current had reached 85% of its peak value (i_{pc}).[16] Where no anodic current peak (i_{pa}) was observed, an estimate of the value of $E_{1/2}$ was obtained from the cathodic potential at which i_c reached 85% of the maximum value, i_{pc}. Comparable procedures were followed to obtain the oxidation potentials. Half-life estimates for the various oxidized and reduced species were obtained by a previously described procedure[15] in which the scan rates and switching potentials (E_λ) in reductions were adjusted until $i_{pa} = 1/2(i_{pc})$. The half-life for reduced species was than taken to be the elapsed time as the potential was swept from E_{pc} to E_λ to E_{pa}. In instances where the intermediate was either too unstable or too stable to allow a variation in i_{pa} with time, the minimum or maximum values of the half-life were estimated. Comparable procedures were followed for the oxidations. The results of these measurements are summarized in Table IV. The effect of added H_2O on the stability of various oxidized and reduced species was explored by adding known amounts of H_2O (1.0 *M* for reductions and 0.2 *M* for oxidations) to the anhydrous solution and then repeating the measurements previously described.

(16) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964); **37**, 178 (1965).

Registry No.—**1a**, 1714-09-6; **1b**, 602-55-1; **1c**, 1714-19-8; **1d**, 33522-35-9; **1e**, 33522-39-3; **2**, 33522-27-9; **3**, 38305-27-0; *cis*-**4**, 38309-51-2; *trans*-**4**, 38309-52-3; **5**, 38305-28-1; **6**, 38305-29-2; **7**, 90-44-8; **8a**, 2395-96-2; **8b**, 784-04-3; **9**, 1714-15-4; **10a**, 38305-34-9; **10b**, 38305-35-0; **11**, 33522-37-1; **12a**, 38305-37-2; **12b**, 38305-38-3; **13**, 38305-39-4; **14**, 38305-40-7; **15a**, 38305-30-5; **15b**, 38305-31-6; **16a**, 602-60-8; **16b**, 37170-96-0; **17**, 22362-90-9; **18**, 14381-66-9; **19a**, 129-42-0; **19b**, 38313-16-5; **19c**, 82-43-9; **19d**, 30877-00-0; **20a**, 605-02-7; **20b**, 1038-67-1; anthracene, 120-12-7; 1-anthramine, 610-49-1.

The Reaction of Cyclic α-Ketal Acids with Phosphorus Pentachloride. A New Stereospecific Route to Esters of Halohydrins

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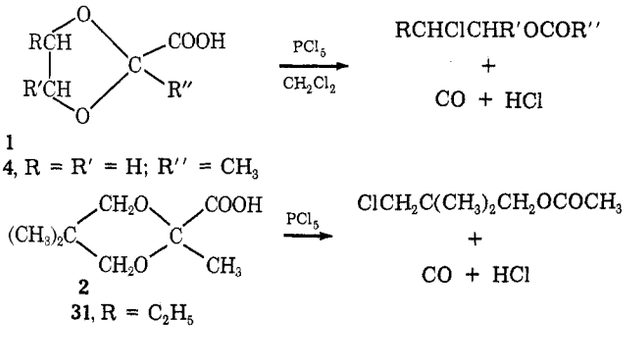
Treatment of a number of cyclic α-ketal acids containing 1,3-dioxolane, 1,3-dioxane, and 1,3-dioxepane rings with phosphorus pentachloride in methylene chloride yielded esters of 1,2-, 1,3-, and 1,4-chlorohydrins, respectively. Evidence is presented to show that 2-chloro-2-methyl-1,3-dioxolane (**5**) and 2-chloro-2,5,5-trimethyl-1,3-dioxane (**9**) are formed directly at −60° from 2-carboxy-2-methyl-1,3-dioxolane (**4**) and 2-carboxy-2,5,5-trimethyl-1,3-dioxane (**8**), respectively. On warming to 0° **5** and **9** rearrange to 2-chloroethyl acetate (**6**) and 3-chloro-2,2-dimethylpropyl acetate (**10**), respectively. Similar reactions with optically active 1,3-dioxolanes yield stereospecific products in which inversion of configuration occurs at the carbon–oxygen bond which is converted to a carbon–chlorine bond. In unsymmetrical 1,3-dioxolanes, the regiospecific products of the reaction are those predicted by assuming an SN2 type mechanism for opening of the 1,3-dioxolane ring. The synthetic utility of these reactions for the synthesis of optically active epoxides is demonstrated.

In a preliminary communication, the conversion of several 2-carboxy-1,3-dioxolanes (**1**) and a 2-carboxy-1,3-dioxane (**2**) into esters of halohydrins by treatment



1

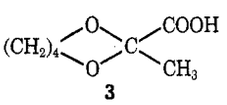
4, R = R' = H; R'' = CH_3

2

31, R = C_2H_5

with phosphorus pentachloride in methylene chloride were described.[2] A more detailed account of this and additional work is presented herein.

The preparation of the requisite 2-carboxy-1,3-dioxolanes and 1,3-dioxanes from diols and pyruvic and benzoylformic acids was accomplished in moderate yields under acid catalysis by either or both of two methods: A, treatment of the α-keto acid with excess diol; and B, treatment of the diol with excess α-keto acid.[3] When method A was used an alkaline treatment was needed during the work-up to hydrolyze any ester formed. Yields of 1,3-dioxanes were better than those of 1,3-dioxolanes (see Table I, Experimental Section). In the only case of a 1,4-diol studied, 1,4-butanediol and pyruvic acid reacted to give 2-carboxy-2-methyl-1,3-dioxapane (**3**) in 63% yield. In a few cases, benzoylformic acid afforded α-ketal acids in about the same yields as when pyruvic acid was used.



