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Examining the Bromination of Benzobicyclooctadiene by ab Initio Methods

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The bromination of 5.8-diacetoxy-1,4-dihydro-1,4-ethanonaphthalene was reported several years ago to yield a single stereospecificly formed dibromide. Given related cases from the literature, the result was interpreted as indicating a significant interaction between the aryl and olefin π-electron systems. This paper reports an ab initio study of the mechanism of the bromination of benzobicyclooctadiene. It is proposed that the stereochemistry is best accommodated by an asynchronous concerted electrophilic addition of bromine across carbons 1 and 3, and that it proceeds via an ion pair transition structure in which the Wagner−Meerwein portion of the reaction has already occurred. All final results were calculated at the Becke3LYP/6-31G* level.

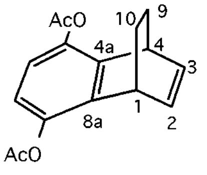
Introduction

The addition of electrophiles to benzobicyclooctadiene (BBO) and various derivatives has proven a challenging mechanistic problem over the years. Early work suffered from the inadequacies of then current NMR techniques for determinations of such complex structures. This problem began to turn around in the early 1980s as higher field instruments and 2-D techniques became available. In 1981, Paquette and co-workers[1] carried out an extensive study on a range of electrophilic additions to 2-methyl-1,4-dihydro-1,4-ethanonaphthalene and its 5,8-dimethoxy and 5,6,7,8-tetrafluoro analogues. The conclusion was drawn that electrophile addition was predominantly syn to the aromatic side of the olefin π-bond. Support was offered by early MINDO/3 calculations suggesting that there was no interaction between the π-electrons of the aryl ring with the corresponding electrons in the olefin bond or with the developing cationic center.

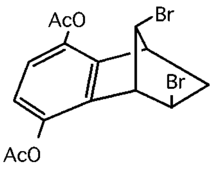
Subsequently, it was found that the epoxidation of a series of 5,8-disubstituted-1,4-dihydro-1,4-ethanonaphthalenes was strongly solvent dependent.[2] The electrophilic strength of the peracid was controlled by employing a series of solvents exhibiting different abilities to hydrogen bond to the peracid. Reaction rates and epoxide stereochemistry were found to vary in a rational pattern. In strong hydrogen bonding solvents rates were slow and attack by the peracid on the olefin face anti to the aryl ring became important.

When unsymmetrical two-part reagents of the type ROI (R = methyl, H, or Ac) were used as electrophiles, two Wagner−Meerwein rearrangement products were formed.[3] As the reagent's electrophilic strength decreased, increasing amounts of the product from initial anti attack on the double bond was found to occur. These results were interpreted again as indicative of the increasing importance of aryl π-electron stabilization of the developing cationic TS or intermediate.

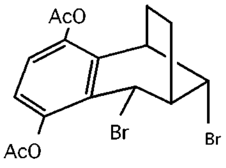
An extreme example of the rearrangement reaction was found in the bromination of 5,8-diacetoxy-1,4-dihydro-1,4-ethanonaphthalene (**A**) at room temperature in chloroform as solvent.[4] The reaction was extremely rapid at room temperature under either room light or totally dark conditions. A quantitative yield of one product only was found, and an extensive NMR study was required to establish the structure as **B**. In light of the results mentioned above, the absence of any **C** was surprising.



A



B



C

Olefin brominations have been demonstrated to exemplify a spectrum of mechanistic possibilities. Olefins such as cyclohexene, *cis*- and *trans*-2-butene, and maleic and fumaric acids give products of anti addition proceeding through bromonium ion intermediates.[5] In contrast, the bromination of either *cis*- or *trans*-1-phenylpropene leads to mixtures of products of both syn and anti addition to the double bond suggesting secondary benzyl-type cations as intermediates.[6] Molecular rearrangements resembling Wagner−Meerwein rearrangements are also known to occur during olefin brominations. The addition of bromine to a mixture of methylenecyclopentane and 1-methylcyclopentene gave "almost entirely" 1,2-dibromo-1-methylcyclopentane[7] while the addition of bromine to norbornene leads to six dibromide products of which the *trans*-2,3 dibromide is only 4% of the total yield.[8]

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[1] Paquette, L. A.; Bellamy, F.; Wells, G. J.; Bohm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1981**, *103,* 7122.

