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EFFECTS OF RING SIZE ON THE REACTIONS OF CYCLIC OLEFINS

HALOHYDRINS FROM METHYLENECYCLOALKANES[1,2]

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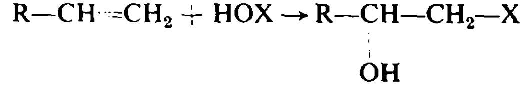
Abstract—Addition of HOCl to methylenecycloalkanes (ring sizes C_4 through C_7) gave mixtures of chlorohydrins with abnormal orientation predominating with the 4- and 6-membered ring compounds. Addition of HOBr to these olefins gave 1-bromocycloalkylmethanols as the only bromohydrin product. Cycloalkanecarboxaldehyde, in amounts dependent on ring size, accompanied the formation of bromohydrin from olefin oxide and HBr solution.

An interpretation of these results is included.

As part of a study of the effects of ring size on the reactions of cyclic olefins,[3] we have included additions of hypohalous acids to a series of methylenecycloalkanes (ring sizes C_4 through C_7). Although we observed no orientation effects when hydrogen bromide was the addend,[3b] significant differences among these olefins were obtained with hypohalous acids.

Additions of hypohalous acids to acyclic 1-alkenes occur predominantly or exclusively with normal orientation (primary halogen).[4]



$$R{-}CH{=}CH_2 + HOX \rightarrow R{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2{-}X$$

These additions are pictured as stepwise processes initiated by attack of a positive halogen or its kinetic equivalent on the olefin,[4a-b,5] probably through a pi-complex. Electrical effects are generally regarded to be of major importance in determining orientation. Substituted olefins may give rise to abnormal orientation in the halohydrin product,[4c,5] but in the absence of serious steric factors[6] unsubstituted acyclic olefins give very largely (or exclusively) the halohydrin to be expected on the basis of the usual electron-releasing effects of alkyl groups.

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[2] Taken from the Ph.D. dissertation submitted by O. S. Pascual to Louisiana State University, 1956. Reported in part at the 131st Meeting of the American Chemical Society, Miami, April, 1957. A Preliminary Communication appeared in *J. Amer. Chem. Soc.* **79**, 2341 (1957).

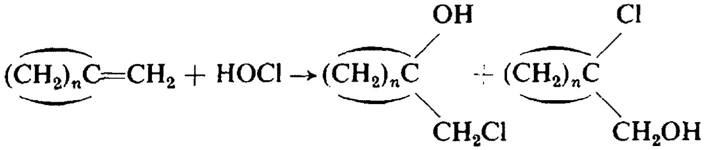
[3] Previous papers in this series include: (a) J. G. Traynham and M. F. Sehnert, *J. Amer. Chem. Soc.* **78**, 4024 (1956); (b) J. G. Traynham and O. S. Pascual, *J. Org. Chem.* **21**, 1362 (1956); (c) J. G. Traynham and J. R. Olechowski, *J. Amer. Chem. Soc.* **81**, 571 (1959).

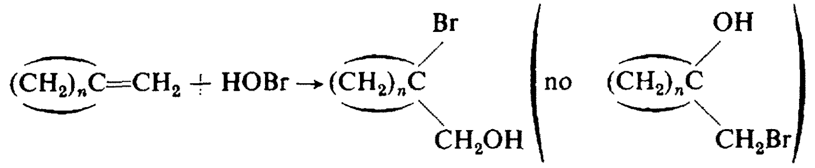
[4a] J. Hine, *Physical Organic Chemistry* pp. 212–213, McGraw-Hill, New York (1956); [b] P. B. D. de la Mare and A. Salama, *J. Chem. Soc.* 3337 (1956); [c] L. Smith and S. Skyle, *Acta Chem. Scand.* **4**, 39 (1950) and **5**, 1415 (1951).

[5] P. B. D. de la Mare and J. G. Pritchard, *J. Chem. Soc.* 3910 (1954).