3

The reactions of the cyclic acids above described with phosphorus pentachloride or thionyl chloride in methylene chloride took place rapidly at room temperature or below. The evolution of hydrogen chloride and carbon monoxide occurred rapidly under all conditions. Comparable results were obtained when a suspension of the dried sodium salts of **1** and **2** in methylene chloride was treated with thionyl chloride or phosphorus pentachloride. In two cases when thionyl chloride was used, the results were qualitatively the same but the yields of pure halo esters obtained were inferior. Accordingly, in all further work only phosphorus pentachloride was used.

With regard to the mechanism of the reaction, we wished to know whether the acid chloride was formed and lost carbon monoxide or an alternate path was involved. Accordingly, a solution of 2-carboxy-2-

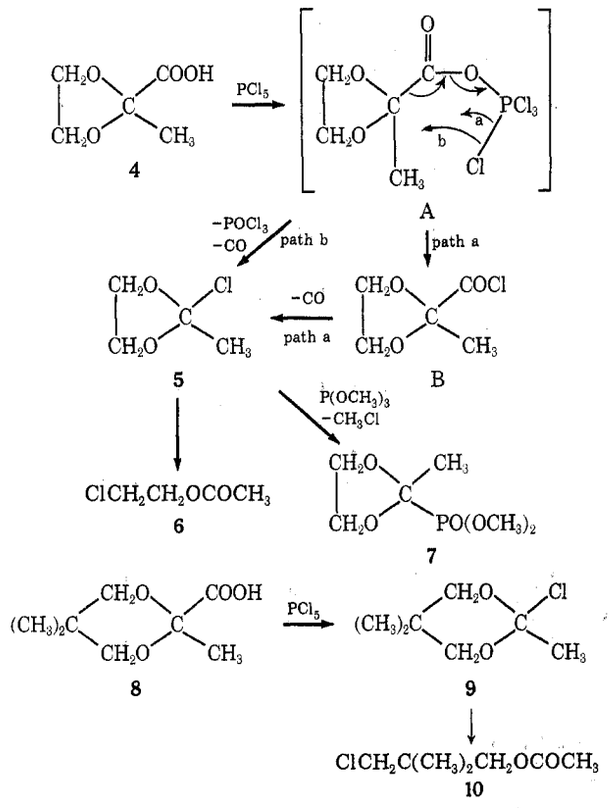
(1) Postdoctoral Fellow. This work was supported by Grant No. GP-12445X of the National Science Foundation.

(2) M. S. Newman and C. H. Chen, *J. Amer. Chem. Soc.*, **94**, 2149 (1972).

(3) E. Vogel and H. Schinz, *Helv. Chim. Acta*, **33**, 116 (1950).

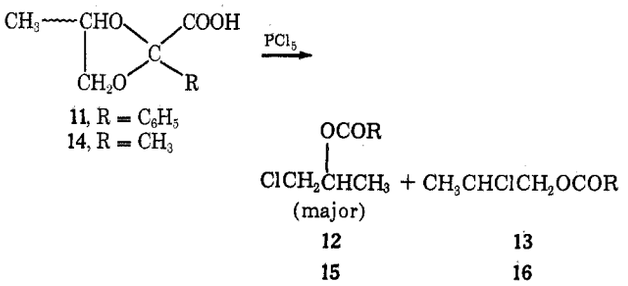
methyl-1,3-dioxolane (**4**) in methylene chloride was added to a suspension of phosphorus pentachloride in methylene chloride at −60°. Evolution of carbon monoxide and hydrogen chloride was instantaneous. The nmr spectrum of the product was consistent with the structure 2-chloro-2-methyl-1,3-dioxolane (**5**).[4] On warming to 0° the spectrum changed to one consistent with the structure 2-chloroethyl acetate (**6**), the product isolated. That **5** was present at −60° was confirmed by treatment of the product formed at −60° with trimethyl phosphite to yield dimethyl (2-methyl-1,3-dioxolanyl)phosphonate[4] (**7**). The lack of induction period observed in all the reactions of cyclic α-ketal acids with phosphorus pentachloride in methylene chloride, and the fact that the addition of galvinoxyl[5] to a reaction of the sodium salt of **4** with thionyl chloride in methylene chloride did not inhibit the reaction by which **4** was converted into **6**, make a free-radical path unlikely.

A similar result was obtained when phosphorus pentachloride was treated with 2-carboxy-2,5,5-trimethyl-1,3-dioxane (**8**) to yield 2-chloro-2,5,5-trimethyl-1,3-dioxane (**9**) at −60° which on warming rearranged into 3-chloro-2,2-dimethylpropyl acetate (**10**). As a result of the above facts the following mechanism for the formation of **5** and **9** is offered (illustrated only with **4**).

