# Influence of Solvent and Brominating Agent on the Steric Course of Bromine Addition to Substituted Cyclohexenes

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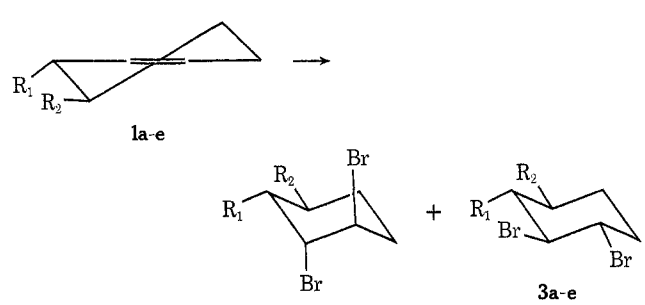
The addition of bromine to several 3- and 4-substituted cyclohexenes in chloroform always produces nonequilibrium mixtures of diaxial and diequatorial dibromides in ratios dependent on the size, position, and polarity of the substituent. 3-Substituted olefins yield higher amounts of diequatorial adducts than the corresponding 4-substituted compounds; particularly, 3-*tert*-butylcyclohexene gives the diequatorial dibromide as the major product. These results may be ascribed to a direct steric effect of the substituent in both the electrophilic and the nucleophilic steps of the addition, which is considered to proceed through the irreversible formation of cyclic bromonium ion intermediates. In contrast, the use of either ethyl ether as the solvent or pyridine perbromide and pyridinium hydrobromide perbromide as the brominating agents, or even the mere presence of tertiary amines in the reaction medium, always leads to a decrease in the amount of the diequatorial products. It is suggested that under these conditions the electrophilic attack could be a reversible prerate-determining step, the steric course of the addition being controlled by the steric interactions in the transition states of the nucleophilic step.

It is generally accepted[1] that the polar addition of bromine to nonconjugated alkenes is an anti stereospecific process, which involves the formation of cyclic bromonium ion intermediates, as was first postulated by Roberts and Kimball.[2] This belief has also recently been supported by stereochemical,[3] kinetic,[4] spectroscopic,[5] and thermochemical[6] evidence. On the basis of the results obtained with steroidal olefins[7-9] and related cyclohexene derivatives,[10] diaxial attack is considered to be strongly favored in the bromine addition to the cyclohexene ring. However, our investigations on the asymmetric bromination of 3- and 4-substituted cyclohexenes[11-13] have shown that diequatorial as well as diaxial dibromides are always produced; moreover, the presence of an asymmetric catalyst, such as a *Cinchona* alkaloid, causes, beside optical activity of the dibromides, a decrease in the amount of the diequatorial adducts. The asymmetric selection was attributed to the intervention of an alkaloid–bromine complex as the brominating agent; we therefore thought that also the use of a simple preformed amine–bromine complex, like pyridine perbromide, or the mere presence of bases in the reaction medium, could possibly change the ratio between diaxial and diequatorial adducts formed in the bromination of cyclohexene derivatives. We accordingly have undertaken an investigation of the steric course of these electrophilic additions to obtain some information about the influence of such factors as the nature and position of ring substituents and the solvent and the brominating agent employed. Two conformationally biased, 4- and 3-*tert*-butylcyclohexene (**1a** and **1b**), and three mobile systems, 4-methylcyclohexene (**1c**), methyl cyclohex-3-enecarboxylate (**1d**), and 3-methylcyclohexene (**1e**), have been studied.

## Results

The ratios between the dibromides **2** and **3** obtained from **1a** and **1b** in various conditions are reported in Table I; the results of the brominations of **1c–e** are




**a**, $R_1$ = H; $R_2$ = *t*-Bu
**b**, $R_1$ = *t*-Bu; $R_2$ = H
**c**, $R_1$ = H; $R_2$ = Me
**d**, $R_1$ = H; $R_2$ = $CO_2Me$
**e**, $R_1$ = Me; $R_2$ = H

summarized in Table II. The halogenations with free bromine were carried out by adding solutions of $Br_2$ in $CHCl_3$ to solutions of the olefins in the various solvents at the temperatures reported; when auxiliary amines were used, they were added in equimolar amounts to the olefin solutions. To avoid the formation of mixed adducts arising from a nucleophilic attack by the solvent on the ionic intermediates, only nonpolar aprotic solvents were generally employed. The brominations with pyridine perbromide ($C_5H_5NBr_2$) and pyridinium hydrobromide perbromide ($C_5H_5NHBr_3$) were carried out by adding the solid brominating agents to solutions of the substrates; when such brominating agents were insoluble in the solvent used, the mixtures were stirred until the solid disappeared. Analyses of the products were performed both by nmr[14] and glpc; the two techniques gave identical results. Only the dibromides arising from **1b**, owing to easy thermal isom-