[6] W. H. Purterbaugh and M. S. Newman, *J. Amer. Chem. Soc.* **79**, 3469 (1957), report exclusive abnormal addition of the elements of Br—OCH_3 (from bromine in methanol) to t-butylethylene and some abnormal addition to 1-hexene.

In striking contrast to these results with acyclic alkenes, we have found that addition of HOCl to methylenecycloalkanes gives mixtures of chlorohydrins, with abnormal orientations predominating with the 4- and 6-membered ring compounds,[7] and that addition of HOBr to these olefins gives only abnormally oriented bromohydrins.





The distribution data are summarized in Table 1.

EXPERIMENTAL[8]

Preparations of the *methylenecycloalkanes* have been previously described.[3b]

Authentic 1-*chloromethylcycloalkanols* (except for 1-chloromethylcyclobutanol) were synthesized by the selective hydrolysis of the appropriate 1-chloro-1-chloromethylcycloalkane.[9] Suspensions of approximately equal molar quantities of olefin dichloride and $CaCO_3$ in water were refluxed for 6 hr.[13] Appreciable amounts of the dichloride were removed from the insoluble organic material along with low yields (28–39%) of the chlorohydrin (primary chloride). These chlorohydrins all gave precipitates with NaI in acetone and with alcoholic $AgNO_3$ (slowly), produced immediate cloudiness with Lucas reagent, reduced $KMnO_4$ and showed infrared absorption near 7·25 μ (tertiary alcohol). Physical properties are given in Table 2.

1-*Chlorocycloalkylmethanols.* Methylenecycloalkane oxides were prepared by treatment of the halohydrin with aqueous KOH or, in the case of methylenecyclohexane oxide, as by-product in the preparation of cycloheptanone from cyclohexanone and diazomethane:[14] methylenecyclobutane

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[7] Formation of 1-chlorocyclohexylmethanol only from methylenecylohexane and HOCl has been reported by M. Tiffeneau, P. Weill and B. Tchoubar, *Compt. rend.* **205**, 144 (1937).

[8] Atomic refractions for calculation of MR and chemical classification tests taken from R. L. Shriner, R. C. Fuson and D. Y. Curtin, *The Systematic Identification of Organic Compounds* (4th Ed.). John Wiley, New York (1956).

[9] Prepared in poor yields by the addition of chlorine to chilled solutions of olefins in CCl_4. Although the addition of bromine to these methylenecycloalkanes gave the expected dibromides in fairly good yields, the product mixtures from chlorine additions contained considerable amounts of polymeric material and some chloromethylcycloalkene. (Similar results were obtained with chlorine and methylenecyclohexane in the presence of solid $NaHCO_3$ by Arnold and Lee.[10]) The dichlorides isolated were: 1-chloro-1-chloromethylcyclobutane,[11] b.p. 49–50° (14 mm), n_D^{20} 1·4777, d_4^{20} 1·175; 1-chloro-1-chloromethylcyclopentane, b.p. 55–56° (7 mm), n_D^{20} 1·4982, d_4^{20} 1·191, MR_{calc} 37·4, MR_{expt} 37·7; 1-chloro-1-chloromethylcyclohexane,[10] b.p. 85–87° (15 mm), n_D^{20} 1·4915, d_4^{20} 1·169; and 1-chloro-1-chloromethylcycloheptane, b.p. 61–62° (3·3 mm), n_D^{20} 1·4910, d_4^{20} 1·105, MR_{calc} 46·7, MR_{expt} 47·5.

Methylenecyclobutane gave, in addition to the desired dichloride, 2 other products whose molar refractivities agreed fairly well with structure assignments based on the detailed study[12] of bromine addition to methylenecyclobutane: 1,1-*bis*(chloromethyl)cyclopropane, b.p. 56–57° (14 mm), d_4^{20} 1·180, n_D^{20} 1·4832, MR_{calc} 33·5, MR_{expt} 33·7; and 1,2,4-trichloro-2-chloromethylbutane, b.p. 55–56° (6 mm), d_4^{20} 1·305, n_D^{20} 1·4945, MR_{calc} 44·7, MR_{expt} 46·9. These products gave precipitates with NaI in acetone but did not reduce $KMnO_4$ nor show infrared absorption characteristic of olefins.

