Tetrahedron Letters No. 19, pp 1549 - 1552, 1976. Pergamon Press. Printed in Great Britain.

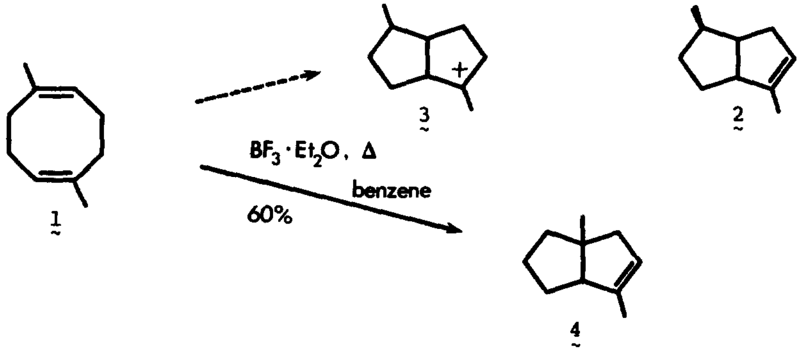
TRANSANNULAR REACTIONS
CONVERSION OF A CYCLOOCTADIENE TO BICYCLO[3.3.0] AND [3.2.1] SYSTEMS

James K. Whitesell*, Randall S. Matthews, and Paul A. Solomon
Department of Chemistry, The University of Texas at Austin
Austin, Texas 78712

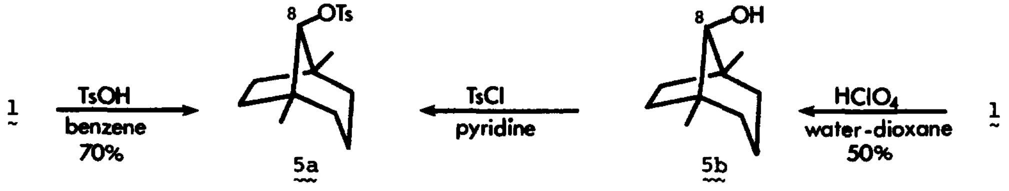
(Received in USA 29 January 1976; received in UK for publication 23 March 1976)

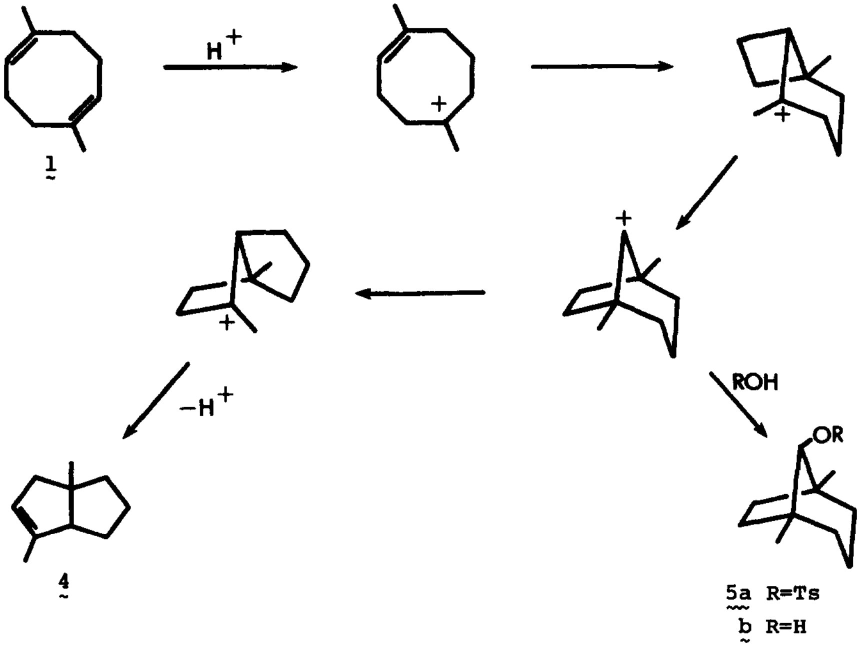
Our interest in the synthetic utility of transannular reactions (1,2) has led us to examine the acid catalyzed reactions of 1,5-dimethyl-1,5-cyclooctadiene **1**. We had previously (2) converted the diene **1** via a multistep sequence to the bicyclic isomer **2**, and sought to effect this isomerization by simple acid catalysis. Though such a transformation would formally require protonation of the diene to afford a secondary rather than a tertiary cation, we felt that there was potential for transannular assistance in the protonation step leading then directly to the bicyclic tertiary cation **3**.

In the event, the diene **1** (3) underwent an acid catalyzed rearrangement with either *p*-toluenesulfonic acid or better, with boron trifluoride etherate in refluxing benzene to afford not **2**, but rather 2,5-dimethylbicyclo[3.3.0]oct-2-ene, **4** (4,5). The process is clearly not a simple one as the initial head-to-tail dimer of isoprene **1** has been transformed into a formal head-to-head arrangement in **4**.

