tography on silica gel (Et_2O/hexane (1:1)) to give **14** and **20**.

14 (0.33 g, 65%): an oil; $[\alpha]^{20}_D$ = +45.3° (*c* 1.72, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.85 (d, 1 H, *J* = 3.4 Hz), 7.33 (d, 1 H, *J* = 3.4 Hz), 4.57 (ddd, 1 H, *J* = 7.2, 4.7, 4.1 Hz), 4.45 (ddd, 1 H, *J* = 8.7, 6.3, 5.7 Hz), 4.29 (dd, 1 H, *J* = 7.2, 2.0 Hz), 4.22 (dd, 1 H, *J* = 8.7, 6.3 Hz), 4.14 (dd, 1 H, *J* = 8.7, 5.7 Hz), 3.91 (dd, 1 H, *J* = 6.3, 2.0 Hz), 3.05 (s, 3 H), 2.79 (dd, 1 H, *J* = 15.2, 4.7 Hz), 2.29 (dd, 1 H, *J* = 15.2, 4.1 Hz), 1.47 (s, 3 H), 1.42 (s, 3 H), 1.36 (s, 3 H), 1.19 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 172.38, 143.84, 120.38, 109.70, 99.76, 99.58, 74.89, 72.07, 71.37, 70.75, 67.02, 49.87, 36.46, 26.96, 26.31, 25.70, 24.90. Anal. Calcd for $C_{17}H_{25}NO_6S$: C, 54.97; H, 6.78; N, 3.77. Found: C, 55.16; H, 6.71; N, 3.93.

20 (0.05 g, 11%): an oil; $[\alpha]^{20}_D$ = +119.7° (*c* 0.33, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.72 (d, 1 H, *J* = 3.2 Hz), 7.38 (d, 1 H, *J* = 3.2 Hz), 6.01 (d, 1 H, *J* = 3.3 Hz), 4.92 (dd, 1 H, *J* = 6.2, 3.3 Hz), 4.53 (m, 2 H), 4.27 (m, 2 H), 4.01 (m, 1 H), 1.50 (s, 3 H), 1.43 (br s, 9 H); ^{13}C NMR ($CDCl_3$) δ 164.06, 148.13, 144.64, 120.41, 111.64, 110.38, 101.35, 77.42, 74.68, 72.43, 69.68, 67.07, 28.38, 27.22, 27.13, 25.63. Anal. Calcd for $C_{16}H_{21}NO_5S$: C, 56.62; H, 6.24; N, 4.13. Found: C, 56.01; H, 6.11; N, 4.46.

More of compound **20** was produced, as TLC and ^1H NMR analysis showed, when the reaction time was increased.

1,4-Anhydro-6,7-*O*-isopropylidene-2,3-deoxy-1-(2-thiazolyl)-α-D-*manno*-hept-2-enopyranose (19). The method described above for the acetonization of **13** was applied to **18** (0.1 g, 0.41 mmol) to give, after column chromatography on silica gel (Et_2O/hexane (2:3)), 0.086 g (75%) of **19**: a white solid; mp 114-116 °C; $[\alpha]^{20}_D$ = +35.0° (*c* 0.82, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.81 (d, 1 H, *J* = 3.2 Hz), 7.31 (d, 1 H, *J* = 3.2 Hz), 6.97 (d, 1 H, *J* = 3.6 Hz), 6.51 (dd, 1 H, *J* = 3.6, 0.8 Hz), 4.93 (dd, 1 H, *J* = 5.1, 3.5 Hz), 4.49 (ddd, 1 H, *J* = 6.7, 5.6, 5.1 Hz), 4.15 (dd, 1 H, *J* = 9.8, 5.6 Hz), 4.08 (dd, 1 H, *J* = 9.8, 6.7 Hz), 2.62 (dd, 1 H, *J* = 3.5, 0.8 Hz), 1.50 (s, 3 H), 1.41 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 158.74, 155.23, 149.31, 144.14, 118.48, 110.49, 110.19, 110.07, 77.36, 68.07, 65.49, 26.49, 25.06. Anal. Calcd for $C_{13}H_{15}NO_4S$: C, 55.50; H, 5.37; N, 4.98. Found: C, 55.61; H, 5.95; N, 4.70.

Methyl 4,5:7,8-Di-*O*-isopropylidene-3-deoxy-α-D-*manno*-2-octosulo-2,6-pyranoside (15). The method described above for converting **5b** to **6** was applied to methyl pyranoside **14** (0.33 g, 0.88 mmol). After column chromatography on silica gel (hexane/Et_2O (1:1)), 0.2 g (73%) of the pure aldehyde **15** was obtained: an oil; $[\alpha]^{20}_D$ = +47.8° (*c* 0.55, $CHCl_3$); IR ($CHCl_3$) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.49 (s, 1 H), 4.52 (ddd, 1 H, *J* = 7.8, 3.6, 2.6 Hz), 4.40 (ddd, 1 H, *J* = 7.8, 6.3, 4.5 Hz), 4.33 (dd, 1 H, *J* = 7.8, 1.9 Hz), 4.18 (dd, 1 H, *J* = 8.8, 6.3 Hz), 4.04 (dd, 1 H, *J* = 8.8, 4.5 Hz), 3.67 (dd, 1 H, *J* = 7.8, 1.9 Hz), 3.28 (s, 3 H), 2.50 (dd, 1 H, *J* = 15.7, 3.6 Hz), 1.82 (dd, 1 H, *J* = 15.7, 2.6 Hz), 1.45 (s, 6 H), 1.40 (s, 3 H), 1.33 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 200.71, 110.21, 109.98, 99.24, 74.14, 72.60, 72.20, 70.07, 67.34, 50.93, 32.40, 27.09, 26.23, 26.37, 24.94. Anal. Calcd for $C_{15}H_{24}O_7$: C, 56.95; H, 7.65. Found: C, 56.78; H, 7.83.

