and there is a reaction between aqueous periodate and *p*-hydroxyphenyl phosphate which gives *p*-quinone and inorganic phosphate, and which is very much faster than the direct hydrolysis of the phosphate.[20]

(1958); T. Wieland and F. Pattermann, *Angew. Chem.*, **70**, 313 (1958); A. Lapidot and D. Samuel, *J. Am. Chem. Soc.*, **86**, 1886 (1964).
(19) T. C. Bruice and S. Benkovic, "Bio-organic Mechanisms," Vol. II, W. A. Benjamin, Inc., New York, N. Y., 1966, p 92.

For reactions of *p*-hydroxyphenyl phosphate in the presence of oxidizing agents both phosphorus– and carbon–oxygen fission is observed.[18,19] In our reactions the very low solubility of the carboxylic esters in water makes it very difficult to use tracer methods to differentiate between the two possible bond fissions.

(20) J. Hellyer, unpublished results.

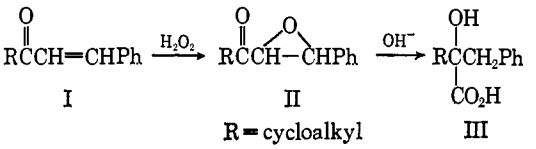
The Base-Induced Rearrangements of α-Epoxy Ketones

Gino R. Treves, Hugo Stange, and R. A. Olofson

Contribution from the Chemical Research and Development Center, FMC Corporation, Princeton, New Jersey 08540. *Received May 31, 1967*

Abstract: Although 1,3-diaryl-2,3-epoxypropanones generally yield glycolic acids *via* a benzylic acid type rearrangement on treatment with aqueous or alcoholic alkali, the related 1-aryl-3-cycloalkyl-2,3-epoxypropanones ordinarily react by a different pathway. The 3-cyclohexyl, 3-cyclopentyl, and 3-cyclobutyl derivatives rearrange to a mixture of γ-lactones and β,γ-unsaturated acids. The 3-cyclopropyl derivative is, however, converted into the glycolic acid on base treatment.

In connection with work in these laboratories on the biological activity of certain glycolate esters, a variety of acids of the general structure III were required. The planned synthetic procedure involved the conversion by known methods of the appropriate α,β-unsaturated ketone I *via* the epoxy ketone II to the glycolic acid III.

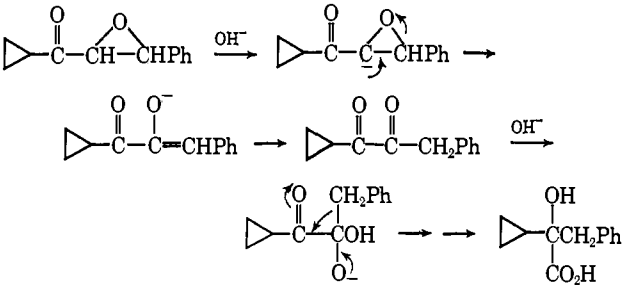


I II R = cycloalkyl III

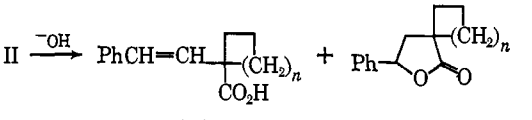
The readily synthesized α,β-unsaturated ketones I appear to be the *trans* isomers as judged by the nmr chemical shifts and coupling constants (Table I). These were successfully converted to the α-epoxy ketones II with hydrogen peroxide and sodium hydroxide in an aqueous–ethanolic–acetone solution. An examination of the nmr coupling constants between the two epoxide protons reveals that these compounds are also of the *trans* configuration (Table I). Further, Black and Lutz[1] have shown that both the *cis* and *trans* isomers of chalcone react with alkaline hydrogen peroxide to produce the same *trans*-epoxy ketone.