[10] R. T. Arnold and W. W. Lee, *J. Amer. Chem. Soc.* **75**, 5396 (1953).

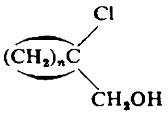
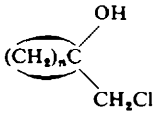
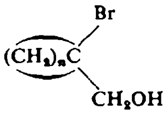
[11] N. J. Demjanow and N. Dojarenko, *Ber.* **55B**, 2730 (1922).

[12] D. E. Applequist and J. D. Roberts, *J. Amer. Chem. Soc.* **78**, 874 (1956).

[13] C. E. Sparks and R. E. Nelson, *J. Amer. Chem. Soc.* **58**, 1010 (1936).

[14] E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, *J. Amer. Chem. Soc.* **61**, 1057 (1939).

TABLE 1. PRODUCT DISTRIBUTIONS IN HYPOHALOUS ACID ADDITIONS TO METHYLENECYCLOALKANES

Ring size	Hypochlorous acid				Hypobromous acid		
	Total yield %	Proportion of total			Total yield %	Proportion of total	
				Other product			Other products
4	72	60	40	none[a]	78	99	1[b]
5	64	41	58	1[b]	67	91	9[c]
6	92	67	32	1[b]	89	98	2[d]
7	86	35	64	1[b]	87	87	13[d]

[a] No rearrangement products were found. [b] Slight absorption attributable to a carbonyl group (probably in cycloalkanecarboxaldehyde) appeared in the infrared spectrum of the product. [c] Methylenecyclopentane oxide. [d] Cycloalkanecarboxaldehyde.

TABLE 2. PHYSICAL PROPERTIES OF METHYLENECYCLOALKANE HALOHYDRINS

Compound[a]	B.p. (mm)	d_4^{20}[b]	n_D^{20}[b]	MR	
				calc.	expt.
$ClCH_2—C_4—OH$[11]	56–60°	—	—		
	(20)	1·135	1·4688	30·0	29·6
$Cl—C_4—CH_2OH$	69–70°	1·154	1·4760	30·0	29·5
	(20)	1·153	1·4765		29·5
$ClCH_2—C_5—OH$	57–58°	1·143	1·4841	34·1	33·7
	(6)	1·144	1·4834		33·6
$Cl—C_5—CH_2OH$	62–63°	1·182	1·5036	34·1	33·7
	(3)	1·183	1·5038		33·7
$ClCH_7—C_6—OH$	54–55°	1·127	1·5024	38·7	38·9
	(4)	1·128	1·5030		39·0
$Cl—C_6—CH_2OH$[7]	53–54°	1·113	1·4905	38·7	38·6
	(2)	1·113	1·4910		38·7
$ClCH_2—C^7—OH$	56–58°	1·118	1·4997	43·3	42·8
	(2)	1·119	1·4990		42·7
$Cl—C_7—CH_2OH$	70–71°	1·128	1·5114	43·3	43·2
	(2)	1·127	1·5110		43·2
$Br—C_4—CH_2OH$	64–65°	1·506	1·5041	32·9	32·5
	(10)	1·506	1·5036		32·4
$Br—C_5—CH_2OH$	45–46°	1·463	1·5126	37·0	36·8
	(2)	1·463	1·5126		36·8
$Br—C_6—CH_2OH$[7]	55–56°	M.P. 82–83°	—		—
	(2)				
$Br—C_7—CH_2OH$	73–74°	1·339	1·5232	46·2	47·3
	(3)	1·340	1·5225		47·2

[a] C_4, C_5, etc., represent cycloalkylidine structures with the number of ring carbons indicated.
[b] The first value in each case is that for independently synthesized ("authentic") halohydrin; the second value is that for the product obtained by hypohalous acid addition to the olefin.

