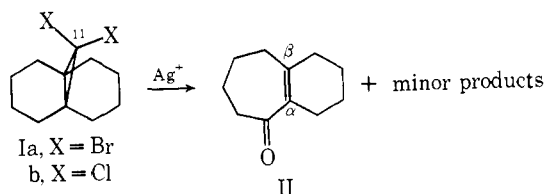


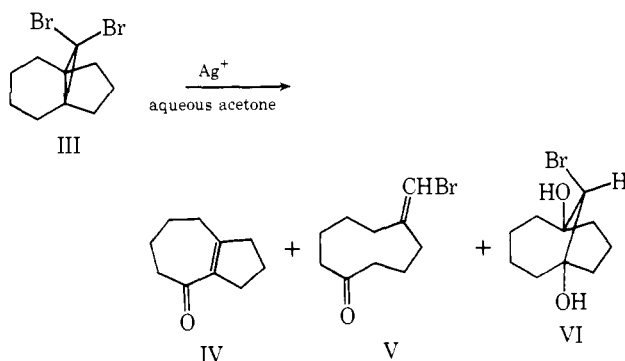
Propellanes. VI.¹ Bridgehead Double Bond Formation in the Solvolysis of 11,11-Dihalotricyclo[4.4.1.0^{1,6}]undecane²

Sir:

We wish to reopen the question of the mechanism of Ag^+ -assisted solvolysis of 11,11-dihalotricyclo[4.4.1.0^{1,6}]undecane (I). Previously Ledlie³ and Reese⁴ have found enone II to be a major constituent of the solvolysate from Ia (X = Br). Both these workers have postulated that II is formed



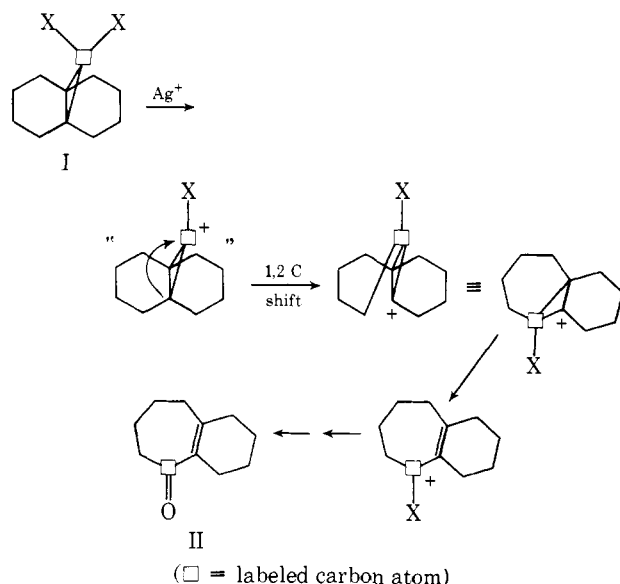
via an alkyl shift mechanism, where the shift involves conversion of one cyclopropyl cation to another (Scheme I).⁵ Reese^{6,7} has also found that solvolysis of the analogous [4.3.1]propellane (III) gives rise to an enone (IV), together with products (V and VI) attributable to an intermediate



