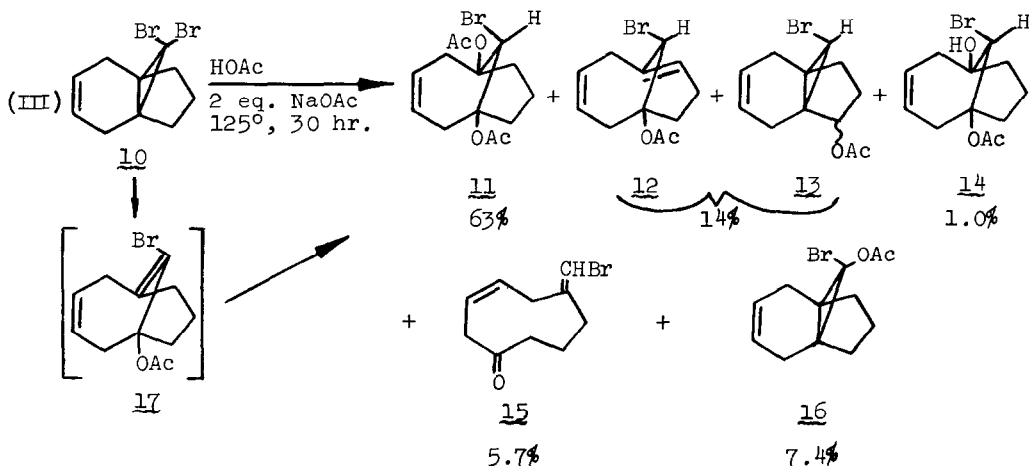


The buffered acetolysis of a 0.26M solution of 10,10-dibromo[4.3.1]-propella-3-ene (10) resulted in the products shown in equation III. Thus compounds 11<sup>7</sup>, 12<sup>7</sup>, 14<sup>7</sup>, and 15<sup>7</sup> are the unsaturated analogs of molecules 2-5, 10% Ac<sub>2</sub>O eliminated the formation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

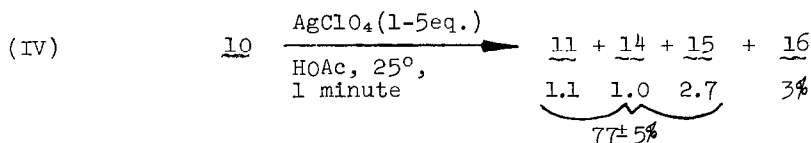


of Gassman.<sup>8</sup> The formation of 3 and 12, to the exclusion (or nearly so) of isomeric bridgehead olefins<sup>5b</sup> with the double bond in the four carbon bridge, can be due to several factors. In the first place, the  $\Delta$ 1,2 isomers appear to be more strained than the ones observed (examination of Dreiding models).

However, the stereochemistry of reaction of 6 (and 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 7, H-7-exo may be better aligned for elimination than H-5. We doubt that 6 yields 3 directly via a 1,3[H] shift.

Propellane 16<sup>7</sup> arises from collapse of the initially formed ion at the cyclopropyl position.<sup>9,10</sup> The stereochemistry is assigned by analogy to similar systems,<sup>4</sup> but is unproven. Basic hydrolysis<sup>11</sup> leads to bicyclo-[4.3.0]non-3-en-1-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<sub>4</sub>.<sup>12</sup> Neither 12 nor 13 were found under the silver-assisted conditions.