(1) R. C. Fahey in "Topics in Stereochemistry," Vol. 3, E. L. Eliel and N. L. Allinger, Ed., Interscience, New York, N. Y., 1968, p 286.
(2) I. Roberts and G. E. Kimball, *J. Amer. Chem. Soc.*, **59**, 947 (1937).
(3) J. H. Rolston and K. Yates, *ibid.*, **91**, 1469, 1477 (1969).
(4) J. E. Dubois and E. Goetz, *J. Chem. Phys.*, **63**, 780 (1966).
(5) J. E. Dubois and F. Garnier, *Tetrahedron Lett.*, 3961 (1965), 3047 (1966).
(6) K. Yates and R. S. McDonald, *J. Amer. Chem. Soc.*, **93**, 6297 (1971).
(7) D. H. R. Barton and E. Miller, *ibid.*, **72**, 1066 (1950).
(8) D. H. R. Barton and W. J. Rosenfelder, *J. Chem. Soc.*, 1048 (1951).
(9) G. H. Alt and D. H. R. Barton, *ibid.*, 4284 (1954).
(10) E. L. Eliel and R. G. Haber, *J. Org. Chem.*, **24**, 143 (1959).
(11) G. Bellucci, C. Giordano, A. Marsili, and G. Berti, *Tetrahedron*, **25**, 4515 (1969).
(12) G. Bellucci, G. Berti, F. Marioni, and A. Marsili, *ibid.*, **26**, 4627 (1970).
(13) G. Bellucci, F. Marioni, A. Marsili, and R. Cinelli, *Chim. Ind. (Milan)*, **52**, 89 (1970).
(14) P. L. Barili, G. Bellucci, G. Berti, F. Marioni, A. Marsili, and I. Morelli, *J. Chem. Soc., Perkin Trans. 2*, 58 (1972).

TABLE I

| Compd | Solvent | Temp, °C | Brominating agent | Added base | Ratio of 2:3 |
|---|---|---|---|---|---|
| 1a | $CHCl_3$ | 0 | $Br_2$ | | 94:6 |
| | $CHCl_3$ | −70 | $Br_2$ | | 95.5:4.5 |
| | $CHCl_3$ | 0 | $Br_2$ | $Et_3N$ | 96:4 |
| | $CHCl_3$ | −70 | $Br_2$ | $Et_3N$ | 98:2 |
| | $CHCl_3$ | 0 | $C_5H_5NHBr_3$ | | >98:<2 |
| 1b | $CHCl_3$ | 0 | $Br_2$ | | 43:57 |
| | $CHCl_3$ | −70 | $Br_2$ | | 42:58 |
| | $CHCl_3$ | 0 | $Br_2$[a] | | 44:56 |
| | $CHCl_3$ | 0 | $Br_2HBr$[b] | | 45:55 |
| | $C_6H_6$ | 7 | $Br_2$ | | 50:50 |
| | $Et_2O$ | 0 | $Br_2$ | | 68:32 |
| | $CCl_4$ | 0 | $Br_2$ | | 50:50 |
| | $CHCl_3$ | 0 | $Br_2$ | $Et_3N$ | 63:37 |
| | $CHCl_3$ | 0 | $Br_2$ | Quinuclidine | 61:39 |
| | $C_6H_6$ | 7 | $Br_2$ | $Et_3N$ | 59:41 |
| | $CHCl_3$ | 0 | $Br_2$ | $C_5H_5N$ | 71:29 |
| | $CHCl_3$ | 0 | $Br_2$ | $C_5H_5N$[c] | 72:28 |
| | $CHCl_3$ | 0 | $Br_2$ | 2-$MeC_5H_5N$ | 72:28 |
| | $CHCl_3$ | 0 | $Br_2$ | 4-$MeC_5H_5N$ | 70:30 |
| | $CHCl_3$ | 0 | $C_5H_5NBr_2$ | | 67:33 |
| | $CCl_4$ | 0 | $C_5H_5NBr_2$ | | 71:29 |
| | AcOH | 20 | $C_5H_5NHBr_3$ | | 68:32 |
| | $CHCl_3$ | 0 | $C_5H_5NHBr_3$ | | 73:27 |

[a] Added with bubbling oxygen. [b] 1 *M* solution of $Br_2$ in $CHCl_3$ saturated with HBr gas. [c] Fivefold excess with respect to **1b**.

