5.35 (br s, 1 H, 5-H), 5.91 (br q, J = 5 Hz, 1 H, 2-H), 7.00–7.70 (m, 10 H, aromatic protons).

Anal. Calcd for $C_{16}H_{15}O_2N$: C, 75.87; H, 5.97; N, 5.53. Found: C, 76.03; H, 6.00; N, 5.55.

1,3-Diphenyl-3-hydroxy-4-methylazetidin-2-one (3k): mp 175–176.5 °C; IR (KBr) 3300, 1725 cm^{-1}; NMR ($CDCl_3$) δ 1.03 (d, J = 6 Hz, 3 H, CH_3), 4.03 (s, 1 H, OH), 4.36 (q, J = 6 Hz, 1 H, 4-H), 6.95–7.55 (m, 10 H, aromatic protons).

Anal. Calcd for $C_{16}H_{15}O_2N$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.98; H, 6.01; N, 5.51.

1,3,4-Triphenyl-3-hydroxyazetidin-2-one (31): mp 172–174 °C; IR (KBr) 3550, 3300, 1735, 1715 cm^{-1}; NMR ($CDCl_3$) δ 5.19 (s, 1 H, 4-H), 6.90–7.72 (m, 15 H, aromatic protons).

Anal. Calcd for $C_{21}H_{17}O_2N$: C, 79.98; H, 5.43; N, 4.44. Found: C, 79.83; H, 5.24; N, 4.42.

Quantum Yield Determinations. Benzophenone–benzhydrol actinometry was used for quantum yield determination. The 313-nm line was isolated with a filter solution containing 0.002 M potassium chromate in 5% aqueous potassium carbonate. Samples (0.10 M solution) in Pyrex tubes were degassed to ca. 10^{-3} mm in three freeze–thaw cycles and sealed. The samples were irradiated individually in succession. Photolyses were carried out to 30–50% conversion. The degree of reaction was determined by NMR spectroscopy. Concentrations of the sensitizer were adjusted so that 5% or less of the incident light was absorbed by the oxoamides (**1b** and **1j**).

Acknowledgment. We thank Dr. Choji Kashima for his useful suggestions. Partial financial support by a Matsunaga Research Grant is gratefully acknowledged.

Registry No.—**2b,** 64201-17-8; **2b-d_1,** 64201-16-7; **2c,** 64201-15-6; **2d,** 64201-14-5; **2e,** 64201-13-4; **2f,** 64201-12-3; **2g,** 64201-11-2; **2h,** 64201-10-1; **2i,** 64201-09-8; **2k,** 64201-08-7; **3e,** 64201-07-6; **3f,** 64201-06-5; **3g,** 64201-05-4; **3h,** 64201-04-3; **3c,** 64201-03-2; **3j,** 64201-01-0; **3k,** 64200-99-3; **3l,** 64201-21-4.

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Regio- and Stereoselectivity of the Formation of Halohydrins from 3-Methyl- and 3-*tert*-Butylcyclohexene and from the Corresponding Epoxides

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In order to explain large variations in product regio- and stereochemistry observed in several types of ionic additions to cycloalkenes involving different reagents, the product compositions obtained in some reactions leading from 3-methyl- and 3-*tert*-butylcyclohexene to chlorohydrins, bromohydrins, and bromoacetoxy derivatives have been investigated in detail. Whereas with *N*-chlorosuccinimide, preformed HOBr, or CH_3COOBr electrophilic attack was nonstereoselective for the methyl and anti stereoselective for the *tert*-butyl derivative, with NBS a high syn stereoselectivity was observed for the attack by electrophilic bromine, which indicated that repulsive steric effects operating during the nucleophilic step should be the main product-determining factor in the latter case, and that this step should be the rate-limiting one. Support of this hypothesis was brought by the reactions of the corresponding epoxides with HBr and HCl, since the observed regioselectivities of these reactions, which can be taken as models for the nucleophilic opening of the halonium intermediates of the electrophilic additions to olefins, are in agreement with those deduced from the product compositions of the latter reactions.

As a part of a research program concerning the influence of steric, polar, and conformational effects on electrophilic additions involving different types of reagents and different mechanisms,[1-4] we undertook a comparative product and kinetic study of additions to 3-alkylcyclohexenes involving epihalonium ion intermediates and of the ring-opening reactions of diastereoisomeric couples of 3-alkyl-1,2-epoxycyclohexanes, which can be taken as models for the nucleophilic steps of the additions. A methyl and a *tert*-butyl group were chosen as alkyl substituents having, respectively, a relatively small and very large size. In this paper, we report the results of the product study.[5]

Results

3-*tert*-Butylcyclohexene Derivatives. As reported by Richer,[6] the epoxidation of 3-*tert*-butylcyclohexene (**1a**) with peroxyacids yielded a 90:10 mixture of the trans and cis epoxides **2a** and **3a.** Opening of this mixture with hydrogen bromide afforded three isomeric bromohydrins, which were separated by column chromatography. The most abundant compound was identified as the diequatorial bromohydrin **5c** on the basis of its NMR spectrum[7] and of its conversion back to **2a** by treatment with base. The other two isomers were trans diaxial bromohydrins, as shown by the narrow signals, due to equatorial protons α to bromine and hydroxyl, appearing in the medium-field part of their NMR spectra; they were identified as **4c** and **6c** by conversion, respectively, into the epoxides **2a** and **3a.**

This method was convenient for the preparation of the pure trans epoxide **2a,** since the separation of bromohydrin **5c** from

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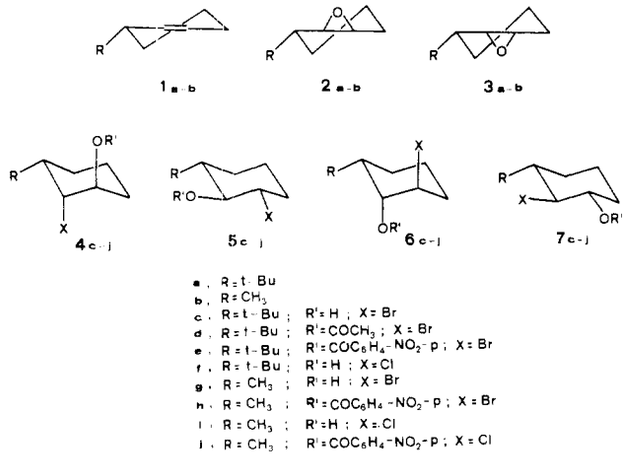
Table I. Product Distributions for Additions to 3-*tert*-Butylcyclohexene[a]

Reagent	Solvent	Products Type	Distribution, % 4	5	6	7
NBS	Me_2SO–H_2O (95:5)	**c**	78	4	3	15
NBS	H_2O	**c**	54	4	19	23[b]
NBA	Dioxane–H_2O (7:3)	**c**	81	3	4	12
NBA	Dioxane–0.2 N aq $HClO_4$ (7:3)	**c**	76	4	5	15
HOBr (aq)	Dioxane	**c**				[c]
AcOBr	CCl_4	**d**	13	2	9	76
NCS	H_2O	**f**	14	3	25	58[d]

