

must be greater than 10^{10} sec^{-1} . The predicted value for k_{-1}' is also reasonable. The rate constants for the elimination of amine ($\text{p}K_a \approx 9$) from **6** and of hydroxylamine ($\text{p}K_a \approx 6$) from **7** are 7×10^8 ¹¹ and about 10^9 sec^{-1} ,¹² respectively. Expulsion of very weakly basic water ($\text{p}K_a = -1.74$) should occur even more readily.

In summary, the data supporting the mechanism of eq 2 are (1) the estimated rate constants for the partitioning of **4**, based on assumptions as to the $\text{p}K_a$ of the intermediate and the equilibrium constant for its formation, are near the diffusion limit; (2) the rate constants for the breakdown of analogous intermediates in other reactions are correspondingly large; (3) the Brønsted $\beta \approx 0$ is consistent with a diffusion-limited deprotonation of **3**; and (4) the change in slope of the Brønsted plot near $\text{p}K_a = -0.5$, which should correspond to the $\text{p}K_a$ of **3** for a diffusion-limited mechanism, is reasonable in terms of the structure of **3**.

The Brønsted plot for ethyl trifluorothioacetate,

(11) R. E. Barnett and W. P. Jencks, *J. Amer. Chem. Soc.*, **90**, 4199 (1968); **91**, 2358 (1969).

(12) J. E. Reimann and W. P. Jencks, *ibid.*, **88**, 3973 (1966).

which has a much poorer leaving group, has a small ($\beta \approx 0.2$) but nonzero slope, implying that for this ester the concerted mechanism (eq 1) rather than the diffusion-limited mechanism holds. This is analogous to the behavior of the hydroxide catalyzed decomposition of hemithioacetals^{10,13} in which it was observed that, when the $\text{p}K_a$ of the departing thiol is less than 8, the diffusion-limited mechanism prevails, while for less acidic thiols it does not.

Since the original suggestion by Moffat and Hunt¹⁴ that equilibration of the various ionic forms of a tetrahedral intermediate may not always be fast compared to making and breaking of bonds to carbon, diffusion-limited mechanisms have been implicated in thiolester hydrolysis, thiolester aminolysis,^{11,15,16} amide hydrolysis,¹⁷ and hemithioacetal decomposition.¹⁰ It seems possible that such mechanisms will be found to be a relatively common phenomena.

(13) G. E. Lienbard and W. P. Jencks, *ibid.*, **88**, 3982 (1966).

(14) A. Moffat and H. Hunt, *ibid.*, **81**, 2082 (1959).

(15) R. K. Chaturvedi and G. L. Schmir, *ibid.*, **91**, 737 (1969).

(16) G. M. Blackburn, *Chem. Commun.*, 249 (1970).

(17) L. D. Kershner and R. L. Schowen, *J. Amer. Chem. Soc.*, **93**, 2014 (1971).

Stereospecific Introduction of Double Bonds via Thermolysis of β -Lactones¹

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Contribution from the Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico 00931. Received July 9, 1971

Abstract: The direct cyclization of β -hydroxy acids with benzenesulfonyl chloride in pyridine at 0–5° has been shown to be a general reaction affording tri- and tetrasubstituted β -lactones in high yield. The β -lactones are decarboxylated at moderate temperatures (140–160°) into the corresponding olefins with retention of the initial geometry and without double bond isomerization. At elevated temperatures (45–55°) benzenesulfonyl chloride in pyridine promotes the dehydrocarbonation of β -hydroxy acids directly to the desired olefins. This novel dehydrocarbonation of β -hydroxy acids, which are now readily prepared by the condensation of α -metalated carboxylate salts with ketones and aldehydes, constitutes a convenient alternative to the Wittig olefin synthesis.

A number of synthetic methods have become available in recent years for the stereospecific and stereoselective introduction of double bonds in carbon skeletons.³ Of particular interest is the work of Corey and coworkers for the novel preparations of tri- and tetrasubstituted olefins.⁴ β -Lactones are known to decompose at moderate temperatures into olefins and carbon dioxide essentially quantitatively.⁵ This ther-

mal lability imparts to this oxetanone ring system the unique property of serving as a convenient olefin carrier in which the carbon dioxide moiety acts as a vise for fixing double bonds.

It is surprising that this synthetic approach has not been utilized more extensively.⁶ Presumably the reason for this is the fact that no convenient methods are available for the synthesis of β -lactones. Besides the classical approach which consists of internal nucleophilic displacement of halide ion from β -halocarboxylate salts,⁷ some alternative methods working with variable degrees of success are deaminative cyclization of β -amino acids,⁸ the cycloaddition of ketones to ketenes,⁹ the

(1) The general aspect of this work (J. C. Liu) was presented at Metrochem 71, Regional Meeting of the American Chemical Society, New York–New Jersey, Puerto Rico Sections, April 29 to May 2, 1971, San Juan, Puerto Rico. The stereochemical study (J. Baeza) was presented at the 23rd International Congress of Pure and Applied Chemistry (IUPAC), July 25–30, 1971, Boston, Mass.

(2) M.Sc. Degree, University of Puerto Rico, Nov 1970.

(3) J. Reucroft and P. G. Sammes, *Quart. Rev.*, **Chem. Soc.**, **25**, 135 (1971).

(4) E. J. Corey, H. Yamamoto, D. K. Herron, and K. Achiwa, *J. Amer. Chem. Soc.*, **92**, 6635 (1970); E. J. Corey and H. Yamamoto, *ibid.*, **92**, 6636, 6637 (1970); E. J. Corey, H. A. Kirst, and J. A. Katzenellenbogen, *ibid.*, **92**, 6314 (1970); E. J. Corey and H. Yamamoto, *ibid.*, **92**, 226 (1970).

(5) H. E. Zaugg, *Org. React.*, **8**, 305 (1954); H. Kröper in Houben-

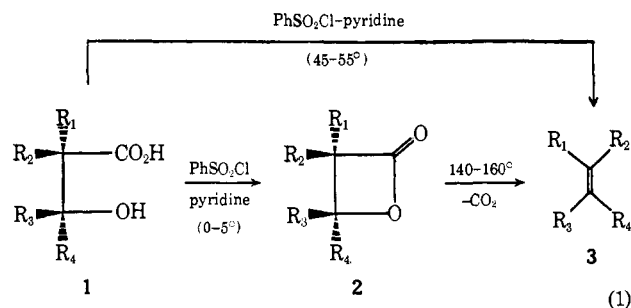
Weyl, "Methoden der Organischen Chemie," Vol. 6, Part 2, Georg Thieme, Stuttgart, 1962, p 511; A. Rosowsky in "Technique of Organic Chemistry," Vol. 19, Part 1, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, p 1.

(6) M. N. S. Sultanbawa, *Tetrahedron Lett.*, 4569 (1968); J. A. Marshall and H. Fauble, *J. Amer. Chem. Soc.*, **92**, 948 (1970).

(7) D. S. Noyce and E. H. Banitt, *J. Org. Chem.*, **31**, 4043 (1966).

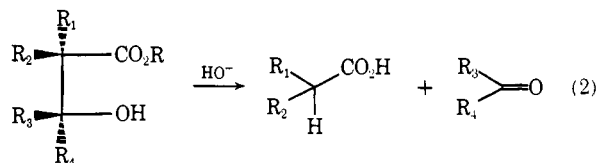
photocyclization of cinnamic acids,¹⁰ and the photo-oxidation of 2-alkoxyoxetanes.¹¹ The direct cyclization of β -hydroxy acids, using cyclants such as acetic anhydride,¹² ethyl chloroformate,¹³ benzoyl chloride,¹⁴ and thionyl chloride¹⁵ all in pyridine as solvent, as well as isopropyl carbodiimide,¹⁶ phosphorus pentoxide,¹⁷ and orthoformate¹⁸ gives β -lactones in modest yields.

