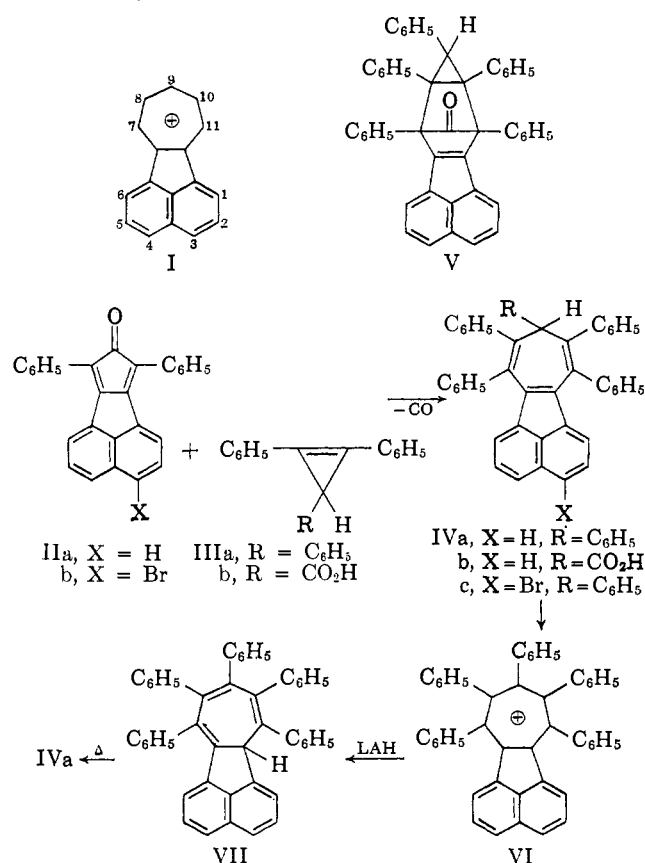each reaction was identical in all respects with the hydrocarbon obtained from the xylene reaction. In addition, the room temperature reaction yielded small amounts of a bright yellow crystalline ketone, m.p. 195–197° dec. (*Anal.* Calcd. for $C_{48}H_{32}O$: C, 92.28; H, 5.16. Found: C, 92.12; H, 5.14), formulated as V on the basis of its thermal behavior (vigorous evolution of gas on melting) and strong carbonyl absorption at 5.65 μ.[2,7]

Solutions of IVa in bromine–carbon tetrachloride slowly evolved hydrogen bromide over a period of several days while depositing in very poor yields the crude amorphous bromide salt VI. The major product in almost 70% yield was a bromine-containing orange solid, m.p. 195–198° (*Anal.* Calcd. for $C_{47}H_{31}Br$: C, 83.55; H, 4.62; Br, 11.83. Found: C, 83.42; H, 4.38; Br, 11.96.), soluble in carbon tetrachloride, benzene and acetonitrile, λ_{max}^{MeCN} 410 (4.17), 342 (4.22), 309 (4.42) and 252 (4.67) mμ. It seemed clear that nuclear substitution of the naphthalene ring had occurred and that the 3-position was the most likely for attack. This was confirmed by direct comparison and identification of the brominated product with independently prepared IVc, available from triphenyl-cyclopropene (IIIa) and 3-bromoacecyclone (IIb), the latter prepared from 3-bromoacenaphthoquinone and dibenzyl ketone.

I

V

X

IIa, X = H　　IIIa, R = C_6H_5
b, X = Br　　b, R = CO_2H

IVa, X = H, R = C_6H_5
b, X = H, R = CO_2H
c, X = Br, R = C_6H_5

IVa ←—Δ—

VII　　　　　　　　　　VI

N-bromosuccinimide in refluxing carbon tetrachloride (catalytic amounts of azobisisobutyronitrile added) improved the yields of pure VI to about 30% after digestion of the crude solid in acetonitrile–acetone. The amorphous crimson salt, m.p. 321–324° dec. (*Anal.* Found: C, 83.36; H, 4.64; Br, 11.63) showed absorption maxima in acetonitrile solution at 475 (4.17), 355 (4.35) and 278 (4.35) mμ. Addition of one drop of ammonium hydroxide completely destroyed this spectrum with the appearance of new bands at

(7) C. F. H. Allen, T. Davis, D. W. Stewart and J. A. VanAllan, *J. Org. Chem.*, **20**, 306 (1955).

355 (4.13) and 337 (sh) (4.02) mμ, λ_{min} 311 (3.87) mμ. Fluoroboric acid restored the original spectrum with virtually no change, establishing the reversibility of hydrolysis without rearrangement.