[a] For experimental conditions, see Experimental Section. [b] About 30% of trans dibromides were also formed. Complete thermal isomerization of the diequatorial into the diaxial dibromo adduct under the GLC conditions prevented the determination of their ratio (see ref 25). [c] An accurate determination was prevented by overlap of the peak of **5** with an unidentified by-product in the chromatogram. However, **7** was evaluated to amount to more than 50% of the total products. [d] Diaxial and diequatorial dichlorides (about 35%) in a 4:6 ratio were also formed.



its isomers was easy, but not for that of the diastereoisomer **3a,** because of the small amount of **6c** that could be isolated. In the search for a stereoselective route to **3a,** the addition of the elements of hypobromous acid to **1a** followed by cyclization of the resulting bromohydrins were investigated. This method has been frequently used to obtain the diastereoisomeric epoxide formed in lower yield by direct epoxidation.[8] In contrast with the expectation, bromohydrin **4c,** having the hydroxyl trans to the *tert*-butyl group, was however isolated as the main product of the reactions of **1a** by the usual methods,[9-11] both with *N*-bromosuccinimide (NBS) in Me_2SO–water and with *N*-bromoacetamide (NBA) in dioxane–water, and this preference for attack by electrophilic bromine syn to the *tert*-butyl group was confirmed by the fact that base-promoted cyclization of the crude bromohydrin mixtures gave an excess of epoxide **2a.**

However, when the addition to **1a** was carried out with an aqueous solution of preformed hypobromous acid, the main product was **7c** (identified by NMR[7]). Its isolation by column chromatography gave a low yield owing to decomposition and isomerization to **6c,** but cyclization of the crude addition mixture with potassium hydroxide gave the two epoxides **2a** and **3a** in a 20:80 ratio.

A 15:85 mixture of **2a** and **3a** was finally obtained by addition of preformed acetyl hypobromite to **1a** in carbon tetrachloride followed by refluxing of the resulting crude acetoxy bromo adducts **4d–7d** with potassium carbonate in aqueous methanol. Opening of the latter mixture of epoxides with hydrogen bromide and column chromatography afforded a fairly good yield of bromohydrin **6c,** the cyclization of which gave pure **3a.** Alternatively, **3a** was conveniently obtained by potassium carbonate treatment of the major product **7d,** formed in the acetoxybromination of **1a** and separated from the accompanying isomers **4d, 5d,** and **6d** by column chromatography.

Table II. Regioselectivity of Opening Reactions of 2a and 3a with Hydrogen Halides in CCl_4

Epoxide	Hydrogen halide	Products Type	4:5 ratio	6:7 ratio
2a	HBr	**c**	29:71	
2a	HCl	**f**	38:62	
3a	HBr	**c**		93:7
3a	HCl	**f**		93:7

Because of the very marked dependence of the steric course of the additions to **1a** on the reagent used as the source of positive bromine, complete stereo- and regioselectivity data were sought by direct GLC analysis of the addition products. The reaction of **1a** with *N*-chlorosuccinimide (NCS) in water was also investigated. This reaction proceeded conveniently at 90–100 °C.[12] The reference trans chlorohydrins **4f–7f** had already been described.[13] The product distributions found for the various addition reactions, as reported in Table I, confirm the largely different steric courses between the *N*-bromoamide-promoted reactions on one hand and the additions of HOBr or AcOBr on the other (Table I).

In contrast, no such difference was apparent in the steric course of the chlorohydrin formation by the NCS reaction, which was very similar to that reported for the addition of chlorine in the presence of aqueous sodium carbonate.[13]

For comparison purposes, the reaction of epoxides **2a** and **3a** with hydrogen bromide and chloride was also examined. The percentages of the two isomeric trans halohydrins formed from each epoxide are reported in Table II.

3-Methylcyclohexene Derivatives. The peroxyacid oxidation of 3-methylcyclohexene (**1b**) afforded about equal amounts of the diastereoisomeric epoxides **2b** and **3b,**[14] which could not be separated by the usual techniques. Opening of the mixture with hydrogen chloride and esterification of the formed trans chlorohydrins with *p*-nitrobenzoyl chloride gave, after several crystallizations, a *p*-nitrobenozyl derivative previously isolated by Rickborn.[14] Structure and relative configuration shown in **6j** resulted from the NMR spectrum of this compound (Table III), the multiplicity and coupling constants of the δ 5.16 signal, due to the proton α to the ester group, clearly establishing a vicinal cis relationship between *p*-nitrobenzoyloxy and methyl substituents. This confirmed the cis configuration **3b** assigned on the basis of hydride reduction[14] to the epoxide obtained by potassium carbonate treatment of **6j.**

The trans-epoxide **2b,** which had never been obtained pure, was prepared by a similar cyclization of the bromohydrin

Table III. NMR Data of *p*-Nitrobenzoates of Halohydrins[a]

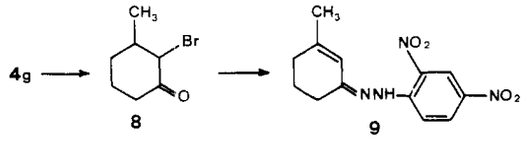
Compd	Registry no.	$-CH_3$ δ	$-CH_3$ J, Hz	>CHX δ	>CHX W	>CHX J, Hz	>CH–O– δ	>CH–O– W	>CH–O– J, Hz	$-C_6H_4NO_2$-p, δ
4h	64162-82-9	1.06 (d)	6.4	4.40 (t)		3.7	5.45 (m)	12		8.27 (s)
5h	64162-83-0	0.99 (d)	6.0	4.15 (m)	25		5.09 (t)		9.3	8.35 (s)
6h	64199-95-7	0.98 (d)	7.0	4.46 (m)	15		5.29 (d of d)		3.4, 5.2	8.30 (s)
7h	64199-96-8	1.23 (d)	6.0	3.80 (t)		10.3	5.22 (m)	25		8.27 (s)
4j	64162-84-1	1.09 (d)	6.7	4.25 (t)		3.9	5.37 (m)	12		8.30 (s)
5j	64162-85-2	1.00 (d)	6.0	4.02 (m)	25		5.05 (t)		9.8	8.35 (s)
6j	64199-97-9	0.99 (d)	6.7	4.31 (m)	14		5.16 (d of d)		3.4, 5.2	8.25 (s)
7j	64199-98-0	1.20 (d)	6.0	3.71 (t)		10.0	~5.1 (m)	*b*		8.25 (s)

[a] In $CDCl_3$. [b] Not measured owing to overlap with the signal at δ 5.16 of the contaminating isomer **6j**.