In this study we show that β -hydroxy acids **1** can be converted in high yield to β -lactones **2** by treatment with benzenesulfonyl chloride in pyridine at subambient temperatures or dehydrocarbonated to olefins **3** at elevated temperatures. Heating of the β -lactones **2** in their pure state affords the respective olefins **3** quantitatively and stereospecifically without geometrical isomerization (eq 1).



Results and Discussion

Synthesis of β -Hydroxy Acids. Basic hydrolysis of β -hydroxy esters, prepared by the Reformatsky reaction,¹⁹ is the usual source of β -hydroxy acids. Unfortunately this method works well only for β -hydroxy acids mono- or disubstituted at the β -carbon since with mono- or disubstitution at the α -carbon, the β -hydroxy acids on basic hydrolysis suffer a retro-Reformatsky reaction into acid and ketone (eq 2).²⁰



This difficulty can be circumvented in part by using *tert*-butyl instead of the ethyl α -bromo esters which with zinc and THF are cleaved to the β -hydroxy acids directly in the Reformatsky synthesis.²¹

(8) E. Testa, L. Fontanella, G. Cristiani, and L. Mariani, *Justus Liebigs Ann. Chem.*, **638**, 176 (1961).

(9) D. Bormann and R. Wyler, *Chem. Ber.*, **99**, 1245 (1966).

(10) O. L. Chapman and W. R. Adams, *J. Amer. Chem. Soc.*, **90**, 2333 (1968).

(11) S. H. Schroeter, *Tetrahedron Lett.*, 1591 (1969).

(12) N. J. Toivonen, *et al.*, *Acta Chem. Scand.*, **3**, 991 (1949).

(13) P. A. Diassi and L. M. Dylion, *J. Amer. Chem. Soc.*, **80**, 3746 (1958).

(14) G. H. Boswell, W. G. Dauben, G. Ourisson, and T. Rull, *Bull. Soc. Chim. Fr.*, 1598 (1958).

(15) E. Testa, L. Fontanella, and L. Mariani, *J. Org. Chem.*, **26**, 3516 (1961).

(16) J. C. Sheehan, K. Hasspacher, and Y. L. Yeh, *J. Amer. Chem. Soc.*, **81**, 6086 (1959); A. W. Burgstahler and D. E. Wetmore, *J. Org. Chem.*, **26**, 3516 (1961).

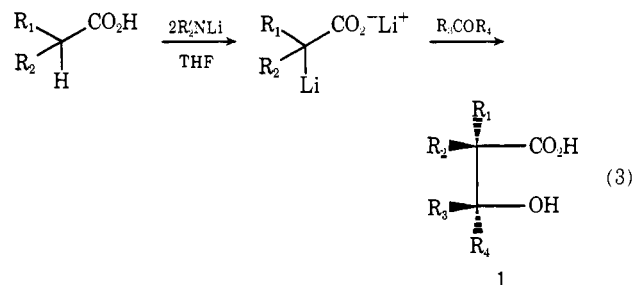
(17) I. L. Knunyants and Yu. A. Cherburkov, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 808 (1961).

(18) R. C. Blume, *Tetrahedron Lett.*, 1047 (1969).

(19) R. L. Shriner, *Org. React.*, **1**, 1 (1942).

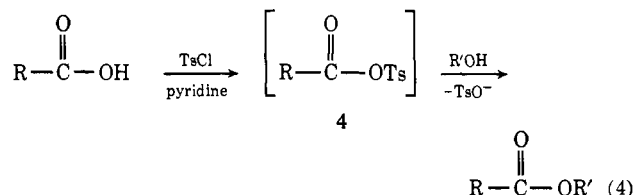
(20) C. S. Rondestvedt, Jr., and M. E. Rowley, *J. Amer. Chem. Soc.*, **78**, 3804 (1956).

On the other hand, β -hydroxy acids can be prepared directly *via* the Ivanov reaction;²² however, this reaction is limited in scope and yield. Recently Creger²³ developed a convenient method of α -alkylating aliphatic carboxylic acids by treating α -lithio carboxylate salts, generated from the aliphatic acid with lithium diisopropylamide in THF, with alkyl halides. It occurred to us that the condensation of α -lithio carboxylate salts with ketones and aldehydes should present an attractive alternative to the Ivanov reaction in affording β -hydroxy acids directly (eq 3). Indeed,



via this method we have been successful in preparing a variety of β -hydroxy acids (**1a** to **1k** in Table I) in fair yields. No efforts were made in optimizing the yields. In the meantime,¹ the same method has been reported by Moersch and Burkett.²⁴

Synthesis of β -Lactones. The Brewster-Ciotti procedure has been successful in preparing esters derived from acid sensitive alcohols and/or acids.²⁵ The mechanism of this reaction (eq 4) presumably involves



the mixed anhydride **4** because in the absence of alcohol the respective carboxylic anhydride is formed. It appeared to us worthwhile to explore the possibility of cyclizing β -hydroxy acids **1** directly into the β -lactones **2** using this simple reagent. Initial attempts did produce the desired β -lactones in low yield accompanied by substantial amounts of unreacted acid or olefin, probably formed by decarboxylation of the β -lactones. In view of the fact that β -lactones are acid labile,⁵ we observed that the β -lactones can be isolated in excellent yields *via* this procedure if the residual pyridine is removed at reduced pressure rather than by extraction with dilute hydrochloric acid. It was also found to be important not to allow the reaction mixture to warm up above $5-10^\circ$ since appreciable amounts of olefin were produced. The β -lactones **2a-2j**, **2o**, and **2p** (Table I) have been prepared in high yields by this method, except for **2b** which always was accompanied by large amounts of olefin.

(21) D. A. Cornforth, A. E. Opara, and G. Read, *J. Chem. Soc. C*, 2799 (1969); A. E. Opara and G. Read, *Chem. Commun.*, 679 (1969).

(22) H. E. Zimmerman and M. D. Traxler, *J. Amer. Chem. Soc.*, **79**, 1920 (1957).

(23) P. L. Creger, *ibid.*, **92**, 1397 (1970); **89**, 2500 (1967).

(24) G. W. Moersch and A. R. Burkett, *J. Org. Chem.*, **36**, 1149 (1971).

(25) J. H. Brewster and C. J. Ciotti, *J. Amer. Chem. Soc.*, **77**, 6214 (1955).

