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INVESTIGATIONS IN THE CYCLOBUTANE SERIES XXV (1)
THE ADDITION OF BROMINE TO 3.4-BENZOTRICYCLO [4.2.1.$0^{2,5}$]NONA-3.7-DIENE

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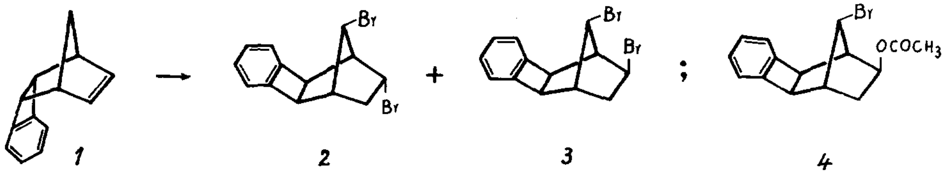
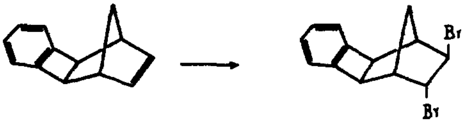
The existence of stable three and five-membered ring halonium ions, in antimony pentafluoride-sulfur dioxide solution at -60°, was recently demonstrated by n.m.r. spectroscopy (2, 3, 4). We now wish to report about a four-membered ring halonium ion which may appear as intermediate in the addition of bromine to 3.4-benzotricyclo[4.2.1.$0^{2,5}$]nona-3.7-diene (benzocyclobutenonorbornene).



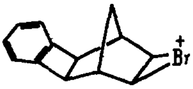
endo-3.4-Benzotricyclo[4.2.1.$0^{2,5}$]nona-3.7-diene 1 (5) gave with bromine, in dichloromethane solution, as main products (91%), a mixture of 83.5% 9-syn-7-endo-dibromo-exo-3.4-benzotricyclo[4.2.1.$0^{2,5}$]nona-3-ene 2, m. p. 108° and 16.5% 9-syn-7-exo-dibromo-exo-3.4-benzotricyclo [4.2.1.$0^{2,5}$] nona-3-ene 3, m. p. 76°. Solvolytic addition of bromine in acetic acid led to 9-syn-bromo-7-exo-acetoxy derivative 4, m. p. 122°.

The *exo* isomer 5 (6) gave, under the same conditions, a single dibromo compound, namely *trans*-7.8-dibromo-*exo*-3.4-benzotricyclo$[4.2.1.0^{2,5}]$ nona-3-ene, 6, m.p. 84°.



5 6

The dibromo derivative 6 is a product of normal, *trans* addition, resulting probably from the bromonium ion 7. The open ion 8 with localized charge should not be favoured by the nonpolar solvent. An effective intervention of the nonclassical ion 9 may be excluded since we did not find the corresponding products, namely those resulting from *exo* attack of Br^- at the 1 and 8 positions.



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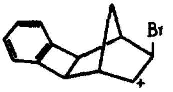

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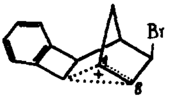

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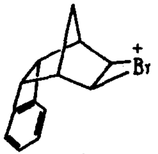
The formation of 2 and 3, during the addition of bromine to the *endo* olefin 1, involves a rearrangement of the skeleton. In order to explain this result we must admit that the initial ion 10 (or 11) rearranges to the nonclassical ion 12. This intermediate accounts for the dibromo-derivative 3 as well as for the solvolytic addition product 4.

As in the previous case, the open ion 11 is probably unfavoured by the nonpolar properties of the medium. The absence of the *trans*-7.8-dibromo-derivative, 6, among the reaction products could be due to the field of the phenyl π-electron system which prevents the _endo_ attack by the bromide ion of the intermediates 10 (or 11).



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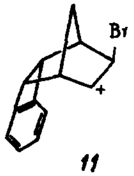

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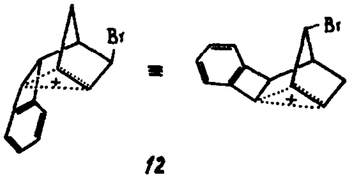

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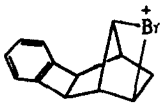
However, the nonclassical ion 12 cannot explain the formation of the dibromo compound 2. One possibility which cannot be ruled out off-hand is the epimerization of 3 to 2. We checked this hypothesis and found that such a transformation does not actually take place in our reaction conditions.

The formation of the dibromo derivative 2 as the main reaction product can be explained if we admit the intervention of the four-membered ring bromonium ion 13. The latter should result by supplying the electron deficit at the 7-positive centre of the ion 12 with the unshared electrons of the nearby bromine atom. The bromonium ion 13 can be attacked by Br⁻ only from _endo_, affording thus the product 2.



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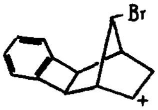

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An open ion 14 is probably unfavoured, as in the previous case, by the nonpolar properties of the medium.

Bromonium ions of 13-type should possess an intermediate stability between the three- and the five-membered ring ones (2, 4). In our case the formation of a four-membered ring bromonium ion was favoured by the rigidity of the molecular system.

N.m.r. spectra and elemental analyses of the reaction products were consistent with the assigned structures.

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