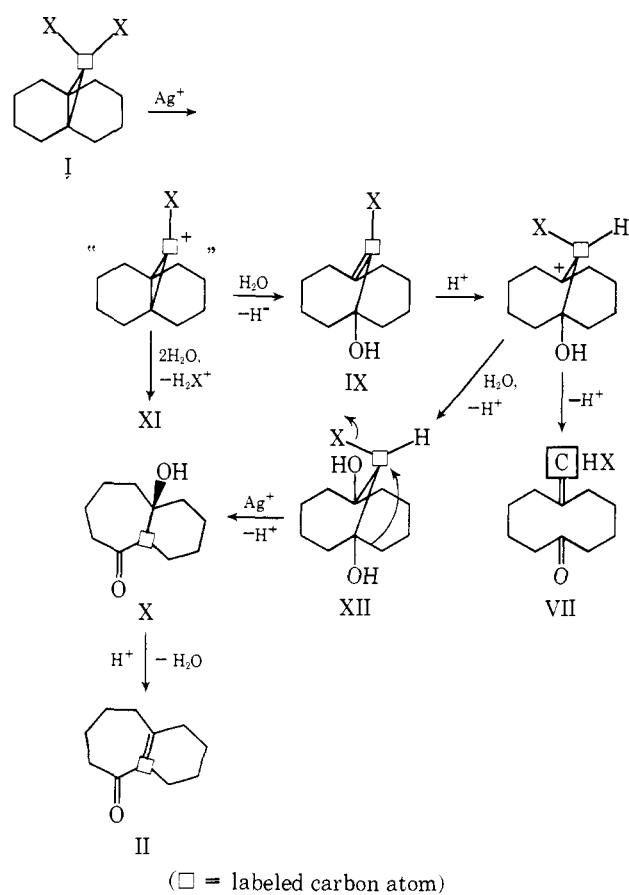
species containing a bridgehead double bond. However, the absence of products of the latter type in the solvolysate from Ia was emphasized.⁶

Our attention became focused on Ia due to our desire to compare its rate of solvolysis (in the absence of Ag^+)⁸ with that of III and similar compounds.⁹ As part of our studies, we checked the products derived from Ia in HOAc-NaOAc

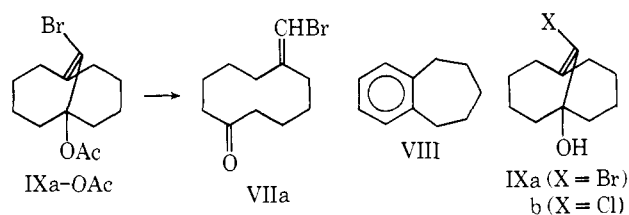
Scheme I



Scheme II



(125°), and found them to be II (36%), VIIa (19%), VIII (21%),¹⁰ and an unidentified acetate (ca. 18%); VIIa clear-



ly^{6,7} arises from an intermediate containing a bridgehead double bond (IXa-OAc). We then rechecked the solvolysis of Ia in 90% aqueous acetone,⁴ and found that VIIa was a minor product (spotted first by ir, $\nu_{\text{C}=\text{O}} = 1710 \text{ cm}^{-1}$, and NMR, δ 5.95 for vinyl H, and positively identified by GLC-mass spectrometry¹¹ as being formed in ca. 0.4% yield) while II was indeed the predominant one.

It thus occurred to us that an alternate pathway for formation of II, involving the intermediacy of IXa, was possible. At least three alternate mechanisms, two of which involve IXa and all of which leave an initially labeled C₁₁ at C α of the α,β -unsaturated enone system, have become apparent. The mechanism we favor (vide infra) is outlined in Scheme II.¹² Clearly, the actual labeling pattern had to be established first. We thus prepared I¹³ with ¹³C enrichment at C₁₁ via standard procedures,¹³ utilizing ¹³C-enriched CHCl_3 (Merck).

When Ib was allowed to react at room temperature with 5 equiv of AgClO_4 in 90% aqueous acetone, at least seven products were formed after 24 hr (note the roughly 50-fold rate deceleration compared to Ia⁴). We have identified four¹⁴ of these, and the absolute yields of product (GLC on 20% SE30, corrected, and/or column chromatography) are

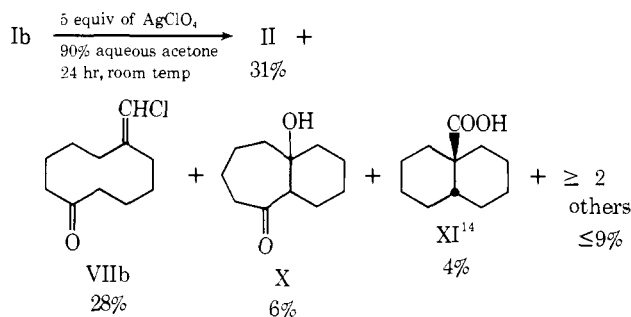
Table I. FT NMR Data for Enone II

| Compound | Relative area | | | No. of pulses (20-sec intervals) |
|-----------------------------|---------------|----------------|----------------|----------------------------------|
| | Carbonyl C | C _α | C _β | |
| Unenriched II | 1.02 | 0.62 | (1.00) | 2000 |
| ¹³ C enriched II | 0.84 | 5.06 | (1.00) | 1710 |