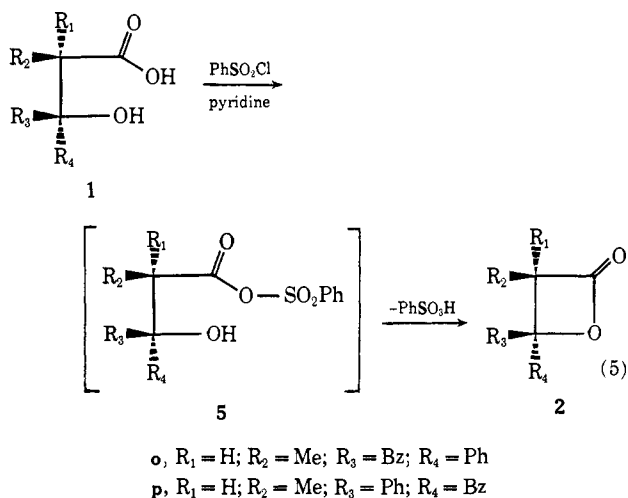
Table I. Yields (%) of β -Hydroxy Acids,^a β -Lactones, and Olefins Prepared in This Work

System	Substituents				Yields (%)		
	R ₁	R ₂	R ₃	R ₄	1	2	3
a	H	Ph	Ph	Ph	81	70	100
b	H	Me	Ph	Ph	76	37 ^b	100
c	H	<i>t</i> -Bu	Ph	Ph	15	100	100
d	Me	H	Me	Ph	25	87	100
e	Me	Me	Ph	Ph	50	95	100
f	Me	Me	Me	Ph	24	92	100
g	Me	Me	Bz	Ph	27	85	100
h	Me	Bz	Bz	Ph	30 ^c	78 ^c	100 ^c
i	Me	Me	H	Ph	31	95	100
j	Me	Me	(-CH ₂) ₆	Ph	75	67	100
k	H	H	Ph	Ph	17		55
l	H	H	Bz	Ph			64
m	H	H	Et	Ph			60
n	H	H	<i>i</i> -Pr	Ph			82
o	H	Me	Bz	Ph	d	93	99.3 ± 0.3
p	H	Me	Ph	Bz	d	90	97.6 ± 0.2

^a No efforts were made to optimize the hydroxy acid yields. ^b Over 50% olefin **3b** was formed. ^c 2.5:1.0 trans/cis mixture by nmr. ^d Stereospecific syntheses of **1o** and **1p** shall be described elsewhere.

Attempts to cyclize the hydroxy acids **1k** to **1n** via this procedure failed. Apparently mono- or disubstitution at the β -carbon of the hydroxy acid is essential for cyclization into β -lactones. However, for tri- and tetrasubstituted β -lactones we feel that our method is the best available to date. More important, the β -lactones are formed stereospecifically with retention of the geometry of the β -hydroxy acid precursor. For example, erythro acid **1o** is converted essentially quantitatively into isomerically pure *E* lactone **2o**, while the threo acid **1p** affords isomerically pure *Z* lactone **2p**, as evidenced by their nmr spectra. The rigorous structure proof *via* olefins **3o** and **3p**, respectively, is discussed in the next section.

Of course, retention of the geometry of the initial β -hydroxy acid in the β -lactone product is expected in this reaction. The β -hydroxy group serves as the internal nucleophile of displacing the benzenesulfonate ion in the mixed anhydride **5** (eq 5).



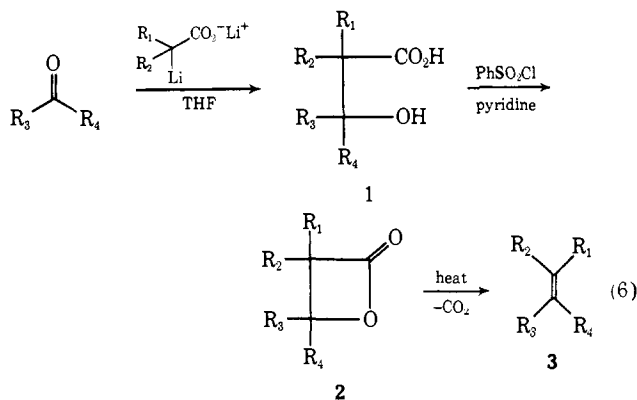
In addition to the synthetic procedures described here, we have explored alternative cyclants. For example, trifluoroacetic anhydride, cyclohexylcarbodiimide, and *N,N*-carbonyldiimidazole²⁶ were utilized

to cyclize the β -hydroxy acid **1a** to its β -lactone **2a**. Although the yields (50–80%) in these cyclizations were competitive with the benzenesulfonyl chloride–pyridine method, the convenience of work-up and availability of the reagents make our reaction the procedure of choice.

Synthesis of Olefins. With a convenient β -lactone synthesis on hand, it was our interest to assess the usefulness of these compounds as synthetic intermediates in the fixation of double bonds in carbon skeletons. At intermediate temperatures (140–160°) all of the β -lactones prepared in this work gave quantitatively the respective olefins. Of particular interest are β -lactones **2g** and **2j** which gave on thermolysis the desired 1,2-diphenyl-3-methyl-2-butene (**3g**) and isopropylidene-cyclohexane (**3j**), respectively. As expected, under the reaction conditions employed neither **3g** nor **3j** isomerized into the more stable α -isopropylstilbene and 1-isopropylcyclohexene, respectively. The fact that no isomerization had taken place was rigorously established by ozonolysis of **3g** and **3j** in the presence of tetracyanoethylene, which produced as exclusive ozonolysis products acetone and deoxybenzoin from **3g** and acetone and cyclohexanone from **3j**, respectively. Even the Wittig reaction is too basic and extensive isomerization of olefins such as **3g** to their stilbene isomers takes place. Besides, the Wittig reaction for the introduction of the isopropylidene group works in modest yields.²⁷ Consequently, an attractive alternative method to the now classical Wittig olefin synthesis is available (eq 6).

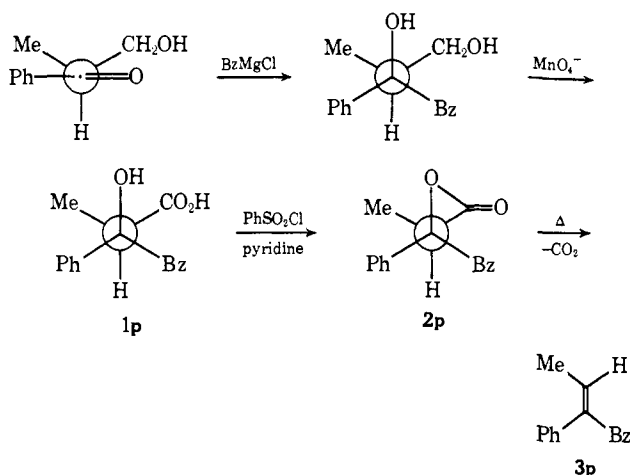
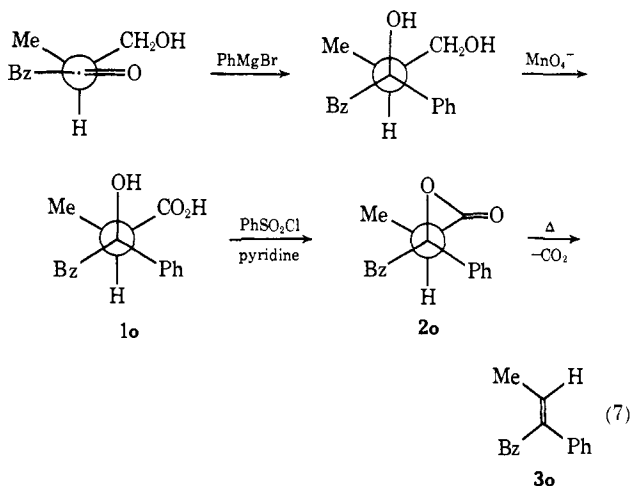
Since the hydroxy acids **1k** to **1n** did not cyclize to the respective β -lactones when treated with benzenesulfonyl chloride in pyridine at 0–5°, we explored the possibility of converting these acids directly to the desired olefins without attempting to isolate the lactones. Indeed, these β -hydroxy acids could be dehydrocarbonated directly to their olefins in respectable yields (55–82%) when the benzenesulfonyl chloride–pyridine reaction is run at 45–55° (eq 1). Again no isomer-

(26) H. A. Staab and A. Mannschreck, *Chem. Ber.*, **95**, 1284 (1964).
 (27) A. Maercker, *Org. React.*, **14**, 270 (1965).



ization of the double bond in the case of 2,3-diphenylpropene to the more stable α -methylstilbene took place under these conditions. This direct dehydrocarbonation of β -hydroxy acids into olefins constitutes a convenient olefin synthesis.