Table IV. Regioselectivity of Opening Reactions of 2b and 3b with Hydrogen Halides in $CHCl_3$

Epoxide	Hydrogen halide	Products Type	Products 4:5 ratio	Products 6:7 ratio
2b	HBr	**g**	64:36	
2b	HCl	**i**	62:38	
3b	HBr	**g**		90:10
3b	HCl	**i**		93:7

p-nitrobenzoate **4h,** easily obtained from the reaction of **1b** with NBS in Me_2SO–H_2O followed by esterification with *p*-nitrobenzoyl chloride and fractional crystallization. This established a trans relationship between hydroxyl and methyl groups in the parent bromohydrin formed as the main product of the NBS reaction. This product, isolated by column chromatography, was shown to have bromine vicinal to the methyl group (**4g**) by oxidation to bromo ketone **8** and subsequent dehydrobromination with 2,4-dinitrophenylhydrazine[15] to the known derivative **9**.[16]



The reaction of the trans-epoxide **2b** with hydrogen bromide yielded, besides **4g,** the alternative product of trans ring opening, **5g,** which was separated by column chromatography. Isomer **6g** was obtained from the similar opening of the cis-epoxide **3b.** The fourth bromohydrin (**7g**), formed in too small amount both in the NBS reaction of **1b** and in the hydrogen bromide opening of **3b,** was instead isolated as its *p*-nitrobenzoate from the reaction of preformed hypobromous acid with **1b** by a combination of column and thin-layer chromatography.

In a similar way, chlorohydrins **4i** and **5i** were isolated from the opening reactions of **2b** with hydrogen chloride, while **6i** was obtained from the cis-epoxide **3b.** The fourth isomer **7i** was not isolated in a pure state, but a mixture of **6i** and **7i** enriched in the latter isomer was separated by chromatography from the products of the reaction of **1b** with NCS in water.

Structures, relative configurations, and conformations of all bromohydrins **4g–7g** and chlorohydrins **4i–6i** were demonstrated or confirmed by the NMR spectra of their *p*-nitrobenzoates (Table III), on the basis of the multiplicity and coupling constants of the signals for the protons α to acyloxy and halogen.

Compounds **5** and **7** exhibited the expected triequatorial conformations, as shown by the high value[17] of the coupling constants of the protons α to the halogen and ester group between themselves and with the proton α to methyl. The low *J* values in the spectra of compounds **4** were consistent[17] with a high preference for conformations with equatorial methyl and axial halogen and ester group. In products **6,** instead, one of the coupling constants of the proton α to the *p*-nitrobenzoyloxy group was slightly higher than expected for an equatorial proton, probably because of some contribution to the conformational equilibrium by the alternative chair form with equatorial halogen and ester group and axial methyl.

Table V. Product Distributions for Additions to 3-Methylcyclohexene[a]

Reagent	Solvent	Products Type	Distribution, % 4	5	6	7
NBS	Me_2SO–H_2O (95:5)	**g**	77	5	11	7
NBS	H_2O	**g**	76	4	15	5
HOBr (aq)	Dioxane	**g**	47	3	33	17
NCS	H_2O	**i**	47	9	26	18

[a] For experimental conditions, see Experimental Section. Only traces of trans dihalides were formed in all these reactions.

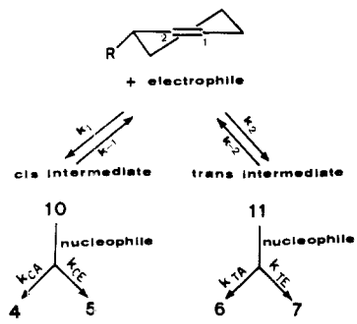
The percentages of the two isomeric halohydrins obtained by GLC analysis of the products of ring opening of **2b** and **3b** with hydrogen bromide and chloride are quoted in Table IV.

Finally, Table V shows the product distributions found in several addition reactions to **1b.** As in the additions to 3-*tert*-butylcyclohexene (**1a**), the formation of products of type **4** decreased, although less markedly, in favor of those of type **6** and **7** on passing from NBS to preformed HOBr and to NCS as the electrophilic reagents. These results excluded the possibility that HOBr, which could have been formed by hydrolysis of NBS or NBA, was the actual reactant in all *N*-bromoamide reactions of **1a** and **1b,** and rather pointed to a direct transfer of bromine from nitrogen to the double bond. In contrast, the similarity in the steric courses observed in the NCS–water and in the hypohalous acid reactions of both **1a** and **1b** suggested hydrolysis of NCS to HOCl before the electrophilic attack.

Discussion

Representative stereo- and regioselectivity data for additions to alkenes **1a** and **1b,** extracted from Tables I and V, are compared in Table VI.[18] The regioselectivity of the attack by the different nucleophiles (water, Me_2SO,[19] acetate) anti to the alkyl substituent, which is given by the **4:5** ratio, is always high and very similar for both alkenes under all examined conditions. Also, the regioselectivity of the syn attack, given by the **6:7** ratio, exhibits a fairly constant trend for each olefin, but is markedly affected by the size of the allylic substituent. Moreover, the observed trends are comparable to those found in the ring-opening reactions of epoxides **2** and **3** with hydrogen halides (Tables II and IV).[20] This analogy, which had been observed also with other cyclohexene derivatives bearing electron-withdrawing substituents,[1,4,21,22] strongly suggests

Scheme I



for all examined reactions two-step addition mechanisms in which bridged intermediates are formed in the electrophilic stage, the main factors affecting the regioselectivity of the subsequent nucleophilic attacks being similar to those operating in the ring opening of the corresponding epoxides.

Nucleophilic attack on the cis-intermediates **10** (Scheme I), as well as on cis-epoxides **3**, occurs preferentially at C(1) to give mainly the expected diaxial products (**4** from **10** or **6** from **3**). On the other hand, the formation of diaxial products **6** from the trans-intermediates **11**, or of **4** from the trans-epoxides **2**, involves a nucleophilic attack at C(2) which is subjected to a steric hindrance by the 3-alkyl substituent. When R is methyl, this attack is still slightly predominant (59–66%), but the alternative attack at C(1) to give diequatorial adducts (**7** from **11** or **5** from **2**) becomes favored, in spite of its unfavorable conformational requirements,[23] when R is a bulky *tert*-butyl group.

If one excludes the NBS reactions, the stereoselectivity data of Table VI, giving the relative contributions of intermediates **10** and **11** to the reaction pathways, show that in all additions to **1a** the trans-intermediate **11** is highly predominant, in accordance with a strong steric effect of the *tert*-butyl group during the electrophilic step, as observed also in the epoxidation of **1a** (90% anti attack), whereas no stereoselectivity in the formation of the two intermediates **10** and **11** is observed in the analogous reactions of **1b**, consistent with the lack of any steric effect by the allylic methyl group in the epoxidation of **1b**. All these data can be rationalized on the basis of the mechanism represented in Scheme I, if the formation of intermediates **10** and **11** is practically irreversible and their subsequent reactions to give products are a fast step (k_{CA}, k_{CE}, k_{TA}, $k_{TE} \gg k_1$, k_2, k_{-1}, k_{-2}; $k_2 > k_1$ for **1a** and $k_2 \simeq k_1$ for **1b**).

