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THE EFFECT OF Ag(I) ION ON PRODUCT COMPOSITION IN HYDROLYSIS[1]

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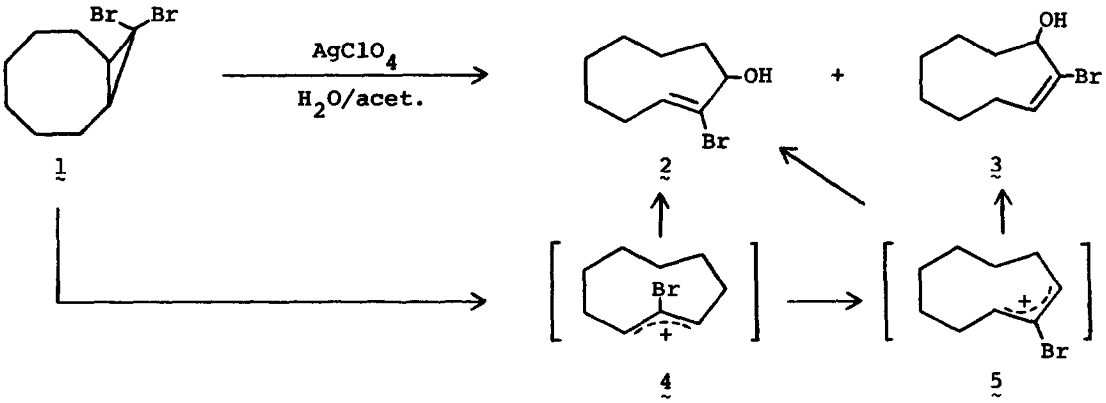
ABSTRACT: The product olefin stereochemistry from the hydrolysis of some cyclopropyl bromides is dependent on $[Ag^+]$.

During the course of our work on the Ag^+-assisted hydrolysis of tricyclic cyclopropyl halides[4], we have been concerned as to the possible effects of Ag^+ on product formation, whether via complexation or otherwise. While this sort of idea is probably not new, our interest was piqued by the report[5] that 1 undergoes reaction with excess Ag^+ at a rate which is both first and second order in $[Ag^+]$. It was also reported[6] that 1 gave both 2 and 3 upon solvolysis, which contrasted with earlier results[7]. By varying the solvent nucleophilicity[6b], Loozen demonstrated that the initially formed cation 4 most likely isomerizes to ion 5, wherefrom emanates 3.



Some of our work drew our attention to the possible relationship between products formed and $[Ag^+]$. Our initial experiments, by which we verified the results of Reese[7b] and Loozen[6a], led us to formulate the hypothesis shown in equations 1-4. At high $[Ag^+]$, the second order term should predominate, and

$$\frac{d[2]}{dt} = (k_1[Ag^+] + k_2[Ag^+]^2)\ [1] \qquad (1)$$

$$\frac{d[3]}{dt} = k'_1[Ag^+][1] \qquad (2)$$

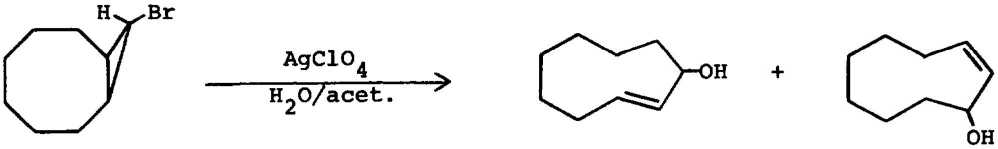
$$\therefore \quad \frac{[2]}{[3]} = \frac{k_2}{k'_1}[Ag^+] + \frac{k_1}{k'_1} \qquad (3)$$

$$\text{and} \quad \frac{k^{\text{second order}}}{k^{\text{first order}}} = \frac{k_2}{k_1 + k'_1} = \frac{\text{slope}}{1 + \text{intercept}} \qquad (4)$$

the product should be almost solely trans (2), while at low $[Ag^+]$, the cis isomer (3) should be formed.