When the epoxy ketones II were treated with an aqueous or aqueous–alcoholic–sodium hydroxide solution only 1-cyclopropyl-3-phenyl-2,3-epoxypropan-1-one (II, R = cyclopropyl) gave the "normal" benzilic acid type rearrangement product, the substituted glycolic acid III (R = cyclopropyl). This rearrangement has been accomplished with a number of related epoxidized benzylideneacetophenones[2] and the mechanism studied in careful detail.[3] By analogy with this work, the mechanism of rearrangement of II (R = cyclopropyl) is pictured in Scheme I.

Scheme I



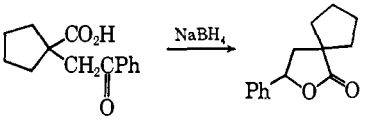
An unexpected rearrangement occurred when the epoxides II (R = cyclohexyl, cyclopentyl, and cyclobutyl) were refluxed in aqueous or aqueous–alcoholic–sodium hydroxide solution. Two product types were isolated and identified by elemental analyses and infrared and nmr spectroscopy as the β,γ-unsaturated acids IV and the γ-lactones V. The acids, as indicated by the nmr coupling constants, appear to be all of *trans* configuration. Compound V (*n* = 2) also was



IV V

n = 1, 2, 3

obtained from the known keto acid VI[4,5] by reduction with sodium borohydride. The mechanism we



VI V (*n* = 2)

(1) W. B. Black and R. E. Lutz, *J. Am. Chem. Soc.*, **75**, 5990 (1953).
(2) O. Widman, *Chem. Ber.*, **49**, 477 (1916); H. Jörlander, *ibid.*, **49**, 2782 (1916); W. Baker and R. Robinson, *J. Chem. Soc.*, 1798 (1932).
(3) C. J. Collins and O. K. Neville, *J. Am. Chem. Soc.*, **73**, 2471 (1951); O. K. Neville, *ibid.*, **70**, 3499 (1948); W. von E. Doering and R. S. Urban, *ibid.*, **78**, 5938 (1956).

(4) S. C. Sen-Gupta, *J. Indian Chem. Soc.*, **11**, 390 (1934).
(5) M. A. Saboor, *J. Chem. Soc.*, 922 (1945).

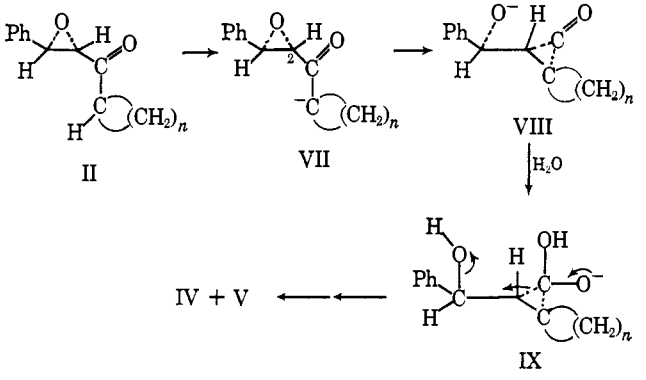
Table I. Nmr δ and J Values (cps) for I and II[a]

	$RCH^A{=}CH^B{-}COPh$		$RCH^A{-}CH^B{-}COPh$ (epoxide)	
	δ (I)[b]	$J_{H^A-H^B}$ (I)	δ (II)[c]	$J_{H^A-H^B}$ (II)
Cyclohexyl	6.72–7.04	16.1	3.40–3.84	1.6
Cyclopentyl	6.71–7.53	16.6	3.37–3.87	2.0
Cyclobutyl	6.64–7.52	17.4	3.49–3.92	2.0
Cyclopropyl	6.81–7.60	16.3	3.53–4.05	1.6
cis-Benzylideneacetone	...	12[d]	...	...
trans-Benzylideneacetone	...	16.5[d]	...	...
cis-3,4-Epoxy-2-butanone	...	...	...	5.54[e]
trans-3,4-Epoxy-2-butanone	...	...	...	1.64[e]
General *J cis*[f]	...	6.5–12.3[g]	...	2.2–5.0[h]
General *J trans*[f]	...	13.7–18.0[g]	...	1.4–2.7[h,i]