Hydroxy acids **1o** and **1p** were prepared to check the stereochemical course of the thermal decarboxylation of β -lactones. The stereospecific synthesis is outlined in eq 7. The experimental details for hydroxy acid **1p** have been described already,²⁸ while the preparation



of hydroxy acid **1o** shall be reported elsewhere. The isomerically pure hydroxy acids **1o** and **1p** were converted in high yields (Table I) into β -lactones **2o** and **2p**, respectively. These isomerically pure β -lactones

(28) W. Adam, Y. M. Cheng, C. Wilkerson, and W. A. Zaidi, *J. Amer. Chem. Soc.*, **91**, 2111 (1969).

on heating in their pure state at 140–160° smoothly decarboxylated into the olefin **3o** consisted of 99.3 \pm 0.3% *E* isomer, while olefin **3p** consisted of 97.6 \pm 0.2% *Z* isomer, indicating a very high degree of stereospecification for this reaction.

Our stereochemical assignment of the β -hydroxy acids **1o** and **1p**, the β -lactones **2o** and **2p**, and the olefins **3o** and **3p** is based on the following results. The (*E*)-1,2-diphenyl-2-butene (**3o**) has been described in the literature, and our nmr data completely match those reported by Casy and coworkers.²⁹ Furthermore, the configuration of the optically active hydroxy acid **1p** was previously assigned by us as (*2S,3R*)-(+)-*threo*-3,4-diphenyl-3-hydroxy-2-methylbutyric acid by correlating it with the literature known (*2S,3R*)-(+)-*threo*-4-dimethylamino-1,2-diphenyl-3-methyl-2-butanol hydrochloride.²⁸ Hydroxy acid **1p** was prepared by the stereospecific route outlined in eq 7 and the Cram-Prelog asymmetric induction rules demand that the *threo* isomer be formed.³⁰ Consequently, on reversal of the order of introducing the benzyl and phenyl groups at the β -carbon, it follows that hydroxy acid **1o** must be the *erythro* isomer. Since this *erythro* isomer **1o**, after conversion to its β -lactone **2o**, afforded the literature known *E* olefin **3o**, it is established that the sequence of transformations **1o** \rightarrow **2o** \rightarrow **3o** proceeded with retention of the geometry of the hydroxy acid. Comparison of the nmr data (Table II) rules out a double inversion in **1o** \rightarrow **2o** \rightarrow **3o** or **1p** \rightarrow **2p** \rightarrow **3p**.

In summary, it is our contention that the thermolysis of β -lactones, the latter now readily prepared *via* the direct cyclization of β -hydroxy acids by benzenesulfonyl chloride in pyridine at subambient temperatures, constitutes a useful synthetic route for the stereospecific fixation of double bonds in carbon skeletons. The availability of β -hydroxy acids by the condensation of α -metalated carboxylate salts with carbonyl compounds and direct dehydrocarbonation of the β -hydroxy acids into olefins should serve as an attractive alternative to the Wittig olefin synthesis.

Experimental Section

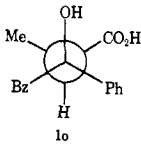
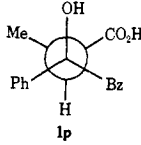
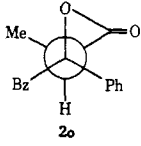
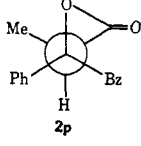
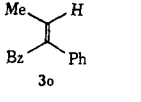
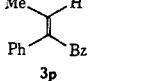
All melting points and boiling points are uncorrected. Solvents were purified according to standard procedures and starting materials were purchased from standard sources unless specifically stated. The ir spectra were measured on a Perkin-Elmer Infracord Model 237B, the nmr spectra on a Varian T-60. For the glpc analyses a Varian Aerograph 202B was used and the specific column conditions are stated in the experimental procedures. Elemental analyses were performed by the A. Bernhardt Analytical Laboratories (Germany) and all new compounds gave satisfactory results.

General Method for the Preparation of β -Hydroxy Acids. A three-necked, round-bottom flask, provided with a magnetic spinbar, a rubber serum cap, and nitrogen inlet and outlet tubes, was flame-dried under a nitrogen atmosphere. The flask was charged with anhydrous tetrahydrofuran (THF) and the required amount of *tert*-butylamine or diisopropylamine to make a 1.0 *M* solution. While stirring magnetically, a stoichiometric amount (equal to the quantity of amine) of *n*-butyllithium in hexane was added through the serum cap by means of a calibrated syringe. About 5–10 min later a stoichiometric amount (half the amount of amine) of the carboxylic acid to be converted into its lithium α -lithiocarboxylate was injected as a 1.0 *M* solution in anhydrous THF and allowed to stir for 1.0 hr. Subsequently, a stoichiometric amount (equal to the quantity of carboxylic acid) of the ketone as a 2.5 *M* solution in anhydrous THF was added at room temperature and the mixture

(29) A. F. Casy, J. L. Myers, and P. Pocha, *Tetrahedron*, **22**, 1001 (1966).

(30) H. E. Zimmerman and J. English, *J. Amer. Chem. Soc.*, **76**, 2294 (1954).

Table II. Nmr Parameters of Isomeric β -Hydroxy Acids, β -Lactones, and Olefins of Systems o and p

Isomer	Solvent	Chemical shifts, ppm ^a				Coupling constants, J_{ab} , Hz
		a -CH ₃	b >CH	c >CH ₂	d -C ₆ H ₅	
 1o	CD ₃ SOCD ₃	1.29 (d)	3.07 (nr)	3.07 (nr)	7.10 (m)	7.0
 1p	CD ₃ SOCD ₃	0.88 (d)	2.98 (q)	3.18 (s)	7.10 (m)	7.0
 2o	CCl ₄	1.59 (d)	3.81 (q)	3.29 (nr)	7.10 (m)	7.0
 2p	CCl ₄	0.88 (d)	3.52 (q)	3.33 (s)	7.15 (m)	7.0
 3o	CCl ₄	1.93 (d)	6.07 (q)	3.90 (s)	7.20 (m)	6.5
 3p	CCl ₄	1.62 (d)	5.56 (q)	3.63 (s)	7.20 (m)	6.5

^a Spectra were taken on a Varian T-60 using 15–20% solutions and TMS as internal standard.

allowed to stir overnight. The reaction mixture was poured on ice and transferred to a separatory funnel. After several extractions with ethyl ether, the aqueous layer was acidified with 6 *N* hydrochloric acid. In those cases in which a solid precipitated, the solid was collected on a Büchner funnel, washed well with water, and dried under vacuum over phosphorus pentoxide. Finally, recrystallization until constant melting point gave the pure β -hydroxy acid. In those cases in which a liquid product separated on acidification, the aqueous mixture was well extracted with ethyl ether, the combined ethereal extracts were dried (MgSO₄), and after evaporation of the solvent at reduced pressure (25 mm), the residue was purified by vacuum distillation, recrystallization, or both. β -Hydroxy acids 1a to 1k (Table I) have been prepared by this procedure and the details of the individual cases are described below.

