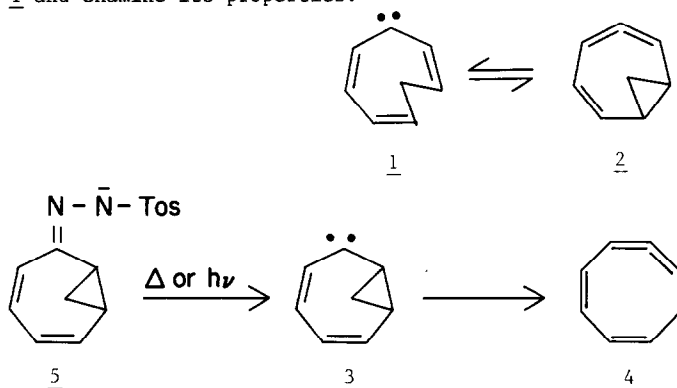


ATTEMPTS TO GENERATE A HOMOCYCLOHEPTATRIENYLIDENE

Richard H. Parker and W. M. Jones
Department of Chemistry, University of Florida, Gainesville, Florida 32611

Abstract. Attempts to generate homocycloheptatrienylidene by dehydrohalogenation of 8-chlorobicyclo[5.1.0]octadiene led to cyclooctatetraene, styrene and heptafulvene.

Oda, Ito and Kitahara¹ have postulated the potentially "homoaromatic" carbene (3) as the precursor to allene 4. Homocycloheptatrienylidene 1 differs from 3 in that the cyclopropyl ring is now part of the allene valence isomer rather than the carbene. Thus, relief of cyclopropyl ring strain should favor the carbene form 1 relative to its corresponding allene in contrast to the Kitahara system where cyclopropyl strain would favor the allene form. We therefore thought it would be interesting to attempt to generate 1 and examine its properties.



There is no obvious straightforward way to prepare the ketone tosylhydrazone analogue to 5 that would yield 1. Our strategy² for generation of this intermediate was to induce elimination of HX from 6 with the hope that the resulting cyclopropene 7 would open to the carbene 1 or its valence 2 in a manner similar to the opening of 2,4,6-bicyclo-(4.1.0)-heptatrienes to cycloheptatrienylidenes³.

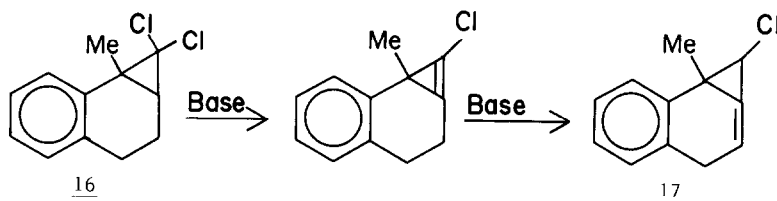
A mixture of 6a and 6b was prepared by reaction of methylene chloride with methyl-lithium in the presence of cycloheptatriene. The known dibromocyclopropane, 6c, was prepared by the method of Van Vuuren et al.⁴

Reaction of a mixture of 6a and 6b with KOt-Bu yielded identifiable products from 6b alone; 6a was very unreactive and when forced, gave only intractables. The products of base induced elimination from 6b varied with temperature. At low temperature, the primary product was cyclooctatetraene (COT) (56% at 25°) with a trace of styrene as the other isolable product. As the temperature was raised, the yield of COT decreased (8% at 90°) and the yield of styrene showed a modest increase (8% at 90°).

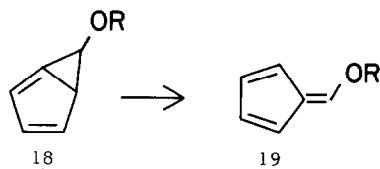
The reduction in the total yield of COT and styrene at elevated reaction temperatures at which these materials are known to be stable hinted at an alternate pathway leading to products unstable to even these moderate reaction temperatures. To study this possibility, the reaction was repeated in tetraglyme at 90° and 1 torr in an apparatus designed to permit collection of volatiles in a liquid nitrogen cooled trap. A red material was trapped which was shown to be heptafulvene (9; Y=H) by conversion to its known dimethylacetylene dicarboxylate adduct.⁶

Reaction of 6c with KOt-Bu at 0° gave no isolable products that could have reasonably originated from mono-dehydrobromination; neither bromocyclooctatetraene nor bromostyrene could be detected. When this reaction was carried out at 0° in the presence of 1,3-diphenylisobenzofuran, a reasonable yield (51%) of the furan: 8-bromoheptafulvene adduct (15) was found.

