Tetrahedron Letters No. 44, pp 3855 - 3858, 1977. Pergamon Press. Printed in Great Britain.

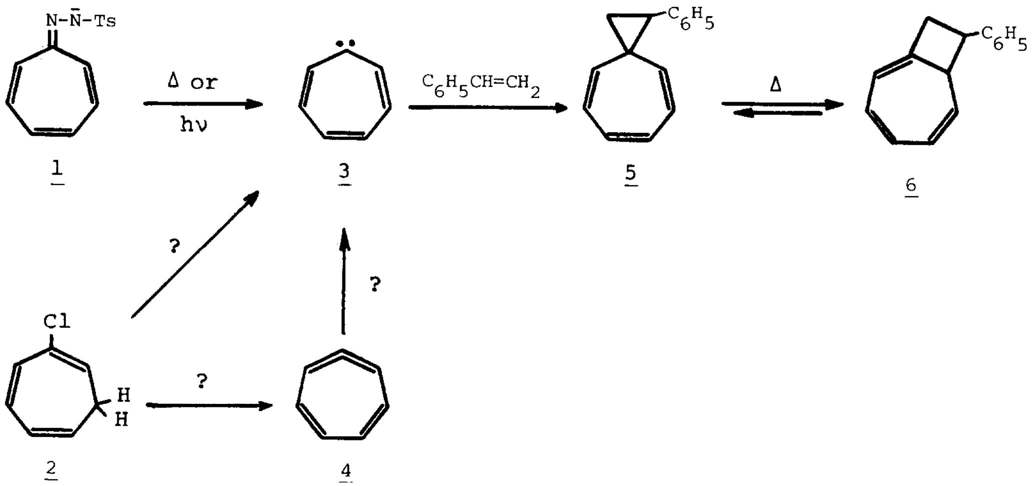
ON THE ORIGIN OF CYCLOHEPTATRIENYLIDENE FROM THE DEHYDROHALOGENATION OF CHLOROCYCLOHEPTATRIENE; EVIDENCE FOR INITIAL FORMATION OF CYCLOHEPTATETRAENE

C. Mayor and W. M. Jones

Department of Chemistry, University of Florida, Gainesville, FL 32611

(Received in USA 27 June 1977; received in UK for publication 16 September 1977)

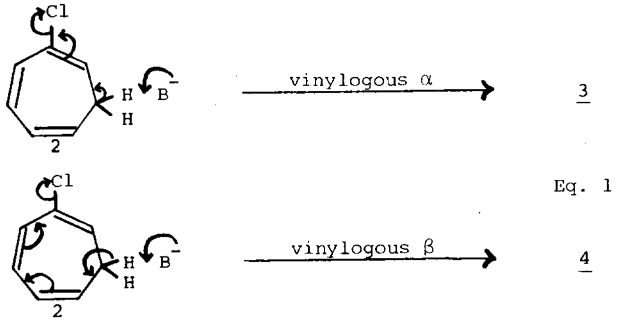
Photolysis or pyrolysis of the sodium salt of tropone tosylhydrazone (1) gives an intermediate that shows chemical properties that have led us[1,2] to assign it the carbene structure 3. This was originally based on expectation -- a tosylhydrazone salt as progenitor -- and formation of cyclopropanes when the intermediate was generated in the presence of appropriately substituted double bonds. However, some years ago, Untch[3] discovered that the dehydrohalogenation of 1-, 2-(2) or 3-chlorocycloheptatriene with strong base gives an intermediate that shows the same properties as those of the intermediate generated from the tosylhydrazone salt 1. Since a reasonable mechanism for the dehydrohalogenation reaction is a beta-elimination (or vinylogous beta-elimination for the 2- and 3-isomers Eq. 1) Untch's observation introduced the interesting possibility that the common intermediate from the two different sources might, in fact, either have an allene structure (4)[4] or, possibly, might best be represented as an interconverting mixture of the two valence isomers 3 and 4. Shortly thereafter it was found that the initially formed spirononatriene adduct of the



intermediate with styrene (5)[2,3] rearranges upon warming to give a more stable isomer, the methylenecyclobutane 6. Since the latter structure is that expected of addition of a strained allene to styrene,[6] it would appear that the intermediate that reacts with double bonds to give cyclopropanes cannot reasonably be represented by the allene structure alone.[7] However, this does not exclude the possibility that the dehydrochlorination reaction intially gives cycloheptatetraene (4) that then isomerizes to a more reactive carbene. And, in fact, theoretical calculations[8] not only support the idea of two intermediates but further suggest that the allene form may actually be the more stable of the two.

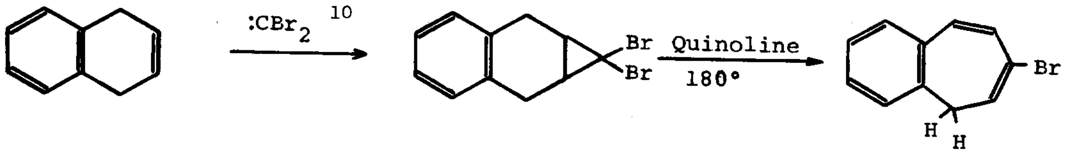
At this time we present experimental evidence that strongly supports allene 4 as a real intermediate for the dehydrochlorination of 2. Our evidence further requires that, unless the allene form can behave like a carbene,[7] in the presence of styrene it isomerizes to the carbene which then reacts to give the spirocyclopropane 5.