4,5:7,8-Di-*O*-isopropylidene-2-*O*-methyl-3-deoxy-α-D-*manno*-2-octulopyranosonic Acid (16). The method described above for oxidizing aldehyde **6** to acid **7** was applied to aldehyde **15** (0.2 g, 0.64 mmol) to give, after the usual workup, 0.21 g (100%) of pure acid **16**: an oil; $[\alpha]^{20}_D$ = +23.2° (*c* 1.25, $CHCl_3$); IR ($CHCl_3$) 1790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.80 (br s, 1 H, exchangeable with D_2O), 4.57 (m, 1 H), 4.36 (m, 2 H), 4.18 (dd, 1 H, *J* = 9.0, 6.0 Hz), 4.00 (dd, 1 H, *J* = 9.0, 4.5 Hz), 3.65 (dd, 1 H, *J* = 7.8, 1.9 Hz), 3.34 (s, 3 H), 2.77 (dd, 1 H, *J* = 15.9, 3.3 Hz), 1.93 (dd, 1 H, *J* = 15.9, 3.0 Hz), 1.50 (s, 3 H), 1.47 (s, 3 H), 1.41 (s, 3 H), 1.37 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 170.28, 110.18, 110.13, 98.56, 73.89, 72.56, 72.03, 70.22, 67.19, 51.39, 32.50, 27.06, 25.53, 25.28, 24.34. Anal. Calcd for $C_{15}H_{24}O_8$: C, 54.21; H, 7.28. Found: C, 54.13; H, 7.08.

(+)-3-Deoxy-D-*manno*-2-octulosonic Acid (12, KDO). A solution of acid **16** (0.2 g, 0.60 mmol) in 90% aqueous AcOH (20 mL) was heated at 90 °C for 30 min. The solution was then concentrated in vacuo, at a temperature not exceeding 50 °C, to afford free KDO, a very hygroscopic white solid, in quantitative yield. This was dissolved in water (15 mL), and the solution was made basic (pH 10) by the introduction of concentrated aqueous NH_3. Evaporation of the solvent in vacuo, at a temperature not exceeding 50 °C, gave a solid residue. This was passed through a reversed-phase column packed with C_{18}-bonded silica gel to give 0.138 g (89%) of the pure KDO ammonium salt: mp 123-126 °C, $[\alpha]^{20}_D$ = +40.9° (*c* 1.05, H_2O) [lit.[32a] mp 125-127 °C, $[\alpha]^{20}_D$ = +41.6° (*c* 2.0, H_2O); lit.[32g] mp 121-124 °C, $[\alpha]^{20}_D$ = +40.3° (*c*, 1.9, H_2O)]. The ammonium salt thus obtained showed TLC behavior ($MeOH/CHCl_3/H_2O$ (10:10:3) and $EtOH/H_2O$/AcOH (4:1:1)) and ^1H and ^{13}C NMR spectra identical with those of an authentic sample.[37]

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Evidence for Ketene Intermediates in the Decarbonylation of 2,4-Dioxo Acids and Esters and 2-Oxobutanedioic Acid Esters

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The mechanism by which α,γ-dioxo carboxylic acid esters **1** and 2-oxobutanedioic acid diesters **2** lose CO was explored. The compounds, 5,5-dimethyl-2,4-dioxohexanoic acid ethyl ester, **1a**, α,2-dioxocyclohexaneacetic acid ethyl ester, **1b**, and α,1-dioxotetrahydro-2-naphthaleneacetic acid ethyl ester, **1c**, lose CO at 170-190 °C to yield the corresponding β-keto esters **3a-c**. When compounds **1** or the parent acids **4** were heated to 170-190 °C with water in a sealed reactor, they yielded ketones resulting from replacement by H of $C(O)CO_2R$ from **1** or $C(O)CO_2H$ from **4**. β-Keto esters suffered replacement by H of the carbethoxy group to yield the corresponding ketones when heated with water at about 105 °C. Acylketenes, such as 4,4-dimethyl-1-pentene-1,3-dione, **6a**, 2-oxocyclohexylidenemethanone, **6b**, 1-oxotetrahydro-2-naphthylidenemethanone, **6c**, 3-methyl-1-butene-1,3-dione, **6d**, and 1-butene-1,3-dione, **6e**, are implicated as the common intermediates that react with water to form β-keto acids that subsequently decarboxylate to yield the ketones **5**. Intense IR frequencies in the region of 2120-2140 cm^{-1}, characteristic of ketenes, are observed when **1**, **2**, or **3** is subjected to GC-FTIR analysis with the injector and light pipe at 280 °C. Loss of carbon monoxide and alcohol at high temperature is required to form **6** from **1**, while only the loss of alcohol at lower temperature is needed to form **6** from **3**.

The quest for a plausible mechanism for the decarbonylation of 2,4-dioxo carboxylic acid esters **1** and 2-oxobutanedioic acid esters **2**, a useful synthetic reaction,[1] has intrigued four generations of chemists. Many useful facts

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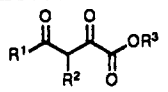
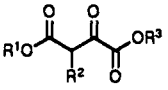
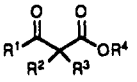
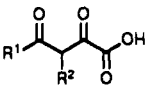
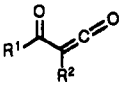
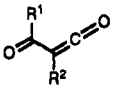
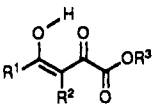
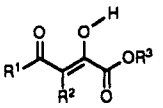
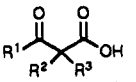
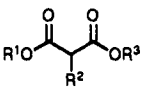
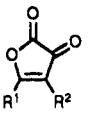
Table I. Compounds Discussed in the Study

compd	R^1, R^2	R^3	notes[a]
			
1a	*t*-Bu, H	Et	A, 2140; B
b	$(-CH_2-)$	Et	A, 2126; B; C
c	$(-C_6H_4(CH_2)_2-)$	Et	A, 2127; B; C; D
d	*t*-Bu, H	Me	
e	$(-CH_2-)_4$	Me	
f	$(-CH_6H_4(Ch_2)_2-)$	Me	C
			
2a	Et, Me	Et	A, 2137; B
b	Me, Me	Et	A, 2137; B
c	Et, Me	Me	A, 2137; B
d	Me, Me	Me	A, 2137; B
			