2,3,3-Triphenyl-3-hydroxypropionic acid (1a) was prepared in 81% yield by the above procedure, mp 207–209° (lit.³¹ mp 205–208°), starting with 1.58 g (11.6 mmol) of phenylacetic acid, 2.12 g (11.6 mmol) of benzophenone, and 23.2 mmol of lithium *tert*-butylamide, obtained from 1.70 g (23.2 mmol) of *tert*-butylamine and 23.2 mmol of *n*-butyllithium.

3,3-Diphenyl-3-hydroxy-2-methylpropionic acid (1b) was prepared in 76% yield by the above procedure, mp 173–175° (lit.³² mp 182–184°), starting with 1.67 g (23.2 mmol) of propionic acid, 4.20 g (23.2 mmol) of benzophenone, and 46.4 mmol of lithium *tert*-butylamide, obtained from 3.40 g (46.4 mmol) of *tert*-butylamine and 46.2 mmol of *n*-butyllithium.

2-*tert*-Butyl-3,3-diphenyl-3-hydroxypropionic acid (1c) was prepared in 15% yield by the above method, mp 143–144.5° (needles from hexane–ether), starting with 1.16 g (10 mmol) of 3,3-dimethylbutyric acid, 1.82 g (10 mmol) of benzophenone, and 20 mmol of lithium *tert*-butylamide, obtained from 1.46 g (20 mmol) of *tert*-butylamine and 20 mmol of *n*-butyllithium. The spectral data are ir (cm⁻¹, KBr) 3475 (m, OH), 3075–2940 (m, aliphatic CH), 1675 (s, -CO₂H carbonyl), 1450 (m), 1375 (m), 1225 (m, C–O), 750 (m), and 700 (m, C₆H₅); nmr (60 MHz) δ (CDCl₃, TMS, ppm) 0.85 (s, 9, C(CH₃)₃), 3.63 (s, 1, -COCH), and 7.20 (s, 10, C₆H₅).

3-Hydroxy-2-methyl-3-phenylbutyric acid (1d) was prepared in 25% yield by the above method, mp 93–106°, starting with 3.6 g (50 mmol) of propionic acid, 6.0 g (50 mmol) of acetophenone, and 100 mmol of *tert*-butylamine and 100 mmol of *n*-butyllithium. Recrystallization from hexane–ether gave 226 mg of white crystals, mp 119–121° (lit.³⁰ mp 121.0–121.5°), of the *threo* isomer.

2,2-Dimethyl-3,3-diphenyl-3-hydroxypropionic acid (1e) was prepared in 50% yield by the above method, mp 166–167° (plates from ethanol) (lit.²⁴ mp 175–176°), starting with 2.20 g (25 mmol) of isobutyric acid, 4.55 g (25 mmol) of benzophenone, and 50 mmol of lithium diisopropylamide, obtained from 5.05 g (50 mmol) of diisopropylamine and 50 mmol of *n*-butyllithium. The spectral data are ir (cm⁻¹, CHCl₃) 3560 (m, OH), 3550 (m, broad OH), 3050–3000 (s, aliphatic CH), 1680 (s, shoulder, CO₂H carbonyl), 1470 (m), 1445 (s), 1385 and 1360 (m, *gem*-dimethyl doublet), 1280 (m), 1160 (s), 1030 (m), and 705 (s, C₆H₅); nmr (60 MHz) δ (CDCl₃, TMS, ppm) 1.25 (s, 3, CH₃) and 7.20 (s, 5, C₆H₅).

2,2-Dimethyl-3-phenylbutyric acid (1f) was prepared in 24% yield by the above method, mp 49–50°, starting with 2.64 g (30 mmol) of acetophenone and 60 mmol of lithium *tert*-butylamide, obtained from 4.38 g (60 mmol) of *tert*-butylamine and 60 mmol of *n*-butyllithium. The spectral data are ir (cm⁻¹, CHCl₃) 3575 (m, OH), 3470 (m, OH), 3080–2870 (s, CH), 1680 (s, shoulder, CO₂H carbonyl), 1460 (m), 1440 (m), 1370 (m), 1280 (m), 1155 (m), 1100 (m),

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1060 (m), and 700 (m, C₆H₅); nmr (60 MHz) δ (CDCl₃, TMS, ppm) 1.12 (s, 6, (CH₃)₂CCO₂H), 1.63 (s, 3, CH₃CO), and 7.30 (m, 5, C₆H₅).

2,2-Dimethyl-3,4-diphenyl-3-hydroxybutyric acid (1g) was prepared in 27% yield by the above method, mp 185–186° (needles from ethanol), starting with 0.88 g (10 mmol) of isobutyric acid, 1.96 g (10 mmol) of desoxybenzoin, and 20 mmol of lithium *tert*-butylamide, obtained from 1.46 g (20 mmol) of *tert*-butylamine and 20 mmol of *n*-butyllithium. The spectral data are ir (cm⁻¹, KBr) 3530 (m), 3460 (s, OH), 3050–2900 (s, CH), 1700 (m), 1680 (s, broad, CO₂H carbonyl), 1505 (m), 1480 (m), 1395 (m), 1300 (s, broad), 1240 (m), 1175 (m, C–O), 1075 (m), and 725 (s, C₆H₅); nmr (60 MHz) δ (DMSO-*d*₆, TMS, ppm) 1.05 (s, 6, CH₃), 3.25 (AB quartet, 2, *J* = 34 Hz, –CH₂–), and 6.95 (m, 10, C₆H₅).

2-Benzyl-3,4-diphenyl-3-hydroxy-2-methylbutyric acid (1h) was prepared in 30% yield by the above method, mp 119–128° (needles from hexane–ether), starting with 2.04 g (13 mmol) of 2-methyl-3-phenylpropionic acid, 2.55 g (13 mmol) of desoxybenzoin, and 26 mmol of lithium *tert*-butylamide, obtained from 1.86 g (26 mmol) of *tert*-butylamine and 26 mmol of *n*-butyllithium. The spectral data are ir (cm⁻¹, KBr) 3530 (m), 3475 (m, broad, OH), 3070–2925 (m, CH), 1705 (s, CO₂H carbonyl), 1495 (s), 1455 (m, CH), 1125 (m), 715 (s, C₆H₅); nmr (60 MHz) shows it to be a 2.5:1.0 mixture of *erythro*- and *threo*-hydroxy acids; *erythro* isomer, δ (DMSO-*d*₆, TMS, ppm) 0.90 (s, 3, CH₃), 3.45 (s, 4, PhCH₂–), and 7.02 (m, 15, C₆H₅); *threo* isomer, 0.90 (s, 3, CH₃), 2.75 (s, 2, PhCH₂CCO₂H), 3.22 (s, 2, PhCH₂COH), and 7.02 (m, 15, C₆H₅).

2,2-Dimethyl-3-hydroxy-3-phenylpropionic acid (1i) was prepared in 31% yield by the above method, mp 134.5–135.5° (lit.³³ mp 134°), starting with 2.04 g (23.2 mmol) of isobutyric acid, 2.46 g (23.2 mmol) of benzaldehyde, and 46.4 mmol of lithium *tert*-butylamide, obtained from 3.39 g (46.4 mmol) of *tert*-butylamine and 46.4 mmol of *n*-butyllithium.