[a] Spectra were run on a Varian Model A-60 spectrometer in deuteriochloroform using tetramethylsilane as an internal reference. [b] The values reported are for the olefinic protons. [c] The values reported are for the epoxide ring protons. [d] H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959). [e] C. A. Reilly and J. P. Swalen, *ibid.*, **32**, 1378 (1960). [f] J_{vic} for ethylenes and epoxides. [g] E. O. Bishop and R. E. Richards, *Mol. Phys.*, **3**, 114 (1959). [h] K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *J. Am. Chem. Soc.*, **86**, 762 (1964). [i] J. L. Pierre, P. Chautemps, and P. Arnaud, *Compt. Rend.*, **261**, 4025 (1965).

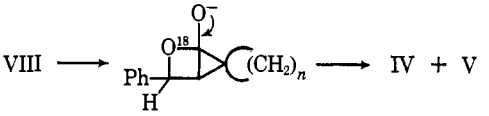
propose for the rearrangement of II to IV and V (Scheme II) is similar to that delineated by Loftfield[6] for the Favorskii rearrangement of 2-chlorocyclohexanone and other α-halo ketones, by Kende[7] for a similar rearrangement of α,β-dihalo ketones, and by Achmad and Cavill[8] for the rearrangement of pulegone dibromide or pulegone epoxide. Our epoxy ketone II first reacts with hydroxide ion to remove the tertiary hydrogen from the cycloalkyl group as a proton. The resulting enolate VII displaces O^- from C-2 of the epoxide ring to produce Loftfield's cyclopropanone intermediate VIII, a species which has received general acceptance as the key intermediate in most Favorskii-type rearrangements.[9] Protonation of the O^- and attack of the carbonyl in the Favorskii manner gives IX which is transformed to IV and V.

Scheme II



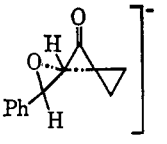
The Loftfield mechanism implies that the formation of the cyclopropanone ring is synchronous with an internal SN2-type displacement on the halogen-bearing carbon atom with consequent inversion at that center. This process suggests that VIII has the stereochemistry pictured. That the Favorskii rearrangement proceeds in a stereospecific manner was shown by Stork and Borowitz[10] for a pair of epimeric 1-chloro-1-acetyl-2-methylcyclohexanes. House and Gilmore,[11] however, have found that the amount of stereospecificity is dependent on the polarity of the reaction medium. The less polar environment, sodium methoxide in 1,2-dimethoxyethane, favors an essentially stereospecific process while in sodium methoxide–methanol a mixture of epimers is formed. A similar result was obtained by Achmad and Cavill[8] (*vide supra*).

An alternate mechanism involving attack of the O^- in Loftfield's intermediate VIII on the cyclopropanone carbonyl to produce the intermediate XI was rejected on the basis of a labeling experiment. 1-Cyclohexyl-



3-phenyl-2-propen-1-one was epoxidized with O^{18} hydrogen peroxide and the resulting epoxide II was rearranged to IV. The intermediacy of species X requires that the carboxylic acid IV be labeled with O^{18} in the carboxyl groups. This was not the case.

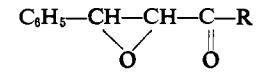
The fact that the cyclopropyl epoxy ketone II does not undergo the above rearrangement is easily rationalized at this point. First, generation of the analogous cyclopropanone requires the intermediacy of the highly strained transition state XI. Second, the epoxy



proton at C-2 should be more acidic than the tertiary cyclopropyl proton because of the electron-withdrawing inductive effect of the epoxy oxygen. (This internal comparison does not necessarily hold for the larger ring system; *vide infra*.) Loss of this former proton constitutes the initial step in the benzilic acid rearrangement observed in this case (Scheme I). Third, when compared with the hydrogen at C-2 the tertiary cycloalkyl hydrogens in four-, five-, and six-membered ring series should be more acidic than the cyclopropyl proton. It is well known that the opposite is true in

(6) R. B. Loftfield, *J. Am. Chem. Soc.*, 73, 4707 (1951).
(7) A. S. Kende, *Org. Reactions*, 11, 278 (1960).
(8) S. A. Achmad and G. W. K. Cavill, *Australian J. Chem.*, **16**, 858 (1963).
(9) N. J. Turro and W. B. Hammond, *J. Am. Chem. Soc.*, 87, 3258 (1965).
(10) G. Stork and L. J. Borowitz, *ibid.*, **82**, 4307 (1960).
(11) H. O. House and W. F. Gilmore, *ibid.*, **83**, 3980 (1961).