TABLE II

| Compd | Solvent | Temp, °C | Brominating agent | Added base | Ratio of 2:3 |
|---|---|---|---|---|---|
| 1c | $CHCl_3$ | 0 | $Br_2$ | | 87:13 |
| | $CHCl_3$ | −70 | $Br_2$ | | 93:7 |
| | $CHCl_3$ | 0 | $Br_2HBr$[a] | | 88:12 |
| | $Et_2O$ | 0 | $Br_2$ | | 96:4 |
| | $CHCl_3$ | 0 | $Br_2$ | $C_5H_5N$ | 97:3 |
| | $CHCl_3$ | 0 | $Br_2$ | $Et_3N$ | 96:4 |
| | $CCl_4$ | 0 | $C_5H_5NBr_2$ | | 98:2 |
| | $CHCl_3$ | 0 | $C_5H_5NHBr_3$ | | 98:2 |
| 1d | $CHCl_3$ | 0 | $Br_2$ | | 90:10[b] |
| | $CHCl_3$ | 0 | $Br_2$ | $Et_3N$ | 93:7 |
| | $CHCl_3$ | 0 | $Br_2$ | $C_5H_5N$ | 94:6 |
| | $CHCl_3$ | 0 | $C_5H_5NHBr_3$ | | 94:6 |
| 1e | $CHCl_3$ | 0 | $Br_2$ | | 78:22 |
| | $CHCl_3$ | −70 | $Br_2$ | | 85:15 |
| | $Et_2O$ | 0 | $Br_2$ | | 89:11 |
| | $CHCl_3$ | 0 | $Br_2$ | $Et_3N$ | 88:12 |
| | $CHCl_3$ | 0 | $Br_2$ | $C_5H_5N$ | 89:11 |
| | $CCl_4$ | 0 | $C_5H_5NBr_2$ | | 92:8 |
| | $CHCl_3$ | 0 | $C_5H_5NHBr_3$ | | 88:12 |

[a] 1 *M* solution of $Br_2$ in $CHCl_3$ saturated with HBr gas. [b] About 10% *cis*-3-hydroxy-*trans*-4-bromocyclohexane-1-carboxylic acid lactone is also formed.

erization[14] of **3b** to **2b** at the injection block temperature, could not be analyzed by glpc.

The additions took place entirely in an anti fashion under all of the conditions examined, to give mixtures of the corresponding diastereoisomeric trans dibromides **2** and **3**. As both **2** and **3** are stable under the reaction conditions, it may be excluded that **3** is formed by secondary isomerization of **2** through a "1,2 interchange."[14,15] This is also confirmed by the finding[11-13] that the chiral centers bearing the bromine atoms in the optically active dibromides **2** and **3** obtained by asymmetric bromination of **1a**, **1c**, **1d**, and **1e** have the same configuration; if compounds **3** were formed by isomerization of **2**, opposite configuration would have resulted. In the addition of free bromine to **1d** ~10% *cis*-3-hydroxy-*trans*-4-bromocyclohexane-1-carboxylic acid lactone and 5% another unidentified product were found beside the dibromo derivatives **2d** and **3d**. In the other cases no formation of products different from **2** and **3** (particularly cis dibromides) was observed, although the analytical procedures could have detected a 1% amount of them.