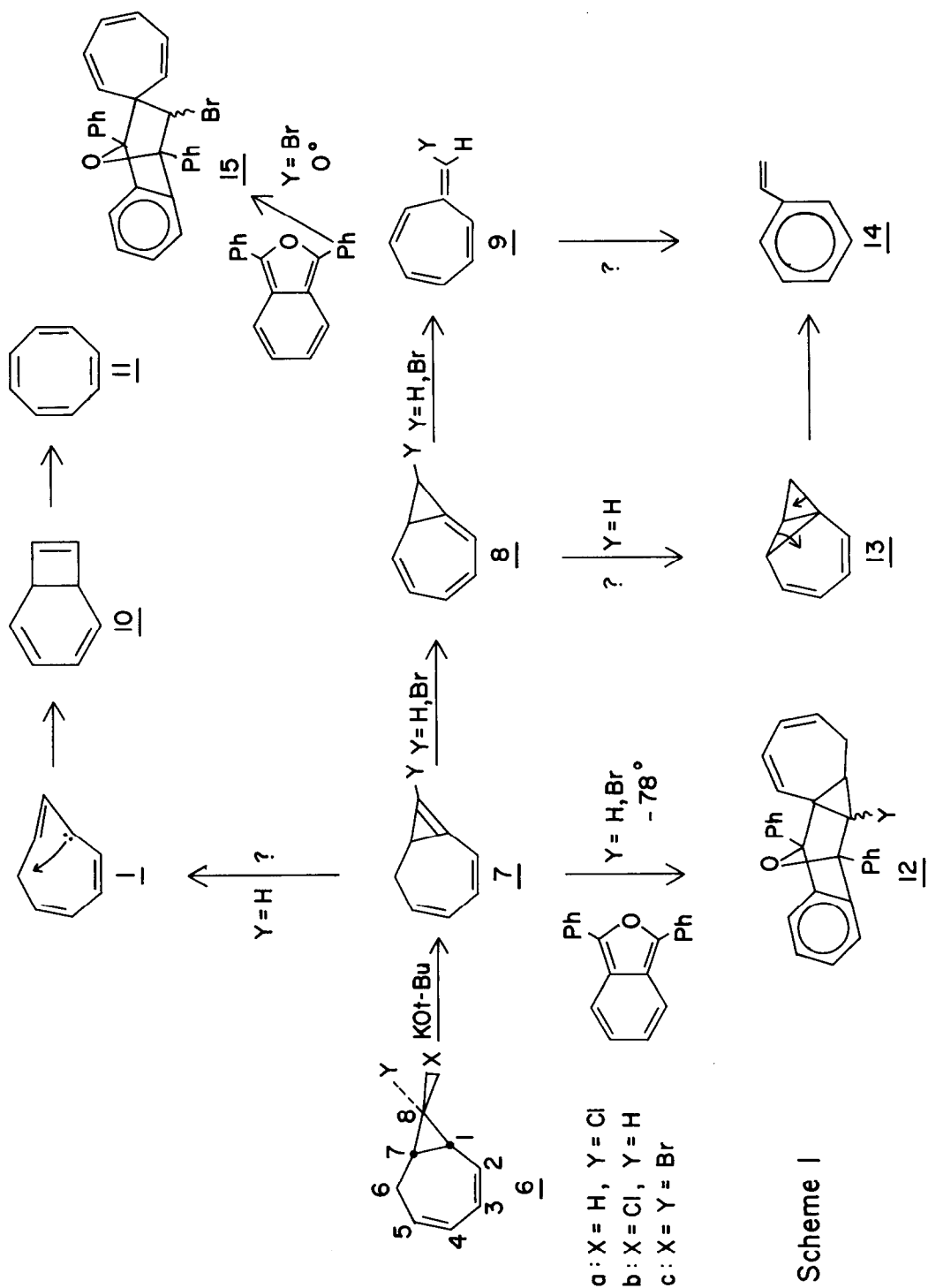
A reasonable mechanism for the formation of heptafulvene and 8-bromoheptafulvene is given in Scheme 1. The first step, dehydrohalogenation, finds ample precedent in the literature^{7,8,9} and the acidity of the allylic hydrogen on C-1 would be expected to dictate the regiochemistry of the elimination. Strong support for 7 (Y=H; Y=Br) as intermediates was obtained by trapping these cyclopropenes with 1,3-diphenylisobenzofuran at -78° (11% and 51% respectively). Base induced tautomerization of 7 to 8 finds ample precedent in the literature, as exemplified by the chemistry of 16.⁸ The last step in the sequence, the opening of 8 to 9 is unique. However, it is analogous to the opening of 18 to 19 in that both can be viewed as methylenecyclopropanes opening to trimethylenemethanes that are