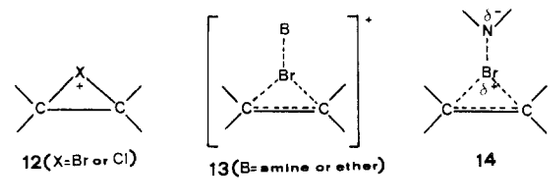
On the other hand, the stereoselectivities observed in the *N*-bromoamide reactions cannot be accounted for on the basis of the same mechanism, since it would imply that $k_1 > k_2$ for both **1a** and **1b**, in contrast with the anticipated retarding effect of the *tert*-butyl and with the expected absence of an accelerating effect by the methyl group on the rates of syn electrophilic attack. The product distributions observed in the latter reactions would be instead consistent with k_{CA}, k_{CE}, k_{TA}, $k_{TE} < k_1$, k_2, k_{-1}, k_{-2}; $k_{CA} + k_{CE} > k_{TA} + k_{TE}$; $k_{CA} \gg k_{CE}$; $k_{TA} > k_{TE}$ for **1b** and $k_{TE} > k_{TA}$ for **1a**. This implies that the electrophilic step be reversible and the cis intermediate **10** be more reactive than the trans intermediate **11**. The latter assumption is supported by the reactivity order found[24] for the hydrogen chloride opening reactions of epoxides **2** and **3**, the protonated forms of which, as previously mentioned, can be considered as fairly reliable models for the bridged intermediates **11** and **10**, respectively.

As far as the nature of the intermediates is concerned, there seems to be no reason for assuming structures different from epihalonium ions **12** (possibly as ion pairs with the appropriate anions) for all examined reactions which appear to proceed through a slow, irreversible electrophilic attack. However, the change in mechanism observed in the *N*-bromoamides reactions can be better explained assuming different bridged species as the intermediates formed in a reversible electrophilic step.

Table VI. Stereo- and Regioselectivities of Additions to 1a and 1b

Reagent	Olefin	Stereoselectivity 10:11	Regioselectivity 4:5	Regioselectivity 6:7
NBS (Me_2SO–H_2O)	**1a**	82:18	95:5	17:83
	1b	82:18	94:6	61:39
HOBr (aq)	**1a**	20:80	$4 \gg 5$	$6 \ll 7$
(dioxane)	**1b**	50:50	94:6	66:34
AcOBr (CCl_4)	**1a**	15:85	87:13	11:89
NCS (H_2O)	**1a**	17:83	82:18	30:70
	1b	56:44	84:16	59:41

Some time ago we proposed[25] that the bromination of compounds **1** with amine–bromine or ether–bromine complexes could occur through a pre-rate-determining equilibrium leading to species of type **13**, in which bromine is bonded both to the base and to the olefinic carbon atoms. A similar intermediate has been later invoked[26] for the bromochlorination of cyclopentadiene with amine–bromine–chloride



complexes. By analogy, we believe that the intermediates of the *N*-bromoamide reactions on olefins may be represented by species **14**, which, being formed rapidly and being conceivably less reactive than bromonium ions, may be subjected to slow rate- and product-determining nucleophilic attack. Similar conclusions have been independently inferred[27] from a study of the relative nucleophilicities of Me_2SO and methanol toward the intermediates formed in the reaction of olefins with bromine and *N*-bromoamides.

In conclusion, all available data indicate the possibility of two different stepwise mechanisms of anti addition to cyclohexene derivatives. In the first, more widely occurring one, the stereoselectivity is controlled during a slow electrophilic step and the regioselectivity during the subsequent nucleophilic steps. In the absence of specific interactions between substituents on the substrate and the electrophile,[4] this mechanism leads to product distributions which can be roughly foreseen on the basis of the stereoselectivity of the peroxyacid oxidation of the substrate and of the regioselectivity of the ring-opening reactions of the resulting diastereoisomeric epoxides. In the second mechanism, both the stereo- and the regioselectivity are instead controlled by steric, electronic, and conformational factors operating during a rate- and product-determining nucleophilic step, and the product distribution can be roughly anticipated on the basis of the relative reactivities of the diastereoisomeric epoxides arising from the substrate.[24] The latter mechanism, which has been proposed also for reactions of dihydropyran derivatives,[28] appears to be peculiar to the reactions of *N*-bromoamides (but not for *N*-chloroamides), iodine compounds,[29-32] amine–halogen and ether–halogen complexes, and to some oxymercuriation reactions.[33]

Experimental Section

Melting points were determined on a Kofler block and are uncorrected. NMR spectra were taken from CCl_4 solutions (except when differently stated) with a Jeol C-60 HL spectrometer using Me_4Si as

internal standard. GLC analyses were performed with a C. Erba Fractovap Model GV and a Perkin-Elmer Model F11 instrument. Neutral silica gel (Schuchardt, 150–300 μ) was always used for column chromatographies. Usual workup of reaction products involved extraction with a solvent (if necessary), washing with H_2O (10% Na_2CO_3 if acidic), drying with $MgSO_4$, and evaporation in vacuo (rotating evaporator). Petroleum ether refers to the fraction of boiling range 40–60 °C.

***t*-2-Bromo-*t*-3-*tert*-butyl-*r*-1-cyclohexanol (4c), *t*-2-Bromo-*t*-6-*tert*-butyl-*r*-1-cyclohexanol (5c), and *t*-2-Bromo-*c*-6-*tert*-butyl-*r*-1-cyclohexanol (6c). A.** A solution of **1a** (12 g, 0.086 mol) in $CHCl_3$ (120 mL) was treated dropwise under stirring at 0 °C with a 0.35 M $CHCl_3$ solution of peroxybenzoic acid (370 mL, 0.13 mol). After standing overnight at 4 °C, the solution was worked up as usual to give a liquid residue (8.8 g) consisting of epoxides **2a** and **3a** in a 90:10 ratio (GLC: 2-m glass column, 2.5-mm i.d., packed with 1% neopentyl glycol succinate on silanized Chromosorb W, 80–100 mesh; column 90 °C, evaporator and detector 200 °C, nitrogen flow 40 mL/min; relative rentention times 1.20:1).

A solution of this mixture in $CHCl_3$ (60 mL) was saturated with dry HBr and worked up after 30 min to give a residue (12.0 g) consisting of bromohydrins **4c, 5c,** and **6c.** A part of this mixture (9.5 g) was chromatographed over a 2.2 × 50 cm column of silica gel (76 g). Petroleum ether eluted pure **5c** (5.0 g) as an oil.[7]

Anal. Calcd for $C_{10}H_{19}BrO$: C, 51.06; H, 8.14; Br, 33.98. Found: C, 50.98; H, 8.30; Br, 33.45.