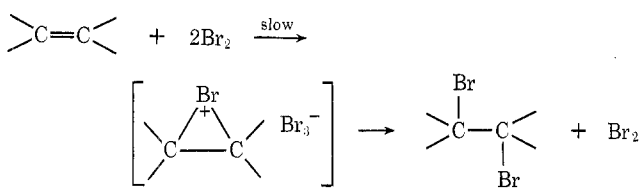
The reaction temperature appears to have no appreciable effect on the ratio between the diastereoisomeric adducts arising from the bromination in $CHCl_3$ of the biased substrates **1a** and **1b**; in contrast, by lowering the temperature the conformationally mobile systems **1c** and **1e** give higher ratios of **2** to **3**. The use of a basic solvent such as ethyl ether instead of $CHCl_3$ strongly decreases the formation of the diequatorial dibromides **3**, whereas benzene and $CCl_4$ have only little effect. The presence of tertiary amines in the reaction medium, or the use of pyridine perbromide or pyridinium hydrobromide perbromide as brominating agents, also leads to a decrease in the amount of the diastereoisomers **3**. In contrast, the presence of hydrogen bromide does not affect the steric course appreciably. The same trend is found in all of the olefins examined, although it is less evident in the case of **1a**, owing to its small tendency to give **3a**. The behavior of **1b**, which gives the highest amount of the diequatorial adduct, has been more thoroughly examined. The fact that the product composition does not change when oxygen is bubbled into the olefin solution during the addition of bromine provides evidence against a free-radical mechanism for the reaction. Pyridine derivatives are more efficient than aliphatic amines in inhibiting the formation of **3b**. However, within analogous sets, neither basic strength nor steric effects around nitrogen seem to be important, as both triethylamine and quinuclidine give substantially similar results, in spite of their different basicities and

(15) D. N. Kirk and M. P. Hartshorn, "Steroid Reaction Mechanisms," Elsevier, Amsterdam, 1968, p 373.

steric hindrances;[16] furthermore no differences are observed in the stereochemical results of the brominations by using different methyl-substituted pyridines as basic catalysts. Even the amount of base does not seem to be important, since, for example, a fivefold excess of pyridine does not appreciably change the results. No acetoxy bromides are formed in the run carried out with pyridinium hydrobromide perbromide in acetic acid, as shown by the absence of acetoxyl protons signals in the nmr spectrum. Finally, it is to emphasize that rather similar ratios of **2** to **3** are obtained from each olefin examined when one uses ethyl ether as the solvent and pyridine perbromide and pyridinium hydrobromide perbromide as the halogenating agent or when pyridine is present in the reaction medium.

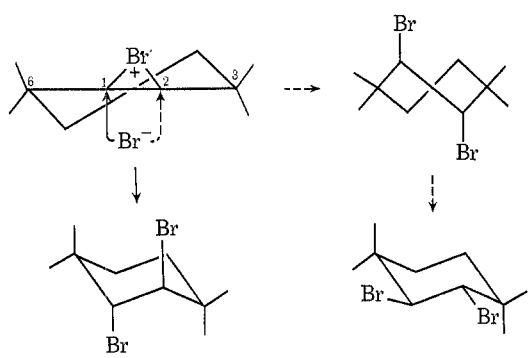
## Discussion

The mechanism of the bromine addition to nonconjugated olefins in nonpolar solvents and in the absence of bromide ions is summarized as follows.[1]



According to Valls and Toromanoff[17] a cyclohexene bromonium ion may undergo two modes of ring opening (Scheme I): (1) nucleophilic attack antiparallel to the

Scheme I



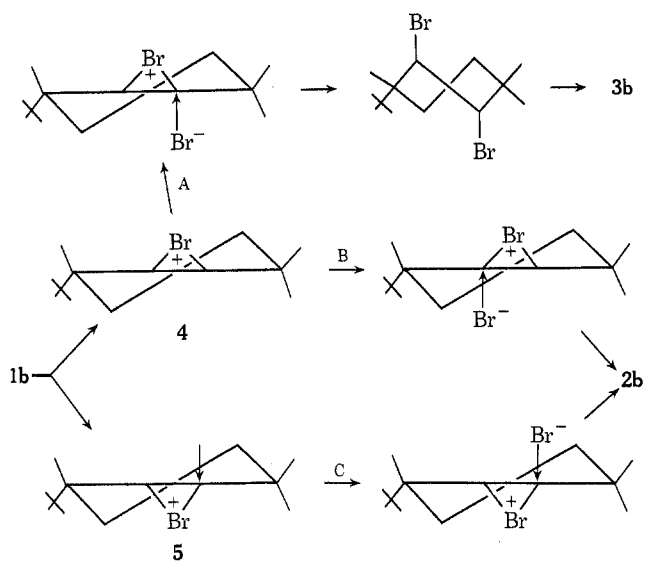
neighboring pseudoaxial bond at C-6, leading to the diaxial adduct through a prechair transition state, as indicated by the full arrow; (2) nucleophilic attack parallel to the pseudoaxial bond at C-3, leading to the diequatorial adduct through a preboat transition state, as indicated by the dotted arrow.