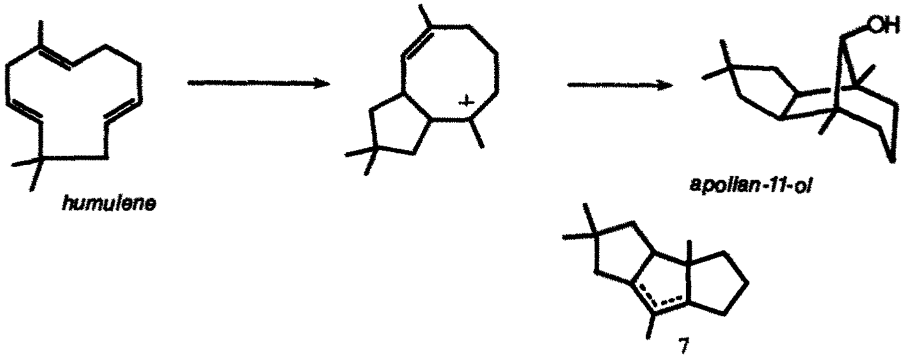


On the other hand, in aqueous systems, or in non-nucleophilic solvents in the presence of equivalent amounts of *p*-toluenesulfonic acid, the isomeric bicyclo[3.2.1]octane system **5** is formed (4). The presence of a symmetrical framework in both the alcohol **5b** and the tosylate **5a** was evident from the presence of only six unique carbon-13 magnetic resonance absorptions for the framework atoms in each of these molecules. A complete three dimensional single crystal x-ray analysis was called upon to firmly establish the assignment as a [3.2.1]octane system as well as to assign the configuration at C-8 in **5a** (6). That the same relative configuration obtains in both the alcohol and the tosylate was confirmed by conversion of the former to the latter. We suggest the following pathway to account for these results:



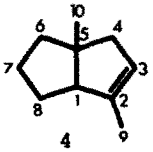


It should be noted that the sequence of cationic rearrangements leading to the alcohol 5b is strictly analogous to that proposed for the corresponding stages of the humulene to apollan-11-ol conversion (7). It is interesting, though, that olefin 7, which might be produced by the same sequence of steps as those leading to olefin 4, has not been reported as a product of an acid catalyzed reaction of humulene (8).

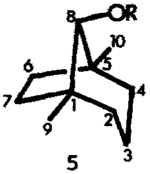


7

Carbon 13 magnetic resonance data (9)



4



5

δ	multiplicity	assignment
15.5	q	9
25.9	t	4
28.9	q	10
30.9	t	6
43.1	t	7
48.3	t	8
49.2	s	5
61.3	d	1
122.8	d	3
141.9	s	2

δ		multiplicity	assignment
R=H	R=Ts		
19.9	19.6	t	3
25.5	25.0	q	9&10
31.0	31.4	t	2&4
32.4	31.9	t	6&7
41.4	41.4	s	1&5
83.1	92.3	d	8

ACKNOWLEDGEMENT

Financial support of this research by the Robert A. Welch Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

REFERENCES and NOTES

1. J. K. Whitesell and P. D. White, Synthesis, 1975, 602.
2. J. K. Whitesell and R. S. Matthews, J. Org. Chem., 40, 3312 (1975).
3. Supplied by Chemical Samples Co., Columbus, Ohio, 43221.
4. Proton and ^{13}C magnetic resonance, infrared, and low resolution mass spectral data as well as elemental analytical data consistent with the proposed structures of all new compounds was obtained.
5. Further evidence for the structure of alkene 4 was provided by its conversion to a ketone with ir λ_{max} 1739 cm^{-1} (CH_2Cl_2 solution) by the sequence: diborane hydroboration, hydrogen peroxide oxidation, chromic acid oxidation.
6. We are grateful to Prof. R. E. Davis for this x-ray analysis, the details of which will be published elsewhere.
7. A. Nickon, T. Iwadare, F. J. McGuire, J. R. Mahajan, S. A. Narang, and B. Umezawa, J. Am. Chem. Soc., 92, 1688 (1970).
8. For recent, leading references see: W. G. Dauben, J. P. Hubbell, and N. D. Vietmeyer, J. Org. Chem., 40, 479 (1975); G. Mehta and B. P. Singh, Tetrahedron Lett., 3961 (1975).
9. ^{13}C nmr spectra were obtained on deuterochloroform solutions with tetramethylsilane as internal standard using a Bruker WH90 purchased with funds from National Science Foundation Grant number GP-41570. We gratefully acknowledge helpful discussions on the interpretation of these spectra with Dr. Ben Shoulders.