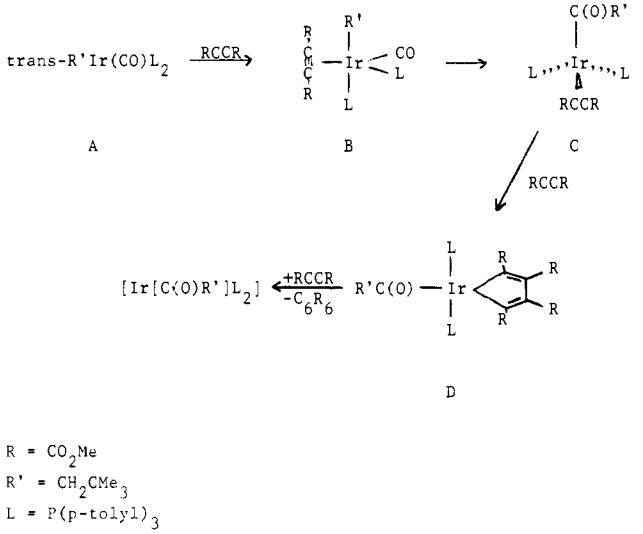


Figure 3. A scheme consistent with the experimental data for the cyclotrimerization of $C_2(CO_2Me)_2$. Structures have been determined for A, B, and C for these complexes and for D with the acyl replaced by Cl. The third acetylene is added in a Diels–Alder type reaction. Where the catalytic cycle is reentered depends on the relative rates of decarbonylation and acetylene association for the $14e^-$ acyl.

is that the complex is a $16e^-$ acyl complex which *does not* undergo alkyl migration to form the $18e^-$ alkyl. Such a migration is observed in five-coordinate benzyl complexes[33] and must be involved in the rearrangement of $Ir(COMe)(CO)_2(PPh_3)_2$ to the $16e^-$ alkyl complex *trans*-$MeIr(CO)(PPh_3)_2$,[34] Indeed, the analogous methyl complex of DMAD exists as the five-coordinate methyl complex, $MeIr(CO)(PPh_3)_2[C_2(CO_2Me)_2]$. Each of these unique features of the neopentyl complex must be attributed to steric interactions. The larger neopentyl group forces the five-coordinate DMAD adduct to rearrange to the $16e^-$ acyl, where steric interactions prevent a square-planar complex and force the tetrahedral arrangement.

Mechanism of Cyclotrimerization. The complexes *trans*-$MeIr(CO)(PPh_3)_2$ and $MeIr(CO)(PPh_3)_2[C_2(CO_2Me)_2]$ are active for cyclotrimerization of DMAD at 300 turnovers/h under ambient conditions. Coordination of a second DMAD molecule probably occurs by a methyl migration leading to $Ir(COMe)(PPh_3)_2[C_2(CO_2Me)_2]_2$ which would rearrange to a metallacyclopentadiene complex.[13] This is supported by three pieces of evidence: (1) the identification of $Ir(COCH_2CMe_3)[P(p\text{-tolyl})_3]_2[C_2(CO_2Me)_2]$ for the neopentyl analogue; (2) the halide analogues, *trans*-$Ir(CO)(PPh_3)_2X$, are inactive for cyclotrimerization;[13] and (3) a metallacyclopentadiene complex was isolated for reaction of DMAD with *trans*-$Ir(N_2)(PPh_3)_2Cl$ since the N_2 ligand readily dissociates.[13] Once the metallacyclopentadiene complex is formed, the addition of the third acetylene molecule could occur by two possible suggested mechanisms. The first involves coordination of an acetylene, formation of metallacycloheptatriene, and then reductive elimination. The second involves a cycloaddition to form a bridged bicyclic complex in a Diels–Alder type reaction. To differentiate between these two steps we used a mixture of DMAD and DMB ($C_2(CH_2OMe)_2$), an acetylene which does not coordinate appreciably to these iridium complexes and is not itself cyclotrimerized. Use of a 1:1 ratio leads to $C_6(CO_2Me)_6$ (62%) and $C_6(CO_2Me)_4(CH_2OMe)_2$ (38%). The presence of *o*-$C_6(CO_2Me)_4(CH_2OMe)_2$ as a product suggests that the third acetylene molecule is added by the second mechanism, a cycloaddition. A scheme describing the mechanism is shown in Figure 3.

Acknowledgment. We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Alfred P. Sloan Foundation for partial support of this research. A loan of $IrCl_3 \cdot xH_2O$ was generously provided by Johnson Matthey Corp.

Supplementary Material Available: Tables of anisotropic thermal parameters and bond distances and angles (5 pages); listing of observed and calculated structure factor amplitudes for $Ir(COCH_2CMe_3)[P(p\text{-tolyl})_3]_2[C_2(CO_2Me)_2]$ (31 pages). Ordering information is given on any current masthead page.

(33) Kubota, M.; Blake, D. M.; Smith, S. A. *Inorg. Chem.* **1971**, *10*, 1430.
(34) Rees, W. M.; Churchill, M. R.; Li, Y. J.; Atwood, J. D. *Organometallics* **1985**, *4*, 1162.

Bromination of Bicyclobutanes: A Possible Case of an Electron-Transfer Mechanism[1]

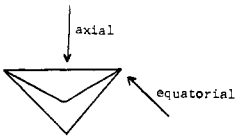
Shmaryahu Hoz,* Mordechai Livneh, and Drora Cohen

Contribution from the Department of Chemistry, Bar-Ilan University, Ramat-Gan, Israel 52100.
Received December 8, 1986

Abstract: The kinetics and product distribution of the bromination of 3-R-bicyclobutanecarbonitrile (R = H, Me, Cl, and Ph) by Br_2 and Br_3^- were studied in MeOH at 25 °C. For the first three substrates, the addition of Br–Br and Br–OMe across the central bond of the bicyclobutane moiety was (within experimental error) 100% syn stereospecific. For the phenylated substrate, where a relatively stable benzylic cation is formed, a mixture of syn and anti addition products was obtained. Reaction rate constants are best correlated by σ^+ with ρ^+ values of −6.2 and −6.4 for Br_2 and Br_3^-, respectively. In both cases the phenylated substrate deviates positively from the Hammett-type plot. With use of ab initio calculations it was shown that the mechanism that promotes the stereospecific syn additions in the acid-catalyzed additions to the same substrates is not operative in the case of the bromination reactions. Analogous to the electrophilic additions to aromatic and olefinic substrates, an electron-transfer mechanism is suggested for these reactions. Ab initio calculations (URHF) show that the bicyclobutane radical cation formed in the first step is more stable in the puckered form by ca. 18 kcal/mol as compared to the planar one.

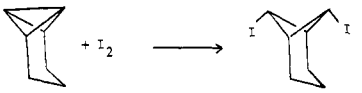
Electrophilic attacks on bicyclobutane could in principle occur from the axial as well as the equatorial directions. However, a literature survey indicates that bicyclobutane undergoes electrophilic attacks exclusively from the equatorial direction.[3] The cause

0002-7863/87/1509-5149$01.50/0 © 1987 American Chemical Society



of this selectivity is probably due to two main factors. The first one is steric in nature and stems from the fact that the bridghead carbons in bicyclobutane have an inverted geometry[4] causing the axial approach to be partly hindered by the bridgehead substituents. The electronic structure of bicyclobutane provides the second reason for this phenomenon. According to theoretical models, the HOMO of the central bond resides heavily in the equatorial direction.[5,6] Hence, governed by HOMO–LUMO interactions, electrophilic reagents will approach bicyclobutane from the equatorial direction, Indeed, to the best of our knowledge, an axial approach has never been demonstrated,

