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# $Ag^+$-ASSISTED METHANOLYSIS OF HALOGENOCARBENE ADDUCTS OF CYCLOHEPTA-1,3-DIENE

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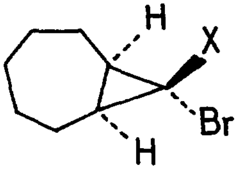
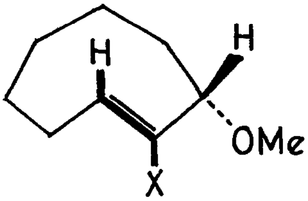
We previously found[2] that when exo-8-bromo- and 8,8-dibromobicyclo-[5,1,0]octanes (**1**a and **1**b) were treated with silver perchlorate in methanol solution at 20°, they underwent rapid methanolysis and high yields of 3-methoxy- and 2-bromo-3-methoxy-trans-cyclo-octenes (**2**a and **2**b), respectively, were obtained. The corresponding bicyclo[5,1,0]oct-3-ene derivatives (**3**a and **3**b) were also found to undergo methanolysis under the same conditions to give 6-methoxy- and 5-bromo-6-methoxy-cis,trans-cyclo-octa-1,4-dienes (**4**a and **4**b), respectively, as the main products.[3]



**1** a; X=H
b; X=Br



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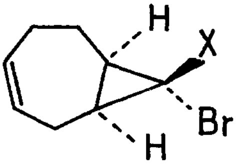
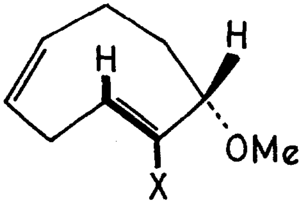
b; X=Br



**3** a; X=H
b; X=Br

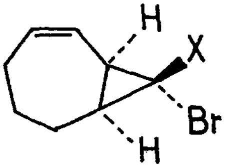


**4** a; X=H
b; X=Br

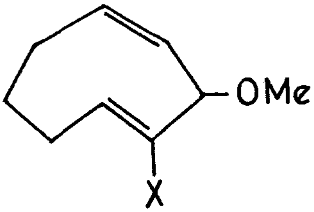
Encouraged by the success of this approach to the preparation of strained trans-cycloalkene derivatives, we have since undertaken a study of the $Ag^+$-catalyzed methanolysis of exo-8-bromo- and 8,8-dibromo-bicyclo[5,1,0]oct-2-enes (5a and 5b). Apart from the synthetic importance of this study, it was of interest to find out if double bonds, conjugated with the cyclopropyl system, had any effect on the site of solvolysis in the ring expansion reaction.

Exo-8-bromobicyclo[5,1,0]oct-2-ene (5a) was treated with silver perchlorate in methanol solution under the usual conditions.[2] After work-up and distillation of the products, an approximately 1:1 mixture of two isomeric methoxycyclooctadienes was obtained in 71% yield. The latter compounds were separated by preparative g.l.c. and isolated as analytically pure oils; they were identified as 3-methoxy-cis,trans-cyclo-octa-1,4-diene (6a) and 5-methoxy-cis,trans-cyclo-octa-1,3-diene (7a) on the basis of their spectroscopic (n.m.r., i.r., u.v., m.s.) properties. In confirmation of these structural assignments, when 6a and 7a were treated with catalytic amounts of iodine[4] in carbon tetrachloride solution they were converted into 3-methoxy-cis,cis-cyclo-octa-1,4-diene (8) and 5-methoxy-cis,cis-cyclo-octa-1,3-diene (9), respectively. The latter compound (9) was obtained as the sole product when endo-8-bromobicyclo[5,1,0]oct-2-ene (10) was treated with silver perchlorate in methanol solution. When 7a was heated at 100° for 45 min, it was converted into an isomer to which structure (11) has been assigned on the basis of spectroscopic evidence.

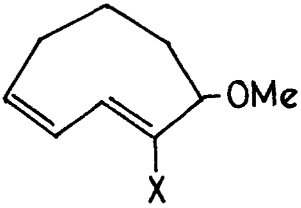
If a free trans,trans-allylic cation[5] is involved as an intermediate[6] in the $Ag^+$-catalyzed methanolysis of exo-8-bromobicyclo[5,1,0]oct-2-ene (5a), then the products obtained (6a and 7a) would result if methanol attacked both ends of this allylic cation at approximately equal rates. No product derived from the attack of methanol on the conjugated cis-double bond could be detected.



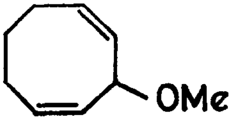
5 a; X=H
b; X=Br



6 a; X=H
b; X=Br



7 a; X=H
b; X=Br



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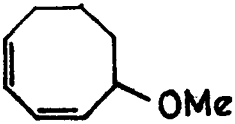

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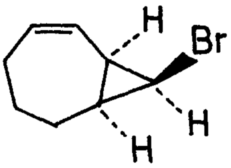

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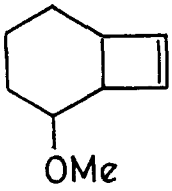

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A similar result was obtained when 8,8-dibromobicyclo[5,1,0]oct-2-ene (5b) was treated with silver perchlorate in methanol solution. Work-up of the products gave a high yield of an approximately 1:1 mixture of two bromomethoxy-cyclo-octadienes which, on the basis of spectroscopic and analytical evidence, are believed to be 4-bromo-3-methoxy-cis,trans-cyclo-octa-1,4-diene (6b) and 4-bromo-5-methoxy-cis,trans-cyclo-octa-1,3-diene (7b).

## References and Footnotes

1. Present address: Department of Organic Chemistry, The University, Newcastle upon Tyne, England.
2. C.B. Reese and A. Shaw, *J. Amer. Chem. Soc.* **92**, 2566 (1970).
3. M.S. Baird and C.B. Reese, *Chem. Comm.*, 1644 (1970).
4. A.C. Cope and C.L. Bumgardner, *J. Amer. Chem. Soc.* **78**, 2812 (1956).
5. R.B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.* **87**, 395 (1965).
6. As methanolysis of *exo*-8-bromo- and 8,8-dibromo-bicyclo [5,1,0]octanes (**1**a and **1**b) leads to diastereoisomerically pure *trans*-cyclo-octene derivatives[2,7] (**2**a and **2**b, respectively), it is possible that free *trans*,*trans*-allylic cations are not involved as intermediates in these transformations.[7] As it appears from their n.m.r. spectra that **6**a and **7**a are also diastereoisomerically pure, the methanolysis of **5**a might also be concerted with ring-expansion.
7. C.B. Reese and A. Shaw, *Chem. Comm.*, 1365 (1970).