Whereas the configurations of the products arising from conformationally biased substrates should reflect the mode of the addition, little information can be obtained from conformationally mobile systems, because products which could be formed in unstable conformations will pass to the more stable ones, which no longer correspond to the addition mode. Therefore the steric course of the bromination of the biased compounds **1a** and **1b** will be discussed in more detail.

(16) W. L. Mosby in "Heterocyclic Systems with Bridgehead Nitrogen Atoms," A. Weissberger, Ed., Interscience, New York, N. Y., 1961, p 1335.
(17) J. Valls and E. Toromanoff, *Bull. Soc. Chim. Fr.*, 758 (1961).

The formation of 5% diequatorial dibromide **3a** beside diaxial isomer **2a** in the bromination of **1a** in $CHCl_3$ even at $-70°$ is consistent with a high but not exclusive preference for the antiparallel opening of both the *cis*- and the *trans*-bromonium ions arising from this olefin. In contrast, no diequatorial bromo chlorides were found in the addition of bromine chloride to **1a**.[18] On the other hand an excess of the diequatorial adduct **3b** is formed in the addition of free bromine to **1b** in $CHCl_3$ and substantial amounts of this diastereoisomer are obtained under all of the conditions employed. Some insight into the steric course of the bromination of **1b** may be obtained from the comparison with the epoxidation of the olefin followed by ring opening of the two epoxides, which may be considered as models for the bromonium ions. It has been shown[19] that **1b** reacts with peroxy acids to give a 9:1 ratio of trans to cis epoxide; while the latter is opened by hydrogen bromide in an exclusively diaxial way, the former undergoes prevalent nucleophilic attack on C-1 to give a diequatorial bromohydrin.[20] Similar results have been obtained also with hydrogen chloride.[21] The steric effect of the *tert*-butyl group should likewise hinder a cis electrophilic attack by bromine and favor a trans attack leading to the *trans*-bromonium ion **4**, which will be preferentially opened in a parallel mode by nucleophilic attack on C-1 (path A) to give an excess of the diequatorial dibromide **3b**. Antiparallel opening of both the *trans*- (**4**) and the *cis*-bromonium ion (**5**) (paths B and C) will afford the diaxial product **2b** (Scheme II).

Scheme II



A direct steric interaction between the *tert*-butyl group and the nucleophile in the transition state for the antiparallel opening of the *trans*-bromonium ion **4** may again account for the preference for path A over path B. Of course, both of these paths should be of higher energy than path C, involving opening of the *cis*-bromonium ion **5** through antiparallel attack on C-1,

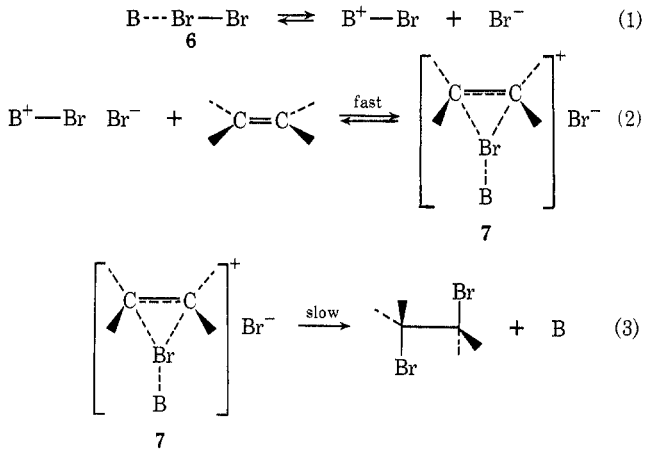
(18) H. J. Hageman and E. Havinga, *Recl. Trav. Chim. Pays-Bas.*, **85**, 1141 (1966).
(19) J.-C. Richer and C. Freppel, *Can. J. Chem.*, **46**, 3709 (1968).
(20) P. L. Barili, G. Bellucci, F. Marioni, A. Marsili, I. Morelli, and G. Ingrosso, *Chim. Ind. (Milan)*, **53**, 789 (1971).
(21) J.-C. Richer and C. Freppel, *Tetrahedron Lett.*, 4411 (1969).

far from the bulky alkyl substituent. However, if the formation of the bromonium ion intermediates is an irreversible step, as it is assumed for the bromination in nonpolar solvents,[1] the steric course of the addition will be controlled first by the relative rates of electrophilic attack on the two faces of the carbon–carbon double bond and then by those of the two alternative modes of nucleophilic opening of the bromonium ions. Whereas this scheme accounts well for the results of the bromination of **1b** in the absence of base, it does not explain the increase in the diaxial:diequatorial ratio when an amine or an ether is present in the system.