oxide,[11] b.p. 90–92° n_D^{20} 1·4207; methylenecyclopentane oxide, b.p. 43–44° (62 mm) n_D^{20} 1·4290, d_4^{20} 0·923, MR_{calc} 27·5, MR_{expt} 27·4; methylenecyclohexane oxide,[14] b.p. 62–63° (37 mm), n_D^{20} 1·4470; methylenecycloheptane oxide, b.p. 84–85° (40 mm), n_D^{20} 1·4552, d_4^{20} 0·938, MR_{calc} 36·8, MR_{expt} 36·5. The olefin oxide (0·01–0·06 mole) was dripped into conc HCl (20 ml) chilled below 5°. The mixture was stirred for an hour and then poured onto ice. Conventional work-up gave poor yields of chlorohydrins whose physical and chemical properties were different from those of the isomeric chlorohydrins described above. These 1-chlorocycloalkylmethanols all gave precipitates with alcoholic $AgNO_3$ (immediately) but none with NaI in acetone, reduced $KMnO_4$, gave negative Lucas tests and showed no infrared absorption near 7·25 μ. Physical properties are given in Table 2.

1-*Bromocycloalkylmethanols.* These bromohydrins were prepared from the olefin oxides and chilled 48% hydrobromic acid. After addition of the oxide was completed and stirring had been continued for an hour longer, the acid was neutralized with solid Na_2CO_3. The mixture was extracted with ether, the ether solution was washed and dried, and the ether was removed by distillation. Distillation of the residue gave the bromohydrins, whose physical properties are listed in Table 2. Each of the bromohydrins formed an immediate precipitate with alcoholic $AgNO_3$ and gave negative tests with Lucas reagent and with NaI in acetone. Acid hydrolysis (refluxing for 5–6 hr with 5 M HCl) of the bromohydrins (5-, 6- and 7-membered rings) gave good yields of the corresponding cycloalkanecarboxaldehydes. These aldehydes had the following properties: cyclopentanecarboxaldehyde,[15] b.p. 55–56° (36 mm), d_4^{20} 0·920, n_D^{20} 1·4343, semicarbazone[15] m.p. 123–124°; cyclohexanecarboxaldehyde,[16] b.p. 49·5° (10 mm), d_4^{20} 0·930, n_D^{20} 1·4490, 2,4-dinitrophenylhydrazone[16] m.p. 172–173°; cycloheptanecarboxaldehyde,[17] b.p. 45·5–46° (4 mm), n_D^{20} 1·4621, semicarbazone[17] m.p. 154–155°.

Except for the preparation from methylenecyclobutane oxide, the initial product mixtures from the olefin oxides contained appreciable amounts of cycloalkanecarboxaldehyde in addition to the bromohydrin. The composition of the residue after evaporation of ether solvent was evaluated by comparison of its infrared spectrum with spectra of known mixtures prepared from distilled samples of 1-bromocycloalkylmethanol and cycloalkanecarboxaldehyde. Fractional distillation of the residue afforded pure samples of bromohydrin and aldehyde as well as confirmation of the spectral analysis.

Table 3 summarizes the data on product compositions. Such a small amount of methylenecyclobutane oxide was used that no product other than bromohydrin could be isolated.

TABLE 3. PRODUCT FROM OLEFIN OXIDES AND HBr

Ring size	Total yield, %	% Bromohydrin	% Aldehyde
5	45	65	35
6	68	95	5
7	87	68	32

Hypohalous acid solutions. HOCl[18] and HOBr[19] solutions were prepared by adding the halogen to well-stirred, chilled aqueous suspensions of HgO or Ag_2SO_4, respectively. The approximately 1·8 M solutions were distilled at reduced pressure in the dark (bath temperature about 40°) and the exact concentrations were determined iodometrically. Because we found that the use of concentrated HOCl solutions sometimes led to the formation of side products, the amount of HOCl solution required for each addition reaction was diluted to 500 ml before use.

