of its ir and nmr spectra with reference spectra. Saponification of 0.0624 g of **5** was accomplished by refluxing with 1 ml of concentrated hydrochloric acid for 20 min, cooling, and then removing the water by placing the mixture in a vacuum desiccator along with a beaker of concentrated sulfuric acid. This procedure furnished a 59% yield of glutaric acid, mp and mmp 96.2–97.2° (lit.[14] mp 97°).

Anal. Calcd for $C_7H_{14}O_4$: C, 52.49; H, 7.55. Found: C, 52.39; H, 7.58.

Compound **6** was proven to be dimethyl adipate by comparison of its ir and nmr spectra with reference spectra. Saponification of 0.0697 g of **6** *vide supra* gave adipic acid in 55% yield, mp and mmp 150.5–151.5° (lit.[15] mp 150–151°).

Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 54.94; H, 7.97.

The yields[16] of esters **3a**, **4**, **5**, and **6** based on **2a** were 13, 16, 9, and 8%, respectively.

Ozonization of **2a** was also carried out in 95% acetic acid at temperatures of 6, 60, and 80°, requiring 3.66, 1.5, and 1.33 hr, respectively, for completion. The yields[16] of esters **3a**, **4**, **5**, and **6** based on **2a** are, respectively, as follows: 19, 17, 8, and 8% for the 6° reaction; 8, 20, 10, and 7% for the 60° reaction; and 8, 29, 7, and 9% for the 80° reaction.

***exo*-7-Phenylnorcarane[2] (2b).** To a stirred solution of 41 g of potassium *tert*-butoxide[8] and 230 ml of dry dimethyl sulfoxide (CaH_2) was added 9.6 g of **2a**[9] (99% pure) and then the mixture was heated to 100° under a nitrogen atmosphere for 25 hr. The reaction mixture was hydrolyzed and extracted with ether, and the extract washed with water and then dried over $CaCl_2$. Evaporation of the solvent and subsequent distillation of the residue, utilizing a Nester/Faust Auto Annular spinning band distillation column, resulted in 8.31 g (87% yield) of **2b** (98% pure), bp 126–127° (11 mm).

Ozonolysis of *exo*-7-Phenylnorcarane[5] (2b). Ozonolysis of **2b** (98% pure) was carried out in exactly the same manner described for **2a**. The time required for this reaction at 25° was 1.16 hr. The order of elution of the four methyl esters obtained is **4**, **3b**, **5**, and **6**. The faster eluting compounds, **4** and **3b**, have previously been identified as methyl benzoate and *exo*-7-carbomethoxynorcarane, respectively.[1]

Compound **5** was shown to be dimethyl glutarate by comparison of its ir and nmr spectra with reference spectra. Saponification of 0.0829 g of **5** *vide supra* gave an 83% yield of glutaric acid, mp and mmp 95.7–96.7° (lit.[14] mp 97°).

Anal. Calcd for $C_7H_{12}O_4$: C, 52.49; H, 7.55. Found: C, 52.58; H, 7.53.

Compound **6** was proven to be dimethyl adipate by comparison of its ir and nmr spectra with reference spectra. Saponification of 0.0805 g of **6** *vide supra* furnished a 68% yield of adipic acid, mp and mmp 150.3–151.8° (lit.[15] 150–151°).

Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.43; H, 8.14.

The yields[16] of esters **3b**, **4**, **5**, and **6** based on **2b** were 25, 11, 10, and 5%, respectively.

Ozonization of **2b** was also carried out in 95% acetic acid at temperatures of 6 and 80°, requiring 1.66 and 0.83 hr, respectively, for completion. The yields[16] of esters **3b**, **4**, **5**, and **6** based on **2b** for the 6° reaction were 23, 8, 7, and 4%, respectively, while the yields for the 80° reaction were 11, 17, 14, and 4%, respectively.

Acknowledgment. The authors wish to acknowledge the financial support (Grant AE-361) of The Robert A. Welch Foundation.

Registry No.—**2a**, 10503-37-4; **2b**, 10503-36-3; **5**, 1119-40-0; **6**, 627-93-0.

