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RESPONSE OF HYPOSTROPHENE AND ITS MONOEPOXIDE TO ELECTROPHILIC REAGENTS

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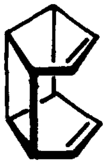
Photoelectron spectroscopy has demonstrated that the two double bonds in hypostrophene (1)[1] experience far more effective through-bond than through-space coupling.[2] In homohypostrophene 2 which lacks laterally fused cyclobutane rings, a return to more normal orbital ordering and dominant through-space interaction is expected. A chemical test of this conclusion is found in the bromination of 2 which proceeds by 1,4 addition to give 3 exclusively.[3] Since experiments designed to evaluate the chemical consequences of high-lying, suitably oriented σ orbitals on π bond reactivity had yet to be performed, the reactivity of 1 toward several electrophilic reagents was investigated. Intriguingly, *eight* of this hydrocarbon's ten constituent carbon atoms participate in the ensuing structural rearrangement.



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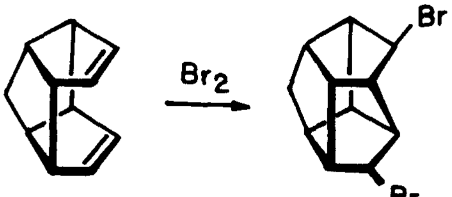
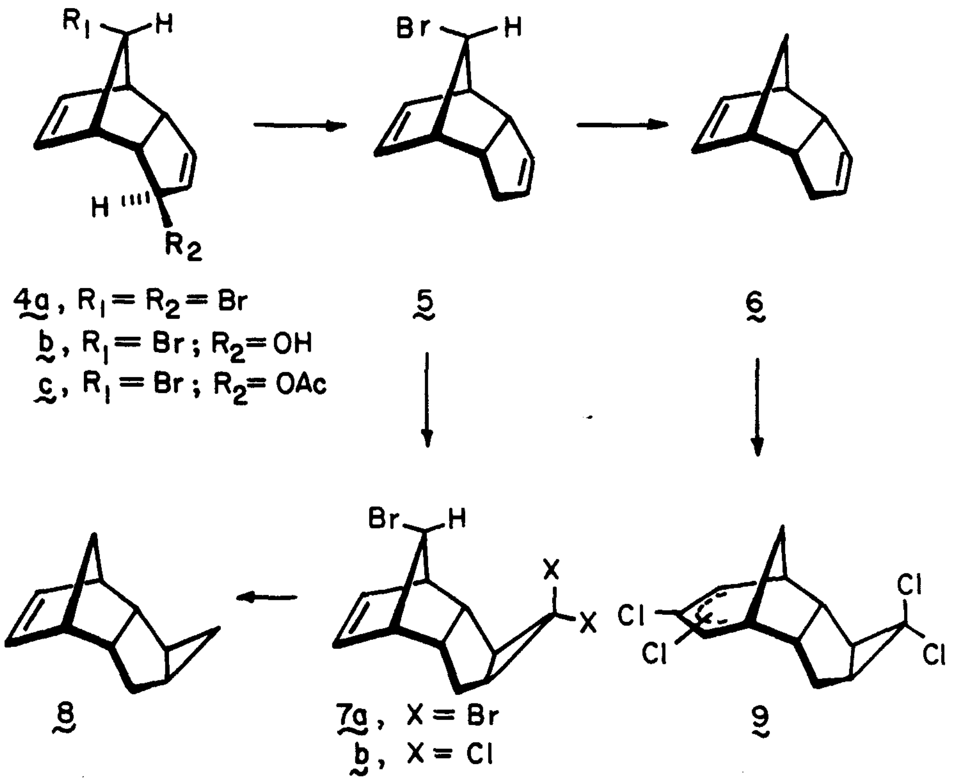


2 **3**

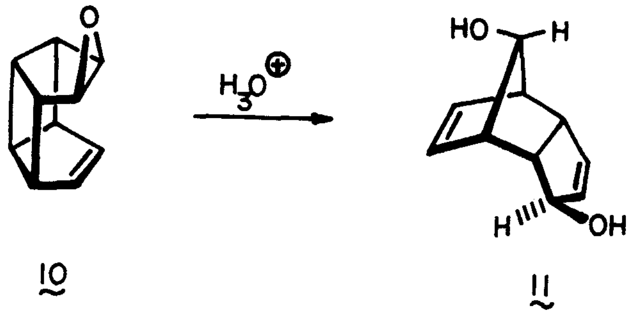
Treatment of 1 at 0° in CCl_4 with 1 equiv of bromine afforded a single oily dibromide [95%; δ($CDCl_3$) 5.92 (m, 2), 5.72 (m, 2), 4.41 (m, 1), 3.92 (m, 1), and 3.7-3.0 (m, 4)], the presence in which of four olefinic protons rules out the operation of simple transannular chemistry as exhibited by 2. That the halogens find themselves in differing chemical environments was clear from the results of subsequent $LiAlH_4$ reduction which gave rise to an isomerically pure monobromide [oil, 75%; δ($CDCl_3$) 5.93 (m, 2), 5.48 (m, 2), 3.92 (m, 1), 3.42-2.40 (m, 5), and 2.27-1.98 (m, 1)]. Since further dehalogenation with sodium in liquid ammonia afforded *endo*-dicyclopentadiene (6), the prior formation of 4a and 5 was implicated. The syn stereochemical assignment to the 8-bromo substituent in these molecules follows from mechanistic reasoning (*vide infra*) and from the selective reactivity of 5 toward dihalocarbene