3a	*t*-Bu, H	H, Et	A, 2138; B
b	$(-CH_2-)_4$	H, Et	A, 2126; B
c	$(-C_6H_4(CH_2)_2-)$	H, Et	A, 2127; B; C
d	Me, Me	H, Et	A, 2121; B
e	Me, H	H, Et	A, 2137; B
f	Me, Me	Me, Et	
g	*t*-Bu, H	H, Me	A, 2138; B
h	$(-CH_2-)_4$	H, Me	A, 2126; B
i	$(-C_6H_4(CH_2)_2-)$	H, Me	A, 2127; B; C
j	Me, H	H, Me	A, 2139; B
k	Me, Me	H, Me	A, 2121; B
			
4a	*t*-Bu, H		A, 2136
b	$(-CH_2-)_4$		A, 2125
c	$(-C_6H_4(CH_2)_2-)$		C; D
			
5a	*t*-Bu, Me		
b	$(-CH_2-)_5$		
c	$(-C_6H_4(CH_2)_3-)$		E
d	Me, Me		
e	Me, Et		

compd	R^1, R^2	R^3	notes[a]
			
	A	B	
6a	*t*-Bu, H		F, in **1a**, **3a**, **3f**
b	$(-CH_2-)_4$		F, in **1b**, **3b,g**, **4b**
c	$(-C_6H_4(CH_2)_2-)$		CF, in **1c**, **3c,h**
d	Me, Me		F, in **3d,k**
e	Me, H		F, in **3e,i**
f	EtOC(O), Me		F, in **2a,b**
g	EtO, Me		F, in **2a,c**
h	MeOC(O), Me		F, in **2c,d**
i	MeO, Me		F, in **2b,d**
			
	A	B	
7a	*t*-Bu, H	Et	
b	$(-CH_2-)_4$	Et	
c	$(-C_6H_4(Ch_2)_2-)$	Et	C
			
8a	*t*-Bu, H	H	F
b	$(-CH_2-)$	H	F
c	$(-C_6H_4(CH_2)_2-)$	H	CF
d	Me, Me	H	F
e	Me, H	H	F
			
9a	Me, Me	Me	
b	Me, Me	Et	
c	Et, Me	Et	
			
10a	*t*-Bu, H		F
b	$(-CH_2-)_4$		F

[a] Notes: (A) ketene C=C=O frequency, cm^{-1}, observed in GC–FTIR peak for compound; (B) in equilibrium with enol tautomer; (C) benzeneethane-2,β-diyl; (D) would not pass through GC column unreacted; (E) benzenepropane-2,γ-diyl; (F) not isolable under conditions of reaction.

have accumulated, but a convincing mechanism has yet to be proposed. Among these facts are that an enolizable hydrogen is required on C-3[2] and that the elimination of carbon monoxide, a first-order process,[3] is from C-1.[4] Here, we account for these facts and other observations[5] thus far not convincingly explained.

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Results and Discussion

The compounds discussed in this study are shown in Table I. When the ethyl esters **1a–c** are subjected to decarbonylation conditions in the presence of an excess of methanol, the decarbonylated products, the β-keto esters **3**, are mainly methyl esters and the gas is mainly carbon monoxide. If ethyl esters **3a–e** are heated with excess methanol in a sealed reactor at a lower temperature (105–120 °C) than that required for decarbonylation (175 °C), the products include the methyl esters **3g–k**. When water is substituted for methanol, ketones **5**, carbon dioxide, and ethanol result. The α,γ-diketo esters **1** do not exchange alkoxy groups appreciably at 105 °C. Heating the esters **1** to 175–190 °C in the presence of water *invariably produces the ketone employed in the original synthesis of 1 and carbon dioxide and carbon monoxide in nearly equal amounts*. Heating the esters, **3a–e** and **3g–k**, with water at about 100 °C yields ketones **5**, carbon dioxide, and ethanol.[6a] However, **3f** is not affected by being heated with water, thus ruling out a pathway involving direct hydrolysis of **3** to a β-keto acid **8** followed by decarboxylation. Heating the acids **4** with or without water leads to the ketones **5**, carbon monoxide, and carbon dioxide.

These results can be explained by the existence of acylketenes[6] **6** as common intermediates[6a] (Scheme I).

Scheme I. Reactions of α,γ-Diketo Esters and β-Keto Esters

$$\mathbf{1a, b, \text{ or } c} \rightleftharpoons \mathbf{7A} \rightleftharpoons \mathbf{7B} \quad (1)$$

$$\mathbf{7B} \rightarrow \mathbf{6} + CO + CH_3CH_2OH \quad (2)$$

$$\mathbf{3a, b, \text{ or } c} \rightleftharpoons \mathbf{6} + CH_3CH_2OH \quad (3)$$

$$\mathbf{6} + H_2O \rightarrow \mathbf{8} \quad (4)$$

$$\mathbf{8} \rightarrow \mathbf{5} + CO_2 \quad (5)$$

$$\mathbf{1} + R'OH \rightarrow \mathbf{5} + RO_2CCO_2R' \quad (6)$$

$$\mathbf{3b} + ROH \rightarrow C_2H_5O_2C(CH_2)_5CO_2R \quad (7)$$

$$\mathbf{3h} + ROH \rightarrow CH_3O_2C(CH_2)_5CO_2R \quad (8)$$

Acylketenes have been generated from 1,3-dioxin-4-ones or **3** and their IR spectra observed by Fourier transform infrared spectroscopy (FTIR).[6l,r,x] We injected samples of the esters **1** into a GC–FTIR instrument with a hot light pipe (240–280 °C) and observed IR frequencies in the region of 2120–2140 cm^{-1} [6h,j–l,o,r,x] in the GC peak corresponding to the starting material. The intensities of these signals increased when the temperature of the light pipe was increased, indicating that reaction occurs during the very brief period after the material emerges from the GC column. Increasing the temperature of the injector has little effect on the intensity at about 2120–2140 cm^{-1} of products that are ketene precursors, but some components emerge at longer retention times than those of the starting materials. The relative amount of decarbonylated product also increases. We interpret this to mean that acylketenes **6** formed in the injector and passing into the initially cool (35 °C) GC column have ample time to combine with the alcohol produced in reaction 2, Scheme I, to polymerize and to produce ketone **5** and diethyl oxalate by a retro-Claisen condensation. Ethanol is observed in the chromatogram when the intermediates **6** are generated from β-keto esters **3a–e**. When mixtures of **3a–e** and methanol are introduced into a 280 °C injector, methyl esters **3g–k** as well as ethyl esters are observed. Ethyl phenylacetate and ethyl pyruvate undergo only slight transesterification with methanol under these conditions. The transesterification of acetoacetic acid esters in solution[6i–k] has been shown to be a first-order reaction with activation parameters fully consistent with a concerted elimination of alcohol to form the intermediate acetylketene **6e**.[6f,r]