Treatment of **5c** (0.30 g, 1.28 mmol) with phenyl isocyanate (0.165 g, 1.38 mmol) on a water bath for 30 min gave the phenylurethane, mp 127–128 °C (from petroleum ether).[7]

Anal. Calcd for $C_{17}H_{24}BrNO_2$: C, 57.62; H, 6.78; Br, 22.59. Found: C, 57.78; H, 6.80; Br, 22.26.

Elution with 98:2 petroleum ether–ethyl ether gave pure **6c** (0.5 g): mp 74–76 °C (from petroleum ether); NMR δ 0.98 [s, $-C(CH_3)_3$, 9 H], 2.16 (s, –OH, 1 H), 4.22 (two overlapping m, >CHOH and >CHBr, $W_{1/2}$ = 5.5 Hz, 2 H).

Anal. Calcd for $C_{10}H_{19}BrO$: C, 51.06; H, 8.14; Br, 33.98. Found: C, 51.30; H, 7.98; Br, 34.26.

Further elution yielded pure **4c** (1.5 g): mp 70 °C (from petroleum ether); NMR δ 1.00 [s, $-C(CH_3)_3$, 9 H], 3.57 (s, –OH, 1 H), 4.11 (m, $W_{1/2}$ = 7.5 Hz, >CHOH or >CHBr, 1 H), 4.29 (m, $W_{1/2}$ = 7 Hz, >CHBr or >CHOH, 1 H).

Anal. Calcd for $C_{10}H_{19}BrO$: C, 51.06; H, 8.14; Br, 33.98. Found: C, 51.05; H, 7.95; Br, 34.50.

B. *N*-bromoacetamide (3.3 g, 0.024 mol) was added to a solution of **1a** (3.0 g, 0.022 mol) in 7:3 dioxane–water (200 mL). After stirring for 1 h at room temperature, the reaction mixture was diluted with water and extracted with ether to yield 4.1 g of mixed bromohydrins **4c–7c.**

A sample of this mixture (0.2 g) was treated with 1 M ethanolic KOH (5 mL). After 30 min, dilution with water and extraction with ether gave epoxides **2a** and **3a** in a 84:16 ratio (GLC).

The remaining mixture was chromatographed on a 1.8 × 57 cm column of silica gel (110 g). Petroleum ether–ethyl ether (98:2 and 95:5) eluted in succession: **5c** (0.13 g), **6c** (0.15 g), mixtures of **4c, 6c,** and **7c** (0.18 g), and **4c** (2.2 g).

C. A solution of **1a** (3.0 g, 0.022 mol) in 95:5 Me_2SO–water (50 mL) was stirred with NBS (4.3 g, 0.024 mol) at room temperature for 1 h. Treatment as described under **B** gave a mixture of **4c–7c** (4.2 g).

The cyclization of a sample of this mixture with ethanolic KOH yielded epoxides **2a** and **3a** in a ratio of 82:18 (GLC).

D. A 0.1 M CCl_4 solution of acetyl hypobromite[34] (540 mL) was added dropwise at 0 °C to a solution of **1a** (6.9 g, 0.05 mol) in the same solvent (20 mL). After the addition was complete, the solution was stirred at 0 °C for 1 h and then washed with saturated aqueous $NaHSO_3$ and worked up. The residue (12.0 g) was dissolved in MeOH (400 mL), a solution of 13.5 g of K_2CO_3 in 40 mL of water was added, and the mixture was refluxed for 2 h with occasional shaking, then diluted with water, and extracted with ether. Distillation of the residue yielded a mixture of epoxides **2a** and **3a** (6.0 g), bp 85–90 °C (20 mm), in a 15:85 ratio (GLC).

Treatment of these epoxides (3.0 g) with dry HBr as reported under **A** gave a mixture of bromohydrins **4c–7c** (4.5 g), which was chromatographed on a 2.2 × 50 cm column of silica gel. Petroleum ether eluted **5c** (0.5 g), 99:1 petroleum ether–ethyl ether eluted **6c** (3.0 g), and 1:1 petroleum ether–ethyl ether yielded **4c** (0.2 g).

***t*-2-Bromo-*c*-3-*tert*-butyl-*r*-1-cyclohexanol (7c).** A 0.7 M aqueous solution of HOBr[35] (57 mL) was added dropwise to a stirred solution of **1a** (5.0 g, 0.036 mol) in dioxane (100 mL) at room temperature. After 30 min the reaction mixture was diluted with water and extracted with ether to afford 6.2 g of a residue, GLC of which revealed the prevailing presence of bromohydrin **7c,** besides isomers **4c, 5c, 6c,** trans dibromides, and other components.

Cyclization of a sample of this mixture (0.2 g) with 1 N ethanolic KOH gave **2a** and **3a** in a 20:80 ratio.

The remaining mixture was chromatographed on a 2.2 × 81 cm column of silica gel (120 g). Elution with petroleum ether gave small amounts of unreacted **1a,** *r*-1,*t*-2-dibromo-*t*-3-*tert*-butylcyclohexane,[36] and **5c** (0.4 g). Elution with 99:1 petroleum ether–ethyl ether yielded fractions containing **7c** and other components (0.7 g), and then pure **7c** (0.5 g) as an oil.[7]

Anal. Calcd for $C_{10}H_{19}BrO$: C, 51.06; H, 8.14; Br, 33.98. Found: C, 51.19; H, 8.19; Br, 33.49.

p-Nitrobenzoate (**7e**): mp 116–118 °C (from EtOH).[7]

Anal. Calcd for $C_{17}H_{22}BrNO_4$: C, 53.13; H, 5.77; Br, 20.79. Found: C, 53.10; H, 5.66; Br, 20.60.

Further elution yielded various mixtures of **7c** and **6c,** pure **6c,** and other components. Bromohydrin **7c** was converted into **6c**[37] on prolonged contact with silica gel.

***t*-2-Bromo-*t*-3-*tert*-butyl-*r*-1-cyclohexanol Acetate (4d).** Prepared from **4c** with Ac_2O in pyridine for 14 h at room temperature as a liquid: NMR δ 0.96 [s, $-C(CH_3)_3$, 9 H], 2.01 (s, CH_3CO–, 3 H), 4.35 (m, $W_{1/2}$ = 6.5 Hz, >CHBr, 1 H), 4.97 (m, $W_{1/2}$ = 6.5 Hz, >CHO-$COCH_3$, 1 H).

Anal. Calcd for $C_{12}H_{21}BrO_2$: C, 51.99; H, 7.63; Br, 28.83. Found: C, 52.40; H, 7.62; Br, 28.35.

