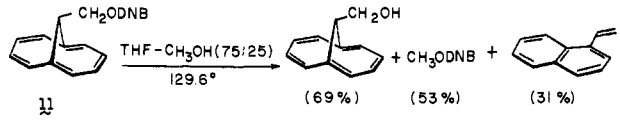
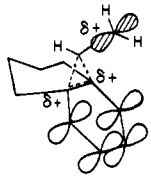
structural features inherent in **12** position both p orbital lobes of the electron-deficient carbon atom sufficiently distant from those of the diene component that *measurable* interaction does not operate.

Since the solvolyses of **7**, **8**, and **11** appear dependent

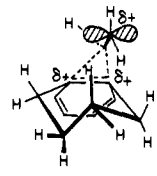


11

upon the operation of a preequilibrium, the observed rate constants comprise in reality a composite of pseudo-first-order rate and equilibrium constants ($k_{obsd} = k_1K_{eq}$). However, it is not imperative to invoke differences in K_{eq} to account for the somewhat more rapid ionization of **7** relative to **8**. A careful study of molecular models reveals that the carbinyl centers in **7** and its tricyclic valence tautomer experience steric compression with the axially disposed hydrogen atoms of the tetramethylene bridge (*cf.* **13**). Similar interactions



12



13

are absent in **8**. To maintain maximum orbital overlap, one hydrogen atom bonded to the carbinyl carbon must be positioned directly in the center of a cluster of ring protons. This nonbonded repulsion may be relieved by the development of some homoallylic character which gives rise to dissymmetric features as in **13**. In contrast, **12** could be a more symmetric ion. Interestingly, these conclusions are compatible with the observed differences in the relevant entropies of activation.

The present solvolyses denote that the large cyclopropyl-assisted rate accelerations available to **1** and **2** owing to their capacity for facile preisomerization to the norcaradienylcarbinyl derivatives **3** and **4**, respectively, are more than adequate to dampen kinetic effects of lesser magnitude. We therefore conclude that the influence of conformation upon the *rates* of solvolysis of 7-cycloheptatrienylmethanol derivatives is of sufficiently small order not to be an important factor *per se* (*i.e.*, $k_1(\mathbf{3}) \approx k_1(\mathbf{4})$. Acceptance of this latter proposal then requires, of course, that the magnitudes of the relevant preequilibria (**1** $\rightleftarrows$ **2**; **1** $\rightleftarrows$ **3**; **2** $\rightleftarrows$ **4**) control whether **3** or **4** is the predominant reaction species during the ionization of 7-cycloheptatrienylmethyl 3,5-dinitrobenzoate (Curtin–Hammett considerations.)

Acknowledgment. The partial financial support of the National Cancer Institute (Grant CA 12115) is acknowledged with gratitude.

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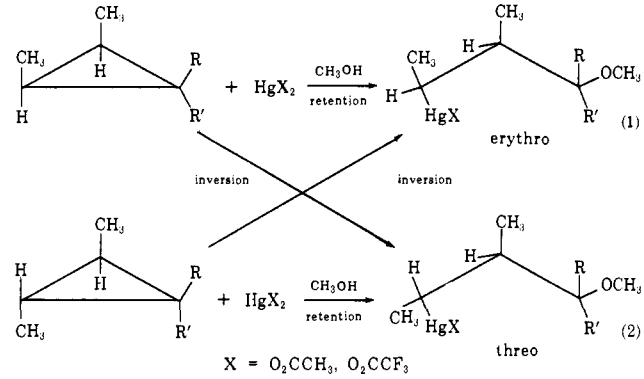
Stereochemistry of the Electrophilic Addition of Mercuric Acetates to Cyclopropanes

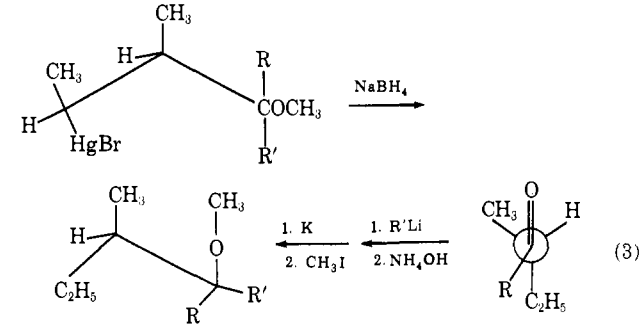
Sir:

The stereochemistry of the reaction of cyclopropanes with various electrophiles has been the subject of a number of investigations, but no general mechanistic pattern has appeared. Thus while cyclopropanes have been shown to react with protons mainly with retention of configuration at the carbon undergoing electrophilic substitution,[1] some examples of inversion are known.[2] Cyclopropanes have been cleaved with mercuric salts with inversion[3] and with positive halogen with inversion[4] and retention.[5] We wish to report the results of a comprehensive study of the reaction of a number of simple cyclopropanes with mercuric acetate and trifluoroacetate in methanol which shows that (1) the stereochemistry of the reaction of the electrophile is generally determined by its attack on the least substituted bond of the ring, (2) the nucleophile reacts almost exclusively with inversion, and (3) in a completely symmetrical system where all ring bonds are identical, inversion predominates slightly in the electrophilic attack.