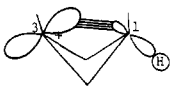
More surprising is the observation that in halogen additions across the central bond, the cis dihalo isomer is preferentially and in some cases even exclusively obtained.[7-12] An electrophilic addition initiated by an equatorial attack must involve a consecutive nucleophilic attack which is also equatorialy directed in order to furnish the syn addition product, Thus, for example, iodination of tricyclo[4,1,0,$0^{2,7}$]heptane affords as expected a product in which both iodine atoms acquire the two equatorial positions[10] (eq 1). This stereospecificity is not unique to halo-



(1)

genation reactions and was shown to dominate the additions of other electrophiles such as acids[2,13-15] and $Hg(AcO)_2$.[16]

In a recent report, we have shown that, in acid-catalyzed additions to bicyclobutane, the protonated intermediate is highly puckered due to a residual bonding across the ring.[2] This puckering, which directs the nucleophilic attack to the equatorial direction leading to an overall syn addition, is probably due to a donation of electron density from the back lobe of the equatorial C–H bond on C(1) to the vacant orbital on C(3).[17]



In cases where the H atom is replaced by an electronegative atom such as Br, puckering is likely to vanish since the C–Br bond is highly polarized in the direction of the Br atom and will not function as an electron density donor. In the absence of any other puckering mechanism, the resulting carbocationic intermediate will be nearly planar. As a result, syn as well as anti additions of the electrophile–nucleophile pair to bicyclobutane will be observed, However, as was mentioned before, literature precedents show that in spite of this difference between Br and H, brominations of bicyclobutanes are highly syn stereospecific.

Practically all the previously reported halogenation reactions of bicyclobutane were performed in apolar solvents, mainly in CCl_4. Therefore, in order to examine the reactions under clearly ionic conditions and also to enable comparison with our previous results for the acid-catalyzed additions to bicyclobutane, the bromination reactions in this study were performed in MeOH,

Table I. First-Order Rate Constants for the Bromination of **1** in MeOH at 25 °C

$[Br^-]$, M	0.48	0.192	0.168	0.12	0.072	0.048	0.024
$10^2 k_{obsd}$, s^{-1}	1.61	1.9	1.95	2.07	2.3	2.61	3.5

Table II. First-Order Rate Constants for the Bromination of **2** in MeOH at 25 °C

$[Br^-]$, M	0.2	0.15	0.08	0.03	0.015	0.010	0.005
k_{obsd}, s^{-1}	0.46	0.5	0.67	1.33	2.0	2.5	3.53

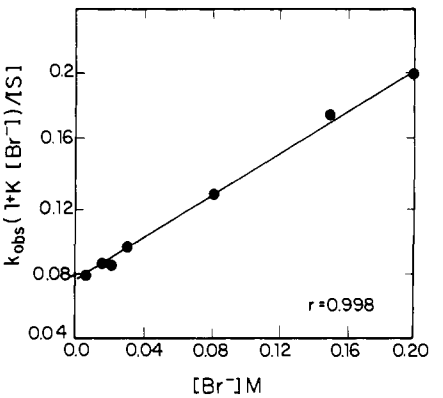
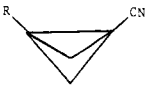


Figure 1. A plot of the left-hand side of eq 3 vs. $[Br^-]$ for the bromination of **4** in MeOH at 25 °C.

Results

The bromination of four derivatives of bicyclobutanecarbonitrile (**1**, **2**, **3**, and **4**) was studied in methanol at 25 °C in the presence of NaBr. Two major aspects were investigated: the kinetics of the reaction and the stereochemistry of the products.



1 R = H
2 R = Me
3 R = Cl
4 R = Ph

Kinetics. The reactions were followed spectroscopically by monitoring the decrease in the absorbance of Br_3^- at 270 nm. The concentrations of NaBr in the reaction mixtures were in the range of 0.005–0.6 M. The initial concentration of Br_2 was always smaller than 0.0001 M and the concentration of the substrate was at least 50 times larger than that of Br_2. The reactions were pseudo-first-order in the brominating agent. Assuming that Br_2 and Br_3^- are the active brominating agents, the reaction rate can be described by eq 2 where S is the substrate.

$$\text{rate} = k_1[Br_2][S] + k_2[Br_3^-][S] \quad (2)$$

This can be further developed into eq 3[18,19]

$$k_{obsd}(1 + K[Br^-])/[S] = k_1 + k_2K[Br^-] \quad (3)$$

(1) Presented in part at the "21st Reaction Mechanism Conference", Austin, Texas, 1986. This is part 13 in the series "Cyclobutane–Bicyclobutane System". For part 12 see ref 2.
(2) Hoz, S.; Livneh, M. *J. Org. Chem.* **1986**, *51*, 4537.
(3) The chemistry of bicyclobutane was recently comprehensively reviewed; see: Hoz, S. In *The Chemistry of the Cyclopropyl Group*; Rappoprt, Z., Ed.; Patai, S., Series Ed.; Wiley: New York, Chapter 19 in press.
(4) Cox, K. W.; Harmony, M. D.; Nelson, G.; Wiberg, K. B. *J. Chem. Phys.* **1969**, *50*, 1976.
(5) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 767.
(6) Paddon-Row, M. N.; Houk, K. N.; Dowd P.; Garner, P.; Schappert, S. *Tetrahedron Lett.* **1981**, *22*, 4799.
(7) Wiberg, K. B.; Lampman, G. M.; Ciula, R. P.; Connor, D. S.; Schertler, P.; Lavanish, J. *Tetrahedron* **1965**, *21*, 2749.
(8) v. Doering, E.; Cobrun, F. F., Jr. *Tetrahedron Lett.* **1965**, 991.
(9) Moore, W. R.; Taylor, G.; Muller, P.; Hall, S. S.; Gaibel, Z. L. F. *Tetrahedron Lett.* **1970**, 2365.
(10) Mazur, S.; Schroder, A. H.; Wiess, M. C. *J. Chem. Soc., Chem. Commun.* **1977**, 262.
(11) Masamune, S. *Tetrahedron Lett.* **1965**, 945.
(12) Hall, H. K.; Blanchard, E. P.; Cherkofsky, S. C.; Sieja, J. B.; Sheppard, W. A. *J. Am. Chem. Soc.* **1971**, *93*, 110.
(13) Blanchard, E. P.; Cairncross, A. *J. Am. Chem. Soc.* **1966**, *88*, 487.
(14) Razin, V. V.; Ermenko, M. V. *Zh. Org. Khim.* **1978**, *14*, 1475.
(15) Razin, V. V.; Ermenko, M. V.; Ogloblin, K. A. *Zh. Org. Khim.* **1975**, *11*, 2439.
(16) Muller, E. *Tetrahedron Lett.* **1973**, 1203.
(17) Wiberg, K. B.; Andes Hess, B., Jr.; Ashe, A. J., III In *Carbonium Ions*; Olah, G. A., von Schleyer, R. P., Ed.; Wiley: New York, 1972; Chapter 26.
(18) Freeman, F. *Chem. Rev.* **1975**, *75*, 439.
(19) de la Mare, D. P.; Bolton, R. *Electrophilic Additions to Unsaturated Systems*; 2nd ed.; Elsevier: New York, 1982.