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[6] Fahey, R. C.; Schneider, H.-J. *Ibid.* **1968**, *90,* 4429.

[7] Wolinsky, J.; Novak, R. W.; Erickson, K. L. *J. Org. Chem.* **1969,** *34,* 490.

[8] Marshall, D. R.; Reynolds-Warnhoff, P.; Warnhoff, E. W. *Can. J. Chem.* **1971**, *49,* 885.

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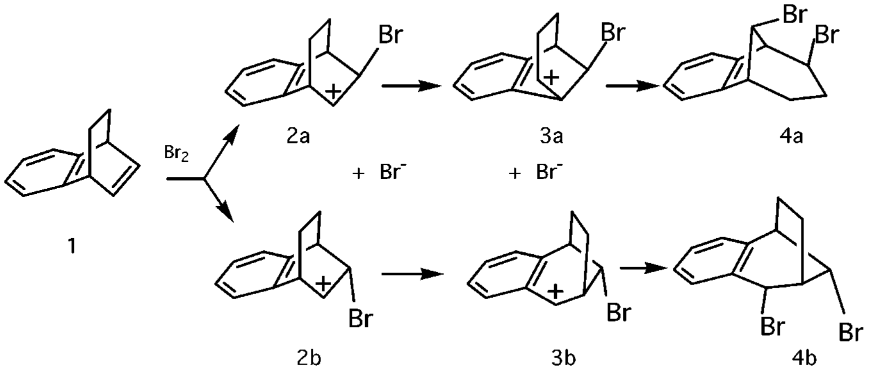
Scheme 1



Given this range of mechanisms, it becomes a matter of some interest to ascertain the reasons behind the stereospecificity noted in the brominations of **A** above. The most obvious solution to this problem is offered by quantum mechanical modeling techniques.[9]

Methods

Low level preliminary calculations were carried out with the programs SPARTAN[10] or Gaussian 94.[11] For the purposes of these computations the acetoxy groups of **A** were omitted. Final structures and energies were determined with the latter program at the Becke3LYP/6-31G* level.[12] Frequency calculations for zero point energy (ZPEs) corrections were carried out (HF/3-21G*) on the Becke3LYP/6-31G*-optimized geometries. This procedure was tested by optimizing and calculating ZPEs for six small molecules at the Becke3LYP/6-31G* level and then redoing the ZPEs at the 3-21G* level. A scaling factor of 1.06 ± 0.005 was found and employed subsequently. Transition structures were first approximated by AM1 "saddle" calculations[13] and then optimized first as HF/3-21G* structures which were then carried on to the Becke3LYP/6-31G* level giving the mandatory single imaginary frequencies. It has been pointed out that in systems where weak interactions are to be expected, basis set superposition errors (BSSE) may become significant.[14] To counter this point Schreiner, Schleyer, and Schaefer[15a] calculated geometries at the Becke3LYP/6-31G* level and energies with the 6-311+G* basis set in the hopes of correcting indirectly for this effect. However, they point out that for such hybrid DFT methods as Becke3LYP, no clear understanding of the role of BSSE exists. The reader should bear in mind that prior to 1994 the largest basis set generally available for bromine atoms was 3-21G*. This changed with the arrival of Gaussian 94. However, at the 6-31G* level each bromine requires 30 basis functions composed of 99 primitive Gaussians. Since computational times scale roughly as the fourth order of the number of basis sets, one quickly runs beyond reasonable time limits on workstations of medium size and speed. Many of the calculations reported here required 1−2 weeks of CPU time. The energy differences to be considered here are sufficiently large that general conclusions are reasonably not influenced.