The reactions whose stereochemistry was studied are shown in eq 1 and 2. The stereochemistry of the prod-



ucts was determined by replacement of the organomercurial with bromine in pyridine under conditions which give exclusively retention of configuration, followed by anti elimination to cis and trans alkenes from the erythro and threo isomer, respectively.[3] The alkenes in turn were synthesized from previously reported[3] compounds of known structure. The stereochemistry of the methoxyl group was determined by removal of the mercury

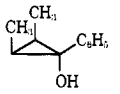
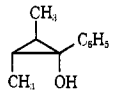
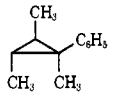
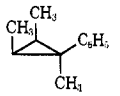
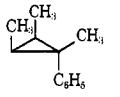
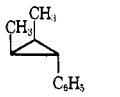
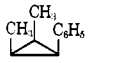
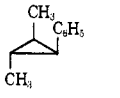
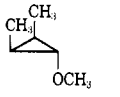
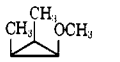
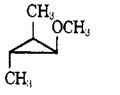
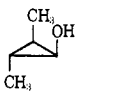
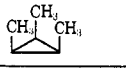


(3)

(1) C. H. DePuy, *Accounts Chem. Res.*, 1, 33 (1968).
(2) R. T. LaLonde, J.-Y. Ding, and M. A. Tobias, *J. Amer. Chem. Soc.*, **89**, 6651 (1967).
(3) A. DeBoer and C. H. DePuy, *ibid.*, **92**, 4008 (1970).
(4) C. H. DePuy, W. C. Arney, Jr., and D. H. Gibson, *ibid.*, **90**, 1830 (1968).
(5) S. J. Cristol, W. Y. Lim, and A. R. Dahl, *ibid.*, **92**, 4013 (1970).

by reduction and synthesis of the resultant ether making use of the Cram–Karabatsos rules (eq 3). The stereochemical results of the ring openings are shown in Table I.

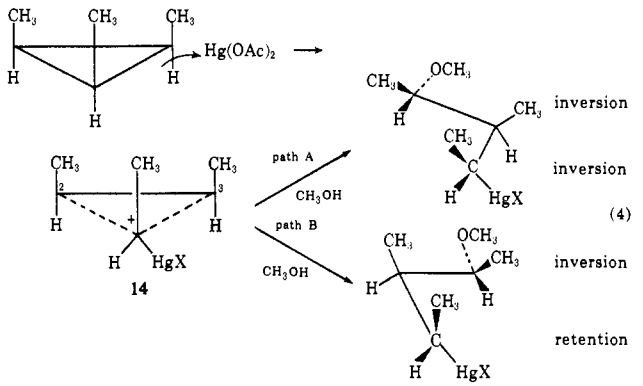
Table I. The Stereochemistry of Cyclopropane Ring Opening with Electrophilic Mercury

Compound	No.	Stereochemistry of electrophilic attack (% inversion)[a]	Stereochemistry of nucleophilic attack (% inversion)[a]
	**1**	100[b]	
	**2**	100[b]	
	**3**	100	100
	**4**	100	100
	**5**	100	100
	**6**	72	75
	**7**	82	91
	**8**	12	90
	**9**	95	
	**10**	40	
	**11**	10	
	**12**	<5	
	**13**	62	100

[a] The remainder is inversion. [b] Reference 3.

The pattern of stereochemistry observed is consistent with a mechanism in which mercuric acetate attacks the least substituted bond in the molecule, with ring opening occurring in the direction of the most stable carbonium ion. If bonds are equally substituted, then a bond with cis substituents is more easily attacked than one with trans substituents. Thus attack at the C2–C3 bond with ring opening to the benzylic cation gives exclusively inversion for electrophilic attack on **1–5**. Compounds **8**, **11**, and **12**, in which the C2–C3 bond is trans, give retention by attack on the disubstituted cis bond. In each case where the stereochemistry of the nucleophile can be determined, it occurs nearly exclusively with inversion of configuration.

In *cis,cis*-1,2,3-trimethylcyclopropane (**13**) all ring bonds are identically substituted, and so the stereochemistry of the reaction of this molecule with mercuric trifluoroacetate in methanol can give insight into the events occurring after attack on one of the ring bonds. We find that its reaction with the electrophile occurs with 62% inversion and 38% retention of configuration and with 100% inversion of configuration by the nucleophile. We believe these results are best accounted for by edge attack on the ring[3] leading to a corner-mercurated cyclopropane ring **14** (eq 4). Attack on **14** by



(4)

solvent from the rear of C2 or C3 leads naturally to nearly equal amounts of electrophilic inversion (path A) or retention (path B), respectively. Further studies with the other electrophiles are in progress.

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Biochemical Importance of the Binding of Phosphate by Arginyl Groups. Model Compounds Containing Methylguanidinium Ion

Sir:

The number of ways in which phosphate esters participate crucially in life processes is legion. We report here some observations on the way in which phosphate groups are bound by guanidinium ions, including those constituting the side chains of arginyl residues in the enzyme *Staphylococcus* nuclease, which we believe to have fundamental importance and possibly wide relevance in structural biochemistry.

In the course of refinement and interpretation of the structure of the ternary *Staph.* nuclease–thymidine di-