Table II. Product Ratios For Various Aqueous Acetone Mixtures.

| % H ₂ O (by volume) | (II + X)/VIIa | % H ₂ O (by volume) | (II + X)/VIIa |
|--------------------------------|---------------|--------------------------------|---------------|
| 10 | ≥160 | 2 | 34 |
| 5 | 43 | 1 | 19 |

shown. While the major product was still enone II, the monocyclic ketone product, VIIb, clearly derived from bridgehead olefin IXb, was also formed in considerable quantity.¹⁶ The presence of X¹⁷ (later identified as a product from



Ia, too) proved to be a key finding; X is presumably cis-fused, although we have not shown that. Brief treatment of X with concentrated HCl (room temperature) gave II, as did exposure of X to the acidic solvolysis conditions.¹²

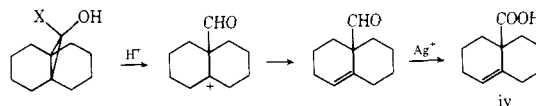
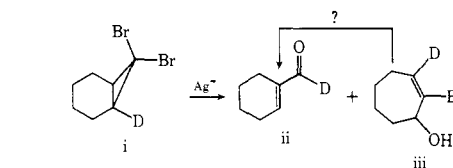
When Ib, enriched at C₁₁ such that C₁₁ contained 5.8% ¹³C (high resolution mass spectrometry, hereafter, hrms), was treated with AgClO₄ as above, the enone II contained one carbon with 5.3% ¹³C (hrms).¹⁸ Unfortunately, the fragmentation of II did not separate the carbonyl carbon from C_α, and thus allowed no mechanistic conclusions. However, the application of ¹³C NMR proved fruitful. The carbonyl, α, and β carbons of II resonate at 205, 135, and 153 ppm, respectively. Table I shows the integrated intensity of these three peaks after data collection at 20-sec pulse intervals. If C_β is taken as a standard (neither mechanism would place the label there), then it is seen that, within experimental error, all of the label winds up at C_α (which would contain 5.6% ¹³C, in good agreement with the hrms results, especially considering the vagaries of integrating FT NMR spectra). This requires that II may be formed via the mechanism shown in Scheme II, i.e., via protonation of the bridgehead double bond intermediate, IX.

Since the mechanism given in Scheme II requires that the ratio of (II + X) to VII varies with the [H₂O] in the solvolytic medium, and since we have been unable to isolate XII,¹² we undertook a study of the aforementioned ratio, beginning with Ia. The results (GLC analysis), summarized in Table II, support Scheme II.

In conclusion, there yet appears to be no case in which an intramolecular shift process competes with ring opening of a "cyclopropyl cation".¹⁹