2-(1-Hydroxycyclohexyl)-2-methylpropionic acid (1j) was prepared in 75% yield by the above method, mp 87–88° (lit.³⁴ mp 90–92°), starting with 2.04 g (23.2 mmol) of isobutyric acid, 0.45 g (4.6 mmol) of cyclohexanone, and 46.4 mmol of lithium *tert*-butylamide, obtained from 3.40 g (46.4 mmol) of *tert*-butylamine and 46.4 mmol of *n*-butyllithium. The spectral data are ir (cm⁻¹, CHCl₃) 3505 (m, OH), 2930 (s), 2850 (s, CH), 1740 and 1680 (s, CO₂H carbonyl), 1470 (s), 1450 (m), 1390 (s), 1280–70 (m), 1180 (m), 1140 (s), 1050 (m, C–O), and 975 (s); nmr (60 MHz) δ (CDCl₃, TMS, ppm) 1.22 (s, 3, CH₃) and 1.55 (s, broad, 5, (CH₂)₅).

3,3-Diphenyl-3-hydroxypropionic acid (1k) was prepared in 17% yield by the above method, mp 221–222° (lit.³⁴ mp 212°), starting with 0.70 g (11.6 mmol) of acetic acid, 2.12 g (11.6 mmol) of benzophenone, and 23.2 mmol of lithium *tert*-butylamide, obtained from 1.70 g (23.2 mmol) of *tert*-butylamine and 23.2 mmol of *n*-butyllithium.

3,4-Diphenyl-3-hydroxybutyric acid (1l) was prepared in 82% yield according to the method of Spring, mp 119–120° (lit.³⁵ mp 120°).

3-Phenyl-3-hydroxyvaleric acid (1m) was prepared in 75% yield according to the method of Schroeter and Wülfing, mp 118–120° (lit.³⁶ mp 118–121°).

4-Methyl-3-phenyl-3-hydroxyvaleric acid (1n) was prepared in 70% yield according to the method of Maroni-Barnaud and coworkers,³⁷ mp 116–117° (lit.³⁷ mp 117°).

***erythro*-3,4-Diphenyl-3-hydroxy-2-methylbutyric acid (1o)** was prepared in 56% yield by permanganate oxidation of *erythro*-3,4-diphenyl-2-methylbutane-1,3-diol following the method of Zimmerman and English,³⁰ mp 113–114°. The spectral data are ir (cm⁻¹, KBr) 3520 (m, OH), 1690 (s, CO₂H carbonyl), 1245 (s, C–O), 1210 (m), and 700 (s, C₆H₅); nmr (60 MHz) δ (DMSO-*d*₆, TMS, ppm) 1.29 (d, 3, *J* = 7.0 Hz, CH₃CH<), 3.07 (m, 3, >CH and –CH₂–), and 7.10 (m, 10, C₆H₅).

***threo*-3,4-Diphenyl-3-hydroxy-2-methylbutyric acid (1p)** was prepared in 55% yield by permanganate oxidation of *threo*-3,4-diphenyl-2-methylbutane-1,3-diol following the method of Zimmerman and English,³⁰ mp 181–182°. The spectral data are ir (cm⁻¹, KBr), 3510 (m, OH), 1675 (s, CO₂H carbonyl), 1235 (s, C–O), and 700 (s, C₆H₅); nmr (60 MHz) δ (DMSO-*d*₆, TMS, ppm) 0.88 (d,

3, *J* = 7.0 Hz, CH₃CH<), 2.98 (q, 1, *J* = 7.0 Hz, >CH), 3.18 (s, 2, –CH₂–), and 7.10 (m, 10, C₆H₅).

General Method for the Preparation of β -Lactones. A solution of the β -hydroxy acid in 20–30 parts of anhydrous pyridine was cooled to 0–5° and 2 mol of benzenesulfonyl chloride per mole of β -hydroxy acid was added. The mixture was well shaken, sealed, and placed into the refrigerator overnight. The work-up consisted of pouring the reaction mixture onto three to four volumes of crushed ice and extraction with several volumes of ether. The combined ethereal layers were washed with saturated sodium bicarbonate and water, and after drying (MgSO₄) the ether was evaporated at reduced pressure. The crude β -lactone was purified by recrystallization from the appropriate solvent. β -Lactones **2a–2j**, **2o** and **2p** (Table I) have been prepared by this procedure and the details for the individual cases are described below.

3,4,4-Triphenyloxetan-2-one (2a) was prepared in 70% yield by the above method, mp 111–112° (needles from hexane–ether), starting with 159 mg (0.5 mmol) of the hydroxy acid **1a** in 3.2 ml of pyridine and 177 mg (1.0 mmol) of benzenesulfonyl chloride. The spectral data are ir (cm⁻¹, CCl₄) 3080–3030 (m, aromatic CH), 1835 (s, carbonyl), 1175 and 1140 (m, C–O), and 700 (s, C₆H₅); nmr (60 MHz) δ (CCl₄, TMS, ppm) 3.28 (s, 1, >CH) and 6.95 (s, 15, C₆H₅).

3-Methyl-4,4-diphenyloxetan-2-one (2b) was prepared in 37% yield by the above method, mp 70–71° (needles from pentane), starting with 252 mg (1.0 mmol) of hydroxy acid **2b** in 5 ml of pyridine and 354 mg (2.0 mmol) of benzenesulfonyl chloride. The spectral data are ir (cm⁻¹, CCl₄) 3085–3025 (w, aromatic CH), 2985–2875 (w, aliphatic CH), 1845 (s, carbonyl), 1165 (m, C–O), and 700 (s, C₆H₅); nmr (60 MHz) δ (CCl₄, TMS, ppm) 1.70 (d, 3, *J* = 7 Hz, CH₃), (q, 1, *J* = 7 Hz, >CH), and 7.00 (s, 10, C₆H₅).

3-*tert*-Butyl-4,4-diphenyloxetan-2-one (2c) was prepared in 100% yield by the above method, mp 117–118° (without purification), starting with 60 mg (0.2 mmol) of hydroxy acid **1c** in 1.5 ml of pyridine and 71 mg (0.4 mmol) of benzenesulfonyl chloride. The spectral data are ir (cm⁻¹, CCl₄) 3085–3020 (w, aromatic CH), 2950–2850 (m, aliphatic CH), 1830 (s, carbonyl), 1150 (m, C–O), and 710 (s, C₆H₅); nmr (60 MHz) δ (CCl₄, TMS, ppm) 0.92 (s, 9, C(CH₃)₃), 3.90 (s, 1, >CH), and 7.30 (m, 10, C₆H₅).

3,4-Dimethyl-4-phenyloxetan-2-one (2d) was prepared in 87% yield by the above method, bp 70–75° (0.05 mm), starting with 96 mg (0.5 mmol) of hydroxy acid **1d** in 2 ml of pyridine and 177 mg (1.0 mmol) of benzenesulfonyl chloride. The spectral data are ir (cm⁻¹, CCl₄) 2985–2885 (m, aliphatic CH), 1835 (s, carbonyl), 1200 (m, C–O), and 700 (m, C₆H₅); nmr (60 MHz) δ (CCl₄, TMS, ppm) 0.85 (d, 3, *J* = 8 Hz, >CHCH₃), 1.83 (s, 3, PhCCH₃), 3.55 (q, 1, *J* = 8 Hz, CH₃CH), and 7.20 (s, 5, C₆H₅).