Table II. α-Epoxy Ketones



R	Bp (mm) or mp, °C	Yield, %	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
Cyclohexyl	124 (0.16)	71	$C_{15}H_{18}O_2$	78.23	7.88	77.78	7.88
Cyclopentyl	110–120 (0.16)	47	$C_{14}H_{16}O_2$	77.75	7.46	77.93	7.63
Cyclobutyl	132–140 (0.005)	50	$C_{13}H_{14}O_2$	77.20	6.98	77.25	6.98
Cyclopropyl	56–57	72	$C_{12}H_{12}O_2$	76.57	6.43	76.65	6.58

simple hydrocarbons; cyclopropyl hydrogens are ordinarily more acidic than similar hydrogens in less strained rings. However, it has been shown by Walborsky[12] that tetrahedral cyclopropyl carbanions are not readily rehybridized to planar sp^2 carbanions even when the possibility of overlap with the π orbital of an adjacent polar multiple bond exists. Therefore, the rate of loss of our tertiary cyclopropyl hydrogen depends only on the intrinsic acidity conferred by the cyclopropane ring and on the electron-withdrawing inductive effect of the adjacent carbonyl. The major rate-enhancing factor assisting the removal of the tertiary hydrogens in the larger cycloalkyl carbonyl systems is not the above but, instead, the much more important resonance stabilization gained as the carbanion forms. In other words, a cyclopropyl carbonyl carbanion is only a carbanion; but a cyclohexyl carbonyl carbanion is an enolate and thus much more readily generated.

Experimental Section

Cycloalkyl Methyl Ketones. All the cycloalkyl methyl ketones have been described by Mariella and Raube[13] who obtained them by the reaction of cycloalkanecarboxylic acid and acetic acid over a manganous carbonate catalyst at 380°. We found it more convenient to utilize the Rupe rearrangement of commercially available 1-ethynylcyclopentanol and 1-ethynylcyclohexanol using the procedure of Newman[14] and subsequent hydrogenation of the known 1-cyclopenten-1-yl[15] and 1-cyclohexen-1-yl[14] methyl ketones to the cyclopentyl and cyclohexyl methyl ketones. Cyclobutyl methyl ketone was prepared by the method of Overberger and Lebovitz[16] utilizing the general procedure of Walker and Hauser[17] involving reaction of an acid chloride with diethyl ethoxymagnesiomalonate followed by hydrolysis and decarboxylation of the acylmalonate. Cyclopropyl methyl ketone was obtained commercially.

Cycloalkyl Styryl Ketones. The cycloalkyl styryl ketones were all prepared by the base-catalyzed condensation of benzaldehyde with the appropriate cycloalkyl methyl ketone and are described by Mariella and Raube,[13] who used as a condensing agent an aqueous sodium hydroxide solution and a reaction period of 7–9 days. We used an aqueous–methanolic solution of sodium hydroxide and a reaction period of 16–22 hr to obtain cycloalkyl styryl ketones in following yields, cyclohexyl 60%, cyclopentyl 71%, cyclobutyl 21%, and cyclopropyl 75%. In the preparation of cyclobutyl styryl ketone some product was obtained directly and from hexane mother liquors a product whose nmr and infrared spectra were consistent with the structure of the aldol intermediate, 1-cyclobutyl-3-hydroxy-3-phenyl-1-propanone, which on treatment with *p*-toluenesulfonic acid gave additional ketone. The nmr δ and J values listed in Table I indicate that the compounds isolated are the *trans* isomers.

