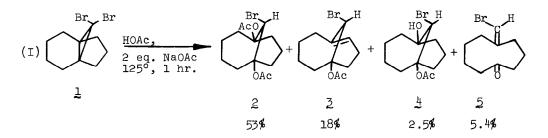
Propellanes. VII.¹ Bridgehead Olefins Via Acetolysis Philip Warner,* Shih-Lai Lu, Elaine Myers, Patrick W. DeHaven and Robert A. Jacobson

Department of Chemistry and Ames Laboratory, U.S.E.R.D.A., Iowa State University, Ames, Iowa 50010 (Received in USA 10 July 1975; received in UK for publication 4 November 1975) We,^{1,2} and others,³ have recently elucidated some of the chemistry involved in the Ag⁺-assisted solvolysis of tricyclic cyclopropyl halides. Evidence has accumulated for the protic capture of bridgehead olefin intermediates. In the course of a kinetic study,⁴ it became necessary to determine the reaction mode under non-assisted conditions. We now report product studies which also implicate bridgehead olefins.

When a $0.17\underline{M}$ solution of 10,10-dibromo[4.3.1]propellane (1) was heated in buffered ($0.34\underline{M}$ NaOAc) glacial acetic acid, compounds $2-5^5$ were isolated (silica gel column chromatography) in the yields shown in equation I. Com-



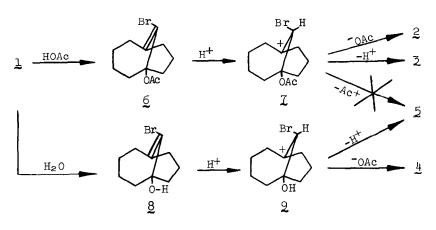
pounds 2, 3 and 5 are kinetic products; 4 may be, although 2 is slowly converted to 4 under the reaction conditions, possibly by hydrolysis with some water in the medium, or further reaction with HOAc. When the reaction was repeated in 10% Ac₂0/HOAc, the products given in equation II were obtained. This seemed to verify that 4 arose via intervention of

(II)
$$\frac{1}{2 \text{ eq NaOAc}} = \frac{1}{2 \text{ eq NaOAc}} + 2$$

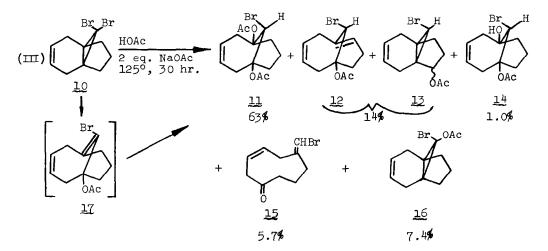
 $125^{\circ}, 1 \text{ hr. } 63\% = 21\%$

water. More importantly, the absence of monocyclic ketone 5 showed that ion 7 cannot fragment (with loss of Ac+), this strongly supports the concept^{3a} of a concerted fragmentation of 9 to 5, with the added requirement of a good departing cation (in this case a proton⁶). It should be noted that 4 does not give 5 under the reaction conditions.





The buffered acetolysis of a 0.26M solution of 10,10-dibromo[4.3.1]propella-3-ene (10) resulted in the products shown in equation III. Thus compounds 11^7 , 12^7 , 14^7 , and 15^7 are the unsaturated analogs of molecules 2-5, 104 Ac₂0 eliminated the formation of 14 and 15. The mixture of acetates (13) (<u>exo/endo</u> = 1.9),⁷ is formed via rearrangement of 12 (this was confirmed via separate isomerization of 12, and constitutes proof for the regionsomeric nature of 12). This process is well precedented by the work



of Gassman.⁸ The formation of $\underline{2}$ and $\underline{12}$, to the exclusion (or nearly so) of isomeric bridgehead olefins^{5b} with the double bond in the four carbon bridge, can be due to several factors. In the first place, the $\underline{1}$,2 isomers appear to be more strained than the ones observed (examination of Dreiding models).

However, the stereochemistry of reaction of $\underline{6}$ (and $\underline{17}$), in which protonation from the right-hand side may leave an acetate ion closer to H-7, may be more significant. Alternatively, depending on the conformation of $\underline{7}$, H-7-<u>exo</u> may be better aligned for elimination than H-5. We doubt that $\underline{6}$ yields 3 directly via a 1,3[H] shift.

Propellane $\underline{16}^7$ arises from collapse of the initially formed ion at the cyclopropyl position.⁹,¹⁰ The stereochemistry is assigned by analogy to similar systems,⁴ but is unproven. Basic hydrolysis¹¹ leads to bicyclof 4.3.0]non-3-en-l-carboxylic acid.

Lastly, the solvolysis of 10 was studied in the presence of silver ion, the results are summarized by equation IV. The relatively larger amounts of 14 and 15 can be ascribed to the very hygroscopic nature of $AgClO_4$.¹² Neither 12 nor 13 were found under the silver-assisted conditions.