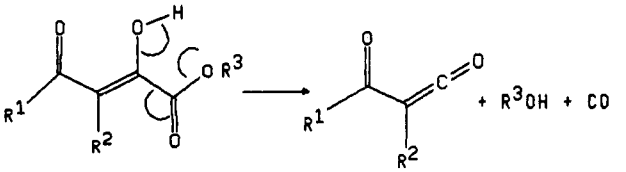

Figure 1. Decomposition of enolic ester.

An acylketene intermediate could be formed from **1a–c** by elimination of ethanol and carbon monoxide (Figure 1). A concerted elimination of ethanol and carbon monoxide from an enol such as **7B** accounts for the need for an enolizable hydrogen on the β-carbon atom of **1**. An acylketene intermediate formed from **1** should react with any alcohol present to form **3**. To test this, mixtures of **1a–c** and methanol in nearly equimolar amounts were introduced into a hot injector (280 °C) packed with finely divided carborundum. Carbon monoxide, carbon dioxide, methanol, and ethanol together with both methyl and ethyl esters **3g–i** and **3a–e** were observed.

The ease of decarbonylation of **1** varies with structure. We found that **1b** is the most reactive followed by **1c** and confirmed the report[1x] that **1a** is rather resistant to the loss of CO. The proportion of enol **7** present in the starting materials **1** appears directly related to the ease of decarbonylation. Powdered soft glass is often introduced[1c,l,m,o] when the decarbonylation reaction of **1** is employed in synthesis. Soft-glass catalysis was reported in decarbonylation of compounds of type **1**[1l] but without effect with type **2**.[1m,n] We demonstrated that catalytic effects rather than surface effects are attributable to powdered soft glass by using an injector packed with soft glass instead of carborundum. Greatly increased yields of the methyl esters **3** were observed under otherwise comparable reaction conditions. Quite possibly the soft glass catalyzes the equilibration of keto and enol forms.

Injecting methanol solutions of the acids **4a** and **4b** into the GC–FTIR or GC–MS yielded primarily the corresponding ketones **5a** and **5b** and minor amounts of methyl esters **1d** and **1e** and the decarbonylated methyl esters **3g**

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and **3h**. These products may result from a dehydration–cyclization of the acids[7a] to the corresponding 2,3-furandiones **10a** and **10b**, which might decarbonylate[6t,v] to form the acylketenes **6a** and **6b**. Subsequent reaction with water or methanol would afford **5a** or **5b** and carbon dioxide or **3g** and **3h**, respectively. Attack of methanol on the 2-position of the furandione ring could lead to the undecarbonylated methyl esters **1d** and **1e** (Scheme II).

Scheme II. Thermal Decomposition of Acids 4

$$\mathbf{4a} \rightarrow \mathbf{10a} + H_2O \quad (1)$$

$$\mathbf{10a} \rightarrow CO + \mathbf{6a} \quad (2)$$

$$\mathbf{6a} + H_2O \rightarrow \mathbf{8a} \quad (3)$$

$$\mathbf{8a} \rightarrow CO_2 + \mathbf{5a} \quad (4)$$

$$\mathbf{10a} + CH_3OH \rightarrow \mathbf{1d} \quad (6)$$

$$\mathbf{4b} \rightarrow \mathbf{10b} + H_2O \quad (7)$$

$$\mathbf{10b} \rightarrow CO + \mathbf{6b} \quad (8)$$

$$\mathbf{10b} + CH_3OH \rightarrow \mathbf{1e} \quad (9)$$

$$\mathbf{6b} + H_2O \rightarrow \mathbf{8b} \quad (10)$$

$$\mathbf{8b} \rightarrow CO_2 + \mathbf{5b} \quad (11)$$

$$\mathbf{4c} \rightarrow H_2O + CO + \mathbf{6c} \quad (12)$$

$$\mathbf{6c} + H_2O \rightarrow \mathbf{8c} \quad (13)$$

$$\mathbf{8c} \rightarrow CO_2 + \mathbf{5c} \quad (14)$$

The behavior of the diethyl ester **2a** and dimethyl ester **2d** is more complex than that of the esters **1** because two different acylketenes can form from each (reactions 3, 4, 14, and 15, Scheme III). Loss of ethanol from **2a** occurs

Scheme III. Cross-Over Experiments with 3-Methyl-2-oxobutanedioic Acid Esters 2

$$\mathbf{2a} + CH_3OH \rightarrow CH_3O_2CCO_2C_2H_5 + C_2H_5CO_2C_2H_5 \quad (1)$$

$$\mathbf{2a} + C_2H_5OH \rightarrow C_2H_5O_2CCO_2C_2H_5 + C_2H_5CO_2C_2H_5 \quad (2)$$