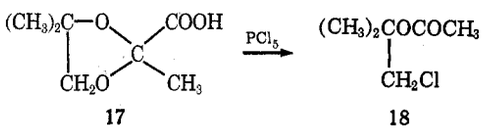


Reactions involving PCl_5 undoubtedly involve attack at oxygen by the PCl_4^+ ion.[6] In the case of ordinary acids this first-formed product usually collapses to yield the acid chloride (path a). However, in the cases of α-ketal acids, path b (as shown in A) involving loss of carbon monoxide with direct formation of **5** is apparently preferred, as judged by the fact that carbon monoxide is formed simultaneously with hydrogen chloride. At low temperatures **5** is stable (see Experimental Section for nmr spectrum). As warming occurs **5** rearranges to **6**.[4] The mechanism by which the rearrangement occurs is of interest and was examined further in substituted analogs.

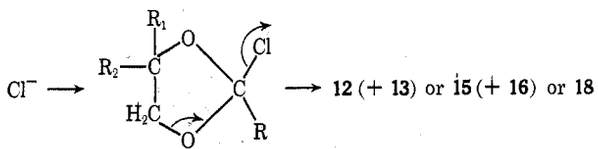
On treatment of 2-carboxy-4-methyl-2-phenyl-1,3-dioxolane (**11**) with phosphorus pentachloride there was obtained in 92% yield a mixture which consisted of 1-chloro-2-propyl benzoate (**12**) and 2-chloro-1-propyl benzoate (**13**) in the ratio of 19:1, respectively.[7] Similarly, 2-carboxy-2,4-dimethyl-1,3-dioxolane (**14**) afforded an 80% yield of a 93:7 mixture of 1-chloro-2-propyl acetate (**15**) and 2-chloro-1-propyl acetate (**16**).[7] In the case of 2-carboxy-2,4,4-trimethyl-1,3-



dioxolane (**17**) only 1-chloro-2-methyl-2-propyl acetate (**18**) was obtained.



These results suggested that the reactions proceed by the formation of 2-chloro-4-methyl-2-phenyl-1,3-dioxolane (**19**), 2-chloro-2,4-dimethyl-1,3-dioxolane (**20**), and 2-chloro-2,4,4-trimethyl-1,3-dioxolane (**21**), which open to **12** (and **13**), **15** (and **16**), and **18** by an S_N2 type displacement by chloride ion (formed by the tendency of **19**, **20**, and **21** to ionize[8]) as shown. This

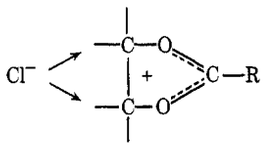


19, R_1 = H; R_2 = CH_3; R = C_6H_5
20, R_1 = H; R_2 = CH_3; R = CH_3
21, R_1 = R_2 = CH_3; R = CH_3

mechanism requires inversion at the carbon undergoing reaction with chlorine. Alternately, the chloride ion (or a chlorine-containing species) might react with ion C[8b] by an S_N2 type reaction (inversion required) or an

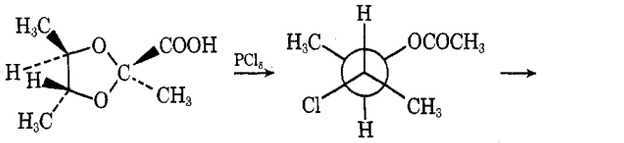
(4) H. Gross, J. Freiberg, and B. Costisella, *Chem. Ber.*, **101**, 1250 (1968).
(5) G. M. Coppinger, *J. Amer. Chem. Soc.*, **79**, 501 (1957).
(6) For examples involving ketones see M. S. Newman and L. L. Wood, Jr., *ibid.*, **81**, 4300 (1959). In A, an alternate formulation would place the phosphorus atom on the oxygen containing the hydrogen.
(7) We previously reported[2] the formation of pure **12**. However, by the use of Eu(DPM)$_3$, K. J. Eisentraut and R. E. Sievers, *ibid.*, **87**, 5254 (1965), the presence of a small amount of the isomer was estimated by nmr spectral studies.
(8) For references and a discussion of the type of cation produced by this ionization see (a) S. Winstein and R. E. Buckles, *ibid.*, **65**, 613 (1943), and (b) S. Hunig, *Angew. Chem., Int. Ed. Engl.*, **3**, 548 (1964). Such ions were produced by participation of a neighboring acetoxy groups in the ionization of a halide or tosyl group, whereas in the present case ions are produced (we assume) by ionization of the chlorine of **5**, **19**, **20**, and **21**.

intimate ion pair involving C and a chloride ion might collapse to product (which would require mostly retention).

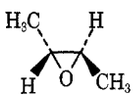


C

To test these hypotheses D-(−)-2,3-butanediol was converted into D-(−)-2-carboxy-2,4,5-trimethyl-1,3-dioxolane (**22**), which yielded L-(+)-*erythro*-3-chloro-2-butyl acetate (**23**) on treatment with phosphorus pentachloride. That inversion had occurred in going from **22** to **23** was established by the fact that treatment of **23** with strong base produced D-(+)-2,3-epoxybutane (**24**),



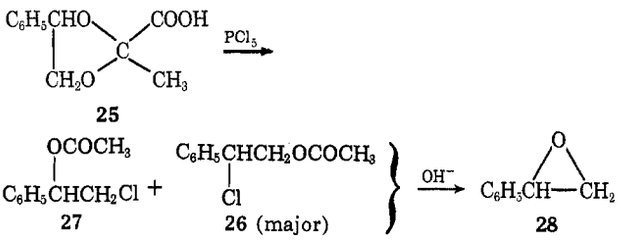
22 **23**



24

a reaction known to proceed with inversion at the carbon–halogen bond.[9] This result excludes the intimate ion pair mechanism.

