Lead Tetraacetate Oxidations of Stereoisomeric 2-Methyl-3-phenylbutyric Acids[1a,b]

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Lead tetraacetate oxidations of carboxylic acids yield products through alkyl radical or alkyl cation intermediates, depending on reaction conditions. We have investigated these reactions in the well-known phenylethyl system by use of *erythro*- and *threo*-2-methyl-3-phenylbutyric acids. Both substitution and elimination products are obtained. Radical and cationic conditions produce different erythro:threo ratios of substitution products, but each kind of product mixture is independent of the configuration of the starting acid. Radical conditions produce mainly a mixture of 2-chloro-3-phenylbutanes (erythro:threo, 1:1.4); cationic conditions produce mainly a mixture of 1-methyl-2-phenyl-1-propyl acetates (erythro:threo, 1.7:1). The cationic product mixtures are different from those obtained from both solvolytic and deamination reactions of 1-methyl-2-phenyl-1-propyl systems.

Studies of various β-phenylethyl systems have provided a wealth of data, interpretation, and controversy about carbocation processes.[2-7] The kind and extent of rearrangement, the stereoselectivity in product formation, and the degree of participation by neighboring phenyl depend upon the method of generation of the carbocation intermediate and have been attributed to differing degrees of association of cation with leaving group and solvent.[2,8,9] We have investigated the oxidative decarboxylation of *threo*- and *erythro*-2-methyl-3-phenylbutyric acids by lead tetraacetate, using conditions which generate intermediate 1-methyl-2-phenyl-1-propyl cations, and have compared the products formed with those from other carbocation processes. The same mixture of diastereomeric acetates is obtained from both diastereomers by oxidative decarboxylation, and migrations of neighboring hydrogen and methyl do not occur. Phenyl participation does not seem to be important enough to influence the ratio of diastereomeric acetate products.

Lead tetraacetate decarboxylations proceed by way of radical and/or cationic intermediates.[10] The course of a particular reaction is dependent on the structure of the carboxylic acid, the solvent, the relative proportions of reactants, and the nature of the catalyst. Copper(II) salts catalyze the reaction and promote the radical pathway;[11] pyridine, on the other hand, causes a shift to a cationic pathway.[11-13]

Separate lead tetraacetate decarboxylations of *cis*- and *trans*-4-*tert*-butylcyclohexanecarboxylic acids in the presence of pyridine gave the same mixture of *cis*- and *trans*-4-*tert*-butyl-1-cyclohexyl acetates, leading to the conclusion that the same carbocation intermediate is formed from the diastereomeric reactants.[14]

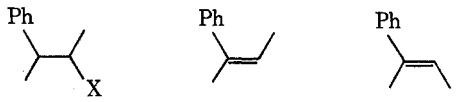
We considered it of interest to investigate whether a β-phenyl substituent would influence the stereochemistry of carbocation product formation in lead tetraacetate decarboxylations. Product formation by solvolysis of 1-methyl-2-phenyl-1-propyl systems is stereospecific,[2,15] but deaminations of the corresponding amines are less stereoselective.[16] Carbocations generated by various means from 1-methyl-2-phenyl-1-propyl systems have been found to give substitution and elimination products resulting from phenyl, methyl, hydrogen, and no rearrangement.[2] Stereochemistry and phenyl rearrangement data have been rationalized in terms of phenyl-bridged cationic intermediates, both symmetrical[15] and unsymmetrical,[7] both providing assistance for the separation of the leaving group and formation after departure of the leaving group. Phenyl-bridged transition states between rapidly equilibrating unbridged cationic intermediates have also been proposed to account for the observed stereochemistry.[5] Recent spectroscopic evidence demonstrates the existence of stable phenyl-bridged cations in superacid solutions.[17]

The acids required for our study were the *erythro*- and *threo*-2-methyl-3-phenylbutyric acids, a mixture of which was synthesized by conventional methods from acetophenone through a sequence of Reformatsky, dehydration, hydrogenation, and saponification reactions and from 2-phenylpropionaldehyde through a Grignard, chlorodehydroxylation, and Grignard carbonation sequence. The mixture of diastereomers (approximately 1:2 theo:erythro) was resolved by fractional crystallization and distillation.