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Oxidation of Olefins by Mercuric Salts. The Alkaline Decomposition of Oxymercurials

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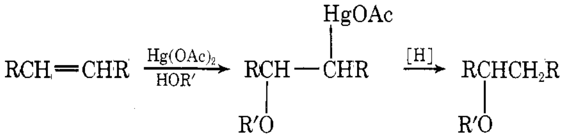
The increasing interest shown in the oxymetalation of olefins in the past few years has mirrored the fast growing field of organometallic chemistry. Among oxymetalation reactions oxymercuration occupies a position of considerable importance and the number of recent reviews is a clear testimony to this.[1-4]

The interaction of alkenes with mercuric salts yields oxymercurials which can either be reduced as typical organo-



$$RCH{=}CHR \xrightarrow[HOR']{Hg(OAc)_2} \underset{R'O}{\underset{|}{RCH}}{-}\overset{HgOAc}{\overset{|}{CHR}} \xrightarrow{[H]} \underset{R'O}{\underset{|}{RCHCH_2R}}$$

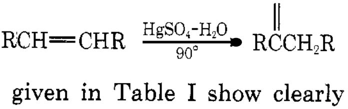
mercury compounds[5] or be thermally decomposed in acidic medium as in the Denigés reaction to give directly oxidized organic moieties and reduced mercury species.[6]

We have studied the thermal decomposition of these organomercurials in alkaline medium and found quite a different behavior from that observed in acidic medium. Thus when basic solutions containing oxymercurials are heated, a mixture of ketone and epoxide as the oxidized organic moiety is obtained.[7]

Results and Discussion

The study was first carried out under experimental conditions analogous to the Denigés reaction[6] and then by synthesizing the desired oxymercurial and following its thermal decomposition in a chosen medium.

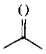
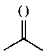
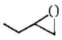
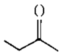
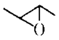
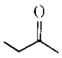
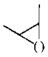
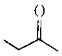
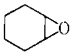
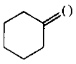
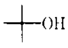
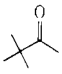
Aqueous Medium. The general procedure was to stir a suspension of mercuric salt in the presence of olefin. The solution obtained was then made basic and heated. At the end of the reaction, addition of hydrochloric acid regenerated the starting olefin and thus allowed an estimation of the advancement of the reaction, *i.e.*, per cent conversion.



$$RCH{=}CHR \xrightarrow[90°]{HgSO_4\text{-}H_2O} R\overset{O}{\overset{\|}{C}}CH_2R$$

The results given in Table I show clearly lower yields with propene and 1-butene. This can easily be explained if one considers the possibility of allylic oxidation of α-olefins analogous to that observed in acidic medium; such oxidations generally yield α,β-unsaturated carbonyl compounds which can be expected to be unstable under the reaction conditions.[6] This was shown to be the case by introducing compounds such as acrolein or methyl vinyl ketone in the

Table I
Oxidation of Olefins with Mercuric Salts at pH 13[a]

Substrate	Salt	Products (%)[b]		Total yield, %[c]	Conversion, %[d]
Propene (115-07-1)	$HgSO_4$ (7783-35-9)	 (6)	 (94)	51	7
Propene	$Hg(OAc)_2$ (1600-27-7)	 (4)	 (96)	43	9
1-Butene (106-98-4)	$HgSO_4$	 (7)	 (93)	30	13
2-Butene (trans) (624-64-6)	$HgSO_4$	 (64)[c]	 (36)	72	49
2-Butene (cis) (590-18-1)	$HgSO_4$	 (44)[e]	 (56)	62	56
Cyclohexene (110-83-8)	$HgSO_4$	 (84)	 (16)	48	f
Isobutene (115-11-7)	$HgSO_4$	 (32)	 (68)	63	11
2,3-Dimethyl-2-butene (563-79-1)	$HgSO_4$	 (100)		g	f

[a] Registry nos. are given below each compound. [b] Relative amount by glpc analysis. [c] Total yield by glpc analysis using an internal standard. [d] % olefin reacted based on olefin regenerated upon hydrochloric acid addition. [e] 95% isomeric purity. [f] Not determined. [g] Could not be determined accurately because decomposition occurred partially during the organomercurial preparation.