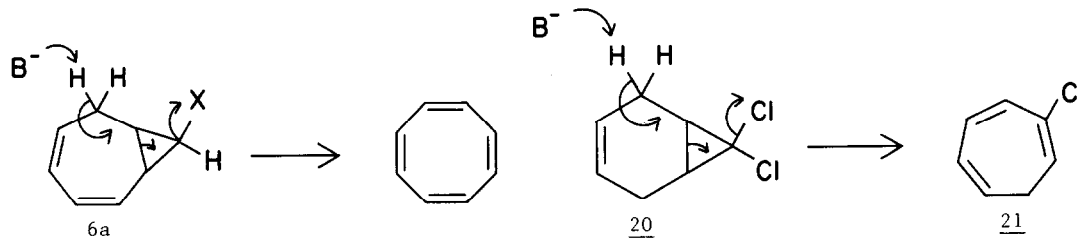
simply resonance forms of the closed shell heptafulvene and fulvene, respectively. It is therefore no surprise that this reaction is exceedingly facile.



There is much less in the way of either concrete data or precedent for the origin of either styrene or COT from 6b. In principle, the former could arise from COT but, in fact, this known isomerization is too slow to account for this product. Possible alternatives for styrene formation include: 1) closure of 8 to its norcaradiene 13 followed by electrocyclic opening to styrene and 2) aromatization of heptafulvene 9.



One possible mechanism for COT formation is concerted opening of 6 as depicted below. We feel, however, that this is unlikely on two counts. First, an analogous concerted elimination to explain 21 from 20 has been unequivocally excluded¹⁰. Second, as in electrocyclic ring openings of bicyclo [n.1.0]alkanes an endo chlorine should be



eliminated faster than its exo isomer¹¹. In fact, 6a is much less reactive than 6b (vide supra) and when forced gives no COT.

A second possible mechanism for COT formation is initial dehydrochlorination of 6b to 7 followed by ring opening to the desired homocycloheptatrienylidene 1. Intramolecular C-H insertion would give 10 which is known to rapidly open to the observed product. Models suggest that the insertion is sterically viable. However, if 1 is formed, it must undergo the insertion very rapidly because all attempts to trap the carbene failed. Unsuccessful trapping agents included styrene, tetramethylethylene, *t*-butanol, butadiene and cyclopentadiene.

Acknowledgement. We gratefully acknowledge the financial support of the National Science Foundation.

REFERENCES

1. M. Oda, Y. Ito and Y. Kitahara, *Tetrahedron Lett.*, 2587 (1975).
 2. We also attempted to prepare cyclopropene 7 from thermolysis or photolysis of the tosylhydrazone i. Unfortunately, under no conditions were we able to suppress electrocyclic closure of the intermediate vinylidiazalkane to the pyrazole.
-
3. T. T. Coburn and W. M. Jones, *J. Amer. Chem. Soc.*, 96, 5218 (1974), and references contained therein.
 4. P. J. Van Vurren, R. J. Fletterick, J. Meinwald and R. E. Hughes, *J. Amer. Chem. Soc.*, 93, 4394 (1971).
 5. This low reactivity with base is duplicated in other halocyclopropanes in which cis-elimination is not possible. See W. E. Billups, L. E. Reed, E. W. Casserly and L. P. Lin, *J. Org. Chem.*, 46, 1329 (1981).
 6. W. von E. Doering and E. Wiley, *Tetrahedron*, 11, 183 (1960).
 7. For a review of reactions of this type see W. E. Billups, *Accnts. Chem. Res.* 11, 245 (1978).
 8. W. E. Billups and L. E. Reed, *Tetrahedron Lett.*, 2239 (1977).
 9. W. N. Washburn, R. Zahler and I. Chen, *J. Amer. Chem. Soc.*, 100, 5863 (1978).
 10. J. Prestien and H. Gunther, *Angew. Chem. Int. Ed.*, 13, 276 (1974).
 11. F. A. Carey and R. J. Sundberg, "Advanced Organic Chemistry", Part A: Structure and Mechanism, Plenum Publishing Corporation, New York, N.Y., 1977, p. 436.

(Received in USA 23 August 1983)