Oxidative decarboxylation was carried out on each isomeric acid separately with pyridine as catalyst and an excess of lead tetraacetate.[12] Product analysis was achieved by comparison of gas chromatographic (gc) data with those of authentic samples; an internal standard was employed for quantitative determinations. The results are summarized in Table I. The only substitution products formed in the oxidation of either isomeric carboxylic acid are acetates obtained without rearrangement due to hydrogen or methyl migration. Rearranged acetates were looked for, but not detected, in the gc chromatogram of the product mixture. Phenyl migration could not be observed under the reaction conditions employed. Such participation, either in generating the intermediate cation or in subsequent reactions of the cation, must be at most a minor factor, however, on the basis of the isomer distribution of the acetates. Phenyl participation is expected to favor erythro acetate considerably more substantially than is found (It-OAc/Ie-OAc ~ 0.20).[18]

The formation of identical (within experimental error) erythro:threo ratios of acetates from both isomeric acids demonstrates the existence of a single cationic intermediate in the oxidation. This observation is supported by the results of the separate halodecarboxylation, a reaction proceeding by a radical pathway,[20] of the isomeric acids. The results are given in Table II. Since the same ratio of erythro:threo chlorides results from the isomeric reactants, a common radical intermediate must be formed after loss of carbon dioxide. The ligand transfer step[21] which follows is then the same for the two isomers and identical product distributions result. It follows that the cation resulting from an electron transfer step[22] must likewise be independent of the stereochemistry of the parent compound, resulting in identical product distributions from the isomeric acids, as found. The specific values of

Table I
Product Distribution from Oxidative Decarboxylation of Isomeric 2-Methyl-3-phenylbutyric Acids

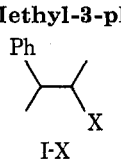


I-X II-Z II-E

Starting acid, mmol	Reaction time, hr	Recovered acid, mol %	Product distribution, mol %[a] I-H	II-Z	II-E	It-OAc	Ie-OAc	It-OAc/Ie-OAc
			A. Erythro					
3.16	9	17	1			38	61	0.62
3.70	9	12		16	2	32	50	0.64
3.03	30	2	0.1	10	0.7	33	56	0.58
3.04	17		0.4	17	3.6	30	49	0.60
4.46	22		0.5	17	4.2	29	49	0.59
							av	0.61 ±0.02
			B. Threo					
2.86	22	31	2.8			33	64	0.52
3.08	21	Trace	0.6	14	3.1	31	52	0.60
2.50	48	3	0.6	17	3.9	30	49	0.61
							av	0.58 ±0.04

[a] It = threo; Ie = erythro.

Table II
Product Distribution of Halodecarboxylation of *erythro*- and *threo*-2-Methyl-3-phenylbutyric Acids



I-X

Configuration of starting acid	Time, hr	Product distribution, mol %[a] Ie-Cl	It-Cl	Ratio It-Cl:Ie-Cl
Erythro	3	41.5	58.5	1.43:1
Threo	4	42.2	57.8	1.37:1

[a] It = threo; Ie = erythro.

the erythro:threo ratios must be determined by the direction of attack on either the radical or cationic intermediate. Several pairs of diastereomeric carboxylic acids which do not have a β-phenyl substituent have previously been found also to give the same proportion of diastereomeric products.[12-14,23,24]

Tables III and IV give summaries of substitution and elimination product distributions from reactions involving 1-methyl-2-phenyl-1-propyl cationic intermediates. Solvolyses occur with high stereoselectivity and little or no methyl and hydrogen migration. Amine deaminations occur with lower stereoselectivity and substantial methyl and hydrogen rearrangements. The pyridine-catalyzed oxidative decarboxylations, which take place with only moderate stereoselectivity but without hydrogen or methyl rearrangements, appear to proceed through a cationic intermediate different from either solvolytic or deamination intermediates.

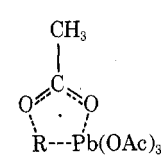
The elimination products likewise illustrate this difference in character of the intermediate cations. The sterically less favored *Z* isomer (steric interaction between the phenyl and methyl groups) is formed from each isomeric parent acid in preference to the thermodynamically more stable *E* isomer.[25]

A small amount of radical product, 2-phenylbutane, is present in the decarboxylation product mixture. The much smaller proportion (2–3% of the hydrocarbon mixtures) of alkane formed from the 2-methyl-3-phenylbutyric acids compared to the amount (~25% of hydrocarbon product) obtained from a similar reaction with 2-methylbutyric acid[11] strongly indicates that conversion of the phenyl-substituted radical to substitution and elimination products (oxidative processes) is easier than it is with the less substituted radical intermediates.