$$\mathbf{2a} \rightleftharpoons \mathbf{6f} + C_2H_5OH \quad (3)$$

$$\mathbf{2a} \rightarrow \mathbf{6g} + C_2H_5OH + CO \quad (4)$$

$$\mathbf{6f} + CH_3OH \rightleftharpoons \mathbf{2b} \quad (5)$$

$$\mathbf{2a} + CH_3OH \rightleftharpoons \mathbf{2b} + C_2H_5OH \quad (6)$$

$$\mathbf{2c} \rightleftharpoons \mathbf{6h} + C_2H_5OH \quad (7)$$

$$\mathbf{6h} + CH_3OH \rightleftharpoons \mathbf{2d} \quad (8)$$

$$\mathbf{2b} \rightarrow \mathbf{6i} + C_2H_5OH + CO \quad (9)$$

$$\mathbf{6i} + C_2H_5OH \rightarrow \mathbf{9b} \quad (10)$$

$$\mathbf{6g} + CH_3OH \rightarrow \mathbf{9b} \quad (11)$$

$$\mathbf{6i} + CH_3OH \rightarrow \mathbf{9a} \quad (12)$$

$$\mathbf{6g} + C_2H_5OH \rightarrow \mathbf{9c} \quad (13)$$

$$\mathbf{2d} \rightleftharpoons \mathbf{6h} + CH_3OH \quad (14)$$

$$\mathbf{2d} \rightarrow \mathbf{6i} + CH_3OH + CO \quad (15)$$

$$\mathbf{2d} + C_2H_5OH \rightleftharpoons \mathbf{2c} + CH_3OH \quad (16)$$

$$\mathbf{6h} + C_2H_5OH \rightleftharpoons \mathbf{2c} \quad (17)$$

$$\mathbf{2d} + C_2H_5OH \rightarrow CH_3O_2CCO_2C_2H_5 + C_2H_5CO_2CH_3 \quad (18)$$

$$\mathbf{2d} + CH_3OH \rightarrow CH_3O_2CCO_2CH_3 + C_2H_5CO_2CH_3 \quad (19)$$

at a relatively low temperature to generate the (carbethoxycarbonyl)ketene, **6f**, which then reacts with whatever else is present to form stable products.[6a] An early observation that heating 2-oxobutanedioic acid diethyl ester produces ethyl pyruvate, carbon dioxide, and ethanol[1a] supports this interpretation. We interpret the decarbonylation of the diethyl ester **2a** to yield **9c**[3] as proceeding by loss of ethanol and carbon monoxide to form the (ethoxycarbonyl)ketene **6g**, which then reacts with ethanol. To test this hypothesis the following cross-over experiment was performed. A mixture of **2a** and methanol (1:2, mol:mol) was injected (280 °C) in the GC–FTIR, and the product mixture was analyzed. A rich array of products was obtained. Scheme III shows the reactions leading to the major products.

A second cross-over experiment with **2d** and ethanol (1:2, mol:mol) was performed and a similar array of products was obtained with the following exceptions. Reactions 14–19 would be predicted to occur but reactions 1–4 and 6 are not expected. In other words, the only different product seen in the second cross-over experiment is methyl propanoate rather than ethyl propanoate.

First-order rate constants were reported[3] for the decarbonylation of **2a**, and activation parameters were computed from these data.[4] We have recomputed the activation parameters for **2a** and find $\Delta H^{\ddagger} = 32.9$ kcal/mol and $\Delta S^{\ddagger} = 0.5$ eu. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for transesterification of ethyl acetoacetate, **3e**, have been reported as 27 ± 2 kcal and −7 ± 5 eu[6f] and 24.7 kcal and −14.2 eu.[6r] This suggests a low energy barrier pathway for ketene formation from β-keto esters and a higher barrier pathway to an acylketene when decarbonylation must also occur. Isotope effects were measured for 2-oxo-3-phenylbutanedioic acid-*1*-^{14}C diethyl ester and are consistent with elimination of CO in the rate-determining step.[4] These workers, however, rejected the possibility of ketene intermediates because they were unable to observe them. Others have expressed guarded skepticism[6v] about the intermediacy of acylketenes. The intermediates can now be observed with the aid of modern instrumentation not available to earlier workers.

We conclude that the reactions of compounds of types 1–4, decarbonylation, transesterification, hydrolysis, and loss of carbon dioxide, are most economically explained by the formation and subsequent reaction of acylketenes or (alkoxycarbonyl)ketenes and that more convoluted pathways are not needed to rationalize the results. Our arguments are bolstered by observation of the expected IR frequencies in reaction components predicted to be ketene precursors in appropriately conducted experiments.

Experimental Section

All temperatures reported are uncorrected.

Gas Chromatography and IR, Mass, and NMR Spectrometry. The GC employed for GC–FTIR analysis was equipped with a flame ionization detector (FID) and arranged so that the effluent could be directed via a transfer line to a Fourier transform IR spectrometer having a resolution of 4 cm^{-1} for condensed-phase and 8 cm^{-1} for vapor-phase spectra. The column oven was programmed to start at either 35 or 50 °C, held for 4 min, increased by 10 °C/min to 250 °C, and held for 15 min. In most instances, starting mixtures for reactions as well as reaction mixtures themselves were analyzed. GC–MS analyses of the same mixtures were also performed using the same type of GC, column, and temperature program as the GC–FTIR. For some of the higher molecular weight compounds a direct insertion probe (DIP) rather than the GC column was used for sample introduction. The relative amounts of carbon monoxide and carbon dioxide produced in sealed reactor experiments were analyzed by GC as described previously.[6a] GC separations for preparative purposes were performed using a 10 ft × $^1/_8$ in. column with 10% OV-1 on 80–100 mesh Chromosorb W.H.P. and a temperature ramping of 2 °C/min. FTIR spectra of liquids and KBr pellets were obtained on the FTIR instrument. Proton NMR spectra were obtained

at 60 MHz or at 300 MHz with $CDCl_3$ as solvent and TMS as an internal standard; ^{13}C spectra were obtained at 75 MHz.

Flash Thermolysis Experiments. Four different fused silica injection ports were used, one empty, another containing powdered soft glass, the third and fourth containing 600 grit and 200 grit carborundum, respectively. The difference in particle size gave no observable effect. Various temperatures of the injector and light pipe were employed, ranging from 170 to 280 °C. The various compounds were injected, and the FTIR spectra were observed and recorded. Cross-over experiments were performed on approximately equimolar mixtures of **1a–c** and methanol, of **3a–e** and methanol, of **4** and methanol, of **2a** with 2 mol of methanol, and **2d** with 2 mol of absolute ethanol. Runs were also made with 1 mol of **2a** and 1 mol of **2d** with 2 mol of ethanol and 2 mol of methanol, respectively.

Preparation of Ketoglyoxylate Esters 1 and 2. Except where noted otherwise, these compounds were all prepared by base-catalyzed condensations of the appropriate ketones or esters with diethyl or dimethyl oxalate. Details are provided in the supplementary material. Reduced pressure distillations were performed on a Kugelrohr apparatus unless otherwise noted, and the temperatures reported by us are oven temperatures. The esters **3a–c** and **g–i** were all prepared by decarbonylation of the appropriate **1**.