(12) H. M. Walborsky, A. A. Youssef, and J. M. Motes, *J. Am. Chem. Soc.*, **84**, 2465 (1962).
(13) R. P. Mariella and R. R. Raube, *ibid.*, **74**, 518 (1952).
(14) M. S. Newman, *ibid.*, **75**, 4740 (1953).
(15) W. J. Rosenfelder and D. Ginsburg, *J. Chem. Soc.*, 2955 (1954).
(16) C. G. Overberger and A. Lebovitz, *J. Am. Chem. Soc.*, **76**, 2722 (1954).
(17) H. G. Walker and C. R. Hauser, *ibid.*, **68**, 1386 (1946).

1-Cycloalkyl-3-phenyl-2,3-epoxypropan-1-ones. The epoxy ketones were all prepared by the reaction of the α,β-unsaturated ketones with alkaline hydrogen peroxide according to the general procedure originally used by Weitz and Scheffer,[18] and by a number of other investigators particularly for the preparation of 1,3-diaryl-2,3-epoxypropan-1-ones. Table II lists the analytical data, physical constants, and yields for the isolated materials. The nmr δ and J values which appear in Table I are consistent with a *trans* configuration for these compounds.

1-Cyclohexyl-3-phenyl-2,3-epoxypropan-1-one. To 62 g (0.29 mole) of 1-cyclohexyl-3-phenyl-2-propen-1-one in 760 ml of a solution of equal parts of acetone and ethanol, 56.8 ml of a 4 *N* sodium hydroxide solution was added, followed by the dropwise addition of 83.4 ml of 30% hydrogen peroxide, the temperature being maintained at 40–47° during this process. The mixture was stirred for an additional hour and poured over ice, the product extracted with toluene and ether, and the organic layer washed with water and dried over magnesium sulfate. The solvent was evaporated under reduced pressure and the epoxide isolated from the residue by distillation.

1-Cyclopentyl-3-phenyl-2,3-epoxypropan-1-one. To 97 g (0.48 mole) of 1-cyclopentyl-3-phenyl-2-propen-1-one in 648 ml of a solution of equal parts of acetone and ethanol, 97 ml of 4 *N* sodium hydroxide solution was added followed by the dropwise addition of 149 ml of 30% hydrogen peroxide. The temperature was maintained at 40–55° during the addition. The reaction mixture was stirred for an additional 18 hr and then poured over ice. The product was isolated according to the above procedure.

1-Cyclobutyl-3-phenyl-2,3-epoxypropan-1-one. To 14 g (0.025 mole) of 1-cyclobutyl-3-phenyl-2-propen-1-one and 18 ml of 2 *N* sodium hydroxide solution in 180 ml of methanol at 10° was added 24 ml of 15% hydrogen peroxide. The reaction mixture then was allowed to stir at room temperature for 1 hr, poured over ice, and extracted with ether. The ether layer was dried over magnesium sulfate and the product isolated by evaporation and distillation.

1-Cyclopropyl-3-phenyl-2,3-epoxypropan-1-one. To a stirred mixture of 103 g (0.6 mole) of 1-cyclopropyl-3-phenyl-2-propen-1-one in 1.5 of methanol and 144 ml of 2 *N* sodium hydroxide solution at 10° was added 192 ml of 15% hydrogen peroxide. The reaction mixture was stirred at 35° for 3 hr and poured over ice. The solid material which precipitated was filtered and recrystalized from hexane.

1-Styryl-1-cyclohexanecarboxylic Acid and 1-(β-Hydroxyphenethyl)-1-cyclohexanecarboxylic Acid γ-Lactone. To 200 ml of 10% sodium hydroxide solution, 43 g (0.187 mole) of 1-cyclohexyl-3-phenyl-2,3-epoxypropan-1-one was added and the mixture heated under reflux for 3 hr. It was then cooled, acidified with dilute hydrochloric acid, and extracted with ether. The ether solution was extracted with a 1 *N* sodium carbonate solution, washed with water, and dried over magnesium sulfate. After removal of the ether, the residue was recrystallized from hexane giving 15 g (35%) of the lactone, mp 68–69°; infrared: 5.69 μ (KBr); nmr: δ 1.67 (broad singlet, ten protons), 1.88 (quartet, one proton, J = 12, 10 cps), 2.61 (quartet, one proton, J = 12, 7 cps), 5.35 (quartet, one proton, J = 10, 7 cps), and 7.32 (singlet, five protons) (CCl_4).

