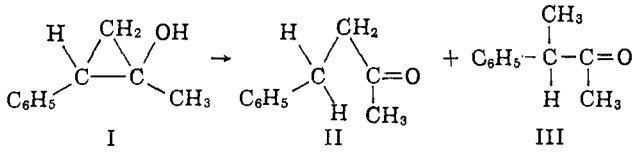
When allowed to react with 0.1 *N* NaOH in 50:50 (v./v.) dioxane–water solution, I is cleaved almost instantaneously. Although in theory either the 1,2 or the 1,3-bond could be broken, in fact II, the product of 1,2 cleavage, is the exclusive product in quantitative yield (Table I). This reaction finds 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 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.*

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%

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]

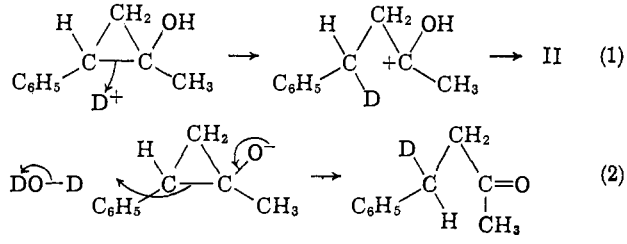
TABLE II

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

	Ketone II[b]	
Alcohol I[a]	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.



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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RECEIVED MARCH 29, 1963

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).

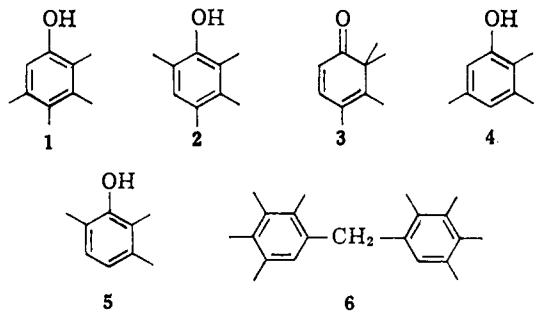
(2) J. D. McClure and P. H. Williams, *J. Org. Chem.*, **27**, 627 (1962).

(3) J. D. McClure, *ibid.*, **28**, 69 (1963).

to phenols and quinones in low yield.[4] We reasoned that coördination of a Lewis acid with an organic peracid might facilitate departure of ionic electrophilic hydroxyl from the latter and furnish a potent oxidant under mild conditions.

This communication reports preliminary results on the use of peroxytrifluoroacetic acid with boron fluoride as a source of positive hydroxyl. Mesitylene was converted directly and rapidly to mesitol in 88% yield, with efficient use of the peracid.[5] Similarly, isodurene gave isodurenol in 62% yield (one experiment).

Extension of the reaction to prehnitene gave, in addition to the expected 2,3,4,5-tetramethylphenol (**1**), a number of other products (**2**–**6**) which reveal the potency of the reactive intermediate formed by this



reagent.[6–9] Attack of OH^+ at a vacant ring position furnishes **1** (9.0%). Similar attack at C-1, followed by a methyl shift, accounts for **2** (3.6%) and **3** (1.8%).[10] The tarry residue (about 27%), which showed no aromatic protons in the n.m.r. and strong C=O and C=C absorption (bands at 1634, 1661, 1695, 1736 and 1750 cm.$^{-1}$), probably contains dimer or polymer from **3** and analogous cyclohexadienones from attack of OH^+ at C-2.

The remaining products (which account for a major fraction of the prehnitene consumed) either lack (**4** and **5**) or have an extra (**6**) carbon atom. Complete absence of trimethylbenzenes and of isomeric trimethylphenols suggests that **4** and **5** arise from loss of the *para* methyl group of **1** and **2**, respectively, according to the scheme shown (for **1**).[11]

(4) J. D. McClure and P. H. Williams, *J. Org. Chem.*, **27**, 24 (1962). It was, however, effective in the Baeyer–Villiger conversion of ketones to esters.

(5) Although the yield when boron fluoride is omitted is reasonably good,[1] the conversion is very poor.

(6) Identification of the products, which were isolated by a combination of distillation and chromatographic techniques, will be described in a full account. All are previously known except **3**, whose structure is based on a satisfactory analysis of its 2,4-dinitrophenylhydrazone, m.p. 153–156°, and on its spectra. In carbon tetrachloride, **3** had bands at 1663 and 1630 cm.$^{-1}$, and in ethanol it had λ_{max} 327 mμ (log ϵ 3.48), which compare favorably with suitable models.[9] Its n.m.r. spectrum in carbon tetrachloride showed singlets at 8.85 and 8.15 τ, corresponding to six protons each, and doublets at 4.19 and 3.15 τ (J = 19 c.p.s.) each corresponding to a single proton.