The increase in the amount of diaxial adduct **2b** must involve an increase of importance of either path B or path C over path A. It does not seem likely that path B is involved since the steric hindrance in the nucleophilic step should not be reduced appreciably in the presence of base.[22] Also the hypothesis, that the more polarized electrophilic bromine in the amine–bromine complex may be sufficiently smaller than $Br_2$ to displace the ratio of ions **4** to **5** in favor of the latter thus making path C more favorable, does not in our opinion appear sufficient to justify the observed increase in diaxial:diequatorial ratio. A third hypothesis which for the present we consider as the most acceptable is that the electrophilic step may be reversible when the reaction is conducted with a bromine–base complex.

If the bromonium ions were formed in a reversible prerate-determining step, the steric course of the addition could be controlled mainly by the difference in the transition-state free energies of the nucleophilic steps, provided that they are sufficiently slower than the formation of the bromonium ions and their reversal to the alkene. In the case of **1b**, since both paths A and B are less favored than path C, the *trans*-bromonium ion **4** would revert in part to the starting olefin and the reaction prevalently would proceed *via* the cis ion **5**, to give an excess of the diaxial dibromide **2b**.

The crystal-structure determination of many amine–halogen addition compounds by X-ray diffraction has shown[23] that a halogen atom is bonded to nitrogen, the "outer" halogen being situated in a linear nitrogen–halogen–halogen arrangement as in **6**. Studies on amine–halogen complexes in solution have also been evidence of their N-donor-type structures.[24] Also ethers form similar addition compounds with halogens through one of the oxygen lone pairs.[23] The dissociation of eq 1 should simultaneously provide an electrophilic agent more effective than bromine itself and the nucleophile; interaction of the electrophilic moiety with the carbon–carbon double bond could establish the prerate-determining equilibrium shown in eq 2, leading to the ion pair **7**, in which the unipositive bromine may be bonded to both the base and to the olefinic carbon atoms. Slow collapse of **7** as outlined in eq 3 would give trans dibromides and free base. This is consistent with the observation that small added amounts of amines and ethers catalyze the halogenation of aro-




matic compounds.[25] Reversible formation of bromonium ions has recently been suggested[26] for the methoxybromination of 1-methyl-4-*tert*-butylcyclohexene in methanol as the solvent; reversibility of the electrophilic step has also been assumed to explain the steric course of the Woodward reaction on the same olefin[27] and of the hydroxymercuration of substituted cyclohexenes.[22,26] Work that is in progress in this laboratory has also shown similar trends in the steric course of the formation of bromohydrins and chloro bromides from **1b**: the presence of bases increases the percentage of electrophilic attack cis to the *tert*-butyl group.[28] One point that is still not clear is the reason why in the case of **1b** aliphatic amines appear to be less effective than pyridine derivatives in promoting diaxial addition.

The results obtained in the brominations with pyridinium hydrobromide perbromide are also consistent with a fast reversible formation of onium intermediates, if the reagent can dissociate to give some $C_5H_5NBr_2$.

In the case of 4-*tert*-butylcyclohexene (**1a**) the presence of base and the use of pyridinium hydrobromide perbromide affect the steric course in a much more limited way, even if in the same direction. The absence of a direct steric interaction between the substituent and the reaction site accounts for this smaller influence. However a certain shielding of the axial H at C-4, which according to the calculation of Altona and Sundaralingam[29] is tilted by ~15° toward the center of the ring, to the antiparallel attack of the nucleophile on the *cis*-bromonium intermediate **8** can justify the formation of some of the diequatorial adduct through parallel attack. Such shielding has been assumed as the cause for the preference for cis attack in the reaction of **1a** with peroxy acids[30] and diborane.[31] Since the C-5 axial H should exert a smaller shielding to the antiparallel attack on the *trans*-bromonium ion **9**, the reversibility of the first step can account for the in-

(22) D. J. Pasto and J. A. Gontarz [*J. Amer. Chem. Soc.*, **93**, 6909 (1971)] have proposed that the steric course of the oxymercuration of 3-substituted cyclohexenes is affected mainly by a torsional angle effect in the nucleophilic step involving the opening of the mercurinium ion. This is based on the assumption of a rather peculiar and unproved geometry for the mercurinium ion, which we do not think could apply to the bromonium ion.