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#### References

- Propellanes, VI P. Warner and S. Lu, *J. Amer. Chem. Soc.*, **97**, 2536 (1975).
- (a) P. Warner, J. Fayos and J. Clardy, *Tetrahedron Lett.*, 4473 (1973), (b) P. Warner, R. LaRose, C. Lee and J. Clardy, *J. Amer. Chem. Soc.*, **94**, 7607 (1972),
- (a) C. B. Reese and M. R. Stebles, *Chem Commun.*, 1231 (1972); (b) C. B. Reese and M. R. Stebles, *Tetrahedron Lett.*, 4427 (1972), (c) D. B. Ledlie, *J. Org. Chem.*, **37**, 1439 (1972), (d) D. B. Ledlie and J. Knetzer, *Tetrahedron Lett.*, 5021 (1973), (e) D. B. Ledlie, J. Knetzer and A. Gitterman, *J. Org. Chem.*, **39**, 708 (1974).
- P. Warner and S. Lu, to be published.
- Identification of compounds 2-5 (a) 2 mp 73-74°, pmr (CCl<sub>4</sub>) δ 5.14 (s, >CHBr), δ 2.7-1.5 (m, 20 H), mass spectrum (10eV) no F<sup>+</sup> ion observed, m/e 232, 230 (P-Ac<sub>2</sub>O) were heaviest ions observed, correct elemental analysis, 2 was independently synthesized from 11 by hydrogenation, (b) 3 mp 85.5-86.5°, ir (CCl<sub>4</sub>) 3020cm<sup>-1</sup> (olefinic C-H), 1734 cm<sup>-1</sup> (s, OAc), 1632 (C=C), pmr (CCl<sub>4</sub>) δ 5.85-5.47 (m, C<sub>4</sub>=C and >CHBr), δ 2.90-0.90 (m, 15 H), cmr (CDCl<sub>3</sub>) δ 170 (-CO<sub>2</sub>Me), 137

( $>C=C$ ), 129 ( $CH=C$ ), 84 ( $C-O-$ ), 57 ( $>CHBr$ ), 40, 36, 32, 24, 23, 22, 21 (7 aliphatic 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 ( $CCl_4$ ) 3560, 3440  $cm^{-1}$  (OH), 1730  $cm^{-1}$  (OAc), pmr ( $CCl_4$ )  $\delta$  4.66 (s,  $>CHBr$ ),  $\delta$  2.35-1.45 (m, 18H), (d) 5 previously reported,<sup>2a,3a</sup> 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),  $\beta = 97.09$  (3),  $\gamma = 116.70$  (4)°. The present discrepancy index is  $R = 0.094$  for 1920 structure factors.

6. In this context, the reported<sup>1</sup> formation of 6-bromomethylenecyclodecanone from the acetolysis of 11,11-dibromo[4.4.1]propellane, likely involved water.
7. Identification of 11-15 (a) 11 mp 90.5-91.5°; pmr ( $CDCl_3$ )  $\delta$  5.60 (s,  $>CHBr$ ), 5.49 (t, 2 olefinic H), 3.1-1.5 (m, 16H), correct elemental analysis, hydrolysis to known diol,<sup>2a</sup> (b) 12 pmr ( $CDCl_3$ )  $\delta$  5.66-5.40 (m, 3 olefinic H plus  $>CHBr$ ), 3.2-2.2 (m, 8H), 2.07 (s, OAc), ir ( $CCl_4$ ) 3020, 1738, 1663  $cm^{-1}$ ; calc'd. for  $C_{12}H_{15}O_2Br$  270.0255, found 270.0254, hydrogenation to same product obtained from 3, (c) 13-exo pmr ( $CDCl_3$ )  $\delta$  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, OAc), ir ( $CCl_4$ ) 3030, 1742  $cm^{-1}$ , calc'd. for  $C_{12}H_{15}O_2Br$  270.0255, found 270.0251, 13-endo pmr ( $CDCl_3$ )  $\delta$  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, OAc), ir ( $CCl_4$ ) 3030, 1742  $cm^{-1}$ , calc'd. for  $C_{12}H_{15}O_2Br$  270.0255, found 270.0251, (d) 14 a single crystal x-ray analysis confirmed the structure. The space group was  $P2_1/n$ , with 4 molecules in a unit cell of dimensions  $a = 10.48$  (1),  $b = 14.44$  (1),  $c = 8.12$  (1) Å, and  $\beta = 93.6$  (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,<sup>2a,3a</sup> (f) 16 mp 51 - 52°, pmr ( $CDCl_3$ )  $\delta$  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, Tetrahedron Lett., 3287 (1973).
9. In a preliminary footnote (ref. 2a, footnote 11), 16 was misidentified. Although 16 does not provide evidence for a bridgehead 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.<sup>4</sup>
11. For a similar case, see J. T. Groves and K. W. Ma, Tetrahedron Lett., 909 (1974).
12. Indeed, use of the less hygroscopic AgOAc results in more 11.