In principle, dehydrochlorination of 2 to 3 could occur by either a vinylogous *alpha*-elimination to give the carbene directly or, as mentioned above by a vinylogous (or direct from the 1-isomer) *beta*-elimination to give 4 initially that could then isomerize to 3. To gain insight into the mechanism of the reaction, 1,2-benzo-5-bromo-1,3,5-cycloheptatriene



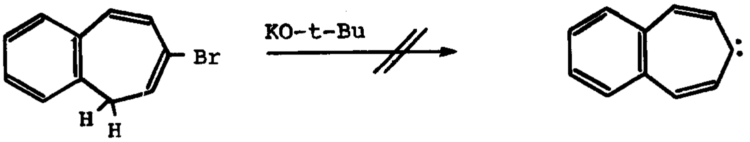
Eq. 1

(8)[9] was synthesized as outlined below.

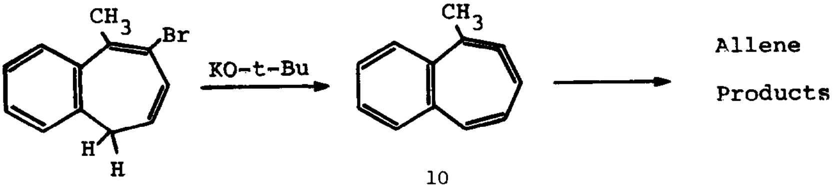


7 8

Dehydrobromination of this compound was then compared with the reported dehydrobromination of 9.[11]



8



9

10

Somewhat to our surprise, whereas 9 undergoes dehydrobromination (Potassium t-butoxide in T.H.F.) to the allene in one hour at zero degrees,[11] 8 is recovered unchanged after one week under the same conditions. It was also found to be unaffected by t-butoxide in either diglyme at 150° (1 hr.) or DMSO at room temp. Finally, the stronger base, n-butyllithium, simply reduces off the bromine.

From these results it is clear that the presence of the benzene ring has little if any retarding effect on the rate of dehydrobromination of the bromocycloheptatriene 9, a molecule that can eliminate to an allene by a vinylogous β-elimination mechanism without breaking aromaticity. In contrast, the benzene ring has a dramatic retarding effect on the rate of dehydrohalogenation of the bromocycloheptatriene 8, a molecule that can, in principle, eliminate via a vinylogous α-elimination mechanism to give the carbene directly but which must break aromaticity to undergo a vinylogous β-elimination to the allene.

Thus it would appear that a halocycloheptatriene can readily dehydrohalogenate to a cycloheptatetraene but cannot eliminate directly to the carbene. Extrapolating from the benz-annelated systems to 2, we are led to the conclusion that the mechanism of the formation of 5 from 2 probably involves two different intermediates; initially a non-planar allene which, by a simple conformational change isomerizes to give the planar carbene 3 which then adds to the double bond.

Acknowledgement. This research was supported by the National Science Foundation to whom the authors express grateful appreciation. C.M. wishes to thank the "Fonds national suisse de la recherche scientifique" for financial support.

References and Notes

1. W.M. Jones and C.L. Ennis, J. Amer. Chem. Soc., 91, 6391 (1969).
2. E.E. Waali and W.M. Jones, J. Amer. Chem. Soc., 95, 8114 (1973).
3. K. Untch, International Symposium on the Chemistry of Non-Benzenoid Aromatic Compounds, Sendai, Japan, August, 1970. Personal Communication.
4. A distorted cycloheptatetraene has recently been postulated[5] to explain products resulting from the debromination of 11,11-dibromo-1,6-methano[10]annulene.
5. J.B. Carlton, R.H. Levin, and J. Clardy, J. Am. Chem. Soc., 98, 6068(1976).
6. Cf. W.R. Moore and W.R. Moser, J. Org. Chem., 35, 908(1970).
7. It is conceivable that a cyclic allene such as 4 could, in fact, react with a double bond in a $\pi^2 + \pi^8$ cycloaddition to give a cyclopropane rather than the methylenecyclobutane that is typical of the two-step addition of allenes to alkenes.[6] At this time this possibility appears remote since models show the symmetry allowed $\pi^2 s + \pi^8 s$ cycloaddition to the more stable diastereomeric form of 4 to be sterically retarded; the more favorable approach of an alkene to the allene would be in a direction that would require a forbidden $\pi^2 s + \pi^8 a$ reaction.
8. R.L. Tyner, W.M. Jones, Y. Ohrn, and J.R. Sabin, J. Am. Chem. Soc., 96, 3765(1974).
9. mp 43-44°; high resolution ms(calc. 220.9864; found 220.9869); ms: (70eV) m/e 222(M+2), 220(M+), 141 (base peak, benzocycloheptatrienyl cation), 115(M-Br-C_2H_2); pmr: $\delta(CDCl_3)$ 3.03(d, J=7.3 Hz, 2H, methylene protons), 6.00 (t, J=7.3 Hz, of d, J=1.2 Hz, 1H, vinylic proton on C-4), 6.45 (d, J=11.3 Hz, of d, J=1.2 Hz, 1H, vinylic proton on C-6), 6.96 (d, J=11.3 Hz, 1H, vinylic proton on C-7), 7.0-7.4 (m, 4H, aromatic protons). The bromo compound was chosen over the chloro to facilitate ring opening of 7 in synthesis. Even so, it was surprisingly sluggish, requiring 8 hours in quinoline at 180° to yield 8 (75%) and 2-methylnaphthalene (10%). Silver assisted solvolysis or heating of 7 to 150° gave only 2-naphthylbromide.
10. R. M. Blankenship, K. A. Burdett, and J. S. Swenton, J. Org. Chem., 39, 2300(1974).
11. E. E. Waali, Jr., D. Lewis, E.A. Lee and A. Chappell, private communication. The authors are indebted to Professor Waali for communicating his results prior to publication. Dehydrochlorination of 1,2-3,4-dibenzo-5-chloro-1,3-5-cycloheptatriene has also been cursorily studied in these labs by E. E. Waali, T. T. Coburn and T. Ives. Their results were consistent with those reported for 9.