Preparation of 5,5-Dimethyl-2,4-dioxohexanoic Acid Ethyl Ester (Keto and Enol), 1a. The fraction distilling at 95–105 °C (1 Torr) [lit.[8a] 124 °C (13 Torr), lit.[8b] 116–118 °C (13 Torr)] was retained. Yield: 6.5 g, 66%. MS *m/z* 43 (72), 55 (8), 57 (46), 69 (54), 81 (10), 83 (13), 115 (30), 127 (100), 128 (8), 143 (10), 144 (8), 200 (1) M^+. FTIR (neat): 2972, 1749, 1734, 1637, 1600, 1286, 1250, 1128, 1111, 1015, 781 cm^{-1}.

Synthesis of α,2-Dioxocyclohexaneacetic Acid Ethyl Ester (Keto and Enol), 1b.[1c] A heart cut boiling at 125–130 °C (1 Torr) was collected. Yield: 4.27 g, 21.6%. MS *m/z*: 43 (11), 53 (9), 55 (26), 68 (9), 69 (10), 79 (9), 125 (100), 126 (8), 198 (6) M^+. FTIR (neat): 2944, 1739, 1617, 1581, 1412, 1282, 1200, 1169, 1019 cm^{-1}.

Synthesis of α,1-Dioxotetrahydro-2-naphthaleneacetic Acid Ethyl Ester (Keto and Enol), 1c.[1j] Recrystallization of the crude product yielded 3.84 g, 16%, mp 44.5–45.5 °C (lit.[1f] mp 48 °C, lit.[1h] 44–45 °C. A second fraction, 1.6 g, 6.7%, was obtained by concentration of the filtrate. MS *m/z*: 63 (16), 89 (22), 90 (16), 91 (29), 105 (34), 115 (76), 116 (21), 117 (23), 145 (14), 173 (100), 246 (6.6) M^+. FTIR (KBr): 1720, 1617, 1594, 1285, 1242, 1174, 912, 744 cm^{-1}.

Synthesis of 5,5-Dimethyl-2,4-dioxohexanoic Acid Methyl Ester (Keto and Enol), 1d.[1p,q,u] Distillation of the crude product yielded 3.5 g, 35%, bp 94–100 °C (3 Torr) (lit.[1p] bp 112–113 °C (11 Torr)). MS *m/z*: 41 (21), 43 (22), 57 (31), 69 (61), 83 (19), 101 (15), 127 (100), 129 (20), 130 (19), 158 (19), 186 (2) M^+. FTIR (vapor): 2971, 1774, 1751, 1637, 1602, 1282, 1254, 1123 cm^{-1}.

Synthesis of α,2-Dioxocyclohexaneacetic Acid Methyl Ester (Keto and Enol), 1e.[1r,s] The fraction boiling at 105–140 °C (3 Torr) was collected (lit.[1r] bp 82–83 °C (0.3 Torr)). Yield: 3.47 g, 37.7%. MS *m/z*: 55 (9), 69 (2), 79 (8), 96 (8), 124 (7), 125 (100), 126 (7), 184 (12) M^+. FTIR (vapor): 2960, 1790, 1758, 1634, 1586, 1273, 1200, 1168 cm^{-1}.

Synthesis of α,1-Dioxotetrahydro-2-naphthaleneacetic Acid Methyl Ester (Keto and Enol), 1f.[1o] Two recrystallizations of the crude product from methanol gave 0.77 g of product, 10.4% yield, mp 65.4–66.2 °C (lit.[1o] mp 65.5–66.5 °C). MS (DIP) *m/z*: 59 (34), 63 (12), 89 (20), 91 (19), 105 (28), 115 (80), 116 (20), 117 (15), 173 (100), 174 (12), 232 (17) M^+. FTIR (KBr): 1721, 1597, 1289, 1244, 1167, 744, 605 cm^{-1}.

Synthesis of 3-Methyl-2-oxobutanedioic Acid Diethyl Ester (Keto and Enol), 2a.[6a] The compound was prepared and characterized as previously described.[6a]

3-Methyl-2-oxobutanedioic Acid 1-Ethyl 4-Methyl Ester (Keto and Enol), 2b.[6a] The compound was produced as a component of the mixture produced when **2a** and methanol in a 1:2 mol ratio was injected in the GC–FTIR.

3-Methyl-2-oxobutanedioic Acid 4-Ethyl 1-Methyl Ester (Keto and Enol), 2c.[6a] The compound was produced as a component of the mixture produced when **2d** and ethanol in a 1:2 mol ratio was injected in the GC–FTIR.

Preparation of 3-Methyl-2-oxobutanedioic Acid Dimethyl Ester. Preparation and characterization was reported previously.[6a]

Preparation of 4,4-Dimethyl-3-oxopentanoic Acid Ethyl Ester (Keto and Enol), 3a. The compound distilled at 105–110 °C (15 Torr) (lit.[7b] 96 °C (15 Torr)). Yield: 0.20 g, 21%. MS *m/z*: 42 (19), 43 (15), 57 (100), 60 (12), 69 (14), 85 (12), 87 (25), 88 (38), 115 (20), 172 (2) M^+. FTIR (neat): 2973, 1748, 1709, 1618, 1367, 1318, 1272, 1211, 1148, 1039 cm^{-1}.

Synthesis of 2-Oxocyclohexanecarboxylic Acid Ethyl Ester (Keto and Enol), 3b.[1c,k] The compound was prepared as previously described,[1c,k] bp 119 °C (18 Torr) (lit.[1c] bp 125–140 °C (40 Torr)), lit.[1k] bp 108 °C (11 Torr)). MS *m/z*: 42 (16), 43 (18), 55 (62), 67 (22), 68 (100), 69 (16), 96 (25), 124 (80), 125 (28), 170 (19) M^+. FTIR (neat): 2941, 1744, 1718, 1652, 1617, 1300, 1261, 1219, 1177, 1082, 834 cm^{-1}.

