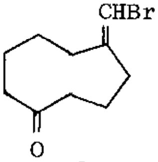

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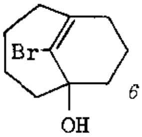

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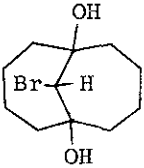

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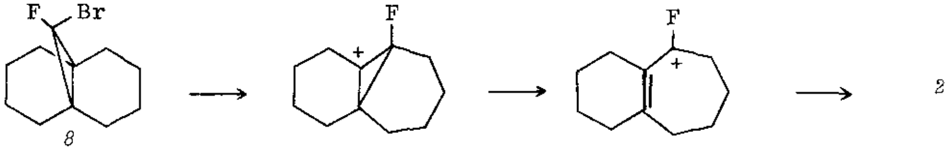
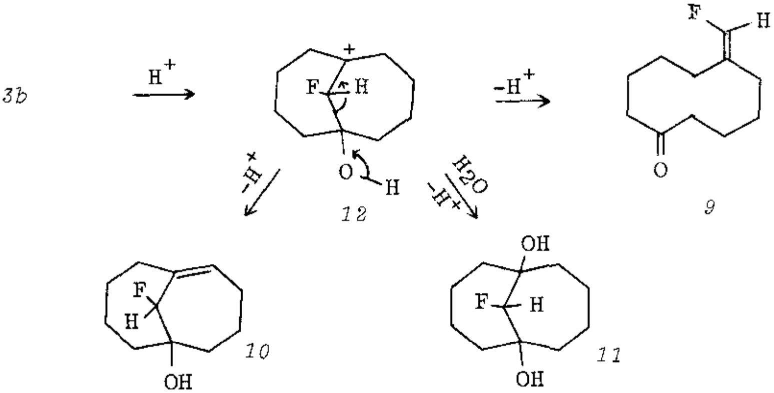
Reaction between $\Delta^{9,10}$-octalin, dibromofluoromethane[5] and potassium t-butoxide in petroleum ether gave 11-bromo-11-fluorotricyclo$[4.4.1.0^{1,6}]$-undecane *(8)* in low yield. It seems reasonable to assume that if the mechanism indicated for the transformation of *1* into *2* in Scheme **1** were correct, treatment of *8* with silver perchlorate in aqueous acetone would also give *2* according to Scheme 2. However, when *8* (2.0 mmole) was treated with silver perchlorate (4.0 mmole) in acetone-water (9:1 v/v; 4 ml) at room temperature, a rapid reaction ensued but no trace of the bicyclic ketone *(2)* could be detected in the products. After chromatography of the latter on silica gel, *9* (28%), *10* (9%) and *11* (m.p. 132-133°, 37%) were isolated as pure compounds.[6]

Scheme 2

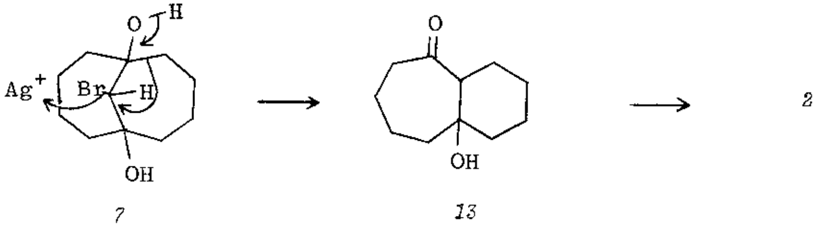


Scheme 3



Compounds *9*, *10* and *11* all appear to be derived (Scheme 3) from an intermediate bridged *trans*-cycloheptene derivative *(3b)*. While fragmentation of *12* leads to *9*, loss of a proton from and hydrolysis of *12* lead, respectively, to *10* and *11*. It therefore seems reasonable to conclude that the silver ion-assisted hydrolysis of *8* proceeds to the extent of at least 74% by initial disrotation to give the bridged *trans*-cycloheptene intermediate *(3b)*. Furthermore, there is no evidence that the latter reaction proceeds to any extent along any other pathway, such as that indicated in Scheme 2.

Scheme 4



It would therefore appear to be extremely unlikely that the reaction pathway outlined in Scheme 1 operates in the silver ion-assisted hydrolysis of the closely-related compound, *1*. The much more likely course for the hydrolysis of *1*, proposed by Warner and Lu[4], consists of the following steps: (i) disrotatory ring opening of *1* to give *3a*, (ii) hydration of *3a* to give *7*, (iii) silver ion-assisted rearrangement of *7* (Scheme 4) to give bicyclo[5.4.0]-undecan-1-ol-6-one *(13)* and (iv) elimination of water from *13* to give *2*. The most notable difference between the chemistry of *(1)* and that of *(8)* in the present context is that *7*, unlike *11*, is susceptible to silver ion-promoted ring contraction (Scheme 4). It remains unclear why virtually no 6-bromomethylene-cyclodecanone (the bromo-analogue of *9*) is formed[7] in the silver ion-promoted hydrolysis of *1*.

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REFERENCES AND FOOTNOTES

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4. P. Warner and S.-L. Lu, J. Amer. Chem. Soc. **97**, 2536 (1975).

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6. Satisfactory microanalytical or high resolution mass spectroscopic data were obtained for all the new compounds described. Compound *9* has $\nu_{max}^{CDCl_3}$ 1695 cm^{-1}; τ($CDCl_3$, 220 MHz): 3.55 (1H, d, *J* = 87 Hz), 7.44 (4H, t, *J* ∿ 6 Hz), 7.85 (2H, m), 8.0 - 8.25 (6H, m), 8.25 - 8.5 (4H, m). Compound *10* has ν_{max}^{film} 3420s cm^{-1}; τ($CDCl_3$, 220 MHz): 4.44 (1H, m), 4.69 (1H, d, *J* = 52 Hz), 7.3 - 7.7 (3H, m), 7.8 - 8.8 (all other protons) [The n.m.r. spectrum of *10* clearly indicates that it is a pure diastereoisomer but its stereochemistry has not been established]. Compound *11* has τ($CDCl_3$, 220 MHz): 5.45 (1H, d, *J* = 49 Hz), 7.0 - 7.5 (2H, m), 8.0 - 8.7 (16H, m).

7. In our original study[1], we did not detect the formation of 6-bromomethylenecyclodecanone but Warner and Lu[4] have estimated that the latter compound is formed in 0.4% yield under their reaction conditions.