HOBr was also formed *in situ* by the hydrolysis of N-bromosuccinimide.[20]

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[15] G. R. Clemo and J. Ormston, *J. Chem. Soc.* 362 (1933).

[16] I. Heilbron, E. R. H. Jones, R. W. Richardson and F. Sondheimer, *J. Chem. Soc.* 739 (1949).

[17] W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Liebegs Ann.* **560**, 62 (1948).

[18] A. Chung and G. C. Israel, *J. Chem. Soc.* 2668 (1955).

[19] S. J. Branch and B. Jones, *J. Chem. Soc.* 2323 (1954).

[20] C. O. Guss and R. Rosenthal, *J. Amer. Chem. Soc.* **77**, 2549 (1955).

Hypohalous acid additions. To a well-stirred, chilled (below 15°) suspension of methylenecycloalkane (approx. 0·12 mole) in water (200 ml) was added about 1/5 of slightly more than the theoretical amount of freshly-distilled, cold hypohalous acid solution. When the mixture no longer turned acidified starch-iodide paper blue, a second portion of hypohalous acid solution was added. The process was repeated until all the hypohalous acid solution had been added. The mixture was stirred for an hour longer and saturated with NaCl. The lower layer was separated, washed with dilute $NaCO_3$ solution and dried with $MgSO_4$. The infrared spectrum and refractive index of this organic material were taken.

The combined aqueous material was extracted with ether to recover the remainder of the product. All of the organic material was fractionally distilled through a Claisen still-head having a vacuum-jacketed Vigreux column approximately 12 × 140 mm. The product components were identified by comparison of their physical and chemical properties and infrared spectra with those of authentic samples synthesized independently.[21]

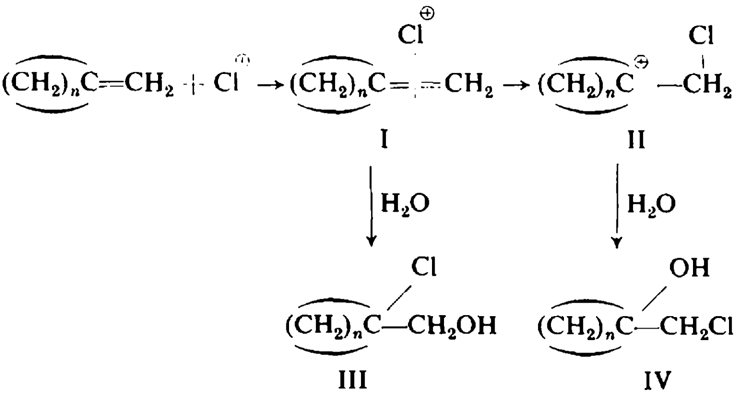
Comparison of the infrared spectrum of the crude product mixture with those of known mixtures prepared from authentic product samples as well as proportions of distillate in the fractions collected afforded data from which product distributions could be estimated. These data are summarized in Table 1.

A suspension of N-bromosuccinimide in water[20] could be substituted for HOBr solution without affecting product distributions.

HOBr *with isobutylene.* Although isobutylene bromohydrin has been prepared in poor yield from isobutylene and an aqueous solution of bromine and bromide,[19] there does not appear to be any report of the addition of relatively pure HOBr solution. Treatment of isobutylene (0·16 mole) with HOBr solution gave a 77% yield of product which was at least 97% 1-bromo-2-methyl-2-propanol[22] (b.p. 66–62·5° (31 mm), d_4^{20} 1·451, n_D^{20} 1·4722) and no more than 3% material tentatively identified as the isomer, 2-bromo-2-methyl-1-propanol.