References and Notes

- (1) For the previous paper in this series, see P. Warner, R. LaRose, and T. Schleis, *Tetrahedron Lett.*, 1409 (1974).
- (2) We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.
- (3) D. B. Ledlie, *J. Org. Chem.*, **37**, 1439 (1972).
- (4) C. B. Reese and M. R. D. Stebles, *Tetrahedron Lett.*, 4427 (1972).
- (5) An analogous deuteride shift mechanism was postulated for the solvolyses of i.⁴ This mechanism now appears incorrect (see text); we are further investigating this case and suspect ii arises from the predominant product, iii.
- (6) C. B. Reese and M. R. D. Stebles, *J. Chem. Soc., Chem. Commun.*, 1231 (1972).
- (7) P. Warner, J. Fayos, and J. Clardy, *Tetrahedron Lett.*, 4473 (1973).
- (8) For rate comparisons in the presence of silver ion, see (a) D. B. Ledlie, J. Knetzer, and A. Gitterman, *J. Org. Chem.*, **39**, 708 (1974); (b) D. B. Ledlie and J. Knetzer, *Tetrahedron Lett.*, 5021 (1973).
- (9) P. Warner and S. Lu, to be submitted for publication.
- (10) VIII is formed via an addition-solvolysis mechanism and is almost the sole product when the acetic acid is unbuffered; VIII was identified by spectral comparison (NMR, uv) with the published data [S. Kabuss, H. Friebolin, and H. Schmid, *Tetrahedron Lett.*, 469 (1965); W. R. Moore, E. Marcus, S. E. Fenton, and R. T. Arnold, *Tetrahedron*, **5**, 179 (1959), respectively].
- (11) We used a Perkin-Elmer 270 GLC-mass spectrometer fitted with a 10 ft X 1/8 in. 3% DEGS on Chromosorb P column; the temperature was programmed (50–180°). Analysis calculated for VIIa (C₁₁H₁₇BrO): *m/e* 244.0463; found, *m/e* 244.0473.
- (12) All three mechanisms will be discussed in our full paper. Also, other work, based on the [4.3.1]- and [3.3.1]dibromopropellane series (P. Warner and S. Lu, to be submitted for publication), serves to establish the mechanism shown in Scheme II.
- (13) E. Vogel, W. Wiedemann, H. Roth, J. Eimer, and H. Günther, *Justus Liebig's Ann. Chem.*, **759**, 1 (1972).
- (14) Acid XI is formed from collapse of the initial ion with retention of the cyclopropane ring, followed by acid-catalyzed ring opening, and is preceded by the work of Groves.¹⁵ Actually, XI appears to be a mixture (ca. 3:1) of XI and iv; iv may be formed via the same acid-catalyzed ring opening which leads to XI but with the proton going to C₁₁ to give an aldehyde, which is subsequently oxidized by Ag⁺.



Both XI and iv are formed from Ia and Ib but in slightly different yields.

- (15) (a) J. T. Groves and K. W. Ma, *Tetrahedron Lett.*, 909 (1974). (b) We thank Professor Groves (see ref 14 of ref 15a) for the ir spectra of XI and its trans isomer, which we utilized to identify XI.
- (16) VIIb: calcd for C₁₁H₁₇OCl, 200.0968; found, 200.0975.
- (17) The spectroscopic identification of X included the following highlights: MS parent ion at *m/e* 182 (rel intes = 10), (P - 18) at *m/e* 164 (rel intes = 100) at 70 eV; ir ν_{OH} 3450 (br), ν_{C=O} 1705 (s) cm⁻¹; ¹³C NMR, the ¹³C enriched sample of X, which gave enriched II as described, showed (relative to TMS) δ 215 (carbonyl carbon), 62 (tertiary carbon α to carbonyl-enriched), 73 ppm (carbon bearing OH).
- (18) This figure was arrived at by assuming that only one carbon position in II was enriched. The natural abundance of ¹³C for the other carbons was subtracted from the total ¹³C content of II, and the remainder was the 5.3% indicated. This includes the natural abundance of the enriched carbon.
- (19) Ledlie^{5a} has overinterpreted our thermodynamic discussion for ring opening of cyclopropyl halides;²⁰ our remarks pertain to uncatalyzed processes only. However, once a "cyclopropyl cation" is formed, ring opening becomes a more facile process.
- (20) P. Warner, R. LaRose, C. Lee, and J. Clardy, *J. Am. Chem. Soc.*, **94**, 7607 (1972).

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Δm = 3 Electron Spin Resonance in a Quartet Molecule

Sir:

In order to confirm the identification of a recently prepared series of organic molecules as electronic quartets,¹⁻⁵ we have sought for and observed the Δm = 3 transition in the electron spin resonance of one of them. The designation