Further evidence about the mechanism was provided by the fact that treatment of (*R*)-(−)-2-carboxy-2-methyl-4-phenyl-1,3-dioxolane[10] (**25**) [prepared from (*R*)-(−)-phenyl-1,2-ethanediol] with phosphorus pentachloride yielded mainly (*S*)-2-chloro-2-phenyl acetate[11] (**26**) containing a small amount (*ca.* 4%) of 2-chloro-1-phenyl acetate (**27**) assumed to be the *R* isomer, as no cleavage of the bond to oxygen should occur. The conversion of **26** (and **27**) to (*R*)-styrene oxide (**28**),



25

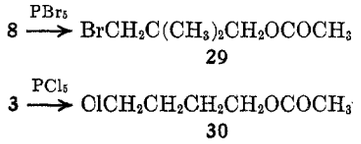
27 **26** (major) **28**

a reaction involving inversion (nor for **27**), confirms the *S* assignment for **26**.

The structure of the major product (**26**) is that which would be predicted by an SN2 mechanism, since the ratio of rate of displacement of chlorine by iodide ion in benzyl chloride and 2-phenylethyl chloride is about 174[12a] or 196[12b] and the rate for 1-phenylethyl chloride (2.5×10^{-5}) is only slightly less than that for benzyl chloride (3.3×10^{-5}).[13]

The smooth stereospecific transformations of **22** to **24** and of **25** to **28** represent an excellent way to prepare optically active epoxides. Since the conversion of an optically active diol to a cyclic ketal does not involve a change in configuration at either carbon and the subsequent steps involve two inversions at one carbon (it may be either carbon if an unsymmetrical diol is used instead of 2,3-butanediol), the resulting epoxide must have the same configuration at each carbon as did the original diol. Thus, if a mixture of halo esters is obtained it need not be separated, as each component must yield the same epoxide.

Further examples of the utility of the reactions described are given by the conversion of 2-carboxy-2,5,5-trimethyl-1,3-dioxane (**8**) to 3-bromo-2,2-dimethylpropyl acetate (**29**), of 2-carboxy-2-methyl-1,3-dioxepane (**3**) to 4-chlorobutyl acetate (**30**), and of 2-carboxy-



5,5-diethyl-1,3-dioxane (**31**) to 3-chloro-2,2-diethylpropyl acetate.

Experimental Section[14]

General Methods of Synthesizing Cyclic α-Ketal Acids. Method A. Preparation of 2-Carboxy-2,5,5-trimethyl-1,3-dioxane (8).—In a typical reaction a mixture of 15.0 g (0.17 mol) of pyruvic acid, 26.6 g (0.256 mol) of 2,2-dimethyl-1,3-propanediol, 150 ml of benzene, and 3 g of acid resin (Amberlite IR-120, Mallinckrodt Chemical Co.) was heated to reflux in an apparatus having a phase-separating head. After 15 hr about 6.5 ml of water was obtained. The filtered reaction mixture was concentrated to give 38 g of residue, which was heated with strong aqueous alkali for 30 min on the steam bath. The resulting alkaline solution was carefully neutralized in the cold with HCl; at the end H_3PO_4 brought the pH to 1. The product was isolated by ether extraction and the dried ($MgSO_4$) extracts were concentrated to afford a creamy solid (33.4 g) which was recrystallized from 2 l. of heptane to give 23.0 g (77% based on pyruvic acid) of **8**** (dried *in vacuo* over P_2O_5): mp 115–116°; nmr ($CDCl_3$) δ 0.77, 1.22 (s, s, 6, 5,5-*gem*-dimethyl), 1.61 (s, 3, 2-Me), 3.58 (s, 4, CH_2), 9.47 (s, 1, COOH). Liquid products were vacuum distilled.

(9) H. J. Lucas and H. K. Garner, *J. Amer. Chem. Soc.*, **70**, 990 (1948). See also C. C. Price and P. F. Kirk, *ibid.*, **75**, 2396 (1953).

(10) The designation *R* refers to the carbon attached to the phenyl group. The compound designated as **25** is a mixture of diastereoisomers (about 3:2 as judged by nmr) because of the new asymmetric center at C-2. No attempt was made to separate these isomers or to determine which was the major component. The same is true for **14**.

(11) The sign of rotation of (*S*)-**26** is negative (neat) but positive in $CHCl_3$. Similarly (*R*)-**28** is positive (neat) but negative in $CHCl_3$. See G. Berti, F. Bottari, and B. Macchia, *Ann. Chim. (Rome)*, **52**, 1101 (1962).

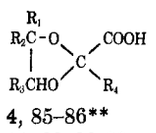
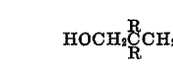
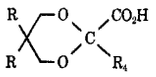
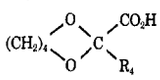
(12) (a) J. B. Conant and W. R. Kirner, *J. Amer. Chem. Soc.*, **46**, 232 (1924); (b) P. Beltrame, L. Olear, and M. S. Monetta, *Gazz. Chim. Ital.*, **89**, 2039 (1959).

(13) J. C. Charlton and E. D. Hughes, *J. Chem. Soc.*, 885 (1956).

