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The Silver Ion Assisted Methanolysis of 11,11- Dibromotricyclo(4.4.1.$0^{1,6}$)undec-3-ene

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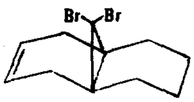
We have recently been interested in the chemistry of "constrained" cyclopropyl halides. That is, systems which because of either steric or electronic factors do not or are loath to undergo "normal" distotatory ring opening under solvolytic conditions (2,3,4). Herein we report on the chemistry of such a constrained system - the title compound 1 (1). In addition, we compare its reactivity to that of the corresponding saturated system 2.



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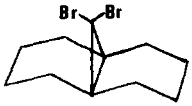

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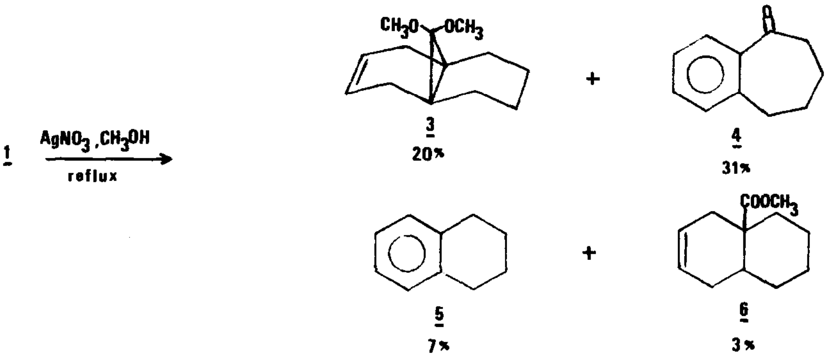
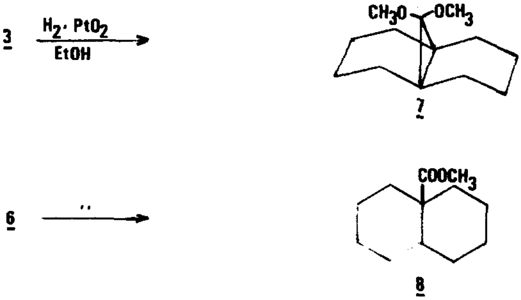
When compound 1 was stirred at reflux for two hours with a four-fold excess of silver nitrate in methanol, four major products (3,4,5,6) were obtained (eqn. 1) (5).



(1)

Both compounds 4 and 5 were identified by comparison of their infrared and nmr spectra with spectra of authentic materials. An nmr spectrum of 3 exhibits absorption at 0.90-2.56ppm (complex absorption, 12 protons), 3.17 and 3.24ppm (2 singlets, 6 protons) and 5.34ppm (broad singlet, 2 protons). Compound 6 exhibits infrared absorption at 3010, 1720, and 1615cm^{-1}. Unambiguous structure proof for compounds 3 and 6 is outlined in Scheme I (6).

SCHEME I

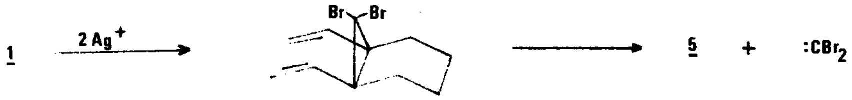


Infrared spectra of 7 and 8 were identical to those of authentic materials (2, 7).

We believe that compounds 3 and 4 arise *via* mechanisms similar to those reported in our study of the solvolytic behavior of 2 (2). Aromatization of diene 9 (oxidation,probably by silver ion) results in the formation of 4 (eqn. 2) (8). Formation of ester 6 ostensibly results from acid catalyzed ring opening of 3. The formation of tetralin (5) can be envisioned as outlined in Scheme II. Precedent for this "oxidation-retro carbene addition"

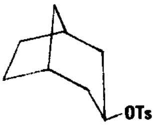
(2)

SCHEME II



is found in the work of Vogel and co-workers (9).

It is interesting to note that the sole product resulting from ring expansion is that which arises from bond migration in the saturated six-membered ring of 1. The migratory aptitude of the corresponding bond in the unsaturated ring *could* conceivably be greatly decreased by an enhanced inductive effect resulting from complexation of the site of unsaturation with silver ion and thus bond migration might be completely mitigated (10). If indeed this is correct, the relative rate of solvolysis of 1 as compared to 2 should also reflect the effect of complexed silver ion. Kinetic studies demonstrate that at 25° compound 1 is approximately forty times less reactive than 2 (11). Recently LeBel has reported on the solvolytic behavior of 10 and 11 (12). It was found that 10 was some three times more reactive than 11 at 25°. Thus it would seem that silver ion plays a significant role in influencing the product distribution as well as rate in the silver ion assisted methanolysis of systems such as 1. Further, product and kinetic studies indicate no significant participatory role of the double bond in the solvolysis of 1.



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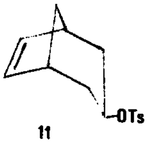

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1) Prepared according to the method of Vogel - see *Liebigs Ann. Chem.*, **759**, 1 (1972).

2) D.B. Ledlie, *J. Org. Chem.*, **37**, 1439 (1972).

3) D.B. Ledlie and W.H. Hearne, *Tetrahedron Lett.*, 4837 (1969).

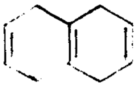
4) D.B. Ledlie and E.A. Nelson, *ibid*, 1175 (1969).

5) All yields were determined by gas chromatography.

6) Although this does not constitute rigorous proof of the location of the double bond in either **3** or **6**, it does establish the structure of the carbon skeleton. Mechanistic considerations, however, lead us to believe that our assignments as to the location of unsaturation in **3** and **6** are correct.

7) We are indebted to Professor F.D. Greene for supplying us with an infrared spectrum of compound **8**.

8) Calculations indicate that in the gas phase the reaction is thermodynamically favorable - see S.W. Benson, *et al.*, *Chem. Rev.* **69**, 279 (1969). We have also demonstrated that silver ion and a trace of nitric acid in either methanol or diglyme quantitatively converts the triene **12** to naphthalene.



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9) E. Vogel, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, **12**, 215 (1968).

10) F.R. Hartley, *Chem. Rev.*, **73**, 163 (1973).

11) This is an extrapolated value. Second order rate constants were determined *via* pseudo-first order techniques. Silver perchlorate 0.23M (20-fold excess) in 95% methanol was employed as the reaction medium.

12) N.A. LeBel and R. Maxwell, *J. Amer. Chem. Soc.*, **91**, 2307 (1969).