***t*-2-Bromo-*t*-6-*tert*-butyl-*r*-1-cyclohexanol acetate (5d),** obtained from **5c** and Ac_2O in pyridine after 21 days, had mp 32–34 °C (from petroleum ether): NMR δ 0.90 [s, $-C(CH_3)_3$, 9 H], 2.04 (s, CH_3CO–, 3 H), 3.85 (m, W = 25 Hz, >CHBr, 1 H), 4.92 (t, J = 9.6 Hz, >CHOCOCH$_3$, 1 H).

Anal. Calcd for $C_{12}H_{21}BrO_2$: C, 51.99; H, 7.63; Br, 28.83. Found: C, 52.20; H, 7.35; Br, 28.40.

***t*-2-Bromo-*c*-6-*tert*-butyl-*r*-1-cyclohexanol acetate (6d)** was obtained as a liquid from **6c** and Ac_2O after a reaction time of 160 h: NMR δ 0.88 [s, $-C(CH_3)_3$, 9 H], 2.04 (s, CH_3CO–, 3 H), 4.31 (m, $W_{1/2}$ = 6.5 Hz, >CHBr, 1 H), 5.17 (m, $W_{1/2}$ = 6.5 Hz, >CHOCOCH$_3$, 1 H).

Anal. Calcd for $C_{12}H_{21}BrO_2$: C, 51.99; H, 7.63; Br, 28.83. Found: C, 52.41; H, 7.60; Br, 28.55.

***t*-2-Bromo-*c*-3-*tert*-butyl-*r*-1-cyclohexanol Acetate (7d).** A mixture of acetoxy bromides **4d–7d** (4.5 g), obtained by the addition of acetyl hypobromite to **1a** as described above, was chromatographed on a 2.8 × 70 cm column of silica gel (140 g). Petroleum ether eluted in succession mixtures of **4d** and **6d** (0.6 g), mixtures of **4d, 6d,** and **7d** (0.6 g), and pure **7d** (2.5 g): mp 55 °C (from petroleum ether); NMR δ 1.08 [s, $-C(CH_3)_3$, 9 H], 2.02 (s, CH_3CO–, 3 H), 3.88 (t, J = 8.8 Hz, >CHBr, 1 H), 4.90 (m, W = 23 Hz, >CHOCOCH$_3$, 1 H).

Anal. Calcd for $C_{12}H_{21}BrO_2$: C, 51.99; H, 7.63; Br, 28.83. Found: C, 52.05; H, 7.58; Br, 29.10.

***trans*-3-*tert*-Butyl-1,2-epoxycyclohexane (2a).** Bromohydrin **5c** (1.0 g, 4.2 mmol) was dissolved in 2-propanol (20 mL) and titrated with 1 N aqueous NaOH at room temperature, with phenol phthalein as the indicator. The consumption of base amounted to 4.2 mL. Dilution with water, extraction with ether, and usual workup gave pure (GLC) **2a**[6] (0.6 g), bp 92–94 °C (20 mm).

The same epoxide was also obtained by similar treatment of **4c.**

***cis*-3-*tert*-Butyl-1,2-epoxycyclohexane (3a). A.** Cyclization of bromohydrin **6c** (1.0 g) under the same conditions as employed for **4c** and **5c** afforded pure (GLC) **3a**[6] (0.55 g), bp 82–83 °C (18 mm).

B. A solution of K_2CO_3 (2.0 g) in water (5 mL) was added to **7d** (2.0 g) dissolved in CH_3OH (50 mL). After refluxing for 2 h, dilution with water, extraction with ether, and usual workup gave 0.8 g of pure **3a.**

***cis*-3-Methyl-1,2-epoxycyclohexane (3b).** The procedure of Rickborn[14] was modified as follows: a 0.36 M $CHCl_3$ solution of peroxybenzoic acid (300 mL) was added dropwise to **1b** (8.5 g, 0.088 mol) dissolved in $CHCl_3$ (25 mL) at 0 °C. After 12 h the solution was washed with saturated aqueous Na_2CO_3 and water, dried, and evaporated to give a mixture of **2b** and **3b** (8.0 g) in a ratio of 52:48 (GLC: 50-m capillary column coated with polypropylene glycol; column 90 °C, evaporator and detector 140 °C, nitrogen flow 1 mL/min; relative retention times 1.10:1). A solution of this mixture in $CHCl_3$ (25 mL) was saturated with dry HCl at 0 °C. After 5 min, usual workup yielded a residue (9.0 g) consisting of chlorohydrins **4i–7i,** which was dissolved in anhydrous pyridine (100 mL) and treated with *p*-nitrobenzoyl chloride (11.5 g). After 10 h at room temperature the reaction mixture was poured onto 10% aqueous HCl and ice and extracted with petroleum ether. Usual workup gave a solid which was crystallized from CH_3OH. Six crystallizations yielded 3.0 g of the pure *p*-nitrobenzoate **6j,** mp 112–113 °C (lit.[14] mp 109–110 °C).

A solution of **6j** (3.0 g) in CH_3OH (45 mL) and water (5 mL) was refluxed for 1 h in the presence of K_2CO_3 (3.5 g). Dilution with water, extraction with ether, and distillation of the dried extract afforded pure (GLC) **3b**[14] (0.8 g), bp 48 °C (18 mm).

***trans*-3-Methyl-1,2-epoxycyclohexane (2b).** NBS (9.5 g, 0.053 mol) was added portionwise to a stirred solution of **1b** (5.0 g, 0.052 mol) in Me_2SO–water (95:5, 100 mL) at room temperature. The reaction mixture was stirred for 30 min, diluted with water, and extracted with ether. Usual workup gave 9.3 g of mixed bromohydrins **4g–7g**, which were dissolved in anhydrous pyridine and esterified with *p*-nitrobenzoyl chloride (9.5 g) in the usual way. Crystallization of the resulting *p*-nitrobenzoates from ethanol yielded pure **4h** (9.5 g), mp 118–119 °C.

Anal. Calcd for $C_{14}H_{16}BrNO_4$: C, 49.14; H, 4.71. Found: C, 49.14; H, 4.86.

Hydrolysis of **4h** (9.5 g) with K_2CO_3 in aqueous CH_3OH as described for **6j** afforded 2.5 g of pure (GLC) **2a**, bp 48–49 °C (18 mm).

***t*-2-Bromo-*t*-3-methyl-*r*-1-cyclohexanol (4g).** A mixture of **4g–7g** (3.0 g) obtained by reaction of **1b** with NBS in Me_2SO–water as described above was chromatographed on a 1.8 × 50 cm column of silica gel (70 g). Elution with petroleum ether–ethyl ether (96:4) yielded small amounts of mixtures and finally pure **4g**, as a liquid: NMR δ 1.03 (d, J = 6.5 Hz, $-CH_3$, 3 H), 3.52 (s, –OH, 1 H), ~4.05 (two overlapping m, >CHOH and >CHBr, 2 H).