(14) Melting points are uncorrected and were determined on a Thomas-Hoover capillary melting point apparatus. Infrared spectra were obtained on a Perkin-Elmer Infracord Model 137 spectrophotometer as films on NaCl plates. Nuclear magnetic resonance spectra were determined on a Varian 60 high-resolution spectrometer using TMS as an internal standard. The mass spectra were determined in an AEI MS-902 double-focusing mass spectrometer. Optical rotations were measured on a Perkin-Elmer Model 141 polarimeter (accuracy to 0.001°) using a 10-cm Micro-cell with inner glass tube diameter of 3.4 mm and a cell volume of 1 ml. In a typical rotation determination, the sample was weighed on a Fisher Gram-Atic balance (accurate to 0.0001 g) and dissolved in a suitable solvent in a 1-ml Kimax volumetric flask, and the prepared solution of known concentration was transferred into the Micro-cell for immediate measuring in the instrument. Measuring accuracy with micro cells is claimed to be approximately ±0.2% for rotations >1° by the manufacturer. Elemental microanalyses were determined by Galbraith Laboratories, Knoxville, Tenn., and by M-H-W Laboratories, Garden City, Mich. All new compounds designated by a double asterisk had analyses within ±0.3% of theory for the elements listed in parentheses by M-H-W Laboratories, or Galbraith Laboratories. All known compounds designated by ≠ had nmr, ir, and mass spectra (parent peak) which were consistent with the assigned structures.

TABLE I

PREPARATION OF CYCLIC KETALS FROM α-KETO ACIDS

Registry no.	Diol $R_1COHCHOHR_3$ R_2	Keto acid $R_4COCOOH$	Bp.°C, of 1,3-dioxolane[a] 	Elemental analysis	Yield, %
107-21-1	$R_1 = R_2 = R_3 = H$	$R_4 = CH_3$[l]	**4**, 85–86**	$[(C_5H_8O_4),C,H]$	55[b]
57-55-6	$R_1 = R_2 = H$; $R_3 = CH_3$	$R_4 = CH_3$	**14**, 89–90[c]**	$[(C_6H_{10}O_4),C,H]$	70[d]
558-43-0	$R_1 = R_2 = CH_3$; $R_3 = H$	$R_4 = CH_3$	**17**, 91–92[e]**	$[(C_7H_{12}O_4),C,H]$	48[d]
5396-58-7	$R_1 = R_3 = CH_3$; $R_2 = H$[f]	$R_4 = CH_3$	**22**, 77.5–78**	$[(C_7H_{12}O_4),C,H]$	51[d]
93-56-1	$R_1 = R_2 = H$; $R_3 = Ph$[g]	$R_4 = CH_3$	**25**, 133–134[h]**	$[(C_{11}H_{12}O_4),C,H]$	51[d,k]
	$R_1 = R_2 = R_3 = H$	$R_4 = Ph$[m]	76.5–77.5[i]**	$[(C_{10}H_{10}O_4),C,H]$	53[b]
	$R_1 = R_2 = H$; $R_3 = CH_3$	$R_4 = Ph$	**11**, 147.0–150.5[c]**	$[(C_{11}H_{12}O_4),C,H]$	51[b]
					
126-30-7	$R = CH_3$	$R_4 = CH_3$	**8**, 115–116[j]**	$[(C_8H_{14}O_4),C,H]$	78[b]
115-76-4	$R = C_2H_5$	$R_4 = CH_3$	**31**, 90.5–91.5[j]**	$[(C_{10}H_{18}O_4),C,H]$	89[d]
110-63-4	$HO(CH_2)_4OH$				
		$R_4 = CH_3$	**3**, 105–107**	$[(C_7H_{12}O_4),C,H]$	63[d]

[a] All boiling points are in the range of 0.5–1.0 mm. [b] Prepared by method A. [c] A mixture of stereoisomers.[10] [d] Prepared by method B. [e] At 8.5 mm. [f] D-(−)-2,3-butanediol, $[\alpha]^{22}D$ −12.9°, neat. [g] (*R*)-(−)-phenylethanediol, $[\alpha]^{19.5}D$ −39.2° (*c* 0.0304, ethanol). [h] At 0.06 mm. [i] Melting point, recrystallized from hexane. [j] Melting point, recrystallized from heptane. [k] Crude product suitable for further reaction. [l] Registry no., 127-17-3. [m] Registry no., 611-73-4.

Method B. Preparation of D-(−)-2-Carboxy-2,4,5-trimethyl-1,3-dioxolane (22).—In a typical reaction, D-(−)-2,3-butanediol[15] [10.0 g, 0.11 mol, $[\alpha]^{22}D$ −12.9° (neat)] was added dropwise in 2.5–3 hr to a well-stirred mixture of 29.3 g (0.33 mol) of pyruvic acid and 1 g of acidic resin (Amberlite IR-120) in 150 ml of benzene held at reflux as in method A. After a further 30 min at reflux 2.8 ml of water had been collected. After cooling and filtration, distillation and redistillation afforded 8.9 g (50% based on diol) of **22**:** bp 77–78° (0.6 mm); $[\alpha]^{22}D$ −14° (neat); nmr δ 1.28 (d, *J* = 5.5 Hz, 6, 4-Me, 5-Me), 1.55 (s, 3, 2-Me), 3.81 (m, 2, 4-H, 5-H), 9.47 (s, 1, COOH).