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.49; H, 7.78.

Upon acidification with dilute hydrochloric acid of the combined carbonate and water solutions, 11 g (26%) of the acid, mp 115–122°, was obtained. Recrystallization from hexane raised the melting point to 126–128°; infrared: 3.5 (broad) and 5.97 μ (KBr); nmr: δ 1.5–2.2 (broad, ten protons), 6.07 (doublet, one proton, J = 16 cps), 6.49 (doublet, one proton, J = 16 cps), 7.28 (multiplet, five protons), and 12.25 (singlet, one proton) (CCl_4).

(18) E. Weitz and A. Scheffer, *Chem. Ber.*, **54**, 2327 (1921).

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.17; H, 8.09.

1-Styryl-1-cyclopentanecarboxylic Acid and 1-(β-Hydroxyphenethyl)-1-cyclopentanecarboxylic Acid γ-Lactone. To a mixture of 71 ml of ethanol and 67 ml of 30% NaOH solution, 48 g (0.223 mole) of 1-cyclopentyl-3-phenyl-2,3-epoxypropan-1-one was added and the mixture heated under reflux for 3 hr. Most of the ethanol was then evaporated under reduced pressure; water and toluene were added and the layers separated. The above toluene layer was dried over magnesium sulfate and filtered, the solvent removed, and the residue distilled. There was obtained 17 g (35%) of a fraction bp 130.2° (0.5 mm). A sample of this material was crystallized from hexane, mp 42°; infrared: 5.68 μ (KBr); nmr: δ 1.81 (broad singlet, eight protons), 1.97 (quartet, one proton, J = 13, 9 cps), 2.50 (quartet, one proton, J = 13, 6 cps), 5.31 (quartet, one proton, J = 9, 6 cps), and 7.27 (singlet, five protons) (CCl_4).

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.96; H, 7.20.

Acidification of the aqueous alkaline layer precipitated the crude acid which was recrystallized from hexane to give 7 g (14%) of the acid, mp 122–124°; infrared: 3.4 (broad) and 5.96 μ (KBr); nmr: δ 1.5–2.4 (multiplet, eight protons), 6.45 (triplet, very high center, two protons, J = 17.3 cps), 7.3 (multiplet, five protons), and 10.8 (singlet, one proton) ($CDCl_3$).

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.81; H, 7.86.

1-(β-Hydroxyphenethyl)cyclopentanecarboxylic Acid γ-Lactone. The 1-phenacylcyclopentanecarboxylic acid required for this preparation was obtained according to the method of Sen-Gupta,[4] who erroneously, as pointed out by Saboor,[5] thought it to be the isomeric 1-benzoylcyclopentaneacetic acid.

To a stirred mixture of 5.8 g (0.025 mole) of 1-phenacylcyclopentanecarboxylic acid, 50 ml of water, and 7.5 ml of 0.5 N sodium hydroxide solution, 0.5 g of sodium borohydride in 20 ml of water was added dropwise. The reaction mixture was stirred at room temperature for 30 min, then filtered to remove a small amount of insoluble material and acidified with dilute hydrochloric acid. The crystalline precipitate that separated upon acidification was collected, washed with water, and then dissolved in ether. The ether solution was extracted with 1 N sodium carbonate and dried over magnesium sulfate. After removal of drying agent and solvent, the residue was crystallized from hexane yielding 1.5 g (25%) of product, mp 40–42°. The mixture melting point and infrared and nmr spectra showed the sample to be identical with that obtained by the rearrangement of 1-cyclopentyl-3-phenyl-2,3-epoxypropan-1-one.