The apparent absence of any significant stabilization of one conformation of an intermediate 1-methyl-2-phenyl-1-propyl cation by neighboring phenyl participation causes one to consider seriously an alternative to an alkyl cation intermediate in the processes leading to alkyl acetate products. A ligand-transfer reaction, parallel to that in halodecarboxylation and involving transfer of AcO· to R·, is, at first thought, an attractive alternative. However, we presume that the stereochemical influences for Cl· and AcO· transfer from Pb(IV) species to R· will be quite similar. The reversed ratios of threo:erythro products for the RCl and ROAc mixtures strongly argues for different mechanisms in the two processes.

It is also conceivable that the alkyl acetates are formed by an SNi-type reaction from an alkyllead intermediate.

$$R\cdot + Pb(OAc)_4 \longrightarrow RPb(OAc)_4$$

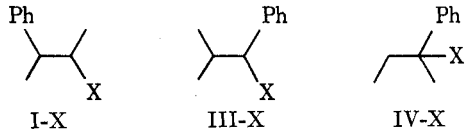


$\longrightarrow$ ROAc + $Pb(OAc)_3$

Again, however, there is no apparent reason for one stereochemical pathway (threo product) being preferred for alkyl chloride formation [ligand transfer from Pb(IV) to R·] and the other (erythro product) for alkyllead bond formation [between Pb(IV) and R·] in the intermediate. One would expect the SNi reaction, as illustrated above, to occur with retention of configuration at the carbon bound to lead.

Finally, the alkyllead intermediate, formed with the same stereochemical preference as is RCl in the ligand-transfer step and pictured above, may undergo SN2-type displacement by acetate. Although this process would be consistent with the stereochemical results in the present study, it cannot be a general pathway for the formation of alkyl acetates from those systems, such as norbornyl,[12,24] which yield rearranged products extensively or exclusively, and the composition of the hydrocarbon fraction of the

Table III
Summary of Substitution Products from the 1-Methyl-2-phenyl-1-propyl System



I-X III-X IV-X

Configuration of starting material	Reagent	X	Product distribution,[a] mol % Ie-X	It-X	III-X	IV-X	Ref
Ie-OTs	HOAc	OAc	94	5			27
Ie-OTs	HCOOH	OCHO	100	9			27
Ie-OH	$SOCl_2$	Cl	90				28
Ie-NH_2	HOAc, HONO	OAc	68	6	6	20	16a
Ie-COOH	$Pb(OAc)_4$, py	OAc	63	37			
Ie-COOH	$Pb(OAc)_4$, Cl^-	Cl	42	58			
It-OTs	HOAc	OAc	4	96			27
It-OTs	HCOOH	OCHO	0	100			27
It-OH	$SOCl_2$	Cl		95			28
It-NH_2	HOAc, HONO	OAc	19	25	32	24	16a
It-COOH	$Pb(OAc)_4$, py	OAc	63	37			
It-COOH	$Pb(OAc)_4$, Cl^-	Cl	42	58			

[a] Ie-X = erythro; It-X = threo.

Table IV
Summary of Elimination Products from the 1-Methyl-2-phenyl-1-propyl System

Configuration of starting material	Reagent	Temp, °C	Yield of olefin, %	Product distribution, mol % II-E[a]	II-Z[a]	V[b]	VI[c]	Ref
Ie-OTs[d,f]	HOAc	75	23	56	8	23	13	29
Ie-OBs[e]	HOAc	30	6	59	13	13	15	29
Ie-OTs	CH_3CN	82	50	45	22	12	21	29
Ie-OCS_2CH_3		180	91	5	50	38		26
Ie-OTs	$LiAlH_4$	25	22	22				30
Ie-$NO(CH_3)_2$	THF	25	*g*	0	95	5		31
Ie-COOH	$Pb(OAc)_4$, py	80	9	18	82			
It-OTs[d]	HOAc	75	35	42	28	24	6	29
It-OBs	HOAc	30	12	24	55	13	10	29
It-OTs	CH_3CN	82	67	34	34	9	23	29
It-OCS_2CH_3		180	76	36	12	38		26
It-OTs	$LiAlH_4$	25	21		21			30
It-$NO(CH_3)_2$	THF	25	80	95	0	5		31
It-COOH	$Pb(OAc)_4$, py	80	6	18	82			
IV-OAc[h]	HOAc	75	90	54	3	43		29
IIZ, IIE or V	HOTs	75	100	79	18	3		32