Scheme I

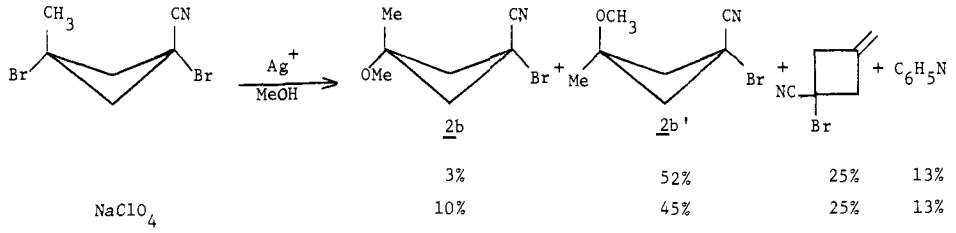


Table III. First-Order Rate Constants for the Bromination of **3** in MeOH at 25 °C

$[Br^-]$, M	0.6	0.48	0.36	0.24	0.192	0.168	0.12	0.096	0.072	0.048
$10^3 k_{obsd}$, s^{-1}	2.12	2.3	2.68	3.08	3.4	3.26	3.7	4.65	5.55	7.1

Table IV. First-Order Rate Constants for the Bromination of **4** in MeOH at 25 °C

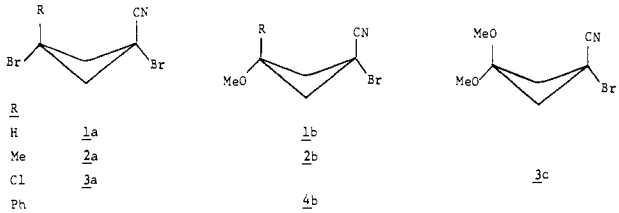
$[Br^-]$, M	0.2	0.15	0.08	0.03	0.02	0.015	0.005
k_{obsd}, s^{-1}	16.3	18.8	25.1	45.5	56.1	69.3	126

Table V. Second-Order Rate Constants for the Bromination of Substrates **1–4** in MeOH at 25 °C

substrate	k_1, M^{-1} s^{-1}	k_2, M^{-1} s^{-1}
1	20.2 ± 1.7	2.24 ± 0.07
2	2535 ± 60	111 ± 3
3	6.9 ± 0.4	0.22 ± 0.008
4	75800 ± 1400	3537 ± 80

where $K = [Br_3^-]/[Br_2][Br^-]$ and k_{obsd} is the observed pseudo-first-order rate constant. Under the reaction conditions (i.e., MeOH at 25 °C) the value of K is known to be 177 M^{-1}.[20] The values of k_{obsd} as a function of bromide concentrations are given in Tables I–IV. A plot of the left-hand side of eq 3 vs. $[Br^-]$ gives straight lines for all substrates. An example is shown in Figure 1 (correlation coefficients in all cases are better than 0.994 with at least 7 points on each line). The values of k_1 and k_2 were evaluated from the slopes and the intercepts of these lines. The values of these two rate constants for the four substrates at 25 °C are given in Table V.

Products and Stereochemistry. In general, the bromination of the substrates yields two types of products: dibromo derivatives (**1a**, **2a**, and **3a**) and bromomethoxy derivatives (**1b**, **2b**, and **4b**). The phenylated substrate **4** is the only substrate that fails to add Br_2 across its central bond and undergoes only bromomethoxylation. Bromomethoxylation of **3** gives the ketal **3c** as the end product.



The reactions were performed under conditions similar to those employed in the kinetic experiments with the exception that the bromine concentration used was larger. This was done in order to increase the concentration of the products so an accurate GC analysis could be performed. In several control experiments, reaction mixtures taken from the kinetic experiments were concentrated by evaporation and analyzed by GC. The product ratio was similar to the one obtained in the reaction with a higher bromine concentration.

The reactions are relatively very fast and are completed within seconds from the addition of the substrate to the reaction mixture. In the bromomethoxylation reaction, HBr is released. The solution becomes acidic therefore and the excess of the substrate undergoes an acid-catalyzed addition of methanol. It was found that the acidity of the medium did not affect the ratio of the two major products of the reaction. This side reaction could be suppressed by quenching the solutions with an aqueous 5% $NaHCO_3$ solution following immediately the addition of the substrate to the reaction mixture. With the exception of **4** where two isomers of the bromomethoxylation product were obtained, the reactions were found to be highly stereospecific. Only one isomer of both the dibromo and the bromomethoxy derivatives was obtained.

Table VI. Product Ratios in the Bromination of **1**, **2**, and **3** in MeOH at 25 °C as a Function of Bromide Ion Concentration[a]

[NaBr], M	**1a**/**1b**	**1a**/**1b**[b]	**2a**/**2b**	**3a**/**3c**
0.06	0.64	0.71	0.059	
0.12	1.28	1.27	0.125	0.132
0.18	1.82	1.77	0.156	0.21
0.24	2.5	2.23	0.247	0.3
0.3	2.78	2.68	0.313	0.325
0.48	3.7	3.97	0.46	0.595
0.6				0.676

[a] Substrate concentrations are in the range of 0.01–0.025 M; Br_2 concentrations are in the range of $1–5 \times 10^{-3}$ M. [b] Calculated with eq 6 and 7, see text.

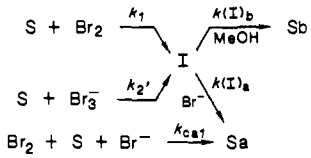
The stereochemistry of the isomer obtained in the aforementioned reactions is cis (with respect to the added Br–nucleophile pair). This configuration assignment is based on the following evidence: The two isomers of the dibromo adduct of **1** are known in the literature.[12] The NMR spectrum of **1a** is identical with that of the cis isomer. An X-ray analysis of **2a** showed that the two bromine atoms are located cis to each other. It is only reasonable to assume that **3a** and the two bromomethoxy derivatives **1b** and **2b** are also obtained by syn addition reactions. The latter assumption can be further supported by data from solvolytic reactions. We have found that when the two geometrical isomers of 3-methyl-3-bromocyclobutanecarbonitrile undergo solvolysis in MeOH in the presence of $AgNO_3$, the major product is the one in which Br is replaced by MeO with an inversion of configuration.[21] The dibromo derivative **2a** was also solvolyzed in MeOH in the presence of $AgNO_3$ (0.2 M). As can be seen from Scheme I, the major product (**2b'**) is the bromomethoxy derivative of **2a** and is not identical with the addition product **2b**. Assuming that solvolysis is accompanied by inversion of configuration as before, it is clear that in **2b** the Br and the MeOH group are syn to each other. It is interesting to note that in the presence of $NaClO_4$ the amount of the retention product **2b** is increased, probably due to a double inversion process. In these reactions an unidentified product (C_6H_5N according to GCMS) was also observed.

The product ratio (dibromide to bromomethoxy) was determined at 25 °C in the presence of variable amounts of NaBr. The data are presented in Table VI. The stereochemistry of the bromination of **2** was examined also in the presence of $NaClO_4$. The reaction was performed in the presence of 0.3 M NaBr and

(20) Dubois, J. E.; Herzog, H. *Bull. Soc. Chim. Fr.* **1963**, 57.

(21) Hoz, S.; Livneh, M., unpublished results.
(22) Bartlett, P. S.; Trabell, D. S. *J. Am. Chem. Soc.* **1936**, *58*, 466.
(23) De Young, S.; Berliner, E. *J. Org. Chem.* **1979**, *44*, 1088.
(24) Dubois, J. E.; Huynh, X. Q. *Tetrahedron Lett.* **1971**, 3369.

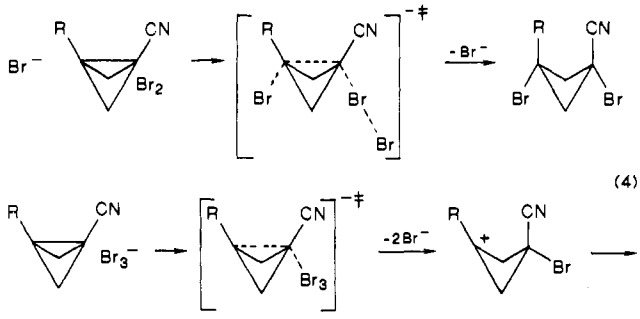
Scheme II



0,3 M $NaClO_4$. In addition to the two original products **2a** and **2b**, 3–4% of **2b'**, which is the trans addition isomer of **2b**, was obtained.