Table 1. Becke3LYP/6-31G* Energies (hartrees) for This Study with Zero Point Energies

structure	total energy (h)	ZPEs (hartrees)
bromide	−2571.761339	
bromine	−5143.399129	0.000644
BBO (**1**)	−464.484136	0.220171
3a	−3035.938306	0.221921
3b	−3035.950029	0.209075
4a	−5607.921201	0.227204
5a	−3035.938305	0.192843
5b	−3035.922235	0.221505
6a	−5607.832458	0.220899
6b	−5607.820998	0.219505

Results and Discussion

As an entrée to the complexities of the BBO bromination, the discussion starts from the viewpoint of conventional carbocation rearrangements, i.e. the Whitmore mechanism. The steps are given in Scheme 1. Classical ions **2a** and **2b** were found to differ only by 2.1 kcal/mol, favoring **2a** and retaining the geometries depicted in Scheme 1 when calculated with the AM1 Hamiltonian. No evidence of a π-interaction was found.

Schleyer and co-workers[15] have studied in some detail the affects of computational method and basis set selection on the determination of carbocation structures. They concluded that valid structures could be obtained with Becke3LYP/6-31G* calculations. Optimizations of **2a** and **2b** at this level gave the structures in Figure 1. Optimization of the cation **2a** results directly in the formation of phenonium ion **5a**; while ion **2b** closes spontaneously to the bromonium ion **5b.** The energy gap between **5a** (favored) and **5b** has now widened to 28.1 kcal/mol. There is no point in dwelling on the disposition of **5b** since no product of syn attack was found. The energies and ZPEs for all species concerned with forming **5a** and **5b** are given in Table 1.

The enthalpy of formation of bromophenonium ion **5a** plus a bromide ion is 96.6 kcal/mol. The corresponding value for ion **5b** and bromide is 125.7 kcal/mol. One may

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[9] Hehre, W. J.; Radom, L.; v.R. Schleyer, P.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

[10] Wavefunction, Inc., Irvine, CA.

[11] Gaussian 94, Revision D.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.

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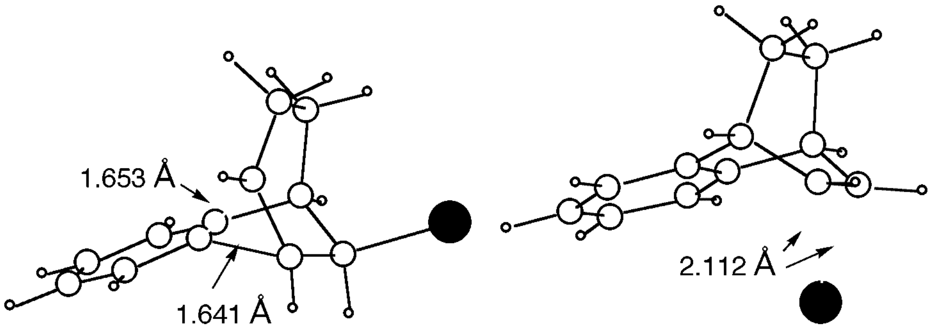
[13] Dewar, M. J. S.; Healy, E. F.; J. J. P. Stewart *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 227.

[14] Feller, D. *J. Chem. Phys.* **1992**, *S13*, 225.

[15] (a) Schreiner, P. R.; v. R. Schleyer, P.; Schaefer, H. F. *J. Org. Chem.* **1997**, *62*, 4216. (b) v. R. Schleyer, P.; Maeker, C. *Pure Appl. Chem.* **1996**, *67*, 755.



5a **5b**

Figure 1. The Becke3LYP/6-31G* structures formed by minimization of structures **2a** and **2b**.