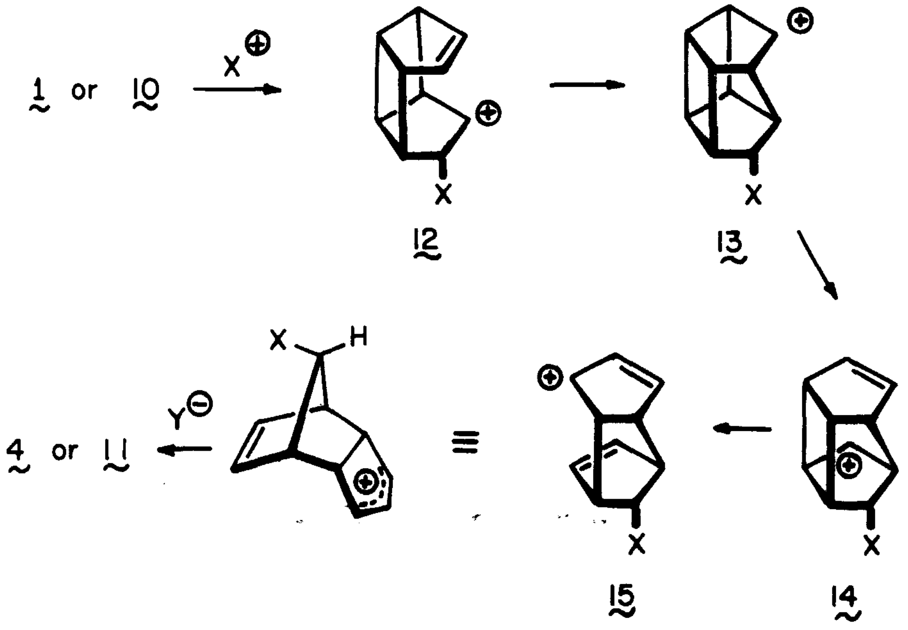
generated under phase-transfer conditions.[4] As a consequence of the steric shielding generated by the 8-bromo substituent (possible only when syn oriented), 5 is subject only to monoaddition with formation of 7a (mp 105-106°, 55%) and 7b (mp 78-79°, 71%) under conditions where parent hydrocarbon 6 undergoes reaction at both olefinic sites to give 9. When dehalogenated, 7a and 7b gave the known hydrocarbon 8.[5]

Dalton and coworkers[6] have reported that the addition of NBS in wet DMSO to a wide variety of olefins leads regio- and stereospecifically to the corresponding bromohydrins.[6] The one exception noted by these workers, in that rearrangement occurred, was norbornene. Contrary to early reports,[6] no 2,3-bromohydrin results. In the present study, no partially rearranged intermediates were trapped when 1 was allowed to react with NBS/H_2O/DMSO. Rather, bromo alcohol 4b, identical in all respects to the hydrolysis product of 4a, was isolated (74%) and characterized as its acetate 4c [mp 90-91°; δ ($CDCl_3$) 6.20-5.55 (m, 4), 4.95 (m, H_1), 3.98 (m, H_8), 3.60-3.25 (m, 2), 3.25-3.0 (m, 1), 2.60-2.45 (m, 1), and 2.02 (s, -CH_3)].

Because the structural framework in hypostrophene monoepoxide (10) is fixed so as to permit electrophilic ring opening with initial formation of a cation related to those believed to intervene above, the fate of 10 in 10% aqueous perchloric acid (25°, 2 hr) was examined. This reaction was found to provide uniquely the known 1-exo-8-syn diol 11.[8]



What there is to say at present about these rearrangements is based on the assumption that electrophilic attack with exo approach to generate 12 is followed by transannular bonding with the normal kinetic preference for 5-ring closure. Once 13 is generated, two sequential cyclobutane bond cleavages follow. The first phase is probably controlled by strain release since the cationic center in 14 is not particularly stabilized relative to that in 13. The energetic value of the second phase which delivers 15 probably lies chiefly in the developments of allylic resonance, although a further diminution in strain also occurs. As a direct consequence of its symmetry, nucleophilic capture by 15 can occur with equal probability at either allylic terminus.



Because of our inability to intercept such hypostrophene rearrangements short of the dicyclopentadiene stage, even with most reactive uniparticulate electrophiles such as TCNE and CSI,[9] it is perhaps preferable to view the conversion of **12** to **15** as a concerted electronic reorganization. In this interpretation, the synchronous flow of electron density which undulates between the two "sandwiched" cyclopentane rings such that 80% of the carbon atoms experience rehybridization can be viewed as the result of the extensive σ, π orbital mixing which prevails. Certainly, if any barriers to bond-making and bond-breaking do exist on this energy profile, their magnitudes have been greatly reduced as compared to the situation in **2** and other structurally related compounds.

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