Discussion

Interpretation of the Kinetic Terms. While the first term in eq 2 represents bromination by a single bromine molecule, the second term in this equation can be interpreted as representing either a catalytic mechanism (eq 4) or an electrophilic addition of Br_3^- (eq 5).[18,19,22,23]



(4)

product (5)

The catalytic route refers to a mechanism in which there is a simultaneous attack by Br_2 and Br^- on the two bridgehead carbons, Therefore, the reaction will be first order in each of these species. However, this cannot be kinetically distinguished from the case where Br_3^- itself functions as an electrophile, since the product $[Br_2][Br^-]$ is equivalent to $[Br_3^-]$,

In the following discussion we will show that the experimental results can be best explained by assuming the electrophilic mechanism (eq 5) for the reaction of Br_3^- with all four substrates with an additional contribution of a catalytic path for the reaction of **1**. Support for this can be gained from the work of Dubois and co-workers, who investigated in depth bromination reactions of olefins.[24] Analysis of the kinetic data for the reactions of over 30 olefins showed that the ratio B ($B = k_2K/k_1$ where k_1 and k_2 are the rate constants in eq 2 and K is the equilibrium constant for the formation of Br_3^-) is especially high at the two ends of the substrates' reactivity range (most and least reactive olefins). High B values are expected for highly reactive olefins since they display a low selectivity toward the electrophiles Br_2 and Br_3^-. However, for the least reactive olefins the catalytic route must be invoked. On this basis it is clear that out of the four substrates **1** is indeed the best candidate for the catalytic mechanism since it possesses a relatively low reactivity and the highest B value (the B values for substrates **1–4** are 19.7, 7.7, 5.6, and 8.3, respectively). In addition, it presents the least steric hindrance for the approach of Br^- to C(3). Thus, the overall scheme for the bromination reactions of the bicyclobutanes (S) in this study involves three possible reaction paths as shown in Scheme II (Sa and Sb are the dibromo and the bromomethoxy products, respectively). According to this scheme, and assuming that the intermediates formed by the reactions of Br_2 and Br_3^- are either identical or display the same selectivity toward Br^- and MeOH, the ratio Q will be expressed by eq 6

$$Q = \frac{[S_a]}{[S_b]} = \frac{k(I)_a[I][Br^-] + k_{cal}[S][Br_2][Br^-]}{k(I)_b[I]} \quad (6)$$

where $k(I)_b$ includes the effective concentration of MeOH.

In the absence of any contribution from the catalytic route, a plot of Q vs. $[Br^-]$ should result in a straight line with a zero intercept. This was indeed found for substrates **2** and **3** (correlation coefficients and intercepts are 0,9950, 0.003, 0.9938, and 0.00083, respectively). However, the same plot for substrate **1** gives a curved rather than a straight line. Assuming a steady-state concentration for the intermediate I in Scheme II, eq 6 obtains the following form (see Appendix),

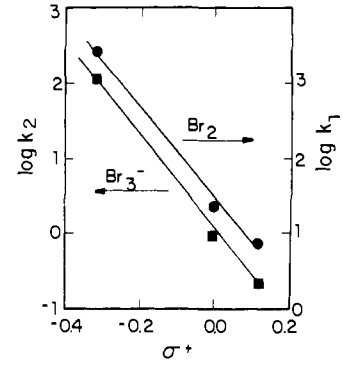


Figure 2. Hammett-type plots for the bromination of **1**, **2**, and **3** by Br_2 (k_1) and Br_3^- (k_2 for **2** and **3**; k_2' for **1**). The phenylated substrate **4** deviates positively from both lines by 1.3 log units (using $\sigma^+ = -0.34$ according to Noyce, D. S.; Fike, S. A. *J. Org. Chem.* **1973**, *38*, 2433).

$$k_{cal} = \frac{(Q - X[Br^-])(k_1 + k_2K[Br^-])}{[Br^-](Q + 1)} \quad (7)$$

In which $X = k(I)_a/k(I)_b$. This equation was solved numerically to give $k_{cal} = 231\ M^{-2}\ s^{-1}$. Using this value one can recalculate the ratio Q for various concentrations of Br^-. In Table VI, the experimental data are displayed along with the calculated data. The data show that the percent of the catalytic route ranges from 19% to 53% for Br^- concentrations of 0.024 and 0.48 M (see Table I), respectively. Having determined the catalytic rate constant one can determine now the rate constant for the electrophilic attack of Br_3^- (k_2'). Its calculated value $(k_2 - k_{cal})/K$ is 0.93 $M^{-1}\ s^{-1}$.

The previously calculated value of B for **1** was 2–3-fold larger than the B value for the other substrates. This discrepancy was indicative of the catalytic component in the reaction of **1**. Knowing the electrophilic rate constant (k_2') for the reactions of Br_3^- with **1**, one can recalculate its B value (8.2). This value clearly falls in the range of the B values for the other three substrates providing an additional support for the existence of the catalytic path for **1**. This conclusion is further substantiated by the Hammett-type plot in which the dissection of k_2 into k_2' and k_{cal} brings the point for **1** to the line.

Substituent Effect. Probably the most suitable substituent parameter for electrophilic reactions in which the positive charge is developed at an α position to the substituent is σ^+.[25] This substituent constant was successfully employed by Tidwell and co-workers[26] in correlating a vast number of alkenes' hydration reactions. Plots of log k_1 and log k_2 (using k_2' for **1**) vs. σ^+ give a good correlation for the three substituents H, Me, and Cl with ρ^+ values of −6.2 and −6.4, respectively (Figure 2). There is, however, a marked positive deviation of the phenylated substrate **4**. Such a deviation was previously reported for somewhat similar reactions.[26,27] Of greater importance, however, is the similarity in the ρ^+ values for the reactions of Br_2 and Br_3^-. Although based on three points only, the quality of the lines seems to justify the conclusion that the two ρ^+ values are nearly identical. This indicates that the two transition states have similar structure.

Transition State. The early recognition that electrophilic aromatic substitution reactions may involve an electron-transfer component[28] has been well established during the last 5 years mainly by Kochi and his co-workers.[29] It was shown that the

(25) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.
(26) Oyama, K.; Tidwell, T. T. *J. Am. Chem. Soc.* **1976**, *98*, 97.
(27) Nowlan, V. J.; Tidwell, T. T. *Acc. Chem. Res.* **1977**, *10*, 252.
(28) Perrin, C. L. *J. Am. Chem. Soc.* **1977**, *99*, 5516.
(29) (a) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 7240. (b) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 7599.

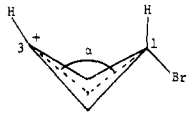
Table VII. Ab Initio Calculations of the Energy as a Function of the Puckering Angle α of the Two Isomers of Bromobicyclobutane Radical Cation

equatorial Br[a]		axial Br	
α, deg	E, au	α, deg	E, au
115	-38.13050	120	-38.13545
120	-38.13373	126.83	-38.13609[b]
125	-38.13587	130	-38.13598
135	-38.13807	135	-38.13558
155	-38.14204	140	-38.13573
165	-38.14313	145	-38.13686
169.44	-38.14323[b]	150	-38.13831
175	-38.14312	160	-38.14076
		170	-38.14215

[a] See Scheme III. [b] Fully optimized.

transition state in the reactions of aromatic[29] as well as olefinic[33b] substrates with a variety of electrophiles strongly resembles the ion pair produced by excitation of a donor–acceptor charge-transfer complex. Viewing these reactions as nucleophilic attacks of the electron-rich moiety on the electrophile is highly consistent with our model for nucleophilic reactions with LL (low LUMO) substrates.[30,31] According to this model, the transition state in these reactions has a large diradicaloid character, the magnitude of which increases as the LUMO of the substrate is lowered. Eventually, with substrates having sufficiently low LUMO (such as the electrophiles at hand, Br_2 and Br_3^-), a complete electron transfer takes place. We believe that the observed stereospecificity of the reaction and the substituent effect suggest that electron transfer is also an essential feature in the bromination of bicyclobutane.