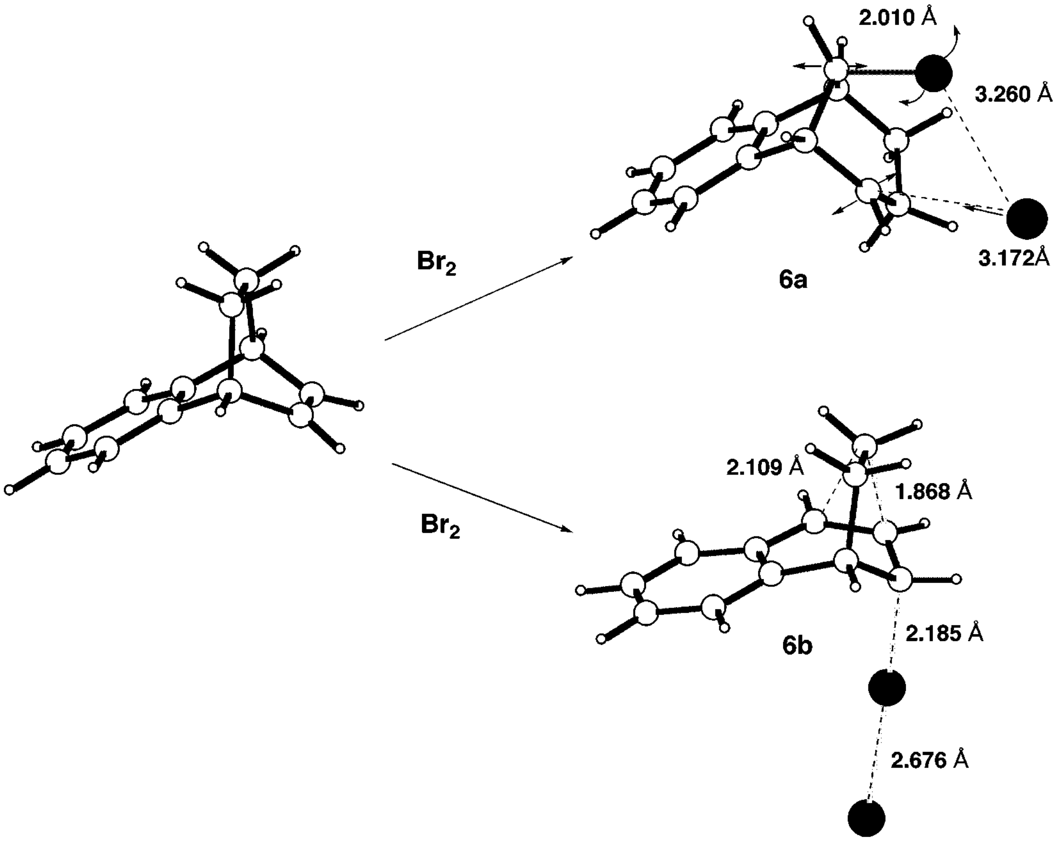


Figure 2. The Becke3LYP/6-31G* transitions structures from the concerted addition of bromine to BBO.

presume that in a solvent of low dielectric constant such as chloroform ($\epsilon = 4.8$ D) these ions would exist as ion pairs of unknown separation. Thus, these enthalpies probably represent maximum values. Present methods of ab initio solvent corrections are based on the reaction field model of Onsager[16] and offer no mechanism to take into account specific solvation effects. Nor could one optimize a combination of ion **5a** plus a bromide ion except as nonsolvated species inside a cavity. It is common knowledge that the bulk dielectric constant is a poor gauge of the solvent's ability to facilitate ion or ion pair formation in the transition state. In reference to ion pairs and related aggregates in the S_N2 reaction, Streitweiser and colleagues[17] have stated, "The energy changes calculated in this paper apply to isolated gas-phase systems. The energies required for these ion-pair processes in solution would undoubtedly be lower, but because the reaction species remain overall neutral throughout the reaction, solvation energies will be much lower than for corresponding ionic reactions; accordingly the transition structures calculated are probably reasonable models for the corresponding solution systems." This statement applies particularly to the mechanism now to be proposed.