[a] II-Z = (*Z*)-2-phenyl-2-butene; II-E = (*E*)-2-phenyl-2-butene. [b] V = 2-phenyl-1-butene. [c] VI = 3-phenyl-1-butene. [d] I = 1-methyl-2-phenyl-1-propyl; Ie = erythro; It = threo. [e] OBs = *p*-bromobenzenesulfonate. [f] OTs = *p*-toluenesulfonate. [g] Yield of olefin was not determined. [h] IV-OAc = 1-methyl-1-phenyl-1-propyl acetate.

present product mixture appears to require cationic intermediates.

Experimental Section

The reagents used in all syntheses were reagent commercial chemicals; unless otherwise indicated, these chemicals were used as received. The solvents used were dried by storage over calcium hydride. Pyridine was stored over potassium hydroxide.

Infrared (ir) spectra of thin films on sodium chloride plates or of solid solutions in potassium bromide disks were obtained with a Perkin-Elmer Infracord Model 137 spectrometer. Proton nuclear magnetic resonance (nmr) spectra of carbon tetrachloride or chloroform-*d* solutions (10–20%) were obtained with a Varian Associates Model A-60A spectrometer or, with the assistance of D. Latour, with a Varian Associates Model HA100 spectrometer; tetramethylsilane (TMS) was used as internal reference. Gas chromatographic (gc) data were obtained with a Hewlett-Packard Model 700 instrument equipped with a hydrogen flame ionization detector and 0.125-in. aluminum columns.

Melting points were obtained with a Thomas-Hoover melting point apparatus and are uncorrected. Spinning band distillations were performed on a 24-in. Nester/Faust Annular Teflon Spinning Band Distillation Column.

Synthesis of the 2-Methyl-3-phenylbutyric Acids. A. A 3:1 mixture of the diastereoisomeric ethyl 3-hydroxy-2-methyl-3-phenylbutyrates[33] was prepared[34] in 56% yield (68.6 g) from zinc, acetophenone (0.57 mol), and ethyl 2-bromopropionate (0.55 mol) in benzene (125 ml) solution: bp 109–111° (2.4 mm); nmr (CCl_4) major isomer δ 0.90 (m, 3, OCH_2CH_3), 1.27 (d, J = 7.0 Hz, 3, CH_3CH), 1.36 (s, 3, CH_3COH), 2.91 (q, J = 7.0 Hz, 1, $CHCH_3$), 3.25 (s b, 1, OH), 3.84 (q, J = 7.0 Hz, 2, OCH_2CH_3), 7.30 (m b, 5, C_6H_5); minor isomer δ 0.90 (m, 3, OCH_2CH_3), 1.20 (d, J = 7.0 Hz, 3, CH_3CH), 1.49 (s, 3, CH_3COH), 2.75 (q, J = 7.0 Hz, 1, $CHCH_3$), 4.16 (q, J = 7.0 Hz, 2, OCH_2CH_3), 7.30 (m b, 5, C_6H_5).

The mixture of hydroxy esters (0.31 mol) was dehydrated[33] with potassium hydrogen sulfate (0.32 mol) to **ethyl 2-methyl-3-phenyl-3-butenoate**[35] in 71% yield (44.5 g): bp 109–113° (2.2 mm); nmr (neat) δ 1.11 (t, J = 7.2 Hz, 3, CH_2CH_3), 1.36 (d, J = 7.0 Hz, 3, CH_3CHCO_2Et), 3.67 (q, J = 7.0 Hz, 1, $CHCO_2Et$), 4.08 (q, J = 7.2 Hz, 2, CH_2CH_3), 5.27 (b s, 1, cis HC=CPh), 5.37 (s, 1, trans HC=CPh), 7.33 (m, 5, C_6H_5).