With the exclusion of **4** where a stable benzylic carbenium ion is formed, the other three substrates undergo, within experimental error, a 100% stereospecific syn addition. In the case of the analogous acid-catalyzed addition reactions to bicyclobutane, the high stereospecificity was found to be due to a high degree of puckering in the first formed cyclobutyl cation.[2] The initiative for this study was based on the assumption that, unlike the equatorial C–H bond, the C–Br bond cannot function effectively as an electron donor and therefore cannot induce such puckering in the analogous bromocyclobutyl cation. In order to substantiate this assumption we have calculated, using GAUSSIAN 80,[32,33] a cross section of a potential surface of the bromocyclobutyl cation. The geometry of the cation was fully optimized for various values of the puckering angle α with the restriction of C_s symmetry. As



can be seen from the data presented in Table VII and Figure 3 (extramum points fully optimized), the puckered structure has no stability and is transformed to the nearly planar structure in a barrierless motion. Placing H in an equatorial position and Br in an axial one will increase the stability of the puckered geometry. The planar geometry, however, is still by far more stable (Figure 3). On the basis of these calculations it is concluded that the mechanism by which the hydrogen at the equatorial position stabilizes the puckered geometry of the cation is not operative in the case where a Br atom occupies the same position.

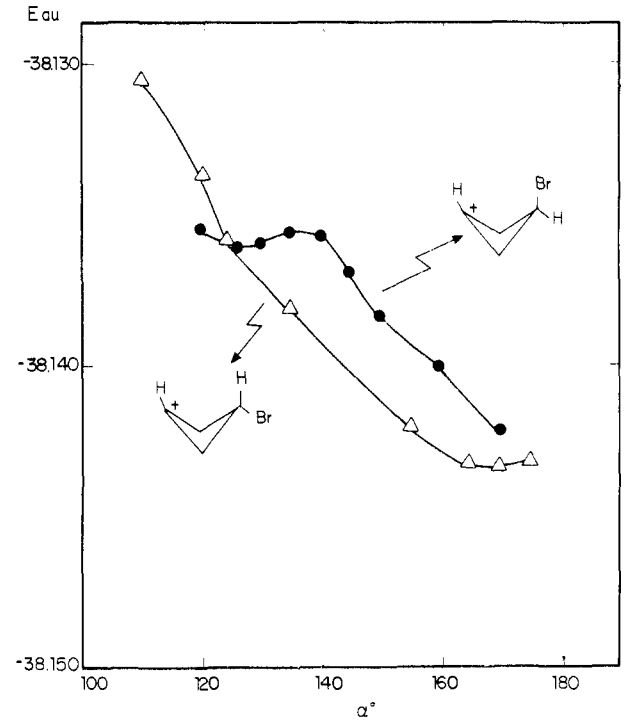
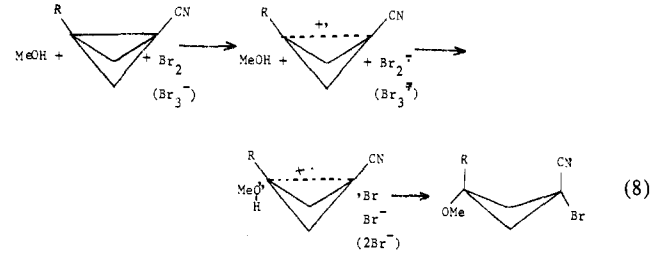


Figure 3. Energy vs. puckering angle (α) for bromobicyclobutyl cation.

It is thus clear that a bromocyclobutyl cation, if initially formed in a highly puckered geometry, will vibrationally relax to the planar geometry at rate orders of magnitude faster than the competing nucleophilic step.[34] As a result, nucleophilic attack on planar bromocyclobutyl cation will lead to stereoconvergance rather than to the observed stereospecificity. Since the "traditional" mechanism in which a covalent bond is formed between C(1) and Br at the transition state cannot accommodate the stereochemical results, this mechanism should be discarded. A possible alternative mechanism is one in which an electron is transferred from the substrate to the brominating agent in the first step. An adiabatic process with respect to solvent (nucleophile) reorganization can be ruled out (see footnote 34). In the vertical process, the first step is followed by solvent (nucleophile) relaxation which brings a MeOH molecule (or a bromide ion) to a reactive position while $Br_2^{\bullet-}$ (or $Br_3^{\bullet-}$) undergo cleavage to $Br^\bullet$ and Br^- (or $2Br^-$).[35]

In the last step, the system collapses to give the observed syn addition product (eq 8).



(8)

Two essential requirements must be met in order to maintain the observed stereospecificity. Solvent reorganization, which for MeOH is probably in the order of ten picoseconds,[36] must precede (1) the covalent C–Br bond formation and (2) planarization of the radical cation of bicyclobutane. Failing to meet either re-

(30) Hoz, S.; Speizman, D. *J. Org. Chem.* **1983**, *48*, 2904.
(31) Hoz, S. In *Advances in Chemistry Series*; Harris, J. M.; McManus, S. P., Ed.; American Chemical Society: Washington, DC, 1987; No. 215, p 182, Nucleophilicity.
(32) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE*, Program No. 406.
(33) The double-ζ basis set and effective potentials that replace the core electrons for carbon and bromine were taken from the work of Stevens et al. (Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026 and private communication). The double-ζ hydrogen atom basis 4 set of Huzynaga (Huzynaga, S. *J. Chem. Phys.* **1965**, *42*, 1293) contracted (3,1) and scaled by (1,2) (Stevens et al.).

(34) A preassociation mechanism or an adiabatic process in which the nucleophile, be it MeOH or Br^-, is already in a reactive position is unlikely. This is because it is equivalent to the catalytic mechanism which was shown not to be operative for all substrates except for a partial contribution in the case of **1**.
(35) The cleavage of the radical anion could occur simultaneously with the electron-transfer step, i.e., dissociative electron attachment, depending on the lifetime of the radical anion.
(36) Garg, S. K.; Smyth, C. P. *J. Phys. Chem.* **1965**, *69*, 1294.

Table VIII. Ab Initio Calculations (3-21G, UHF) of the Energy as a Function of the Puckering Angle α of Bicyclobutane Radical Cation

α, deg	E, au	α, deg	E, au
115.0	−153.711 54	153.0	−153.695 24
120.0	−153.713 17	157.715	−153,694 4[a]
122.68	−153.713 39[a]		(154.568 88)[b]
	(−154.599 32)[b]	160.0	−153.695 37
125.0	−153.713 24	170.0	−153.696 48
130.0	−153.711 95	179.90	−153.696 73[a]
140.0	−153.706 10		(154.569 50)[b]
150.0	−153.697 17		

[a] Fully optimized geometry. [b] UHF/6-31G*/3-21G.

quirement will result in the formation of a planar cation leading ultimately to stereoconvergance.

Regarding the first requirement, it is clear that formation of the C–Br bond lags significantly behind the electron-transfer step, allowing enough time for solvent relaxation. This has already been demonstrated in the electrophilic aromatic substitution reaction where the lifetime of the intermediate is long enough to enable selectivity among the ortho, para, and meta positions on the ring.[29] The reason for a barrier in these reactions probably stems from the fact that the formation of the C–Br bond is not a simple radical combination but rather a radical substitution reaction which involves a rupture of a one-electron bond.

The second requirement deals with the question of whether the radical cation of bicyclobutane[37] in the puckered geometry (**5**), with its HOMO delocalized on C(1) and C(3), is significantly more stable than the localized nearly planar form (**6**).