(23) O. Hassel and C. Rømming, *Quart. Rev., Chem. Soc.*, **16**, 1 (1962).

(24) J. J. Eisch, *Advan. Heterocycl. Chem.*, **7**, 13 (1966).

(25) J. J. Eisch, *ibid.*, **7**, 4 (1966).

(26) D. J. Pasto and J. A. Gontarz, *J. Amer. Chem. Soc.*, **93**, 6902 (1971), footnote 49.

(27) P. L. Barili, G. Bellucci, B. Macchia, F. Macchia, and G. Parmigiani, *Gazz. Chim. Ital.*, **101**, 300 (1971).

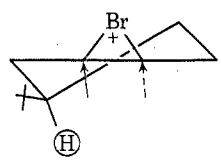
(28) In a paper by J.-C. Richer and C. Freppel, published after this manuscript was submitted [*Tetrahedron Lett.*, 2321 (1972)], about several types of additions involving iodine as the electrophile, the formation of the iodonium ions is considered as reversible, the nucleophilic step being controlled by torsional angle effects of the type advocated by Pasto and Gontarz.[22]

(29) C. Altona and M. Sundaralingam, *Tetrahedron*, **26**, 925 (1970).

(30) B. Rickborn and S. Y. Lwo, *J. Org. Chem.*, **30**, 2212 (1965).

(31) D. J. Pasto and F. M. Klein, *ibid.*, **33**, 1468 (1968).

crease of the **2a** to **3a** ratio when the reaction is carried out in the presence of base. An exclusive formation of **2a** in the bromination of **1a** with $C_5H_5NHBr_3$ in pyridine has been reported by Pasto and Gontarz.[26] In support of our interpretation it can be mentioned that both the methoxybromination and the hydroxymercuration of **1a**, which have been assumed to proceed through reversible formation of onium intermediates,[26] give a slight excess of the products arising from the diaxial opening of the respective *trans*-onium ions, although the electrophilic attack should preferentially occur cis to the *tert*-butyl group.[30,31]

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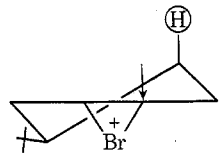


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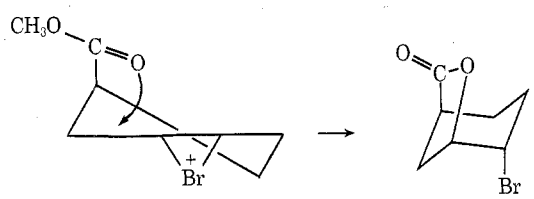
It is more difficult to rationalize the results obtained with the conformationally mobile substrates **1c–e** because of the necessity to take into account also the less stable conformers. While it would be possible to present an explanation which could fit into the same mechanisms proposed for **1a** and **1b**, we shall postpone its discussion until we have more evidence to support it. We want only mention at this point that the formation of bromolactone **11** in the bromination of the unsaturated ester **1d** is practically suppressed in the presence of base. This is also consistent with the mechanism shown in eq 1–3 for the bromination by amine–halogen complexes. Indeed, while the rather high localization of positive charge on the carbon atoms of the bromonium ion **10** may allow an intramolecular attack by




10 11

the poorly nucleophilic methoxycarbonyl group to give **11**, only the more nucleophilic bromide ion should be able to attack an intermediate of the type **7** in eq 2, owing to the greater delocalization of the positive charge and the smaller development of the carbon–bromine bonds.

## Experimental Section

**Starting Materials.**—4-*tert*-Butylcyclohexene (**1a**) was prepared from the commercial mixture of *cis*- and *trans*-4-*tert*-butylcyclohexanols according to the Sicher method.[32] 3-*tert*-Butylcyclohexene (**1b**) was obtained from 2-*tert*-butylcyclohexanone tosylhydrazone with butyllithium.[19] 4-Methylcyclohexene (**1c**) was prepared[33] by dehydration of mixed *cis*- and *trans*-4-methylcyclohexanols with $KHSO_4$. Methyl 3-cyclohexene-1-carboxylate (**1d**) was prepared by Fischer esterification of the commercially (Fluka AG) available acid. 3-Methylcyclohexene (**1e**) was purchased from Fluka AG.