The unsaturated ester (0.22 mol) was hydrogenated in ethanol solution over Pd/C in a Parr apparatus at an initial hydrogen pressure of 40 psig. After removal of solvent by distillation at reduced pressure, nmr analysis [relative intensities of δ 4.12 (OCH_2CH_3, erythro isomer) and 3.87 (OCH_2CH_3, threo isomer) absorptions] of the residue (43.7 g, 98% yield) showed it to be a mixture of **ethyl 2-methyl-3-phenylbutyrates,**[36] *ca.* 2:1 erythro:threo. Pure erythro isomer (gc analysis, 8-ft Carbowax column at 130°) was obtained as the higher boiling fraction from a reduced pressure, spinning-band distillation, bp 101–102° (3.0 mm).

The *erythro*-**2-methyl-3-phenylbutyric acid**[37] was obtained (67% yield after recrystallization from cyclohexane) by saponifi-

cation of the distilled erythro ester: mp 130–131°; ir (KBr) 1672 cm^{-1} (s, C=O); nmr (CCl_4) δ 0.99 (d, J = 6.9 Hz, 3, CH_3CHCO_2H), 1.34 (d, J = 6.6 Hz, 3, CH_3CHPh), 2.56 (dq, $J_{2,3}$ = 10.0, $J_{2,Me}$ = 6.9 Hz, 1, $CHCO_2H$), 2.90 (dq, $J_{2,3}$ = 10.0, $J_{3,4}$ = 6.6 Hz, 1, CHPh), 7.20 (m, 5, C_6H_5), 12.2 (s, 1, CO_2H).

Saponification of the lower boiling ester distillate led to a mixture of crystalline (erythro isomer) and oily acids. The oily material, *threo*-**2-methyl-3-phenylbutyric acid**,[38] was separated by filtration and was distilled: bp 109–110° (0.4 mm); ir (neat, film) 1710 cm^{-1} (s, C=O); nmr (CCl_4) δ 1.08 (d, J = 7.0 Hz, 3, CH_3CHCO_2H), 1.22 (d, J = 7.0 Hz, 3, CH_3CHPh), 2.64 (p, J = 7.0 Hz, 1, $CH_3CHCOOH$), 3.15 (p, J = 7.0 Hz, 1, CH_3CHPh), 7.12 (s, 5, C_6H_5), 10.9 (s, 1, CO_2H).

B. When a 1:1.9 threo:erythro mixture of 2-chloro-3-phenylbutanes was converted through a Grignard reagent to the carboxylic acids, the two diastereomeric 2-methyl-3-phenylbutyric acids were isolated in a 1:1.9 threo:erythro ratio (combined yield, 41%).

2-Chloro-3-phenylbutanes. While the temperature of the mixture was kept below 30°, 3-phenyl-2-butanol (45.9 g, 0.31 mol, 1:1.8 threo:erythro mixture prepared by a Grignard synthesis from 2-phenylpropionaldehyde[39] was added slowly to thionyl chloride (40.1 g, 0.90 mol). This mixture was stirred for 2 hr at room temperature and for 1 hr at reflux temperature, concentrated by distillation, and poured over ice. The alkyl chloride was extracted into pentane, and the pentane solution was washed thoroughly, dried, and concentrated by rotary evaporation. Distillation of the residue gave 43 g (85%) of **2-chloro-3-phenylbutane**,[28] bp 69–69.5° (2 mm). Gc analysis of the distillate (8-ft Carbowax column at 140°) showed it to be a 1:1.9 threo:erythro mixture.[40] The diastereomers were satisfactorily separated by a spinning band distillation. For the lower boiling threo isomer, the nmr absorptions (CCl_4) were δ 0.99 (d, J = 6.6 Hz, 3, CH_3CPh), 1.34 (d, J = 6.9 Hz, 3, CH_3CCl), 2.56 (dq, $J_{2,3}$ = 10.0, $J_{1,2}$ = 6.9 Hz, 1, CHCl), 2.90 (dq, $J_{2,3}$ = 10.0, $J_{3,4}$ = 6.6 Hz, 1, CHPh), 7.20 (m, 5, C_6H_5). For the higher boiling erythro isomer, the nmr absorptions (CCl_4) were δ 1.33 (d, J = 6.8 Hz, 3, CH_3CCl), 1.33 (d, J = 7.2 Hz, 3, CH_3CPh), 3.02 (dq, $J_{2,3}$ = 5.2, $J_{3,4}$ = 7.2 Hz, 1, CHPh), 4.15 (dq, $J_{1,2}$ = 6.8, $J_{2,3}$ = 5.2 Hz, 1, CHCl), 7.13 (m, 5, C_6H_5).