Anal. Calcd for $C_7H_{13}BrO$: C, 43.53; H, 6.76. Found: C, 43.80; H, 6.90. *p*-Nitrobenzoate (**4h**), mp 118–119 °C.

***t*-2-Bromo-*t*-6-methyl-*r*-1-cyclohexanol (5g).** A solution of **2b** (3.0 g) in $CHCl_3$ (75 mL) was saturated with dry HBr. After 15 min, washing with water, 10% aqueous $NaHCO_3$, and water, drying and evaporation gave 4.0 g of a mixture of **4g** and **5g**, which was chromatographed on a 1.8 × 60 cm column of silica gel (75 g). Elution with 96:4 petroleum ether–ethyl ether gave pure **5g** (1.0 g), mp 36–37.5 °C (from petroleum ether); NMR δ 1.08 (highly distorted d, $-CH_3$, 3 H), 2.68 (s, –OH, 1 H), 3.23 (t, J = 8.4 Hz, >CHOH, 1 H), 3.96 (m, W = 25 Hz, >CHBr, 1 H).

Anal. Calcd for $C_7H_{13}BrO$: C, 43.54; H, 6.76; Br, 41.38. Found: C, 43.73; H, 6.84; Br, 41.10.

p-Nitrobenzoate (**5h**): mp 136–138 °C.

Anal. Calcd for $C_{14}H_{16}BrNO_4$: C, 49.14; H, 4.71. Found: C, 49.00; H, 4.85.

Further elution with 95:5 petroleum ether–ethyl ether yielded pure **4g** (2.3 g).

***t*-2-Bromo-*c*-6-methyl-*r*-1-cyclohexanol *p*-Nitrobenzoate (6h).** Opening of **3b** (0.4 g) with dry HBr in $CHCl_3$ followed by esterification of the crude oily product with *p*-nitrobenzoyl chloride in pyridine and crystallization from CH_3OH yielded **6h** (0.5 g), mp 128–130 °C.

Anal. Calcd for $C_{14}H_{16}BrNO_4$: C, 49.14; H, 4.71. Found: C, 49.10; H, 4.90.

***t*-2-Bromo-*c*-3-methyl-*r*-1-cyclohexanol *p*-Nitrobenzoate (7h).** A 1 M aqueous solution of $HOBr$[34] (35 mL) was added dropwise with stirring to **1b** (3.0 g, 0.032 mol) dissolved in dioxane (100 mL). After 30 min at room temperature, dilution with water, extraction with ether, and the usual workup yielded 4.2 g of mixed bromohydrins **4g–7g**, which were chromatographed on a 1.8 × 60 cm column of silica gel. Elution with 97:3, 95:5, and 90:10 petroleum ether–ethyl ether gave various mixtures of **6g** and **7g**, and finally **4g**.

A sample (0.2 g) of an approximate 1:1 mixture of **6g** and **7g** was esterified with *p*-nitrobenzoyl chloride (0.24 g) in anhydrous pyridine (2 mL). The resulting mixed *p*-nitrobenzoates **6h** and **7h** (0.26 g) were subjected to preparative TLC (PSC-Fertigplatten Kieselgel 60 F_{254} Merck). Elution was repeated three times with 97:3 and once with 96:4 petroleum ether–ethyl ether. Extraction of the slower moving band with ethyl ether and purification of the product by further TLC and crystallization from CH_3OH yielded pure **7h** (50 mg), mp 103–104 °C.

Anal. Calcd for $C_{14}H_{16}BrNO_4$: C, 49.14; H, 4.71. Found: C, 48.91; H, 4.95.

Extraction of the faster moving band and crystallization from CH_3OH gave pure **6h** (50 mg).

3-Methyl-2-cyclohexenone 2,4-Dinitrophenylhydrazone (9). A solution of **4g** (0.72 g, 3.7 mmol) in acetone (10 mL) was treated at 0 °C with Jones reagent[36] (1 mL). After 3 h, dilution with water, extraction with ether and usual workup gave bromo ketone 8 (0.65 g) as a liquid: NMR δ 1.08 (d, J = 6 Hz, $-CH_3$, 3 H), 4.20 (m, $W_{1/2}$ = 5 Hz, >CHBr, 1 H). This product was dissolved in warm glacial acetic acid (10 mL), 2,4-dinitrophenylhydrazine (0.70 g) was added under a nitrogen atmosphere, and the solution was heated on a hot plate for 5 min. The hydrazone **9**, precipitated immediately and crystallized several times from chloroform–ethanol, had mp 175–178 °C (lit.[16] mp 177–178 °C).

***t*-2-Chloro-*t*-3-methyl-*r*-1-cyclohexanol (4i) and *t*-2-chloro-*t*-6-methyl-*r*-1-cyclohexanol (5i).** A solution of **2b** (1.0 g) in $CHCl_3$ (50 mL) was saturated with dry HCl. After 15 min, usual workup gave a mixture of **4c** and **5c** (1.2 g) which was chromatographed on a 1.8 × 50 cm column of silica gel. Elution with 96:4 petroleum ether–ethyl ether gave pure **5i** (0.1 g) as a low-melting solid; *p*-nitrobenzoate (**5j**): mp 124–126.5 °C (from CH_3OH).

Anal. Calcd for $C_{14}H_{16}ClNO_4$: C, 56.50; H, 5.40. Found: C, 56.80; H, 5.40.

Further elution with 95:5 petroleum ether–ethyl ether yielded pure **4i** (0.4 g), liquid: *p*-nitrobenzoate (**4j**) mp 98–99 °C (from CH_3OH).

Anal. Calcd for $C_{14}H_{16}ClNO_4$: C, 56.50; H, 5.40. Found: C, 56.75; H, 5.25.

***t*-2-Chloro-*c*-6-methyl-*r*-1-cyclohexanol (6i) and *t*-2-Chloro-*c*-3-methyl-*r*-1-cyclohexanol (7i).** NCS (7.5 g, 0.056 mol) was added to a stirred suspension of **1b** (5.0 g, 0.052 mol) in water (35 mL) heated at 90 °C in a flask equipped with a condenser. Heating was continued until a heavy oil was formed. Extraction with ether, usual workup, and distillation gave a mixture of chlorohydrins **4i–7i** (5.5 g), bp 62–65 °C (2.5 mm), which was chromatographed on a 1.8 × 70 cm column of silica gel. Elution with 98:2 petroleum ether–ethyl ether gave in succession: **5i**, as a low-melting solid; **6i**, as a liquid; mixtures of **6i** and **7i**; mixtures of **7i** and **4i**. Further elution with 95:5 petroleum ether–ethyl ether yielded pure **4i**.

Esterification of **6i** with *p*-nitrobenzoyl chloride gave **6j**, mp 112–113 °C, identical to the *p*-nitrobenzoate used for the preparation of epoxide **3b**. The same compound was also obtained by esterification of the product of ring opening of **3b** with HCl in $CHCl_3$ and crystallization from CH_3OH.