1-(β-Hydroxyphenethyl)-1-cyclobutanecarboxylic Acid γ-Lactone and 1-Styryl-1-cyclobutanecarboxylic Acid. A mixture of 7.7 g (0.038 mole) of 1-cyclobutyl-3-phenyl-2,3-epoxypropan-1-one and 80 ml of 10% sodium hydroxide solution was heated under reflux for 3 hr, cooled, and extracted with ether. The reaction mixture then was filtered from some insoluble material. The aqueous alkaline solution was acidified with dilute hydrochloric acid to produce an oily precipitate which was extracted twice with ether. The combined ether extracts were extracted with 10% sodium bicarbonate solution. The sodium bicarbonate solution was acidified with dilute hydrochloric acid to precipitate 0.5 g (6%) of the γ-lactone. A recrystallized sample melted at 55–56°; infrared: 5.70 μ (KBr); nmr: δ 1.8–3.1 (multiplet, eight protons), 5.34 (quartet, one proton, J = 9, 6 cps), and 7.32 (singlet, five protons) ($CDCl_3$).

Anal. Calcd for $C_{14}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.54; H, 6.77.

When the original oily precipitate was again extracted with 10% sodium bicarbonate solution, which cautiously was acidified with dilute hydrochloric acid, 0.5 g (6%) of the crystalline acid (mp 89–90°) was obtained. An analytical sample with the same melting point was recrystallized from hexane; infrared: 3.4 (broad) and 5.95 μ (KBr); nmr: δ 1.7–2.9 (multiplet, six protons), 6.49 (triplet, very high center, two protons, J = 16.3 cps), 7.3 (multiplet, five protons), and 11.9 (singlet, one proton) ($CDCl_3$).

About 2 g of the original oily precipitate remained; spectral evidence indicated it to be chiefly the γ-lactone.

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.44; H, 6.77.

Benzylcyclopropylglycolic Acid. A stirred mixture of 42 g (0.223 mole) of 1-cyclopropyl-3-phenyl-2,3-epoxypropan-1-one and 200 ml of 10% sodium hydroxide solution was heated under reflux for 3 hr, and then cooled to room temperature. The reaction mixture was extracted twice with ether. The water layer was filtered with Celite and acidified with dilute hydrochloric acid. The precipitate was filtered off and dried; 35 g (76%) was obtained, mp 95–98°; infrared: 2.96 3.4 (broad), and 5.85 μ (broad) (film); nmr: δ 0.1–1.5 (two multiplets [2:1], five protons), 2.8–3.3 (AB quartet, two protons, J = 14 cps), and 7.17 (singlet, five protons), OH and CO_2H very broad (CCl_4).

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.53; H, 7.05

Preparation and Rearrangement of 1-Cyclohexyl-3-phenyl-2,3-epoxy-O^{18}-propan-1-one. 1-Cyclohexyl-3-phenyl-2-propen-1-one, 1.00 g (0.0047 mole), was dissolved in 12 ml of 1:1 acetone–ethanol and the solution placed in a 50-ml, three-necked flask equipped with reflux condenser topped by a $CaSO_4$ drying tube, a mechanical stirrer, and a 1-ml pipet fitted through a rubber stopper. The apparatus was thermostated at 40°, and 0.94 ml of 4 N NaOH was added followed by a slow dropwise addition of 0.79 ml (0.13 mole) of H_2O_2[18] (concentration determined by $KMnO_4$ titration). The product was isolated in the usual manner by distillation; yield 0.9 g (87%), bp 130–140° (0.55–0.60 mm); O^{18} concentration by mass spectrometer: about 45% (not precise because compound shows no molecular ion peak).

The rearrangement was carried out in the usual way with the labeled epoxide and 4.7 ml of 10% NaOH solution. The crude acid (mp 125–130°) was submitted for mass spectrometric analysis without further purification. The amount of O^{18} in the acid was less than 1%.

Acknowledgment. We wish to thank Miss C. Miles for measuring and interpreting the nmr spectra, Mr. D. Hansen for carrying out the O^{18} reactions, and Professor J. O. Edwards for a generous gift of H_2O_2[18].