Preparation of Isomeric Phenylbutenes. 2-Phenyl-2-butenes and 2-Phenyl-1-butene. An ether solution of 2-phenyl-2-butanol obtained by a Grignard synthesis from butanone (0.20 mol) was dehydrated with a warm mixture of sulfuric and acetic acids[41] to a mixture of alkenes from which (*E*)-**2-phenyl-2-butene**[26] (pure by gc) was isolated by repeated distillation: 12.6 g (48%); bp 90–93.5° (22 mm); nmr (CCl_4) δ 1.74 (dq, $J_{1,3}$ = 7.0, $J_{1,4}$ = 1.1 Hz, 3, CH_3CH), 1.95 (m, 3, CH_3CPh), 5.83 (qq, $J_{3,4}$ = 7.0, $J_{1,3}$ = 1.1 Hz, 1, C=CH), 7.25 (m, 5, C_6H_5).

The mixture of alkenes above was equilibrated with *p*-toluenesulfonic acid and distilled.[41] From the lower boiling fraction, (*Z*)-**2-phenyl-2-butene**[26] was obtained by a spinning-band distillation: bp 57–60° (10 mm); nmr (CCl_4) δ 1.56 (dq, $J_{1,3}$ = 6.9, $J_{1,4}$ = 1.5 Hz, 3, CH_3CH), 1.99 (m, 3, CH_3CPh), 5.51 (qq, $J_{1,3}$ = 6.9, $J_{3,4}$ = 1.5, 1, C=CH), 7.17 (m, 5, C_6H_5). In the higher boiling fraction, **2-phenyl-1-butene**[29] was identified [mixed with (*E*)-2-phenyl-2-butene] by gc and nmr data: nmr (CCl_4) δ 1.04 (t, J = 7.0 Hz, 3, CH_3CH_2), 2.45 (m, 2, CH_3CH_2), 5.01 (m, 1, trans HC=CPh), 5.24 (m, 1, cis HC=CPh), 7.3 (m, 5, C_6H_5).

3-Phenyl-1-butene[29] was prepared in 13% yield by a Wittig synthesis[42] from 2-phenylpropionaldehyde (0.11 mol): bp 29.1° (1.2 mm); $n^{24}D$ 1.5108; nmr (CCl_4) δ 1.32 (d, J = 7.0 Hz, 3, CH_3CH), 1.75 (m, 1, CH_3CH), 4.87, m, cis HC=CR), 5.09 (m, 1, trans HC=CR), 5.99 (ddd, $J_{1,2\text{-cis}}$ = 9.3, $J_{1,2\text{-trans}}$ = 17.6, $J_{2,4}$ = 6.1 Hz, 1, C=CHR), 7.14 (s, 5, C_6H_5).

1-Phenyl-2-methyl-1-propene. An ether solution of 2-methyl-1-phenyl-1-propanol, prepared by a Grignard synthesis from benzaldehyde (0.14 mol), was dehydrated by a warm mixture of sulfuric and acetic acids.[41] The alkene[43] was obtained in 26% yield: bp 40–42° (1.8 mm); $n^{24}D$ 1.5371; nmr (CCl_4) δ 1.80 (m, 6, CH_3), 6.40 (m, 1, C=CH), 7.14 (s, 5, C_6H_5).

Synthesis of Isomeric Acetates. A portion of (*E*)-2-phenyl-2-butene was converted by hydroboration[44] to threo alcohol, which was esterified with acetic anhydride and pyridine. Conventional work-up of the pyridine solution gave *threo*-1-methyl-2-phenyl-1-propyl acetate:[16a] bp 97.5–99.6° (3.7 mm); $n^{24}D$ 1.4877; ir (neat, film) 1739 cm^{-1} (s, C=O); nmr (CCl_4) δ 1.10 (d, J = 6.0 Hz, 3, CH_3CHOAc), 1.19 (d, J = 7.0 Hz, 1, CH_3CHPh), 1.80 (s, 3, CH_3CO_2), 2.92 (m, 1, CHPh), 5.05 (m, almost p with separation of 6 Hz, 1, CHOAc), 7.17 (s, 5, C_6H_5).