Lithium aluminum hydride reduction of an ether suspension of VI afforded 78% of a crystalline yellow hydrocarbon isomeric with IVa (*Anal.* Found: C, 94.58; H, 5.42). The infrared and nuclear magnetic resonance spectra of this isomer bear close resemblance to the respective spectra of IVa; however, in the ultraviolet there are striking differences, the yellow isomer showing absorption at 340 (4.23) and 325 (sh) (4.11) mμ, λ_{min} 299 (3.94) mμ. This spectrum is similar to that for hydrolyzed solutions of VI although the bands are somewhat shifted to the blue. On heating to around 200° this same yellow hydrocarbon is converted to the apparently more stable 9H-isomer IVa. While this work was in progress, a report[8] of similar thermal isomerizations of substituted cycloheptatrienes appeared in which evidence was presented that isomerization occurred *via* a 1,5-transannular shift of hydrogen. Consideration of this evidence with the above chemical and physical data leads us to propose VII for the structure of the isomeric hydrocarbon. Further support for this structure was obtained on closer examination of the nuclear magnetic resonance spectra of both IVa and VII.[9] An explanation for the apparent mode of reduction, and perhaps for hydrolysis also, probably lies in steric approach control of the attacking nucleophile.[10]

Further studies of the cyclohept(a)acenaphthylene ring system are currently in progress with immediate attention focused on the preparation of the parent cation I. Simple molecular orbital calculations of the Hückel type suggest I should have unique stability among aryl-fused tropylium ions with a calculated gain in delocalization energy on ionization of 1.99–2.38 β.[11]

(8) A. P. ter Borg, H. Kloosterziel and N. Van Meurs, *Proc. Chem. Soc.*, 359 (1962).

(9) The n.m.r. spectra will be reproduced and fully discussed later in a more detailed publication.

(10) *Cf.* K. Conrow, *J. Am. Chem. Soc.*, **83**, 2343 (1961), for pertinent data on isomer distribution obtained on complex hydride reductions of the methyltropylium ion.

(11) The author is grateful to Dr. J. Nordling and Mr. M. Alvarez of the Quantum Theory Project, University of Florida, for their invaluable aid in the computational programming for these calculations, the details of which will be published separately.

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The Stereospecific Acid- and Base-Catalyzed Ring Opening of a Substituted Cyclopropanol[1]

Sir:

We recently have reported several convenient methods for the synthesis of substituted cyclopropanols.[2] Our interest in these compounds was stimulated originally by reports of their tautomerization. Cottle,[3] for instance, noted that cyclopropanol was readily converted to propionaldehyde in basic solution. Cyclopropanols also undergo acid catalyzed tautomerizations. *We wish to report that cis-1-methyl-2-phenyl-cyclopropanol (I) is isomerized to 4-phenyl-2-butanone (II) by different, stereospecific pathways in acidic and basic solution.*

(1) Supported by a grant from the National Science Foundation.

(2) C. H. DePuy, L. R. Mahoney and K. L. Eilers, *J. Org. Chem.*, **26**, 3616 (1961); C. H. DePuy, G. M. Dappen and R. A. Klein, *ibid.*, **27**, 3742 (1962).

(3) J. K. Magrane, Jr., and D. L. Cottle, *J. Am. Chem. Soc.*, **64**, 484 (1942).

When allowed to react with 0.1 N NaOH in 50:50 (v./v.) dioxane–water solution, I is cleaved almost instantaneously. Although in theory either the 1,2 or the 1,3-bond could be broken, in fact II, the product of 1,2 cleavage, is the exclusive product in quantitative yield (Table I). This reaction finds analogy in the work of Cram and co-workers,[4] who studied the base cleavage of alkoxides. These workers showed that the stereochemistry of the displaced group is dependent on the solvent composition. In solvents of high dissociating power capable of donating protons, inversion of configuration predominates, while in poorly dissociating solvents with a paucity of protons, the reaction occurs with predominant retention. Because the reaction involves carbanions as intermediates, Cram has considered these cleavages to be SE1 reactions (electrophilic substitution at a saturated carbon, monomolecular variety).

Cyclopropanols are also isomerized by acids. For example, I has a half-life of about 40 hr. in 1 M HCl in a 50:50 (v./v.) dioxane–water solution at 50°. This reaction parallels the cleavage of cyclopropanes by HBr and other acids. In contrast to the base-catalyzed cleavage, *acid-catalyzed isomerization of I gives only 40% of II and (60%) of 3-phenyl-2-butanone (III) is*

TABLE I
PRODUCTS FROM THE ACID AND BASE CLEAVAGE OF *cis*-1-METHYL-2-PHENYLCYCLOPROPANOL

	I	II	III
Base catalysis	100%	0%
Acid catalysis	40%	60%

formed. The total yield of the two ketones is quantitative. Because the acid-catalyzed isomerization of cyclopropanols is a bimolecular reaction between the alcohol and a proton,[5] and because of the great differences in product composition between the acid- and base-catalyzed isomerizations, *we consider this acid-catalyzed reaction to be a unique type of an* SE2 *reaction.*