(*R*)-(−)-2-Carboxy-2-methyl-4-phenyl-1,3-dioxolane (25).—By method B, (*R*)-(−)-phenylethanediol, mp 64.5–65.5° [from benzene–petroleum ether (bp 30–60°)], $[\alpha]^{19.5}D$ −39.24° (*c* 0.0304, ethanol),[16] was converted into **25**,[10] bp 133.5–134.5° (0.06 mm), $[\alpha]^{20}D$ −57.37° (*c* 0.0638, $CHCl_3$), in 51% yield. An analytically pure sample of **25**, having the same rotation, was obtained only after a cold aqueous alkaline solution of **25** was extracted with ether and **25** was liberated in the cold with phosphoric acid. The data for the other compounds synthesized are summarized in Table I.

General Methods of Synthesis of Esters of Chlorohydrins from Ketals of α-Keto Acids. A. Reaction of Ketals of α-Keto Acids with PCl_5.—In a typical experiment, 1 g (4.83 mmol) of the diastereoisomeric mixture[10] of **11** in 5 ml of CH_2Cl_2 was added dropwise to a solution of 1.05 g (5.83 mmol) of PCl_5 in 10 ml of CH_2Cl_2 at room temperature in a 50-ml flask fitted with a 10-ml pressure-equalizing dropping funnel and a gas outlet. The gas evolved was passed over a small amount of ammonia to detect HCl, through a test solution[17] to test for carbon monoxide, or measured by collection over water. Carbon monoxide and HCl were immediately detected. The reaction was essentially complete after 15 min. When the gas evolved was not passed through the CO testing solution, the reaction was monitored by the volume of CO collected. After standing at room temperature for 2 hr, dilute Na_2CO_3 was added (with cooling). The CH_2Cl_2 layer was separated, washed with brine, dried over $MgSO_4$, and concentrated. Distillation afforded 0.80 g (84%) of **12**,± bp 98.0–99.5° (1.2 mm), containing about 5% of **13**.± The presence of a small amount of **13** was revealed by nmr analysis [with 15 mol % of $Eu(DMP)_3$ added[18]] and the precentage was estimated by integration. The methyl proton signal of **12** at δ 2.21 (d, *J* = 6.5 Hz) is shifted downfield more (because it is β to the ester function) than is the methyl of **13** at δ 1.8 (d, *J* = 6.5 Hz), which is γ to the ester function.[19]

In a similar manner, the proportions of **15**[20]± (93%) and **16**± (7%) were estimated in the product of reaction of **14** with PCl_5. In addition an authentic sample of a mixture of **15** and **16** was prepared by acetylation of a mixture of 1-chloro-2-propanol and 2-chloro-1-propanol (*ca.* 7:3) obtained from the Columbia Organic Chemicals Co.

B. Reaction of Sodium Salts of α-Ketal Acids with PCl_5 and $SOCl_2$.—In a typical reaction, 0.50 g of the dried sodium salt prepared from **8** (by neutralization with the equivalent of $NaHCO_3$ followed by rotary evaporation of water and drying of the salt by distillation of benzene therefrom) was suspended in 2 ml of CH_2Cl_2 and treated during 15 min with a solution of 0.465 g of PCl_5 in 10 ml of CH_2Cl_2 in an apparatus similar to that described above in part A. Carbon monoxide was evolved immediately and the reaction was complete shortly after the PCl_5 solution had been added. After a conventional work-up there was obtained 0.38 g (90%) of **10**,[21]± bp 95–96° (9.6 mm).

Similarly, when a solution of 5 g of $SOCl_2$ in 3 ml of dry ether at room temperature was added to a suspension of the dried sodium salt, prepared from 1.85 g of **1**, in ether, carbon monoxide[17] and sulfur dioxide[22] were immediately detected. After heating at reflux for 2 hr, the mixture was filtered. Distillation afforded 1.29 g (75%) of **6**,± bp 142.0–142.5°.

C. Reaction of Ketals of α-Keto Acids with $SOCl_2$.—The following is a typical example. Excess thionyl chloride (0.8 g, 6.7 mmol) in 5 ml of anhydrous ether was added to 0.88 g (4.58 mmol) of 2-carboxyl-2-phenyl-1,3-dioxolane at room temperature.

(15) Obtained from the Norse Laboratories, Santa Barbara, Calif. 93103.

(16) J. A. Dale and H. S. Mosher, *J. Org. Chem.*, **35**, 4002 (1970), report $[\alpha]^{25}D$ −39.7° (*c* 4.33, 95% EtOH) for (*R*)-phenylethanediol; hence our diol was about 100% optically pure. We thank Dr. J. D. Morrison for pointing this out to us.

(17) F. Feigl, "Spot Tests in Organic Analysis," 5th Translated English edition, Elsevier, Amsterdam, 1956, p 327.

(18) K. J. Eisentraut and R. E. Sievers, *J. Amer. Chem. Soc.*, **87**, 5254 (1965).

(19) See R. E. Rondeau and R. E. Sievers, *ibid.*, **93**, 1522 (1971), and references cited therein.

(20) A. N. Pudovik and E. M. Faizullin, *Zh. Org. Khim.*, **2**, 798 (1966); *Chem. Abstr.*, **65**, 15214*h* (1966).

(21) M. Bartok, B. Kozma, and A. S. Gilde, *Acta Univ. Szegod., Acta Phys. Chem.*, **11**, 35 (1965), give bp 96–98° (7 mm).