Table II
Influence of Various Variables on the Reaction of *trans*-2-Butene with Mercuric Salts in Alkaline Medium

		Degree of influence		
Variables	Experimental range	% epoxide[a]	% total yield[b]	% conversion[c]
Salt concentration	0.1–0.9 mol/l.	***[d] (−32.2)[e]	*** (12.4)	*** (22.4)
pH	9–13	* (3.4)	* (5.9)	* (−2.7)
Reaction temperature	78–93°	* (−5.5)	*** (31)	*** (25.7)
Reaction time	2–6 hr	** (6.7)	*** (14.1)	*** (13.4)
N_2 flow	4–8 l./hr	0 (−2.9)	0 (−2.9)	0 (−1.7)
Salt nature	$HgSO_4$–$Hg(OAc)_2$	** (−12)	*** (−13.4)	** (8.7)

[a] Relative amount by glpc analysis. [b] Total yield of epoxide and ketone by glpc analysis. [c] % olefin reacted based on olefin regenerated upon hydrochloric acid addition. [d] Degree of significance of the influence measured by statistical methods and symbolized from very significant (***) to not significant (0).[9] [e] Direction and amplitude of the influence obtained from two-level fractional factorial plans.[9]

reaction medium and observing a very rapid polymerization.

The isomeric purity of the oxides obtained from *cis*- or *trans*-2-butene strongly suggests two successive stereoselective steps; most probably a trans addition to give the intermediate oxymercurial followed by a trans intramolecular attack to give the epoxide. The higher yield in epoxide in the case of cyclohexene is also indicative of such a process since it has been shown that with this olefin the hydroxyl group and the mercury atom are trans to each other which through a rapid aa ⇄ ee equilibrium facilitates a trans intramolecular attack.[8]

The use of olefins whose structures do not allow ketone formation did not always give high yields of epoxide; with isobutene a large quantity of *tert*-butyl alcohol was obtained and with 2,3-dimethyl-2-butene the only product was *tert*-butyl methyl ketone.

In order to obtain a deeper insight we studied the various variables that could influence this reaction. *trans*-2-Butene was chosen arbitrarily and a series of reactions was carried out using six variables.

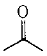
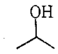
The Variance Analysis Technique was utilized and a relatively limited number (20) of experiments permitted the determination of the influence of each variable on the yield and selectivity of the reaction.[9]

The results given in Table II show firstly a great influence of the oxymercurial concentration and a little or no influence of the pH on the yield and selectivity. If by analogy with the reaction in acidic medium, one considers the formation of the ketone, *via* an intramolecular rearrangement of the oxymercurial accompanied by a 1,2-hydride shift, the first observation is not surprising. What is more unexpected, however, is the nondependence of the hydroxide concentration on the rate of product formation as can be seen from the small influence of the pH on the per cent conversion. Although this is in accord with a ketone formation by the path described above, it forbids a full analogy with the process of epoxide formation from 1,2-chlorohydrins which has been shown to be base dependent.[10]

The results in Table II also show a very significant influence of the temperature and the reaction time on the per cent conversion. This is not unexpected; however, the fact that the selectivity in epoxide fell with reaction time left a doubt as to the possibility of isomerization of epoxide into ketone. Such rearrangements have been reported in the presence of organometals.[11] We thus introduced pure epoxide in a mixture containing mercuric sulfate under identical experimental conditions and at a rate close to which it is formed and observed no ketone formation.

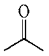
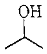
All these observations as well as those given in Table I

Table III
Thermal Decomposition of 1-Chloromercuri-2-hydroxypropane in the Presence of Potassium Alkoxide (ROK) in Alcohol (ROH)

R	ε[a]	Products, %			Yields, %	Conversion, %
						
Ethyl[b]	24.3	60	38	2	20	36
n-Butyl	18.2	78	21	1	21	47
sec-Butyl	15.8	87	11	2	83	94

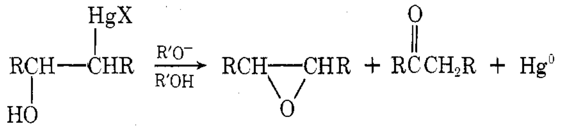
[a] Dielectric constant of the alcohol at 25°. [b] Reaction temperature: refluxing ethanol, 78°.

Table IV
Thermal Decomposition of 1-Halomercuri-2-hydroxypropane in the Presence of Potassium *n*-Butoxide in *n*-Butyl Alcohol

Halogen	Registry no.	Products, %			Yields, %	Conversion, %
						
Cl	52358-07-3	78	21	1	21	47
Br	18832-83-2	35	65		14	50
I	5323-64-8	4	96		36	60

clearly indicate two parallel decomposition paths of the intermediate oxymercurial, one leading to the ketone and one to the epoxide.