The cleavage reactions as written in Table I are not suitable for a study of the stereochemistry of these processes since no asymmetric carbons are generated at the point of reaction. If D^+/D_2O or OD^-/D_2O is used, however, asymmetry may be present in the product since ample evidence exists that an asymmetric center containing one hydrogen and one deuterium atom may give rise to detectable rotations. The stereochemistry of the acid- and base-catalyzed isomerizations was therefore determined by isomerizing optically active I[6] under essentially the conditions described above, using D_2O in place of H_2O. After ring opening was complete, the products were heated in basic dioxane–deuterium oxide solution to racemize any III present and to ensure approximately equal deuteration of the active methylene groups. Deuterated II was isolated in each case by preparative-scale gas chromatography and shown to be pure by analytical g.p.c. and spectroscopic techniques. Its rotation was determined from neat samples in a 10-cm. tube on a precision Rudolph polarimeter. The results of three runs are given in Table II.

(4) D. J. Cram, A. Lagemann, J. Allinger and K. R. Kopecky, *J. Am. Chem. Soc.*, **81**, 5740 (1959), and subsequent papers.
(5) Unpublished work with R. A. Klein.
(6) Optically active alcohol was obtained by resolution of the corresponding carboxylic acid with brucine, conversion of the acid to the methyl ketone and oxidation to the acetate with peroxytrifluoroacetic acid. The alcohol may be prepared in good yield from the acetate.[2]

TABLE II
SPECIFIC ROTATIONS OF $C_6H_5CHDCD_2COCD_3$ OBTAINED FROM ISOMERIZATION OF ALCOHOL I

| Alcohol I[a] | Ketone II[b] | |
	1.0 M DCl	0.1 M NaOD
+41.5°	−0.35°	+0.34°
−41.9°	+0.46°	−0.27°
−41.9°	+0.46°	−0.42°

[a] Measured in absolute ethanol solution. [b] The rotations given are averages of twelve measurements on each sample with average deviations of 2–5%.

It is obvious from these data that the acid- and base-catalyzed reactions are both stereospecific. Since ketones of opposite sign of rotation are obtained from the same alcohol depending upon whether the reaction is carried out in acid or in base, one reaction must involve retention of configuration, the other inversion. Since in open chain systems base-catalyzed cleavages give inversion of configuration in protonic solvents, *we tentatively conclude that acid-catalyzed cleavage of the carbon–carbon bond in cyclopropanols proceeds with retention of configuration.*[7] The mechanisms which we envisage for these reactions are given in eq. 1 and 2.

$$\text{II} \quad (1)$$

$$(2)$$
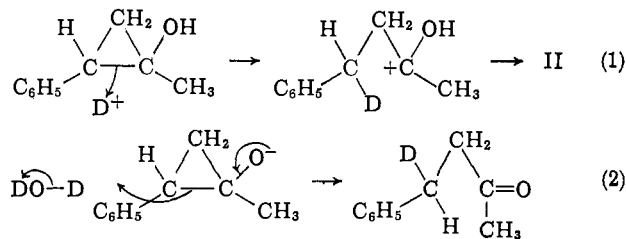
Experiments are now underway in an attempt to determine the absolute configuration of cyclopropanol I and deuterated ketone II by stereospecific syntheses from D-(−)-mandelic acid. In this way an unequivocal conclusion can be drawn about the stereochemistry of the above reactions.

(7) Cyclopropanols also undergo a facile tautomerization when heated in chloroform or carbon tetrachloride solution with at race of oxygen (C. H. DePuy, G. M. Dappen and J. W. Hauser, *J. Am. Chem. Soc.*, **83**, 3156 (1961)). From the data available at that time we concluded that the ring opening reaction was free-radical in character. When suitably substituted cyclopropanols are isomerized under these conditions, however, the product distribution more nearly resembles that expected from an electrophilic attack on the ring. We hope to establish the point conclusively by a stereochemical study of the carbon tetrachloride isomerization. Until that study is complete it seems best to say that our mechanistic conclusions (but not our experimental observations) about the "free-radical" isomerization of cyclopropanols are probably erroneous.
(8) Alfred P. Sloan Foundation Fellow.

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Peroxytrifluoroacetic Acid–Boron Fluoride as a Source of Positive Hydroxyl

Sir:

Peroxytrifluoroacetic acid has been shown to oxidize aromatic hydrocarbons directly to phenols and quinones,[1] to convert aromatic ethers to phenolic ethers[2] and to produce quinones[1] or cyclohexadienones[3] from certain phenols, all presumably by ionic mechanisms. The combination of 90% hydrogen peroxide–boron fluoride etherate also converted aromatic hydrocarbons

(1) R. D. Chambers, P. Goggin and W. K. R. Musgrave, *J. Chem. Soc.*, 1804 (1959).
(2) J. D. McClure and P. H. Williams, *J. Org. Chem.*, **27**, 627 (1962).
(3) J. D. McClure, *ibid.*, **28**, 69 (1963).