(22) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1966, p 553.

Carbon monoxide, SO_2, and HCl were immediately detected as described above.[17,22] The reaction mixture appeared yellow and was stirred at ambient temperature overnight. Distillation afforded 0.67 g (79%) of 2-chloroethyl benzoate, ± bp 98.5–99° (1.4 mm).[23]

Reaction of (*R*)-(−)-2-Carboxy-2-methyl-4-phenyl-1,3-dioxolane (25) with PCl_5.—Addition of a solution of 0.9 g (4.32 mmol) of pure **25**, $[\alpha]^{23}D$ −57.26° (*c* 0.035, $CHCl_3$), in 8 ml of CH_2Cl_2 to a solution of 1.2 g of PCl_5 in 20 ml of CH_2Cl_2 in a similar manner as described above afforded 0.85 g (4.29 mmol) of (*S*)-(+)-2-chloro-2-phenylethyl acetate (**26**)[24] ± [bp 92–93° (1 mm); $[\alpha]^{23.5}D$ 89.91° (*c* 0.032, $CHCl_3$); nmr (CCl_4) δ 2.0 (3, s, CH_3COO–), 4.36 (2, d, *J* = 7 Hz, $-OCH_2$–), 5.0 [1, m, $-(C_6H_5)CHCl$], and 7.32 (5, s, C_6H_5–)] containing *ca.* 3% **27**,[25] ± nmr (CCl_4) δ 2.05 (3, s, CH_3COO–), 3.67 (2, d, *J* = 6.5 Hz, $-CH_2Cl$), 5.84 [1, t, *J* = 6.5 Hz, $-OCH(C_6H_5)$–], and 7.25 (5, s, C_6H_5). The percentage of **27** was estimated by integration of the acetyl methyl signal at δ 2.05 with respect to that of **26** at δ 2.0, through a 50-Hz sweep width. When the sodium salt prepared from crude **25**, $[\alpha]^{20}D$ −57.37° (*c* 0.0638, $CHCl_3$), was treated with PCl_5 as described above there was obtained (*S*)-(+)-**26** (containing *ca.* 4% of (*R*)-**27** as estimated above), $[\alpha]^{20}D$ 73.74° (*c* 0.0747, $CHCl_3$).

L(+)-*erythro*-3-Chloro-2-butyl Acetate (23).[26]—Treatment of D(−)-2-carboxy-2,4,5-trimethyl-1,3-dioxolane (**22**), $[\alpha]^{22}D$ −14° (neat) [made from D(−)-2,3-butanediol, $[\alpha]^{22}D$ −12.9° (neat)] with PCl_5 in CH_2Cl_2 as above afforded **23**, ± bp 87–88° (52 mm), $[\alpha]^{21}D$ 12.74° (neat), in 90% yield. Reaction of **22** with $SOCl_2$ in CH_2Cl_2 afforded **23**, $[\alpha]^{21}D$ 15.16° (*c* 0.0483, CH_2Cl_2), in 80% yield.

3-Chloro-2,2-dimethyl-1-propyl Acetate (10). ±—Treatment of **8** with PCl_5 in CH_2Cl_2 gave **10**,[21] bp 70–71° (8.5 mm), in 85% yield. Yields of **10** were inferior when methods B and C were used.

4-Chlorobutyl Acetate (30). ±—Method A was used to prepare **30**,[27] bp 80–82° (11 mm), from **3** in 85% yield.

Reaction of 8 with PBr_3.—A solution of 1.0 g (3.7 mmol) of PBr_3 in 5 ml of dry ether was added dropwise to a solution of 1.0 g (5.75 mmol) of **8** in 15 ml of ether. The evolution of HBr and CO were detected immediately. After standing overnight, the readily volatile substances were removed under reduced pressure. Nmr analysis showed that the crude residue was essentially pure 3-bromo-2,2-dimethylpropyl acetate. On distillation an analytical sample of this bromo ester (**29**), ± bp 80–81° (8 mm), was obtained.

Chemical and Nmr Evidence for 2-Chloro-2-methyl-1,3-dioxolane (5).—A mixture of 0.2 g of **4** and 0.32 g of PCl_5 in 0.6 ml of CH_2Cl_2 was stirred at −60 to −70° for 3 hr, during which time HCl (g) and CO were detected.[17] Low-temperature nmr (CH_2Cl_2) analysis of the product at −58° revealed that the major product had signals at δ 1.66 (s, 3, C-2 Me) and 4.14 (s, 4, $-CH_2CH_2$–) consistent with the formulation as **5**,[4] which rapidly rearranged on warming to 0° to **6**, nmr (CH_2Cl_2) δ 2.08 (s, 3, CH_3COO–), 3.68 (m, 2), and 4.32 (m, 2), an A_2M_2 pattern for $ClCH_2CH_2O(COCH_3)$. In a similar run the product from 1.85 g of **4** was stirred at −60° until no more CO was evolved (4 hr). Excess trimethyl phosphite was added and the mixture, after stirring at −60° for 4 hr, was allowed to come to room temperature overnight. After removal of methylene chloride and excess trimethyl phosphite, the residue was fractionated to give about 0.75 g (43%) of **6** and 0.78 g (50%) of dimethyl phosphonate,[28] nmr (neat) δ 3.75 [d, 6, J_{POCH} = 12 Hz, $(CH_3O)_2P$], 6.75 (d, 1, J_{PH} = 694 Hz, HP–), and 1.25 g (45%) of **7**,[4] ± bp 73–74° (15 mm), slightly contaminated with dimethyl phosphonate, nmr (neat) δ 1.45 (d, 3, J_{PCCH} = 17 Hz, CH_3CP), 3.69 (d, 4, J_{PCOCH} = 11 Hz, $-OCH_2CH_2O$–), 3.74 (6, d, J_{POCH} = 11 Hz, $2\ CH_3O$–).