(IV) 10
$$\frac{\text{AgClo}_4(1-5\text{eq.})}{\text{HOAc, 25°,}}$$
 11 + 14 + 15 + 16
1 minute 1.1 1.0 2.7 3%

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References

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- 5. Identification of compounds 2-5 (a) 2 mp $73-74^{\circ}$, pmr (CCl₄) δ 5.14 (s, >CHBr), δ 2.7-1.5 (m, 20 H), mass spectrum (loeV) no P ion observed, m/e 232, 230 (P-Ac₂O) were heaviest ions observed, correct elemental analysis, 2 was independently synthesized from 11' by hydrogenation, (b) 3 mp 85.5-86 5°, ir (CCl₄) 3020cm⁻¹ (olefinic C-H), 1734 cm⁻¹ (s, 0Ac), 1632 (C=C), pmr (CCl₄) δ 5.85-5.47 (m, C_L=C and >CHBr), δ 2 90-0.90 (m, 15 H), cmr (CDCl₃) δ 170 (-CO₂Me), 1₂7

(>C=C), 129 (CH=C), 84 (C-O-), 57 (>CHBr), 40, 36, 32, 24, 23, 22, 21 (7 allphatic \overline{C} 's)-no other peaks were visible after 32,768 scans of a 72 mg sample, mass calc'd. for $C_{12}H_{17}O_2Br$: 272.0408, found 272.0412, a variety of chemical evidence for 3 includes the addition of HOAc (p-TsOH, 45°, 11 hr.) to give, in part, 2, (c) 4 mp 87-88°, ir (CCl₄) 3560, 3440 cm⁻¹ (OH), 1730 cm⁻¹ (OAc), pmr (CCl₄) \cdot 84.66 (s, >CHBr), 82.35-1.45 (m, 18H), (d) 5 previously reported, ^{2a,3a} the stereochemistry of 5 was determined via a single crystal x-ray analysis of the 2,4-dinitrophenylhydrazone derivative. space group P₁, unit cell dimensions a = 11.048 (5), b = 11.997 (6), C = 7.514 (2) Å, $\alpha = 98.42$ (3), 8 = 97.09 (3), $\gamma = 116.70$ (4)°. The present discrepance index is R = 0.094 for 1920 structure factors.

- In this context, the reported¹ formation of 6-bromomethylenecyclodecanone from the acetolysis of ll,ll-dibromo[4.4.1]propellane, likely involved water.
- 7. Identification of <u>11-15</u> (a) <u>11</u> mp 90.5-91.5°; pmr (CDCl₃) §5.60 (s, >CHBr), 5.49 (t, 2 olefinic H), 3.1-1.5 (m, 16H), correct elemental analysis, hydrolysis to known diol,^{2a} (b) <u>12</u> pmr (CDCl₃) §5.66-5.40 (m, 3 olefinic H plus >CHBr), 3.2-2.2 (m, 8H), 2.07 (s, 0Ac), ir (CCl₄) 3020, 1738, 1663 cm⁻¹; calc'd. for C_{12H1502}Br 270.0255, found 270.0254, hydrogenation to same product obtained from 3, (c) <u>13-exo</u> pmr (CDCl₃) §5.56 (s, 2 olefinic H), 5.32 (t, J=7, >CHOAc), 3.30 (s, cyclopropyl H), 2.5-1.0 (m, 8H), 2.08 (s, 0Ac), ir (CCl₄) 3030, 1742 cm⁻¹, calc'd. for C_{12H1502}Br 270.0255, found 270.0251, <u>13-endo</u> pmr (CDCl₃) §5.62 (s, 2 olefinic H), 5.45-5.32 (m, >CHOAc), 2.92 (s, cyclopropyl H), 2.8-1.2 (m, 8H), 2.10 (s, 0Ac), ir (CCl₄) 3030, 1742 cm⁻¹, calc'd. for C_{12H1502}Br 270.0255, found 270.0251, (d) <u>14</u> a single crystal x-ray analysis confirmed the structure. The space group was P₂/n, with 4

molecules in a unit cell of dimensions a = 10.48 (1), b = 14.44 (1), c = 8.12 (1) Å, and β = 93.6 (1)°. The refinement (excluding H's), using heavy atom methods, led to a discrepancy index of R=0.097 for the 1044 observed structure factors, (e) 15 previously reported,^{2a,3a} (f) 16 mp 51 - 52°, pmr (CDCl₃). §5 60 (2 olefinic H), 2.7-1.1 (m, 13H), correct elemental analysis, mass parent ions at m/e 270, 272.

- 8. (a) P. G. Gassman, R. N. Steppel and E. A. Armour, <u>Tetrahedron Lett.</u>, 3287 (1973).
- 9. In a preliminary footnote (ref. 2a, footnote 11), 16 was misidentified. Although 16 does not provide evidence for a bridgenead olefin intermediate, we do not see any reasonable alternatives which could explain the formation of the other products.
- 10. Our failure to observe a saturated analog of 16 is also reflected in the kinetics.⁴
- 11. For a similar case, see J. T. Groves and K. W. Ma, <u>Tetrahedron Lett.</u>, 909 (1974).
- 12. Indeed, use of the less hygroscopic AgOAc results in more 11.