(7) When the reaction was repeated with boron fluoride, but without the peracid, prehnitene was recovered (94%) unchanged. Study of the reverse conditions (peracid but no boron fluoride) will be reported in a full account.

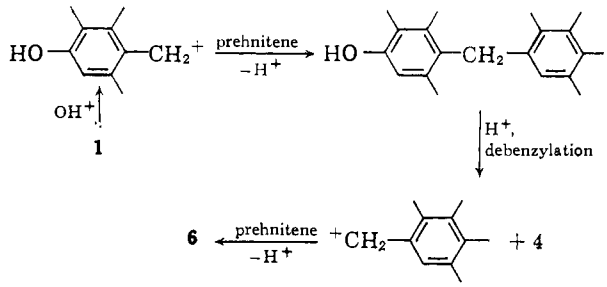
(8) For simplicity, this intermediate will be referred to as OH^+.

(9) See L. Mandell, D. Caine and G E. Kilpatrick, *J. Am. Chem. Soc.*, **83**, 4457 (1961), and leading earlier references therein.

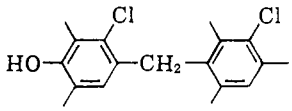
(10) The formation of a cyclohexadienone from 2,6-dimethylphenol and peroxytrifluoroacetic acid[3] is not strictly analogous to the present reaction, since the potential ketonic oxygen was already present in the aromatic substrate. The hydrogen bonding invoked to rationalize the product in ref. 3 is not possible here.

(11) This mechanism requires that the sum of moles of **4** and **5** equal the yield of **6**. In fact, from 0.0332 mole of prehnitene consumed, there was obtained 0.0048 mole of **4**, 0.0017 mole of **5** and 0.0039 mole of **6**. The sum of **4** and **5** is too large, but the yield of these products was determined from v.p.c. curves, whereas that of **6** is of isolated, purified crystalline product and is probably low.

The material balance accounted for 85% of the prehnitene consumed; it is unlikely that any significant products with low molecular weights (under 200) were missed.



Consistent with this scheme is the isolation of **7** as the major product from the reaction of our reagent with



chloromesitylene.[12] The chlorine apparently does not prevent the hydride abstraction, but does inhibit the debenzylation. Nitromesitylene gave a product similar to **7**.

Typical of the experimental procedure is the following preparation of mesitol. To a solution of 56.1 g. (0.468 mole) of mesitylene[13] in 100 ml. of methylene chloride was added peroxytrifluoroacetic acid prepared from 35 g. (0.167 mole) of trifluoroacetic anhydride, 50 ml. of methylene chloride and 4 ml. (0.148 mole) of 90% hydrogen peroxide.[14] Boron fluoride was bubbled through the reaction mixture during the addition, which required 2.5 hr. The reaction was strongly exothermic, and the temperature was kept below 7° by external cooling.[15] After addition was complete, water was added and the organic layer was washed with bisulfite and bicarbonate, dried and distilled. There was obtained 32.0 g. of unchanged mesitylene and 17.7 g. (88%) of mesitol, m.p. 69–70°.

Acknowledgment.—We are grateful to the Petroleum Research Fund of the American Chemical Society for financial support (G-488C).

(12) The structure of **7**, m.p. 142.5–143.5°, is based on a satisfactory analysis, hydroxyl at 3535 cm.$^{-1}$, n.m.r. and mass spectra consistent with the structure, and reduction to products with one or both chlorines removed. We are indebted to Mr. S. Meyerson, American Oil Company, Whiting, Indiana, for mass spectral data and interpretation for **6** and **7**.

(13) Excess hydrocarbon reduces further oxidation of the primary product.

(14) The peracid was prepared by mixing the reagents at 0°, then allowing them to warm to room temperature.

(15) If boron fluoride was omitted, the reaction was much less exothermic and gave mesitol in 47% yield based on peracid; this is, nevertheless, an appreciable improvement over the earlier[1] procedure.

(16) National Science Foundation Coöperative Fellow, 1962–1963.

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RECEIVED MAY 16, 1963

A New Method for the Alkylation of Ketones and Aldehydes: the C-Alkylation of the Magnesium Salts of N-Substituted Imines

Sir:

The difficulties involved in monoalkylating ketones and aldehydes are well known. As we have pointed out in a previous communication,[1] the enamine alkylation procedure which was devised to circumvent some of these difficulties is general only with electrophilic olefins (conjugated ketones, esters, nitriles, etc.). With alkyl halides, however, it has turned out that although

(1) G. Stork, A. Brizzolarra, H. Landesman, J. Szmuszkovicz and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).