In the same manner, (*Z*)-2-phenyl-2-butene was converted into *erythro*-**1-methyl-2-phenyl-1-propyl acetate**:[16a] bp 76–77° (1.5 mm); ir (neat, film) 1730 cm^{-1} (s, C=O); nmr (CCl_4) δ 0.95 (d, J = 6.3 Hz, 3, CH_3CHOAc), 1.24 (d, J = 6.8 Hz, 3, CH_3CHPh), 1.87 (s, 3, CH_3CO_2), 2.80 (m, 1, CHPh), 4.97 (m, 1, CHOAc), 7.17 (s, 5, C_6H_5).

1-Methyl-1-phenyl-1-propyl acetate was prepared by esterification of 2-phenyl-2-butanol with acetic anhydride and pyridine. The pure ester[16a] was isolated in 67% yield after chromatography of a pentane–ethyl ether (97:3, v/v) solution on a 35-cm alumina column: bp 61.0–61.4° (0.5 mm); ir (neat, film) 1710 cm^{-1} (s, C=O); nmr (CCl_4) δ 0.72 (t, J = 7.0 Hz, 3, CH_3CH_2), 1.76 (s, 3, CH_3CPh), 1.94 (s, 3, CH_3CO_2), 2.0 (m, 2, CH_3CH_2), 7.21 (s, 5, C_6H_5).

Esterification of 2-methyl-1-phenyl-1-propanol with acetic anhydride and pyridine gave **2-methyl-1-phenyl-1-propyl acetate**:[16a] bp 68–73° (0.8 mm); $n^{24}D$ 1.4890; ir (neat, film) 1742 (s, C=O), 1385 and 1370 cm^{-1} (s, isopropyl); nmr (CCl_4) δ 0.77 (d, J = 6.6 Hz, 3, CH_3CHCH_3), 0.93 (d, J = 6.6 Hz, 3, CH_3CHCH_3), 1.93 (s, 3, CH_3CO_2), 2.02 (m, 1, Me_2CH), 5.47 (d, J = 7.5 Hz, 1, CHPh), 7.22 (s, 5, C_6H_5).

A sample of 2-benzyl-2-propanol, prepared by a Grignard synthesis from benzyl chloride and acetone, was partly esterified by acetic anhydride and pyridine. Pure ester (1-benzyl-1-methylethyl acetate)[43] was isolated by chromatography of a pentane–ethyl ether (90:10, v/v) solution through a 40-cm silica gel column: $n^{23.5}D$ 1.4911; ir (neat, film) 1730 (s, C=O), 1380 and 1365 cm^{-1} (s, Me_2C); nmr (CCl_4) δ 1.40 [s, 6, $(CH_3)_2C$], 1.88 (s, 3, CH_3CO_2), 3.03 (s, 2, CH_2Ph), 7.17 (s, 5, C_6H_5).

Decarboxylation Procedures. A. Oxidative Decarboxylation.[12] To an ice-cooled, stirred solution of benzene, pyridine, carboxylic acid, and *tert*-butylbenzene (internal standard for gc analysis) (typical quantities, 10 ml, 3.5, 3.0, and 0.5 mmol, respectively), lead tetraacetate (typical, 4.0 mmol) was added all at once. The reaction flask was then placed in a preheated oil bath, and the mixture was refluxed until completeness of reaction was indicated by formation of a white precipitate in a yellow solution. The cooled mixture was filtered, the precipitate was washed with benzene, and the combined benzene solution was washed sequentially with dilute perchloric acid–sodium chloride solution and with saturated aqueous solutions of sodium chloride, sodium bicarbonate, and sodium chloride. The benzene solution was dried and analyzed by gc methods; internal standards were used for quantitative determination of the product distributions, which are summarized in Table I. Unconsumed carboxylic acid was recovered from the bicarbonate wash solution by acidification with 3 *M* hydrochloric acid.

B. Halodecarboxylation.[20] Lithium chloride was added to a solution of benzene (10 ml), carboxylic acid, lead tetraacetate, and *tert*-butylbenzene (gc internal standard). (See Table II for exact quantities.) The mixture was refluxed for 3–4 hr, cooled, and filtered to remove the white precipitate. The benzene solution was treated and analyzed as described for oxidative decarboxylation. The product distributions are summarized in Table II.