Treatment of a mixture of **6i** and **7i** with *p*-nitrobenzoyl chloride followed by several crystallizations from CH_3OH afforded ester **7j** contaminated by ~20% (NMR) of isomer **6j**.

Anal. Calcd for $C_{14}H_{16}ClNO_4$: C, 56.50; H, 5.40. Found: C, 57.00; H, 5.70.

Products Distribution Studies. Additions to Alkenes. The additions reported in Tables I and IV were performed under the same conditions employed for the preparative reactions described above. The reaction of **1a** with NCS in water was carried out as described for **1b**. The additions of NBS–water to both **1a** and **1b** were performed in the following way: the olefin (10 mmol) was added dropwise to a stirred suspension of NBS (2.5 g, 14 mmol) in water (25 mL). The mixture was stirred for 2 h at room temperature and extracted with ether. The extract was washed with water, dried, and evaporated.

All reactions were carried out on a 10-mmol scale and the crude products were subjected to GLC under the following conditions.

Bromohydrins **4c–7c:** 1.5-m glass column, 2.5-mm i.d., packed with 10% ethylene glycol succinate on silanized Chromosorb W 80–100 mesh (column 115 °C, evaporator and detector 200 °C, nitrogen flow 35 mL/min). Relative retention times: **5c**, 1; **7c**, 1.49; **6c**, 2.43; **4c**, 3.22.

Acetoxy bromides **4d–7d:** 1.5-m glass column, 2.5-mm i.d., packed with 1% silicone oil SE_{52} on silanized Chromosorb W 80–100 mesh (column 60 °C, evaporator and detector 150 °C, nitrogen flow 40 mL/min). Relative retention times: **6d**, 1; **4d**, 1.11; **5d** and **7d**, 1.55. Since under these conditions the diequatorial adducts **5d** and **7d** were not separated, only the single percentages of **4d** and **6d** and the total percentage of **5d** and **7d** were obtained. The single percentages of the latter adducts were deduced by combining the data obtained by direct analysis of the mixture of acetoxy bromo adducts with the percentages of epoxides **2a** and **3a** arising from K_2CO_3 hydrolysis of the same mixture.

Chlorohydrins **4f–7f** and **4i–7i** and bromohydrins **4g–7g:** 2-m glass column, 2.5-mm i.d., packed with 10% Carbowax 20 M on silanized Chromosorb W 80–100 mesh. Relative retention times of **4f–7f** (column 170 °C, evaporator and detector 220 °C, nitrogen flow 30 mL/min): **5f**, 1; **7f**, 1.42; **6f**, 2.33; **4f**, 2.96. Relative retention times of **4g–7g** (column 160 °C, evaporator and detector 200 °C, nitrogen flow 30 mL/min): **5g**, 1; **7g**, 1.16; **6g**, 2.28; **4g**, 3.21. Relative retention times of **4i–7i** (column 150 °C, evaporator and detector 200 °C, nitrogen flow 30 mL/min): **5i**, 1; **7i**, 1.17; **6i**, 2.16; **4i**, 2.92.

All products were stable under the reaction conditions and under the GLC conditions. The percentages quoted in Tables I and V for each reaction are averages of at least four experiments, which were reproducible within ±1%.

Opening of Epoxides with Hydrogen Halides. A solution of epoxide **2a, 2b, 3a,** and **3b** (0.1 g) in 5 mL of solvent was saturated with the appropriate dry hydrogen halide. After 15 min at room temper-

ature, the reaction mixture was washed with water and 10% aqueous $NaHCO_3$, dried, and subjected to GLC under the conditions defined above. The results reported in Tables II and IV are averages of three or more experiments, which were reproducible within ±1%.

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Registry No.—**1a,** 14072-87-8; **1b,** 591-48-0; **2a,** 20887-61-0; **2b,** 7443-54-1; **3a,** 20887-60-9; **3b,** 7443-69-8; **4c,** 64199-99-1; **4d,** 64200-00-6; **4g,** 64200-01-7; **4i,** 64162-78-3; **5c,** 38512-63-9; **5c** phenylurethane, 38749-39-2; **5d,** 38512-66-2; **5g,** 64162-79-4; **5i,** 64162-80-7; **6c,** 38512-64-0; **6d,** 64199-91-3; **6g,** 64199-92-4; **6i,** 64199-93-5; **7c,** 38749-36-9; **7d,** 38512-65-1; **7e,** 38749-37-0; **7g,** 64162-81-8; **7i,** 64199-94-6; **8,** 41780-49-8; **9,** 3234-76-2; *p*-nitrobenzoyl chloride, 122-04-3.

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(20) In the latter reactions, nucleophilic attack is carried out by halides on the protonated forms of the epoxides and the **4:5** and **6:7** ratios quoted in Tables II and IV must be respectively compared with the **6:7** and **4:5** ratios of Table VI.
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Epoxycarbinyl Solvolyses. Lack of Significant Participation by Epoxide Oxygen in the Hydrolysis of Acyclic Secondary Epoxycarbinyl Substrates

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The rate constants and activation parameters for solvolysis of the diastereomeric epoxycarbinyl *p*-bromobenzenesulfonate esters **23b** and **24b** (derived from the oxides of *trans*-3-penten-2-ol) in ethanol–water mixtures have been determined. The predominant products (~88–96%) from solvolysis of **23b** and **24b** in 80% acetone–water resulted from inversion at the ionizing carbon. The product distributions suggest that neither significant amounts of oxabicyclobutonium ion intermediates nor highly stabilized epoxycarbinyl cations are formed. The rates of solvolysis of **23b** and **24b** were ~10^6 times slower than the rates of solvolysis of the corresponding cyclopropylcarbinyl analogues.

Numerous publications about the solvolytic reactions of cyclopropylcarbinyl substrates have appeared during the past 20 years.[1] The stabilizing interaction of the cyclopropane ring with a developing positive charge on the carbinyl carbon is generally reflected by enhanced reactivities of cyclopropylcarbinyl derivatives, relative to model compounds without neighboring cyclopropyl groups. The geometry of the cyclopropyl group relative to the developing p orbital on the carbinyl carbon is critical, however. A "bisecting" geometry of the cyclopropyl group is most favorable, whereas a "perpendicular" geometry actually brings about a destabilizing interaction.[1,2]

More recent results have been reported on the reactions of geometrically related "epoxycarbinyl" substrates of general structure **1** under conditions that lead to the development of a positive charge on the carbinyl carbon.[3–5] Most of the reactions of epoxycarbinyl substrates are analogous to those reactions observed in cyclopropylcarbinyl solvolysis. If the intermediate from the solvolysis of **1** possesses a significant positive charge density on the carbinyl carbon (i.e., **2**), then

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