3,3-Dimethyl-4,4-diphenyloxetan-2-one (2e) was prepared in 95% yield by the above method, mp 101–102° (plates from hexane–ether), starting with 1.08 g (4 mmol) of hydroxy acid **1e** in 25 ml of pyridine and 1.41 g (8 mmol) of benzenesulfonyl chloride. The spectral data are ir (cm⁻¹, CCl₄) 3060–3010 (w, aromatic CH), 2980–2880 (w, aliphatic CH), 1830 (s, carbonyl), 1185 (m, C–O), and 720 (m, C₆H₅); nmr (60 MHz) δ (CCl₄, TMS, ppm) 1.15 (s, 6, CH₃) and 7.27 (m, 10, C₆H₅).

3,3,4-Trimethyl-4-phenyloxetan-2-one (2f) was prepared in 92% yield by the above method, mp 33.5–34.5° (needles from pentane–ether), starting with 208 mg (1.0 mmol) of hydroxy acid **1f** in 4 ml of pyridine and 354 mg (2.0 mmol) of benzenesulfonyl chloride. The spectral data are ir (cm⁻¹, CCl₄) 2980–2870 (w, aliphatic CH), 1825 (s, carbonyl), 1125 and 1030 (m, C–O), and 710 (m, C₆H₅); nmr (60 MHz) δ (CCl₄, TMS, ppm) 0.85 (s, 3, PhCCCH₃), 1.40 (s, 3, CH₃CCMe), 1.77 (s, 3, PhCCH₃), and 7.20 (s, 5, C₆H₅).

4-Benzyl-3,3-dimethyl-4-phenyloxetan-2-one (2g) was prepared in 85% yield by the above method, mp 145–146° (needles from hexane–acetone), starting with 568 mg (2 mmol) of hydroxy acid **1g** in 15 ml of pyridine and 706 mg of benzenesulfonyl chloride. The spectral data are ir (cm⁻¹, CCl₄) 3080–3010 (w, aromatic CH), 2980–2860 (w, aliphatic CH), 1825 (s, carbonyl), 1140 (m, C–O), and 720 (s, C₆H₅); nmr (60 MHz) δ (CCl₄, TMS, ppm) 0.95 (s, 3, PhCCCH₃), 1.55 (s, 3, MeCCCH₃), 3.30 (AB quartet, 2, *J* = 22 Hz, >CH₂), and 7.05 (m, 10, C₆H₅).

3,4-Dibenzyl-3-methyl-4-phenyloxetan-2-one (2h) was prepared in 78% yield by the above method, mp 174–177° (from hexane–acetone), starting with 360 mg (1.0 mmol) of hydroxy acid **1h** in 6 ml of pyridine and 353 mg (2.0 mmol) of benzenesulfonyl chloride. The spectral data are ir (cm⁻¹, CHCl₃) 1815 (s, carbonyl), 1155 (m, C–O), and 710 (s, C₆H₅); nmr (60 MHz) consisted of a 2.5:1.0 trans-cis mixture: *trans* isomer, δ (CDCl₃, TMS, ppm) 1.45 (s, 3, CH₃), 3.35 (s, 2, PhCH₂CO–), 3.45 (s, 2, PhCH₂CC=O), and

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7.20 (m, 15, C₆H₅); cis isomer, δ (CDCl₃, TMS, ppm) 0.85 (s, 3, CH₃), 2.40 (s, 2, PhCH₂CO-), 2.50 (s, 2, PhCH₂CC=O), and 7.20 (m, 15, C₆H₅).

3,3-Dimethyl-4-phenyloxetan-2-one (2j) was prepared in 95% yield by the above method, bp 79–83° (0.025 mm), starting with 194 mg (1.0 mmol) of hydroxy acid **1i** in 4 ml of pyridine and 354 mg (2.0 mmol) of benzenesulfonyl chloride. The spectral data are ir (cm⁻¹, CCl₄) 2970–2880 (m, aliphatic CH), 1835 (s, carbonyl), 1100 (m, C–O), and 700 (m, C₆H₅); nmr (60 MHz) δ (CCl₄, TMS, ppm) 0.83 (s, 3, PhCCH₃), 1.50 (s, 3, HCCCH₃), 5.15 (s, 1, >CH), and 7.20 (m, 5, C₆H₅).

3,3-Dimethyl-1-oxaspiro[3.5]nonan-2-one (2j) was prepared in 67% yield by the above method, mp 105–106° (needles from hexane), starting with 372 mg (2.0 mmol) of hydroxy acid **1j** in 10 ml of pyridine and 706 mg (4.0 mmol) of benzenesulfonyl chloride. The spectral data are ir (cm⁻¹, CCl₄) 2980–2900 (m, aliphatic CH), 1815 (s, carbonyl), and 1120 (m, C–O); nmr (60 MHz) δ (CCl₄, TMS, ppm) 1.16 (m, 10, (CH₂)₆) and 1.24 (s, 6, CH₃).

(E)-4-Benzyl-3-methyl-4-phenyloxetan-2-one (2o) was prepared in 92.8% yield by the above method, mp 119–121° (needles from hexane), starting with 218 mg (0.81 mmol) of hydroxy acid **1o** in 5 ml of pyridine and 285 mg (1.1 mmol) of benzenesulfonyl chloride. The spectral data are ir (cm⁻¹, CCl₄) 1830 (s, carbonyl), 1160 (m, C–O), and 700 (s, C₆H₅); nmr (60 MHz) δ (CCl₄, TMS, ppm) 1.59 (d, 3, *J* = 7.0 Hz, CH₃CH<), 3.29 (m, 2, –CH₂–), 3.81 (q, 1, *J* = 7.0 Hz, >CHCH₃), and 7.10 (m, 10, C₆H₅).

(Z)-4-Benzyl-3-methyl-4-phenyloxetan-2-one (2p) was prepared in 90% yield by the above method, mp 103–104° (needles from hexane), starting with 218 mg (0.81 mmol) of hydroxy acid **1p** in 5 ml of pyridine and 285 mg (1.1 mmol) of benzenesulfonyl chloride. The spectral data are ir (cm⁻¹, CCl₄) 1830 (s, carbonyl), 1155 (m, C–O), and 690 (s, C₆H₅); nmr (60 MHz) δ (CCl₄, TMS, ppm) 0.88 (d, 3, *J* = 7.0, >CHCH₃), 3.33 (s, 2, –CH₂–), 3.52 (q, 1, *J* = 7.0, >CH–CH₃), and 7.15 (m, 10, C₆H₅).

General Method for the Preparation of Olefins. The β -lactone (1–2 mmol) was placed into a molecular still and heated in an oil bath at 140–160° at atmospheric pressure until cessation of carbon dioxide evolution. The product was then distilled at reduced pressure. The olefin structure was confirmed by ir and nmr spectra and ozonolysis to the corresponding ketone products. The ozonolysis procedure of Criegee and Günther³⁸ was followed by passing dry ozone gas (generated by means of a Welsbach T-408 ozonator) through an equimolar solution of 1–2 mmol of the olefin and tetracyanoethylene in ethyl acetate at –78° until persistence of the characteristic blue ozone color. The ketone products were individually collected by glpc and identified by comparison of glpc and tlc retention times and ir spectra with the authentic materials. Olefins **3a** to **3j**, **3o**, and **3p** (Table I) were prepared via the thermolysis of β -lactones and the details of the individual cases are described below.