Product Stability Experiments. A benzene solution of a mixture of diastereomeric 1-methyl-2-phenyl-1-propyl acetates was washed, dried, and analyzed as described above for the oxidative decarboxylation product mixture. There was no change in composition of the mixture.

In separate experiments, *erythro*- and *threo*-1-methyl-2-phenyl-1-propyl acetates, 1-methyl-1-phenyl-1-propyl acetate, 2-methyl-1-phenyl-1-propyl acetate, and 2-methyl-1-phenyl-1-propene were substituted for carboxylic acid in the oxidative decarboxylation, and each was unchanged by the procedure.

Registry No. Ethyl 3-hydroxy-2-methyl-3-phenylbutyrate isomer A, 17226-97-0; ethyl 3-hydroxy-2-methyl-3-phenylbutyrate isomer B, 17226-96-9; acetophenone, 98-86-2; ethyl 2-bromopropionate, 535-11-5; ethyl 2-methyl-3-phenyl-3-butenoate, 25289-62-7; ethyl *erythro*-2-methyl-3-phenylbutyrate, 42879-13-0; ethyl *threo*-2-methyl-3-phenylbutyrate, 42879-14-1; *erythro*-2-methyl-3-phenylbutyric acid, 42971-03-9; *threo*-2-methyl-3-phenylbutyric acid, 42879-15-2; *threo*-3-phenyl-2-butanol, 1502-80-3; *erythro*-3-phenyl-2-butanol, 1502-79-0; *threo*-2-chloro-3-phenylbutane, 5706-90-1; *erythro*-2-chloro-3-phenylbutane, 5706-91-2; 2-phenyl-2-butanol, 1565-75-9; (*E*)-2-phenyl-2-butene, 768-00-3; (*Z*)-2-phenyl-2-butene, 767-99-7; 2-phenyl-1-butene, 2039-93-2; 3-phenyl-1-butene, 934-10-1; 2-phenylpropionaldehyde, 93-53-8; 1-phenyl-2-methyl-1-propene, 768-49-0; 2-methyl-1-phenyl-1-propanol, 611-69-8; *threo*-1-methyl-2-phenyl-1-propyl acetate, 42879-20-9; *erythro*-1-methyl-2-phenyl-1-propyl acetate, 42879-21-0; 1-methyl-1-phenyl-1-propyl acetate, 10042-36-1; 2-methyl-1-phenyl-1-propyl

acetate, 5706-87-6; 2-benzyl-2-propanol, 100-86-7; 1-benzyl-1-methylethyl acetate, 151-05-3.

References and Notes

(1) (a) Based on the Ph.D. Dissertation of Sister Alice Theine, Louisiana State University (Baton Rouge), Dec 1972. Grateful acknowledgment is made to the Dr. Charles E. Coates Memorial Fund of the LSU Foundation donated by George H. Coates for financial aid toward the preparation of that dissertation. (b) Presented in part at the Southwest Regional Meeting of the American Chemical Society, Baton Rouge, La., Dec 7, 1972, Paper ORGN 213. (c) Participant in National Science Foundation Summer Institutes for College Teachers of Chemistry, Louisiana State University (Baton Rouge), 1968–1970.

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$$R\cdot + (RCO_2)_4Pb^{IV}X \longrightarrow RX + Pb^{III}(O_2CR)_4 \quad \text{(ligand transfer)}$$

$$X\cdot + (RCO_2)_4Pb^{IV}X \longrightarrow X_2 + Pb^{III}(O_2CR)_4$$

$$Pb^{III}(O_2CR)_4 \longrightarrow R\cdot + CO_2 + Pb^{II}$$

$$R\cdot + X_2 \longrightarrow RX + X\cdot$$

(22) Oxidative decarboxylation[11] involves initial formation of a radical.

$$Pb^{IV}(O_2CR)_4 \longrightarrow Pb^{III}(O_2CR)_3 + R\cdot + CO_2$$

The propagation steps which follow are

$$Pb^{III} \longrightarrow Pb^{II} + R\cdot + CO_2$$

$$R\cdot + Pb^{IV} \longrightarrow R^{+} + Pb^{III} \quad \text{(electron transfer)}$$

$$\downarrow$$

alkene, ester

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