The possibilities of a concerted addition of bromine to an olefin such as BBO seem not to have been explored previously. However, the bond length in bromine (Becke3LYP/6-31G*) is 2.320 Å; while the C1 to C3 distance in BBO is 2.401 Å. To explore this possibility, trial transition structures were determined as described in the Methods. For each case, the bromine was placed end-on ca. 3.0 Å above the appropriate face of the olefin. The resultant TSs were then optimized and confirmed

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[16] Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486.

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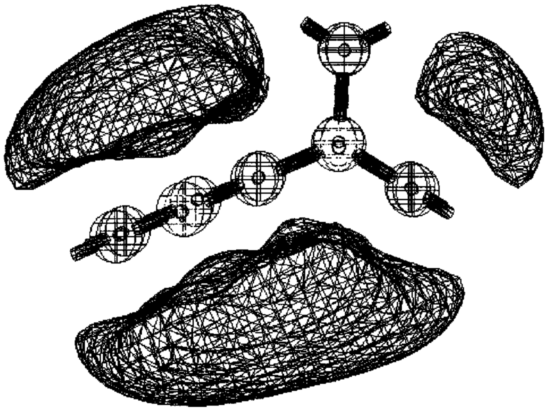

Figure 3. Isosurface of BBO showing excess electron density as computed from the electrostatic potential (Breneman, C. M., Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361) using SPARTAN at the LSA/VWN/DN* level. DN* is numerically equivalent to the 6-31* basis set.

by frequency calculations. When carried out at HF/3-21G*, attack of bromine anti to the aryl ring showed the first bromine to be bonded at C3 while the second bromine was above the C1 atom at a distance of 3.2 Å. The carbon structure was basically that expected of a C2 cation. This picture changes quite dramatically when the optimization is carried at the higher Becke3LYP/6-31G* level. The TS for anti and syn addition are shown in Figure 2 as **6a** and **6b** respectively. Both transitions structures gave single imaginary frequencies.

The structure **6a** has a number of features of interest. At 2.010 Å the methylene C−Br bond is not quite completely formed, the value in the final product **4a** (Scheme 1) being 1.977 Å. The second bromine is some distance from its final position at the original C1. Atomic charges were calculated from electrostatic potentials by the method of Besler, Merz, and Kollman.[18] The "atoms in molecules"[19] method of computing atomic charges failed presumably due to the strange geometry of the TS. The bonded bromine bears a charge of 0.14, while the unbound bromide has a charge of −0.56. As can be seen, the migration of the phenyl has been completed already leading to a TS best described as an ion pair. Recently, Streitwieser has described a similar ion pair TS formed in the course of an S_N2 reaction.[20] The activation enthalpy for the formation of **6a** is 31.9 kcal/mol, while that for the **6b** is 38.3 kcal/mol. Both values are significantly lower than the processes discussed previously for the formation of **5a** and **5b**.

Paquette et al.[1] recognized that phenonium ion formation would obscure the roll of aryl−olefin π-interactions and wisely chose reactions where no rearrangements were possible. The formation of **6a** as the correct TS for the reaction implies that early interactions are over by the time the TS is reached. However, the question of π-interactions in BBO can now be examined in greater detail. Shown in Figure 3 is an isosurface plot of the excess electron density as determined from the electrostatic potential. Clearly an interaction does exist between olefin and aryl π-electrons, and reasonably it must influence the early stages of any electrophilic addition reaction.

Conclusions

The most satisfactory mechanism explaining the rapidity and stereospecificity of the addition of bromine to BBO is an asynchronous concerted process involving an ion pair as the transition structure. Current research is devoted to examining the possibilities of similar mechanisms in other electrophilic processes involving Wagner−Meerwein type rearrangements.

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Supporting Information Available: Summaries of all Becke3LYP/6-31G* data (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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