DISCUSSION OF RESULTS

Attack on an olefin by a positive halogen will lead to an intermediate with carbonium character and with the halogen normally attached to the less substituted carbon.[4a] The data in Table 1 clearly indicate that ring size in these *exo*-olefins has an effect on the orientation in HOCl addition. The preponderance of abnormally oriented chlorohydrins from the 4- and 6-membered rings is consistent with the view that trigonal carbons in those rings are less favored than in 5- and 7-membered ones.[23] Possible reaction paths are indicated in the following equations:



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[21] Although no authentic 1-chloromethylcyclobutanol was prepared independently, the product assigned this name had chemical properties similar to those of the other normal chlorohydrins (primary chloride, tertiary alcohol) and the physical and spectral properties were consistent with the structure assignment.

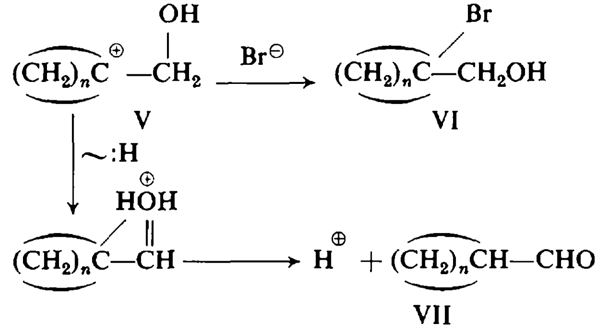
[22] C. M. Suter and H. D. Zook, *J. Amer. Chem. Soc.* **66**, 741 (1944).

[23] H. C. Brown, J. H. Brewster and H. Shechter, *J. Amer. Chem. Soc.* 76, 467 (1954).

The initially formed pi-complex (I) may rearrange as usual to the conventional carbonium ion (II),[4a–b,5,24] or it may suffer direct attack by water to give III, the abnormally oriented product. The carbonium ion II combines with water to give the normally oriented chlorohydrin IV.

Rearrangement of I to II is the less favored path for 4- and 6-membered rings because of the tendency to pass from trigonal to tetrahedral carbons in those rings,[23] but is satisfactory for 5- and 7-membered rings.[25] The formation of large amounts of III even from 5- and 7-membered rings, when acyclic olefins give corresponding products only in small amounts, indicates that this explanation is incomplete and suggests an importance of the ring structure itself in directing orientation.

The proportions of aldehyde and bromohydrin obtained in the treatment of methylenecycloalkane oxides with HBr (see Table 3) give further support to the claim that the relative stabilities of intermediates containing ring trigonal carbon atoms are strongly influenced or determined by ring size. The olefin oxide reacts with acid to give a carbonium ion intermediate (V) which combines with bromide to give bromohydrin.



V may also rearrange by hydride migration to give cycloalkanecarboxaldehyde (VII). Under the conditions used in these experiments (excess conc HBr), bromohydrin formation is the faster process and aldehyde formation becomes appreciable only when the intermediate V is sufficiently unreactive (long-lived) to allow the slower hydride migration to compete. The intermediate carbonium ion derived from methylenecyclohexane is the most reactive and very little aldehyde appears in the product mixture. The intermediates from methylenecyclopentane and methylenecycloheptane however are longer-lived, hydride shift can compete better, and aldehyde constitutes about 1/3 of the product obtained. Only relatively small changes in energy are required to effect these product proportion changes. Our data for methylenecyclobutane oxide are insufficiently complete to permit evaluation in that case.

In the HOBr additions however, ring *size* does not seem to play any role in determining orientation. Only a single bromohydrin was obtained from each methylenecycloalkane. The orientation was opposite to that obtained with the

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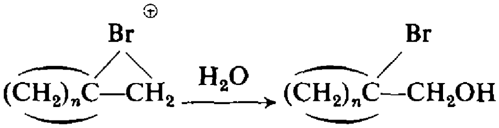
[24] Rearrangement of the protonated olefin (pi-complex) to a more conventional carbonium ion has been shown to be an important part of acid-catalyzed hydration; R. W. Taft, Jr., *J. Amer. Chem. Soc.* **74**, 5372 (1952); R. W. Taft, Jr., E. L. Purlee, P. Riesz and C. A. De Fazio, *J. Amer. Chem. Soc.* **77**, 1584 (1955).