All of the olefins were purified by distillation through a spinning band column and their purities checked by glpc.

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Pyridine perbromide was prepared by mixing carbon tetrachloride solutions of equimolar amounts of bromine and dry pyridine at 0°. The red precipitate, collected, washed, and dried (mp 60–62°, lit.[34] mp 62–63°), was used without further purification.

Pyridinium hydrobromide perbromide was prepared by the Fieser method.[35]

Chloroform was purified by washing with 2 *N* NaOH, concentrated $H_2SO_4$, and $H_2O$ and distillation. Rudi Pont Spectranalyzed reagent grade carbon tetrachloride was used without further purification. Ethyl ether was freed from peroxides by washing with a solution of ferrous sulfate. Benzene was washed with $H_2SO_4$, refluxed on sodium, and distilled.

Bromine was purified[36] by refluxing with calcium bromide and distillation.

Commercial anhydrous triethylamine was purified by distillation. Pyridine and 2-methyl-, 4-methyl-, and 2,6-dimethylpyridine were dried by refluxing with potassium hydroxide and fractionally distilled.

**Bromination Procedures. A. With $Br_2$ in the Absence of Bases.**—A 10% excess of a 1 *M* solution of $Br_2$ in $CHCl_3$ was added dropwise to a stirred solution of 1.5 mmol of the olefin in 5 ml of the appropriate solvent at the temperatures reported in Tables I and II. After the addition was complete, the solution was further stirred for 5 min, then washed with aqueous $NaHSO_3$ and $H_2O$, dried ($MgSO_4$), and evaporated at 30° (rotating evaporator). The residue was directly analyzed.

In the case of **1d**, the ir spectrum of the crude reaction mixture showed in addition to the strong carbonyl band at 5.8 $\mu$ typical of **2d** and **3d**, a weak band at 5.6 $\mu$. Crystallization from pentane allowed to isolate a small amount of the bromolactone **17**, identified by comparison with an authentical sample.[37]

**B. With $Br_2$ in the Presence of Bases.**—A 10% excess of a 1 *M* solution of $Br_2$ in $CHCl_3$ was added to a solution of equimolar amount (1.5 mmol) of the olefin and the appropriate amine in 5 ml of $CHCl_3$. After stirring for 5 min the solution was washed with aqueous $NaHSO_3$, aqueous 2 *N* HCl, and $H_2O$, dried, and evaporated.

**C. With $C_5H_5NBr_2$ or $C_5H_5NHBr_3$.**—A 10% excess of the solid brominating agent was added to a solution of 1.5 mmol of the olefin in 5 ml of the appropriate solvent. The mixture was stirred for 15 min at 0° and then treated as described in B. $C_5H_5NBr_2$ is slightly soluble in $CCl_4$; the same happens for $C_5H_5NHBr_3$ in $CHCl_3$; however, in the presence of the alkenes, these reagents were completely dissolved after few minutes.

The bromination of **1b** with $C_5H_5NHBr_3$ in AcOH was carried out by stirring the reagents at 20° for 30 min, followed by dilution with water, extraction with ether, washing with $H_2O$, aqueous saturated $NaHCO_3$, and $H_2O$, and drying ($MgSO_4$).

In all cases the composition of the mixtures of **2** and **3** did not change after longer reaction times.

**Methods of Analysis.**—The glpc analyses of the reaction mixtures arising from **1a**, **1c**, **1d**, and **1e** were performed with a Carlo Erba Fractovap, Model G.V., column: 1% neopentyl glycol succinate (NPGS) on Chromosorb W, 80–100 mesh. The conditions were previously reported.[11,12,13] Nmr analyses of the same mixtures and of those of **2b** and **3b** were carried out with a JEOL C-60 HL spectrometer, by integration of the signals of the protons $\alpha$ to bromine.[14]

The results listed in Tables I and II were reproducible within ±2%.

**Registry No.**—**1a**, 2228-98-0; **1b**, 14072-87-8; **1c**, 591-47-9; **1d**, 6493-77-2; **1e**, 591-48-0; $CHCl_3$, 67-66-3; $C_6H_6$, 71-43-2; $Et_2O$, 60-29-7; $CCl_4$, 56-23-5; AcOH, 64-19-7; $Br_2$, 7726-95-6; $C_5H_5NHBr_3$, 36812-55-2; $Br_2$+HBr, 36748-62-6; $C_5H_5NBr_2$, 6081-86-3.

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