Triphenylethylene (3a) was obtained quantitatively from β -lactone **2a**, bp 145° (0.4 mm) (lit.³⁹ bp 220° (14 mm)).

1,1-Diphenylpropene (3b) was obtained quantitatively from β -lactone **2b**, bp 284–285° (760 mm), mp 49–50° (lit.⁴⁰ bp 280–281° (760 mm), mp 52°).

1,1-Diphenyl-3,3-dimethyl-1-butene (3c) was obtained quantitatively from β -lactone **2c**, bp 96–98° (0.6 mm). The spectral data are ir (cm⁻¹, CCl₄) 3060–3000 (m, aromatic CH), 2950–2850 (m, aliphatic CH), 1598 (w, double bond), and 700 (s, C₆H₅); nmr (60 MHz) δ (CCl₄, TMS, ppm) 0.94 (s, 9, *tert*-butyl), 5.96 (s, 1, >CH), and 7.06 (m, 10, C₆H₅). Ozonolysis gave benzophenone and pivaldehyde as exclusive products.

trans-2-Phenyl-2-butene (3d) was obtained quantitatively from *trans* β -lactone **2d**, bp 93° (25 mm) (lit.⁴¹ bp 81–82° (12 mm)).

1,1-Diphenyl-2-methylpropene (3e) was obtained quantitatively from β -lactone **2e**, bp 160° (15 mm), *n*_D²⁰ 1.5840 (lit.⁴² bp 293° (760 mm), *n*_D¹⁶ 1.5960). Ozonolysis gave acetone and benzophenone as exclusive products.

2-Methyl-3-phenyl-2-butene (3f) was obtained quantitatively from β -lactone **2f**, bp 100° (25 mm) (lit.⁴³ bp 83° (12 mm)).

1,2-Diphenyl-3-methyl-3-butene (3g) was obtained quantitatively from β -lactone **2g**, bp 160° (15 mm), *n*_D²⁰ 1.5725 (lit.⁴⁴ bp 168° (20 mm)). Ozonolysis gave exclusively acetone and deoxybenzoin.

1,2,4-Triphenyl-3-methyl-2-butene (3h) was obtained quantitatively from β -lactone **2h**, bp 195° (1.0 mm). The nmr (60 MHz) showed it to be a 2.5:1.0 mixture of *trans* and *cis* olefins: *trans* isomer, δ (CCl₄, TMS, ppm) 1.80 (s, 3, CH₃), 3.23 (s, 2, PhC=C–CH₂Ph), 3.67 (s, 2, CH₃C=CCCH₂Ph), and 7.00 (s, 15, C₆H₅); *cis* isomer, δ (CCl₄, TMS, ppm) 1.50 (s, 3, CH₃), 3.60 (s, 2, >C=C–(Ph)CH₂Ph), 3.75 (s, 2, >C=C(Me)CH₂Ph), and 7.0 (s, 15, C₆H₅). Ozonolysis gave phenylacetone and deoxybenzoin as exclusive products.

2-Methyl-1-phenylpropene (3i) was obtained quantitatively from β -lactone **2i**, bp 103° (25 mm) (lit.⁴⁵ bp 76–77° (11 mm)).

Isopropylidenecyclohexane (3j) was obtained quantitatively from β -lactone **2j**, bp 160° (760 mm) (lit.⁴⁶ bp 160–161° (760 mm)). Ozonolysis gave acetone and cyclohexanone as exclusive products.

(E)-1,2-Diphenyl-2-butene (3o) was obtained quantitatively from *E* lactone **2o**, bp 135–138° (0.9 mm), *n*_D²⁰ 1.5880 (lit.²⁹ bp 128–136° (0.9 mm), *n*_D²⁰ 1.5883). The spectral data are ir (cm⁻¹, CCl₄) 3075–3025 (m, aromatic CH), 2960 (w, aliphatic CH), and 700 (s, C₆H₅); nmr (60 MHz) δ (CCl₄, TMS, ppm) 1.93 (d, 3, *J* = 6.5 Hz, CH₃CH=), 3.90 (s, 2, –CH₂–), 6.07 (q, 1, *J* = 6.5 Hz, CH₃–CH=), and 7.20 (m, 10, C₆H₅). Glpc analysis showed that the olefin **3o** is of 99.3 ± 0.3% isomeric purity.

(Z)-1,2-Diphenyl-2-butene (3p) was obtained quantitatively from *Z* lactone **2p**, bp 134–140° (0.8 mm), *n*_D²⁰ 1.5716. The spectral data are ir (cm⁻¹, CCl₄) 3075–3025 (m, aromatic CH), 2910 and 2850 (w, aliphatic CH), and 700 (s, C₆H₅); nmr (60 MHz) δ (CCl₄, TMS, ppm) 1.62 (d, 3, *J* = 6.5 Hz, CH₃CH=), 3.65 (s, 2, CH₂), 5.56 (q, 1, *J* = 6.5 Hz, CH₃CH=), and 7.20 (m, 10, C₆H₅). Glpc analysis showed that olefin **3p** is of 97.6 ± 0.2% isomeric purity.

Direct Dehydrocarbonation of β -Hydroxy Acids. A round-bottomed flask, provided with a spinbar, condenser, and gas outlet tube protected with a calcium chloride drying tube, was charged with a solution of 2–3 mmol of β -hydroxy acid **1** in 20–30 parts of anhydrous pyridine. Two moles of benzenesulfonyl chloride per mole of β -hydroxy acid was added and the reaction mixture stirred overnight at 45–55°. The dark mixture was poured onto three to four volumes of water and extracted several times with ether. The combined ethereal layers were extracted several times with 6 *N* hydrochloric acid and washed with aqueous sodium bicarbonate and finally with water. After drying (MgSO₄), the ether was removed at reduced pressure (25 mm) and the olefin distilled. Olefins **3k–3n** (Table I) were prepared by this method and the details are described below for the individual cases.

1,1-Diphenylethylene (3k) was obtained in 55% yield, bp 145° (15 mm) (lit.⁴⁷ bp 113° (2 mm)), starting with 121 mg (0.5 mmol) of hydroxy acid **2k** in 3 ml of pyridine and 177 mg (1.0 mmol) of benzenesulfonyl chloride.

2,3-Diphenylpropene (3l) was obtained in 64% yield, bp 105° (1.0 mm), *n*_D²⁰ 1.5905 [lit.⁴⁸ bp 170° (22 mm), *n*_D²⁰ 1.5903], starting with 512 mg (2.0 mmol) of hydroxy acid **2l** in 6 ml of pyridine and 708 mg (4.0 mmol) of benzenesulfonyl chloride.

2-Phenyl-1-butene (3m) was obtained in 60% yield, bp 180° (760 mm), *n*_D²⁰ 1.5265 (lit.⁴⁹ bp 181° (760 mm), *n*_D²⁰ 1.5264), starting with 582 mg (3.0 mmol) of hydroxy acid **2m** in 10 ml of pyridine and 1.062 g (6.0 mmol) of benzenesulfonyl chloride.

3-Methyl-2-phenyl-1-butene (3n) was prepared in 82% yield, bp 98° (30 mm), *n*_D²⁰ 1.5180 (lit.⁵⁰ bp 82° (12 mm), *n*_D²⁰ 1.5181), starting with 624 mg (3.0 mmol) of hydroxy acid **2n** in 10 ml of pyridine and 1.062 g (6.0 mmol) of benzenesulfonyl chloride.

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