Synthesis of 1-Oxotetrahydronaphthalene-2-carboxylic Acid Ethyl Ester (Keto and Enol), 3c.[1h] Compound **3c** was prepared in 68% yield, bp 146–154 °C (<1 Torr) (lit.[1h] bp 123–125 °C (0.05 Torr)), mp 34–35 °C. MS *m/z*: 63 (12), 89 (28), 90 (43), 91 (23), 115 (75), 116 (43), 117 (20), 118 (49), 144 (100), 145 (37), 172 (38), 218 (60) M^+. FTIR (neat): 2980, 1740, 1686, 1646, 1618, 1570, 1401, 1325, 1271, 1213, 1085, 1026, 770 cm^{-1}.

Synthesis of 2-Methyl-3-oxobutanoic Acid Ethyl Ester (Keto and Enol), 3d.[9] The product, 52% yield, distilled at 88–92 °C (15 Torr) (lit.[10] 75–76 °C (15 Torr), lit.[9] 93–95 °C (33 Torr)). MS *m/z*: 43 (100), 45 (4), 55 (5), 56 (13), 57 (7), 73 (9), 74 (36), 99 (10), 102 (30), 144 (1) M^+. FTIR (neat): 2987, 1743, 1718, 1455, 1360, 1244, 1204, 1155, 1100, 1084, 1050, 1020 cm^{-1}.

3-Oxobutanoic Acid Ethyl Ester (Keto and Enol), 3e. Ethyl acetoacetate (J. T. Baker) was redistilled.

Preparation of 2,2-Dimethyl-3-oxobutanoic Acid Ethyl Ester, 3f.[11] The compound was prepared from **3e** using NaH and CH_3I; 0.80 g (27.5%) of pure material, bp 98–106 °C (75 Torr) (lit.[11] bp 180–184 °C/atm) was obtained. MS *m/z*: 43 (100), 57 (13), 59 (11), 70 (21), 73 (40), 85 (12), 88 (59), 113 (11), 116 (50), 158 (0.2) M^+. FTIR (neat): 2985, 1716, 1470, 1386, 1365, 1357, 1267, 1155, 1119, 1028 cm^{-1}.

4,4-Dimethyl-3-oxopentanoic Acid Methyl Ester (Keto and Enol), 3g.[1g] The compound was prepared by injecting an equimolar mixture of **1a** or **3a** and methanol into the GC–FTIR or GC–MS with powdered soft glass in the inlet at 280 °C and the light pipe at 200 °C. MS *m/z*: 41 (48), 42 (14), 43 (13), 57 (100), 69 (20), 74 (33), 85 (9), 101 (30), 130 (10), 158 (2) M^+. FTIR (vapor): 2969, 1768, 1725, 1623, 1444, 1314, 1272, 1217, 1150, 1069, 1034 cm^{-1}. The data are in good agreement with mass[12a] and FTIR (vapor) spectra of an authentic sample, yield 0.57 g, 53.8%, bp 68–73 °C (3 Torr) (lit.[1q] bp 91–98 °C (20 Torr)).

2-Oxocyclohexanecarboxylic Acid Methyl Ester (Keto and Enol), 3h.[1s] The compound was prepared from **1b** or **3b** in equimolar mixtures with methanol in the GC–FTIR or GC–MS, inlet at 280 °C, light pipe at 200 °C, MS *m/z*: 41 (45), 42 (20), 55 (68), 67 (23), 68 (100), 69 (25), 96 (30), 100 (16), 124 (100), 125 (29), 156 (39) M^+. FTIR (vapor): 2951, 2972, 1764, 1736, 1672, 1621, 1446, 1362, 1303, 1261, 1225, 1175, 1084 cm^{-1}. The data are in good agreement with the mass and FTIR vapor spectra of an authentic sample, bp 70–105 °C (3 Torr) (lit.[1s] bp 95–107 °C (30 Torr)), yield 42.9%.

1-Oxotetrahydronaphthalene-2-carboxylic Acid Methyl Ester (Keto and Enol), 3i.[1o] The compound was prepared from equimolar mixtures of **1c** or **3c** and methanol in the GC–FTIR and GC–MS, inlet temperature 280 °C, light pipe at 200 °C. MS *m/z*: 89 (27), 90 (56), 115 (53), 116 (28), 117 (23), 118 (62), 144 (100), 145 (38), 172 (28), 204 (84) M^+. FTIR (vapor): 2961, 1763, 1709, 1665, 1624, 1572, 1445, 1361, 1325, 1270, 1214, 1161, 1086 cm^{-1}. The data are in good agreement with the FTIR (vapor) spectrum of an authentic sample, mp 48.8–50.2 °C (lit.[1o] mp 84.5–86.5 °C). ^1H NMR (60 MHz): δ 2.70 (m, CH_2CH_2), 3.83 (s,

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OCH_3), 7.3 (m, C_6H_4), 7.82 (m, C_6H_4), 12.51 (s, enol). FTIR (KBr): 1638, 1616, 1568, 1439, 1366, 1270, 1213, 1201, 1084, 836, 772. MS (DIP) m/z: 59 (16), 63 (17), 89 (39), 90 (38), 91 (20), 115 (100), 116 (53), 117 (19), 118 (34), 144 (57), 145 (24), 172 (36), 204 (48) M^+.

3-Oxobutanoic Acid Methyl Ester (Keto and Enol), 3j.[13] The compound was produced by injecting an equimolar mixture of **3e** and methanol into the GC–FTIR at an inlet temperature of 280 °C and light pipe at 200 °C and in the GC–MS at an inlet temperature of 280 °C. MS m/z: 42 (24), 43 (100), 59 (18), 69 (6), 74 (13), 85 (15), 88 (9), 101 (8), 116 (21) M^+. FTIR (vapor): 1747, 1642, 1445, 1313, 1295, 1160 cm^{-1}. The data are in good agreement with the mass and FTIR spectra of an authentic sample isolated by preparative GC.

2-Methyl-3-oxobutanoic Acid Methyl Ester (Keto and Enol), 3k.[13] The compound was produced from an equimolar mixture of **3d** and methanol in the GC–FTIR, inlet temperature of 280 °C, light pipe at 200 °C. MS m/z: 43 (100), 55 (8), 56 (14), 57 (18), 59 (12), 88 (38), 99 (7), 130 (3) M^+. FTIR (vapor): 2960, 1739, 1672, 1624, 1446, 1349, 1248, 1198, 1157, 1093 cm^{-1}. The data are in good agreement with the mass and FTIR (vapor) spectra of an authentic sample that was prepared and purified by preparative GC.