Nonaqueous Medium. The general procedure consisted of adding to the potassium alkoxide solution the previously prepared halomercurial and heating the resulting mixture.



$$\underset{HO}{RCH}\text{—}\overset{HgX}{CHR} \xrightarrow[R'OH]{R'O^-} RCH\text{—}CHR\ (\text{—O—}) + R\overset{O}{\overset{\|}{C}}CH_2R + Hg^0$$

R′ = H, alkyl

The results given in Table III show that both the yield and the selectivity in epoxide increase with decreasing dielectric constant of the medium. This again points out the dissimilarity with the epoxide formation from chlorohydrins; thus, the formation of an intermediate 1-chloromercuri-2-alkoxide analogous to the 2-chloroethoxide proposed by Swain would be expected to be facilitated in solvents with higher dielectric constants, whereas the opposite was observed.[12]

On the other hand the ease of formation of ketone seems to be influenced by the character of the mercury atom as a leaving group. This was shown by varying the halogen on the oxymercurial. The results are given in Table IV.

The results obtained both in aqueous and nonaqueous medium, although not allowing the establishment of a detailed mechanism, clearly indicate two distinct decomposition paths: one leading to epoxide formation most probably by an intramolecular attack, somehow different from that of 1,2-chlorohydrins, and a second leading to ketone apparently driven by the departure of the mercury atom.

Experimental Section

Materials. All olefins used were commercially available and were used as obtained after verifying their purity by glpc on a 12 m × 6 mm column of 30% dimethylsulfolane on Chromosorb P at 25°. All solvents were purified by distillation following standard methods. Mercuric salts (Prolabo) and alkali metals (Prolabo) were used without further purification.

Oxidation Procedure. The general procedure was discussed in the text. All product analyses were carried out by glpc using tetrahydrofuran as an internal standard. Products were identified by spectroscopic methods on preparative glpc purified samples and compared with authentic samples.

Aqueous Medium. A suspension of 80 mmol of mercuric salt in 150 ml of water was placed under an atmosphere of gaseous olefin. In the case of liquid olefins, the stoichiometric amount of substrate was added to the aqueous suspension and stirring continued for 1 hr. The resulting solution was then placed in the reaction vessel equipped with a gas inlet tube, a mechanical stirrer, and a reflux condenser kept at 60–65°. The mixture was rendered basic (pH 13) by slowly adding 14 g of potassium hydroxide and then heated to 100° for 6 hr. The products formed were swept out by a continuous flow of nitrogen gas (5 l./hr) and collected in two flasks placed in series and cooled to −45°. After cooling the reaction mixture, hydrochloric acid was added and the amount of olefin regenerated was measured.

Nonaqueous Medium. To the desired potassium alkoxide (80 mmol) in 100 ml of alcohol, placed in the reaction vessel described for the aqueous reaction, was added a 100-ml alcoholic solution containing 80 mmol of the previously prepared 1-halo-2-hydroxypropane. Heating the mixture for 6 hr at 82° while nitrogen gas swept the system gave the reaction products which were collected and analyzed in a manner analogous to the reaction in water.

Preparation of 1-Halomercuri-2-hydroxypropane. The procedure followed was the one described by Hofmann and Sand.[13] A 300-ml aqueous solution containing 200 g (0.63 mol) of mercuric acetate was placed under an atmosphere of propene. Vigorous agitation resulted in the absorption of 13.24 l. of gas. The solution obtained was neutralized by adding slowly 40 g (0.7 mol) of potassium hydroxide dissolved in 100 ml of water, adjusted to neutrality with CO_2 and then divided into three aliquots. Each part was then treated separately with 0.21 mmol of sodium chloride, bromide, and iodide to give white precipitates which were filtered and recrystallized from diethyl ether. The products obtained were respectively: 1-chloromercuri-2-hydroxypropane (42 g, 68% yield), mp 51° (lit.[13] 53°); 1-bromomercuri-2-hydroxypropane (54 g, 75% yield), mp 78° (lit.[13] 76°); and 1-iodomercuri-2-hydroxypropane (40 g, 50% yield), mp 65° (lit.[13] 68°). All solids were stored under nitrogen and in the dark before use.

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A Kinetic Study of the Thermal Decomposition of (*Z*)-*N*-*tert*-Butyl-α-phenylnitrone[1,2]

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The vapor-phase pyrolysis of 2-*tert*-butyl-3-phenyloxaziridine (1) was described by Emmons in 1957.[3] The prod-