5 **6**

PRDDO calculations with partial geometry optimization showed that the ion with the neutral geometry was 11 kcal/mol lower in energy than an ion with a planar carbon ring structure.[38] In the present study, ab initio calculations (GAUSSIAN 82)[39] were performed at the 3-21G level[40] (UHF), maintaining C_s symmetry with full geometry optimization for each α value (minima and maximum points were fully optimized). From the data given in Figure 4 and Table VIII it is evident that this radical cation is significantly more stable (10 kcal/mol) in the puckered geometry. Moreover, recalculating the energy of the extramum points (determined with the 3-21G basis set) with a much higher quality basis set (6-31G*)[41] shows that the barrier for planarization is ca. 18 kcal/mol. Hence, it is obvious that solvent reorganization is by far faster than planarization of the radical cation of bicyclobutane which complies with the second requirement. It should be pointed out that the presence of the CN group is bound to decrease the degree of delocalization (moving in the direction from **5** to **6**) due to its inductive effect. However, it has been shown that when the positive charge resides α to the cyano group, the latter exerts a stabilizing mesomeric effect,[42] This, combined

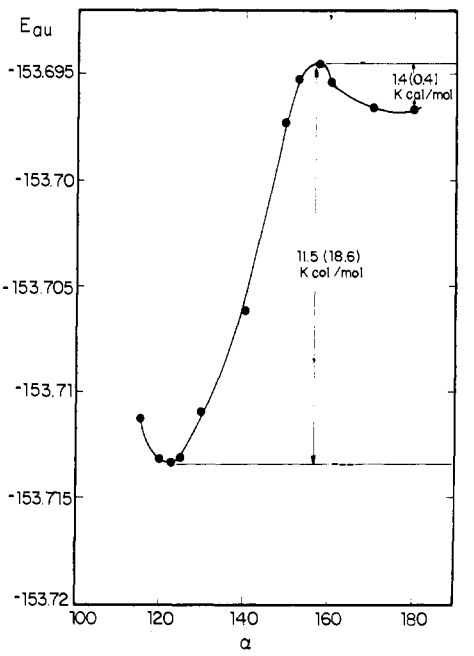


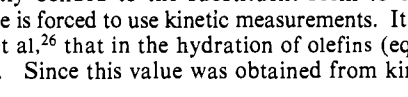
Figure 4. Energy vs. puckering angle (α) for bicyclobutane radical cation.

with the electrostatic effect of the counter negative charge on the bromine, will markedly compensate the inductive effect of the CN. The conclusion of this section is that the electron-transfer mechanism provides a reasonable explanation for the observed syn stereospecificity.

It is interesting to note that radical cations of bicyclobutane produced by an electron transfer to the photoexcited 1-cyanonaphthalene show mixed stereochemistry in their MeOH addition reactions,[43] These reactions, however, differ from the present reactions in several aspects. For example, instead of the collapse of the intermediate in eq 6 with the reactive Br•, a free radical is apparently formed which can undergo either back electron transfer followed by protonation or a hydrogen abstraction,[43] These processes which are relatively slow allow enough time for a loss of any initial sterochemical bias.

An additional support for the electron-transfer mechanism is obtained from the subtituent effect on the reaction rates. Even though the ρ^+ values are based on three data points only, the similarity in the substituents response to the two vastly differing electrophiles, Br_2 and Br_3^-, is amazing. This observation is highly consistent with a transition state that resembles an excited charge-transfer complex. Such a situation is much less likely to be encountered if the reaction would have taken place via the "traditional" covalent bonding mechanism.

Since ρ^+ value are usually employed as a measure for the amount of the effective charge sensed by the substituents, one would like to compare the observed ρ^+ values with that for a unit positive charge. Unfortunately, relevant thermodynamic data for cases where the carbenium ion is not substituted by aryl moieties and is directly bonded to the substituent seem to be lacking. Therefore one is forced to use kinetic measurements. It was found by Tidwell et al,[26] that in the hydration of olefins (eq 9) the ρ^+ value is −12. Since this value was obtained from kinetic mea-



(9)

surements, it can serve as a lower limit for ρ^+ values for an equilibrium reaction in which a unit positive charge is formed. Indeed, a much higher (absolute) value was suggested for such a process by Kosower et al.[44] It is thus clear that the observed

(37) Gassman, P. G.; Yamaguchi, R. *J. Am. Chem. Soc.* **1979**, *101*, 1308. Gassman, P. G.; Mullins, M. J.; Richtsmeier, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5793. Gassman, P. G.; Yamaguchi, R. *Tetrahedron* **1982**, *38*, 1113. Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977. Gassman, P. G.; Olson, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 3704. Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1984**, *106*, 2711.

(38) Richtsmeier, S. C.; Gassman, P. G.; Dixon, D. A. *J. Org. Chem.* **1985**, *50*, 311.

(39) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Rahgavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A., Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA.

(40) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(41) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217. This is the recomended basis set for strained systems: Newton, M. D. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1977; p 234.

(42) Gassman, P. G.; Talley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 1214. Dixon, D. A.; Charlier, P. A.; Gassman, P. G. *J. Am. Chem. Soc.* **1980**, *102*, 3957.

(43) Gassman, P. G.; Carrol, G. T. *Tetrahedron* **1986**, *42*, 6206.

(44) Kosower, E. M.; Dodiuk, H. *J. Am. Chem. Soc.* **1978**, *100*, 4173.

ρ^+ values are well below this limit and consistent with the delocalized electronic structure **5** which indicates that only a fraction of the positive charge resides on C(3). At this stage we would like to speculate about the protonation of bicyclobutane by carboxylic acids, a reaction which we have previously studied.[2] The pertinent information is as follows: The ρ^+ value for this reaction was found[2] to be −7.1 which is surprisingly close to that for the Br_2 and Br_3^- reactions. Carboxylic acids have low LUMOs and are known to be good electron acceptors.[45] Methoxonium ion has a relatively higher LUMO and exhibits a remarkable negative deviation from the Brønsted plot.[2] The major reaction at the cathode in electrolysis of carboxylic acids is hydrogen liberation.[46] These four points are consistent with protonation via an electron-transfer mechanism. The last step in this process will obviously be H transfer from $RCOOH^{\bullet-}$ rather than its decomposition into $RCOO^-$ and $H^\bullet$ followed by radical combination. However, much more experimental support is needed to substantiate such a far reaching conclusion.

Summary and Conclusions. In the bromination of bicyclobutanes **1–4** in MeOH by Br_2 and Br_3^-, the mode of the reaction is substituent dependent. In the case of R = H, the electrophilic attack at C(1) is in part assisted by a simultaneous interaction of a nucleophile with C(3) (eq 4). The contribution of this mechanism to the overall reaction of **1** depends linearly on the concentration of Br^-. The uncatalyzed mechanism is operative in the reactions of all substrates. Substrates **1–3** gave 100% stereospecifically syn addition whereas the phenylated bicyclobutane **4**, where a stable benzylic carbenium ion is formed, gave stereoconvergence.

It was shown that the "traditional" stepwise addition mechanism cannot explain the reaction stereospecificity observed for substrates **1–3** since the bromocyclobutyl cation formed in the first step of this mechanism is transformed to a nearly planar structure at a vibrational rate. Completion of the reaction by nucleophilic attack on this nearly planar cation will lead to the formation of two isomers rather than a single isomer as observed. The stereochemistry of the reaction can be explained at this stage by adopting the electron-transfer mechanism (eq 8) previously suggested for electrophilic reactions with olefinic substrates.[29] In the case of bicyclobutane this mechanism is feasible since its HOMO is higher than that of ethylene.[47] Consistent with this mechanism are also the identity of the ρ^+ values for the reactions of the two vastly different electrophiles Br_2 and Br_3^- and their magnitude which is the one expected from a delocalized charge as in **5**. The seemingly high probability of the electron-transfer mechanism in electrophilic additions to bicyclobutane substantiates further the well-known similarity[3,48] between an olefinic bond and the central bond of bicyclobutane.