Nmr Evidence for 9.—Addition of a solution of 0.2 g (1.15 mmol) of **8** in 0.4 ml of CH_2Cl_2 to 0.26 g of PCl_5 in 0.2 ml of CH_2Cl_2 at −70° as described above afforded essentially pure **9**, nmr (CH_2Cl_2, −57°) δ 1.30 [s, 6, $(CH_3)_2C$], 2.89 (s, 3, C-2 methyl), 4.87 (d, 4, *J* = 1.5 Hz, ring protons), in agreement with the formulation as **9**. On warming to 5° and finally to 35°, the ketal of the acid chloride slowly rearranges to **10**.[21] ± In contrast to **5**, **9** appears to be stable at temperatures up to about −10°, and rearranges much more slowly than **5**.

(*R*)-(−)-Styrene Oxide (28).—A solution of 3.2 g (16.1 mmol) of **26**, $[\alpha]^{27}D$ 89.91° (*c* 0.032, $CHCl_3$), which contained about 3% of **27**, in 4 ml of methanol was added during 20 min to a stirred ice-cold solution of 20 g of NaOH in 25 ml of water. After 3 hr at 0° the product was isolated by $CHCl_3$ extraction. On removal of the $CHCl_3$ crude (*R*)-styrene oxide was obtained in almost quantitative yield. On distillation a center cut was obtained, bp 57.5–58.5° (4 mm), $[\alpha]^{25}D$ 34.1° (neat, 1 dm), $[\alpha]^{25}D$ −22.5 (*c* 2.390, $CHCl_3$), −21.5 ± 1.5° (*c* 0.330, $CHCl_3$).[29]

D-(+)-2,3-Epoxybutane.—A solution of 0.9 g of **23**, $[\alpha]^{22.5}D$ 12.48° (neat), in 1 ml of ethylene glycol was added during 25 min to a stirred solution of 13.5 g of KOH in 7.4 ml of water held at 117° (oil bath). The epoxide was distilled as formed. At the end the oil-bath temperature was raised to 145°. The distillate was thoroughly dried with $CaCl_2$ to yield 0.35 g (81%) of D-(+)-2,3-epoxybutane, ± bp 50–51°, $[\alpha]^{21.5}D$ 76.22° (*c* 0.0613, xylene).[30]

Registry No.—**3**, 38088-73-2; **4**, 5736-04-9; **5**, 38088-74-3; **7**, 17997-31-8; **8**, 36294-83-4; **8** (Na salt), 38808-77-6; **10**, 2163-55-5; **11**, 38088-79-8; **12**, 36220-92-5; **13**, 7022-98-2; **14**, 6413-11-2; **17**, 38088-83-4; **22**, 36220-93-6; **23**, 36220-94-7; **24**, 1758-33-4; **25**, 38088-84-5; **26**, 6509-95-1; **28**, 20780-53-4; **31**, 38088-86-7; Cl_5P, 10026-13-8.

(23) M. V. Prokof'eva, S. R. Rafikov, and B. V. Suvorov, *Zh. Obshch. Khim.*, **32**, 1318 (1962); *Chem. Abstr.*, **58**, 1392e (1963), give bp 118–120° (2 mm).

(24) For the optically inactive compound, see Y. Yukawa and M. Sakai, *Bull. Chem. Soc. Jap.*, **39**, 827 (1966).

(25) An authentic sample, bp 87.0–87.5° (11 mm), was prepared by acetylation of 2-chloro-1-phenylethanol in pyridine. See V. R. Kartashov and I. V. Badrikov, *Zh. Org. Khim.*, **3**, 775 (1967); *Chem. Abstr.*, **67**, 43162e (1967).

(26) For racemic compound, see R. C. Fahey and C. Schubert, *J. Amer. Chem. Soc.*, **87**, 5172 (1965).

(27) J. B. Lee and T. J. Nolan, *Can. J. Chem.*, **44**, 1331 (1966).

(28) Product resulting from dealkylation of $(CH_3O)_3P$ by HCl formed in the reaction. See Ye. L. Geffer and J. Burdon, "Organophosphorus Monomers and Polymers," Vol. 6, International Series of Monographs on Organic Chemistry, Pergamon Press, Elmsford, N. Y., 1962, p 114.

(29) The optical purity of our (*R*)-**28** was about 100% as judged by the fact that D. J. Pasto, C. C. Cumbo, and J. Fraser, *J. Amer. Chem. Soc.*, **88**, 2194 (1966), report $[\alpha]^{25}D$ −34.2° (neat, 1 dm) for (*S*)-**28**. All measurements were made on a Perkin-Elmer 141 polarimeter by Dr. Dan Olson, whom we thank for repeating this preparation.

(30) H. L. Lucas and H. K. Garner, *J. Amer. Chem. Soc.*, **70**, 990 (1948), give $[\alpha]^{25}D$ 59° (neat) for 2,3-epoxybutane.