Our quantitative experiments were performed in both 90% and 95% aqueous acetone, with initial [1] = 0.01M, and initial $[Ag^+]$ ranging from 0.1M to 1.5M. The ionic strength was kept constant by adding appropriate amounts of $LiClO_4$. In all cases, the products were stable and the product ratios were invariant with time (total yields = 89-101%). Figures 1 and 2 graphically depict the data for duplicate runs with $[ClO_4^-]$ = 1.5M in both 90% and 95% aqueous acetone, and a single run in the latter solvent with $[ClO_4^-]$ = 0.5M. The lines drawn are the least squares lines, and all correlation coefficients were ≥0.99 for the points fitting a linear relationship. As shown, the ratio of second order to first order processes is in the range 1.5-3, which is somewhat less than the ratio of ca. 10 observed in MeOH[5].

The mechanistic significance of these results was partly obscured by the presence of two bromines in 1, thus providing the possibility that exo bromine ionization (2nd order in $[Ag^+]$) led to 2, while endo bromine loss (1st order in $[Ag^+]$) afforded 3. To test this possibility, which seemed doubtful on the basis of earlier kinetic studies[8], we investigated the Ag^+-assisted hydrolysis of 6. As shown in Figure 3, equations 1-4 apply to the hydrolysis of 6, too,



6 7 8

although the second order process is much more preferred for 6 than for 1[9]. We thus feel confident that only the exo bromine of 1 undergoes ionization.

At this point, a number of mechanistic possibilities, including various pre-equilibria involving silver ions, may explain the results, and further work is necessary. However, the current observations do explain some anomalies in the literature[6,7], and may have synthetic import.

References and Notes

1. This material was presented at the 4th International Physical Organic Chemistry Symposium, York, England, September 4, 1978, abstract B.4.
2. Alfred P. Sloan Fellow, 1976-80.
3. NSF Trainee, 1974-1977.
4. (a) P. Warner, S. Lu, E. Myers, P. De Haven and R. A. Jacobson, *J. Am. Chem. Soc.*, **99**, 5102 (1977); (b) P. Warner, R. F. Palmer and S. Lu, *ibid.*, **99**, 3773 (1977); (c) P. Warner and S. Lu, *ibid.*, **98**, 6752 (1976); (d) P. Warner, R. LaRose, C. Lee and J. Clardy, *ibid.*, **97**, 5507 (1975).
5. G. M. Blackburn and R. M. Ward, *Chem. Comm.*, 79 (1976).
6. (a) H. J. J. Loozen, W. M. Robben, T. L. Richter and H. M. Buck, *J. Org. Chem.*, **41**, 384 (1976); (b) H. J. J. Loozen, J. W. de Hann and H. M. Buck, *ibid.*, **42**, 418 (1977).
7. (a) M. S. Baird and C. B. Reese, *Tetrahedron Lett.*, 4637 (1971); (b) C. B. Reese and A. Shaw, *J. Am. Chem. Soc.*, **92**, 2566 (1970); (c) C. B. Reese and A. Shaw, *J. C. S. Perkin I*, 2422 (1975). Reese's work was always carried out at high [Ag^+], which accounts for the observed stereospecificity.
8. U. Schöllkopf, *Ang. Chem. Int. Ed.*, **7**, 588 (1968).
9. The increased preference for **7** over **8**, as compared to **2** over **3**, coupled with the greater stability of the *trans*-*trans* allylic ion **i** over **ii** relative to **4** over **5**, may indicate that, mechanistically, the second Ag^+ (in the second order process) may be involved in preventing the conversion of **4** to **5** (or **i** to **ii**). However, the fact that k_2/k_1 for **6** (the ratio of the second order to first order terms for formation of **7**) is larger than k_2/k_1 for **1**, is not interpretable on the basis of a greater stability for **i** vs. **4**.