Experimental Section

General Methods. ^1H NMR spectra (in $CDCl_3$) were recorded on a Varian EM 360A (60MH) or a Bruker AM-300 (300MH) spectrometer. Mass spectra were taken with a Finnigan 4021 mass spectrometer. For analytical purposes a Packard Model 878 (FI detector) gas chromatograph was used whereas for preparative separation a Varian 920 gas chromatograph (TC detector) was employed. In both cases, the column was 5–15% XE60 on Chromosorb W (80–100 mesh). The kinetic measurements were performed on a Gilford 2400 and on a Durrum stopped-flow spectrophotometer. Both spectrophotometers were linked to a PDP-11/40 minicomputer for data aquisition.

Reagents and Starting Materials. Methanol (Frutarom analytical) was dried by the magnesium method. NaBr (Frutarom A.R.) was oven dried before use. Br_2 (Frutarom A.R.) was used without further treatment. $AgNO_3$ (Fluka purum) was used without further purification. Published procedures were employed for the preparation of the four substrates: bicyclobutanecarbonitrile (**1**),[12] 3-methylbicyclobutanecarbonitrile (**2**),[2,15] 3-chlorobicyclobutanecarbonitrile (**3**),[12] and 3-phenylbicyclobutanecarbonitrile (**4**).[12] All substrates were purified by preparative gas chromatography to at least 99% purity and stored at −70 °C.

Preparation of Products. Reaction of Bicyclobutanecarbonitrile (1) with Br_2. To a solution of 0.25 g (0.0032 mol) of **1** in 25 mL of MeOH, a solution of 0.6 g (0.0038 mol) of Br_2 in 10 mL of MeOH was added dropwise over 15 min at room temperature. After an additional 15 min, the solvent was evaporated leaving 0.65 g of yellowish liquid. GC analysis of this liquid showed that it consisted mainly (>95%) of **1a** and **1b**. These products were separated by preparative gas chromatography. 1,3-Dibromocyclobutanecarbonitrile (**1a**) is a known compound and was assigned the syn (dibromo) stereochemistry.[12] 1-Bromo-3-methoxycyclobutanecarbonitrile (**1b**): ^1H NMR δ 2.65–3.03 (m, 2 H), 3.15–3.5 (m, 2 H) 3.25 (s, 3 H, OMe), 4.06–4.17 (p, 1 H); MS, *m/z* (CI) 192, 190, 110. Satisfactory C, H, N, Br analysis was obtained.

Reaction of 3-Methylbicyclobutanecarbonitrile (2) with Br_2. To a stirred cold (0–5 °C) solution of 0.93 g (0.01 mol) of **2** in 10 mL of MeOH, a 10-mL methanolic solution of 1.82 g (0.012 mol) of Br_2 was rapidly added dropwise. Toward the end of the reaction, when the color of the bromine persisted, 10 mL of a 10% sodium bicarbonate solution and 10 mL of saturated sodium thiosulfate solution were added. The reaction mixture was extracted twice with ether, and the ethereal phase was washed with concentrated salt solution, dried over $MgSO_4$, and evaporated. The resulting liquid (2 g) contained 80–90% 1,3-dibromo-3-methylcyclobutanecarbonitrile (**2a**) and 1-bromo-3-methoxy-3-methylcyclobutanecarbonitrile (**2b**) accompanied by ca. 15% 3-methoxy-3-methylcyclobutanecarbonitrile, which is the acid-catalyzed addition product of MeOH to **2**.[2] The amount of this product could be supressed by faster addition of the Br_2 followed by immediate quenching. The products were separated by preparative gas chromatography. **2a** is a known compound.[12] X-ray analysis showed that the two Br atoms are syn to each other. **2b**: ^1H NMR δ 1.47 (s, 3 H), 3.0 (s, 4 H), 3.16 (s, 3 H); MS, *m/z* 206, 204, 174, 172, 152. Satisfactory C, H, N, Br analysis was obtained.

Reaction of 3-Chlorobicyclobutanecarbonitrile (3) with Br_2. A 10-mL methanolic solution of NaBr (0.6 M) containing 0.7 g (0.0044 mol) of Br_2 was added dropwise over 10 min at room temperature to a solution of 0.5 g (0.0044 mol) of **3** in 10 mL of MeOH. After an additional 10 min, the solvent was evaporated, yielding 1.5 g of clear yellow liquid which, according to GC analysis, contained more than 95% of **3a** and **3c**. 3-Chloro-1,3-dibromocyclobutanecarbonitrile (**3a**): ^1H NMR δ 3.7–4.3 (broad singlet for all hydrogens); MS, *m/z* (CI) 276, 275, 274, 273, 240, 238, 236, 197, 196, 195, 194, 193, 192, 116, 114. Satisfactory C, H, N, Br analysis was obtained. 3,3-Dimethoxy-1-bromocyclobutanecarbonitrile (**3c**): mp 42 °C; ^1H NMR δ 2.75–3.5 (m, all hydrogens, the methoxy Me's show singlet at 3.18); MS, *m/z* (EI) 190, 188, 173, 140, 125, 113, 99, 94, 80. Satisfactory C, H, N, Br analysis was obtained. Samples of the purified products were obtained by preparative gas chromatography.

Reaction of 3-Phenylbicyclobutanecarbonitrile (4) with Br_2. To a solution of 1 g (0.0065 mol) of **4** in 10 mL of MeOH, a solution of 1.1 g (0.0069 mol) of Br_2 in 10 mL of MeOH was added dropwise over 5 min. The workup of the reaction mixture was identical with that described for the reaction of **2**. The crude material (1.65 g; 95% yield) was separated by column chromatography (Kieselgel 60, 230–400 mesh) with a 1:1 mixture of methylene chloride–hexane. Two isomers of 3-methoxy-3-phenyl-1-bromocyclobutanecarbonitrile (**4b**) were obtained. The first eluted isomer (60% by GC) has the following characteristics: mp 82 °C; ^1H NMR δ 7.22–7.43 (m, 5 H), 3.0–3.3 (m, 4 H), 2.92 (s, 3 H); MS, *m/z* (CI) 268, 266, 234, 236, 188, 190, 187, 186. Satisfactory C, H, N, Br analysis was obtained. Second isomer: mp 84 °C (40% yield by GC); ^1H NMR δ 7.22–7.32 (m, 5 H), 3.06–3.55 (m, 4 H), 2.98 (s, 3 H); MS, *m/z* identical with the previous isomer. Satisfactory C, H, N, Br analysis was obtained.

Kinetic Measurements. The reactions of the four substrates with bromine in the presence of NaBr in MeOH were followed by monitoring the disappearance of the absorption of Br_3^- at 270 nm. The reactions of **1** and **3** were slow enough to be measured on a Gilford 2400 spectrophotometer. The reaction cell containing 2 mL of NaBr (0.024–0.6 M) solution in MeOH to which 5 μL of Br_2–NaBr methanolic solution was added (total concentration of $Br_2 < 10^{-4}$ M) was incubated in the thermostated cell compartment (25 °C) for ca. 30 min. With use of a microsyringe, 25 μL of the substrate from a methanolic stock solution were injected to the cell. The final concentration of the substrate which was in the range of 0.002–0.008 M was always at least 50-fold larger than the concentration of the bromine. Monitoring and data aquisition by the computer started immediately after the mixing of the reactants. The reactions of the two other substrates were much faster and were therefore monitored by a stopped-flow spectrophotometer with final reactant concentrations similar to those previously described.

Product Distribution Studies. Methanolic solutions of variable concentration of NaBr and constant concentration of Br_2 (in the range of

(45) Siegerman, H. In *Techniques of Chemistry*; Weinberger, N. L., Ed.; Weissberger, A., Series Ed.; Wiley: New York, 1975; Vol. 5, p 667.
(46) Coleman, J. P. In *The Chemistry of Acid Derivatives*; Patai, S., Ed.; Wiley: New York, 1979; Supplement B, Part 2, Chapter 13.
(47) Schulman, J. M.; Fisanick, G. J. *J. Am. Chem. Soc.* **1970**, *92*, 6653.
(48) Pomerantz, M. *J. Am. Chem. Soc.* **1966**, *88*, 5349.