Recent experiments in This Laboratory suggest that the same type of rearrangement is involved in halogen addition to olefins; J. G. Traynham and J. E. Landry, unpublished results.

[25] A more complete discussion of this point is found in reference 3b.

acyclic analog, isobutylene. Here again is an indication that the ring structure itself has an importance in directing orientation. Because of the prevalence of neighboring group participation with bromine, in contrast to the poor participation by chlorine,[26] an additional intermediate (VIII) may be pictured for additions of HOBr (or other reagents involving attack by $Br^{\oplus}$.)



VIII VI

Attack by water molecule on VIII (with Br symmetrically placed between the carbons) would occur far more readily at the primary carbon than at the tertiary one. Bromine in VIII is not necessarily symmetrically placed between the two carbons however, and the tertiary carbon might carry a higher proportion of positive charge than the primary one.[27] Attack would then occur preferentially at the tertiary carbon. This seems to be the case with isobutylene from which normally oriented bromohydrin (by attack on the tertiary carbon) is formed almost exclusively. The role of the ring structure may then be to bring the bromine in an intermediate such as VIII into a more symmetrical position or to make the partially-formed bond between bromine and the ring carbon more resistant to cleavage. The fact that VIII is spirane-like may play a significant part in determining the subsequent fate of such intermediates.

The addition of HOBr to some $\Delta^{9,11}$ unsaturated steroids has been reported to give abnormally oriented bromohydrins.[28] These polycyclic compounds are relatively rigid systems and conformations are quite well fixed. In the cases reported, HOBr addition follows the generalization that intermediates containing 3-membered rings react to open that ring with preservation of the axial bond.[29] The axial bond to Br in an intermediate similar to VIII is preserved even if that means formation of abnormally oriented product.

The formation of an axial bond between the ring carbon and bromine in the intermediate VIII may then be responsible for the exclusive formation of VI from methylenecyclohexane. The classification of axial bonds is less distinct in the other rings used here, but similar considerations may apply. To the extent that chlorine is able to form bridged ions[26,27] the same tendency to preserve the axial bond could account for some of the abnormal chlorohydrins formed. The normal cleavage of the tertiary carbon–oxygen bond in reaction of the epoxides with strong acid contrasts with the unexpected formation of the tertiary carbon-bromine bond in HOBr addition to the olefins. The quite different behavior of the conjugate acid of the epoxides and the analogous intermediate VIII may mean that the ring carbon–oxygen bond in the epoxides is not axial or, more probably, that considerably more bond-breaking has occurred in the transition state derived from the oxygen-containing intermediate than in that from the bromine-containing one.

[26] S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.* **70**, 828 (1949).

[27] An unsymmetrical bridged ion with chlorine has been used to account for the two products obtained from HOCl and allyl chloride; P. B. D. de la Mare and J. G. Pritchard, *J. Chem. Soc.* 3990 (1954).

[28] L. B. Barkley, M. W. Farrar, W. S. Knowles and H. Raffelson, *J. Amer. Chem. Soc.* **76**, 5017 (1954); E. M. Hicks, Jr. and E. S. Wallis, *J. Biol. Chem.* **162**, 641 (1946).

[29] D. H. R. Barton and R. C. Cookson, *Quart. Rev.* **X**, 44 (1956).

Since abnormal products were not obtained from the methylenecycloalkanes with HBr as addend,[3b] it appears that size (or activity[30]) of the attacking cation may have an important role in determining the actual orientation with these olefins. This role may well be associated with the ability to form bridged ion intermediates.[31] We are continuing studies of additions to cyclic olefins in the hope of unveiling more explicit information about these effects.

[30] H. C. Brown and K. L. Nelson, *J. Amer. Chem. Soc.* 75, 6292 (1953).

[31] A similar suggestion has been made to account for the different amounts of abnormal product obtained from allyl chloride with HCl, HOCl and ICl.[27]