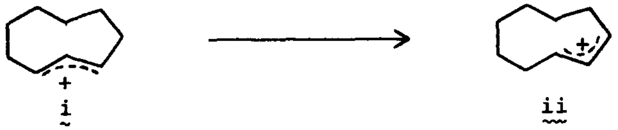


FIGURE 1. HYDROLYSIS OF 1 IN 90% AQUEOUS ACETONE
[**1**]=0.01M, [ClO_4^-]=1.5M

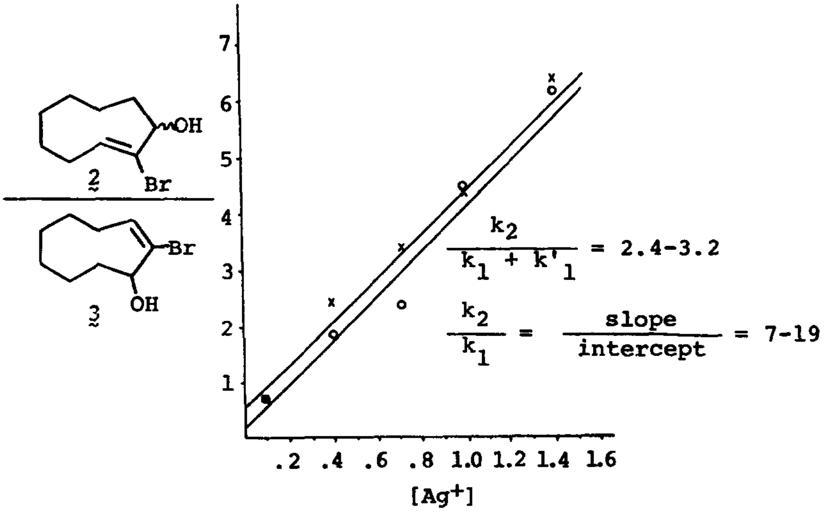


FIGURE 2. HYDROLYSIS OF 1 IN 95% AQUEOUS ACETONE
[1]=0.01M

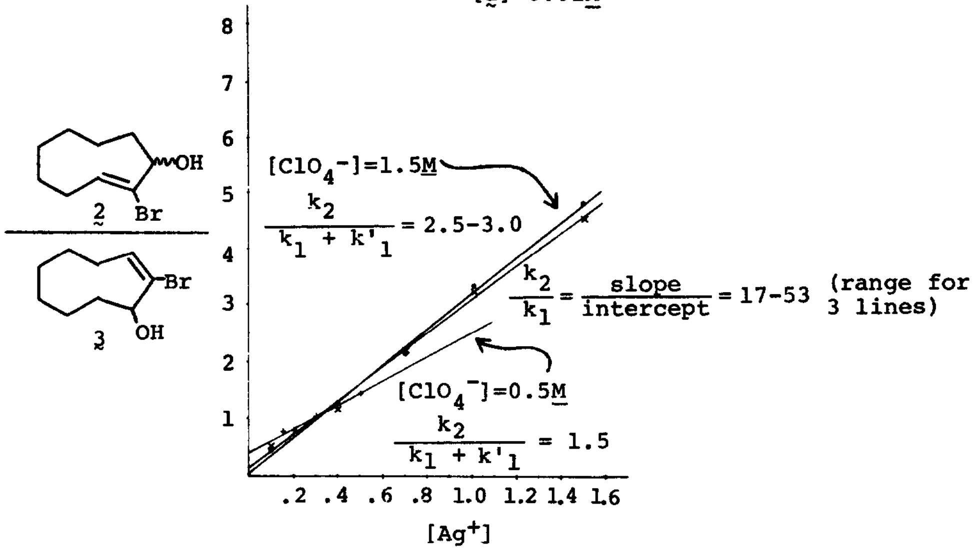
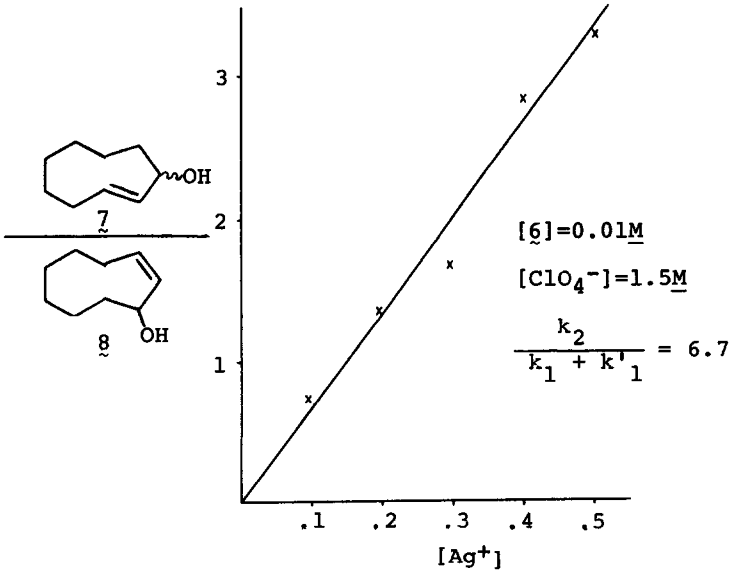


FIGURE 3. HYDROLYSIS OF 6 IN 95% AQUEOUS ACETONE



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