0.001–0.005 M) in 5 mL volumetric flasks were incubated in a thermostated bath. After the desired temperature was reached, 15 μL of the substrate (final concentration ca. 0.02 M) were injected into the solutions. When the reactions were completed (as indicated by the disappearance of the yellow color of the bromine), or shortly before it, 0.1 mL of saturated sodium thiosulfate methanolic solution and 0.1 mL of a 10% solution of sodium bicarbonate in MeOH were injected to quench the reaction. The "dibromo" to "bromomethoxy" ratio was determined by GC analysis. In order to ensure that the same product ratio was also obtained in the kinetic experiments that were performed with less concentrated solutions, samples were also taken from the latter, concentrated, and GC analyzed. The results obtained showed both types of experiments to yield identical results.

Solvolytic Reactions. To a test tube containing 10 mL of 0.2 M $AgNO_3$ methanolic solution, 0.4 g (0.0016 mol) of **2a** were added. The test tube was immersed in a bath at 50 °C for 5 days. The reaction mixture was filtered and the filtrate was washed several times with ether. The combined organic phases were washed twice with water and twice again with salt-saturated water. Evaporation of the ether gave a yellow liquid from which 3-methylene-1-bromocyclobutanecarbonitrile [^{1}H NMR δ 3.35–3.7 (m, 4 H), 4.9–5.17 (t, 2 H); MS, *m/z* 174, 172, 147, 145, 92, 65] (unstable compound, decomposes at room temperature) and 3-methoxy-3-methyl-1-bromocyclobutanecarbonitrile (**2b′**) [^{1}H NMR δ 1.51 (s, 3 H), 3.18, 3.1, 2.78, 2.74 (AB q, 4 H), 3.17 (s, 3 H); MS, *m/z* 206, 204, 174, 172, 125, 110] (satisfactory C, H, N, Br analysis was obtained) were separated by preparative gas chromatography. GC yields of these and the unidentified products are given in Scheme I.

Acknowledgment. The authors are grateful to Dr. F. Frolow of the Weizmann institute for performing the X-ray analysis and to Profs, M, Sprecher, E. M. Kosower, and J. K, Kochi for helpful discussions.

Appendix

Steady-state assumption for I gives

$$[\mathrm{I}] = \frac{k_1[\mathrm{S}][\mathrm{Br_2}] + k_2'[\mathrm{S}][\mathrm{Br_3^-}]}{k(\mathrm{I})_a[\mathrm{Br^-}] + k(\mathrm{I})_b}$$

Substituting this expression for I in eq 6 and using the equation $[\mathrm{Br_3^-}] = K[\mathrm{Br_2}][\mathrm{Br^-}]$ gives

$$Q - \frac{k(\mathrm{I})_a[\mathrm{Br^-}]}{k(\mathrm{I})_b} = \frac{k_{cal}[\mathrm{Br^-}](k(\mathrm{I})_a[\mathrm{Br^-}] + k(\mathrm{I})_b)}{k(\mathrm{I})_b(k_1 + k_2'K[\mathrm{Br^-}])}$$

Since $k_2'K = k_2K - k_{cal}$ one obtains

$$Q - \frac{k(\mathrm{I})_a[\mathrm{Br^-}]}{k(\mathrm{I})_b} = \frac{k_{cal}[\mathrm{Br^-}](k(\mathrm{I})_a[\mathrm{Br^-}] + k(\mathrm{I})_b)}{k(\mathrm{I})_b(k_1 + k_2K[\mathrm{Br^-}] - k_{cal}[\mathrm{Br^-}])}$$

from which eq 7 is easily derived.

Registry No. **1**, 16955-35-4; **1a**, 30628-80-9; **1b**, 109151-11-3; **2**, 694-25-7; **2a**, 109151-12-4; **2b**, 109151-13-5; **2b′**, 109151-14-6; **3**, 23745-75-7; **3a**, 109151-15-7; **3c**, 109151-16-8; **4**, 30494-27-0; **4b** (isomer 1), 109151-17-9; **4b** (isomer 2), 109151-18-0; **6**, 109151-10-2; Br_3^-, 14522-80-6; Br^-, 24959-67-9; methanol, 67-56-1; 3-bromocyclobutyl cation, 109151-09-9; 1-bromo-3-methylenecyclobutylcarbonitrile, 109151-19-1.

Consequences of π/σ Interaction in Bishomoanthraquinones and Their Dimethylene Derivatives. A Structural and PE Spectroscopic Study

Rolf Gleiter,*† Walter Dobler,† Emanuel Vogel,*‡ Stefan Böhm,‡ and Johann Lex‡

Contribution from the Institut für Organische Chemie der Universität Heidelberg, D-6900 Heidelberg, West Germany, and Institut für Organische Chemie der Universität Köln, D-5000 Köln 41, West Germany. *Received December 30, 1986*

Abstract: The syntheses of *syn*- and *anti*-7,14-dihydro-7,14-dimethylene-1,6:8,13-bismethano[14]annulene (**1** and **2**) and of the corresponding 17,17,18,18-tetramethyl compounds (**3** and **4**) starting from *syn*- and *anti*-bishomoanthraquinones (**6** and **7**), respectively, are described. The molecular structures of **6** and **7** have been determined by X-ray analysis. For **6** four independent molecules are found in the unit cell whereas for **7** all molecules are related by symmetry. A great similarity between the molecular parameters of **6** and **7** is observed. As anticipated, both compounds exhibit pronounced bond alternation in the hexatriene systems. The He I photoelectron (PE) spectra of **1**–**6** are reported. Assignment of the bands below 12 eV is based on semiempirical calculations (MINDO/3). A comparison of the PE spectra of **1** and **2** with the spectrum of their planar congener, dibenzo-*p*-quinodimethane (**5**), indicates considerable π/σ interaction in the bridged species. A comparison between **1** and **3** and **2** and **4**, respectively, provides evidence for unusual large Koopmans' defects. Very strong π/σ interactions in **6** and **7** are inferred by comparing the widths of the group of the first six PE bands of these compounds (1.6 eV) with the width of the first peak of **8** (0.8 eV) which contains six transitions.

In planar π systems like ethylene or benzene, symmetry can be used to discriminate between π and σ electrons. If the symmetry is reduced and π and σ systems are no longer orthogonal, mutual interaction occurs. The size of this interaction depends on several factors, e.g., the overlap integral between π and σ system and the energy difference of the corresponding basis orbital energies. In organic chemistry two effects, i.e., hyperconjugation[1] and the through-bond interaction,[2] are due to a sizable conjugation between a planar π system and an adjacent σ framework. In both cases a 2p orbital of a planar π system can interact with an adjacent σ bond as indicated in A (hyperconjugation) or B (through-bond interaction). The electronic nature of the π systems

†Institut für Organische Chemie der Universität Heidelberg.
‡Institut für Organische Chemie der Universität Köln.

(1) Mulliken, R. S. *J. Chem. Phys.* **1939**, *7*, 339. Mulliken, R. S.; Rieke, C. A.; Brown, W. G. *J. Am. Chem. Soc.* **1941**, *63*, 41. Baker, J. W. *Hyperkonjugation*; Oxford, 1952. Coulson, C. A.; Crawford, V. A. *J. Chem. Soc.* **1953**, 2052.

(2) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936. Reviews: Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. Gleiter, R. *Angew. Chem.* **1974**, *86*, 770; *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696. Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245.

0002-7863/87/1509-5156$01.50/0 © 1987 American Chemical Society