Preparation of 5,5-Dimethyl-2,4-dioxohexanoic Acid (Keto and Enol), 4a.[8a] To a flask were added 2.0 g (10 mmol) of **1a**, 1.50 g (10 mmol) of NaI, 1.2 g (10 mmol) of *N,N,N',N'*-tetramethyl-1,2-ethanediamine (TMEDA), and 30 mL of 2-butanone. A solid formed at once. The mixture was heated with stirring. The solid formed initially liquefied and after 5 h was replaced by another solid. The reaction mixture was mixed with an aqueous solution of 0.84 g (10 mmol) of $NaHCO_3$ and extracted with ether. The aqueous layer was acidified with 12 N HCl and extracted with ether. The crude acid, 1.1 g, 64%, sublimed readily to yield a fibrous white solid. Various fractions had melting points ranging from 55 to 75 °C and decomposition above 130 °C (lit.[8a] 60 °C). ^1H NMR (300 MHz) δ 1.24 (s, CH_3), 6.64 (s, CH_2). ^{13}C NMR (75 MHz): δ 208.05 (s, CO), 168.82 (s, CO), 164.23 (s, CO), 97.28 (t, CH_2), 41.21 (s), 26.77 (q, CH_3). MS m/z: 43 (89), 45 (18), 57 (100), 69 (57), 83 (17), 88 (22), 116 (27), 127 (47), 144 (11), 172 (1.4) M^+. FTIR (KBr): 3217, 1776, 1736, 1639, 1599, 1483, 1358, 1190, 1122, 1022, 852, 787, 741, 670 cm^{-1}.

Synthesis of α,2-Dioxocyclohexaneacetic Acid (Keto and Enol), 4b.[1k] The compound was isolated from the aqueous layer remaining after ether extraction from a preparation of **1b**. A solid that was recrystallized from water melted at 113–116.5 °C (0.6 g). This was recrystallized from 3 mL of a 1:1 solution of benzene–hexane to which a few drops of absolute ethanol had been added; mp 119.2–120.2 °C dec (lit.[1k] mp 121 °C). ^1H NMR (300 MHz): δ 1.77 (br), 2.58 (m), 2.77 (m). ^{13}C NMR (75 MHz): δ 168.10 (s, CO), 136.40 (s), 131.94 (s), 102.72 (s), 39.04 (t, CH_2), 26.72 (t, CH_2), 23.23 (t, CH_2), 23.08 (t, CH_2). MS m/z: 43 (20), 45 (22), 53 (23), 55 (51), 68 (21), 69 (22), 79 (20), 96 (21), 125 (100), 152 (10), 170 (6) M^+. FTIR (KBr): 3217, 2949, 1734, 1694, 1448, 1338, 1264, 1200, 1177, 1079, 980, 891, 780, 705 cm^{-1}.

Synthesis of α,1-Dioxotetrahydronaphthalene-2-acetic Acid (Keto and Enol), 4c.[14] To 0.75 g (3 mmol) of **1c** were added 0.45 g (3 mmol) of NaI, 0.38 g (3 mmol) of TMEDA, and enough acetone to make a homogeneous solution. The mixture was allowed to stand for 20 days. The resulting solid was dissolved in water, acidified with HCl, and extracted with ether. The ether extract yielded 0.72 g of an oil that solidified. Some of the solid was recrystallized from CCl_4 yielding the acid, mp 116 °C dec (lit.[14] mp 116 °C). ^1H NMR (60 MHz): δ 3.05 (m, $-CH_2CH_2-$), 7.4 (m, 3 H), 8.1 (m, 1 H), 9.35 (br, –COOH). MS (DIP) m/z: 63 (24), 89 (34), 90 (17), 91 (25), 105 (39), 115 (96), 116 (27), 117 (18), 127 (14), 144 (14), 172 (25), 173 (100.0), 200 (9), 218 (12) M^+. FTIR (KBr): 3265, 1676, 1599, 1414, 1364, 1314, 1232, 1153, 943, 894, 855, 746, 710 cm^{-1}.

3,3-Dimethyl-2-butanone, 5a, cyclohexanone, 5b, 1(2*H*)-3,4-dihydronaphthalenone (α-tetralone), 5c, acetone, 5d, and 2-butanone, 5e, used in synthesis or as spectroscopic standards were used as is if of sufficient purity or, if not, distilled before use.

4,4-Dimethyl-1-pentene-1,3-dione, 6a.[6x] The ketene frequency at 2140 cm^{-1} was observed in the GC–FTIR spectra of **1a**, **3a**, and **3g**.

2-Oxocyclohexylidenemethanone, 6b.[6x] The ketene frequency at 2126 cm^{-1} was observed in the GC–FTIR spectra of **1b**, **3b**, and **3h**.

1-Oxotetrahydronaphthylidenemethanone, 6c. The ketene frequency at 2127 cm^{-1} was observed in the GC–FTIR spectra of **3c** and **3i**. Compound **1c** would not pass through the GC column intact.

2-Methyl-1-butene-1,3-dione, 6d.[6x] The ketene frequency at 2121 cm^{-1} was observed in the GC–FTIR spectra of **3d** and **3k**.

1-Butene-1,3-dione, 6e.[6x] The ketene frequency at 2137 cm^{-1} was observed in the GC–FTIR spectra of **3e** and **3j**.

2,4-Dioxo-3-methyl-3-butenoic Acid Ethyl Ester, 6f. The ketene frequency at 2137 cm^{-1} was observed in the GC–FTIR spectra of **2a** or **2b** when the injector was at 200 °C.

2-Methyl-3-oxo-2-propenoic Acid Ethyl Ester, 6g. The ketene frequency was observed at 2137 cm^{-1} in the GC–FTIR spectra of **2a** or **2c** when the light pipe was at 280 °C.

2,4-Dioxo-3-methyl-3-butenoic Acid Methyl Ester, 6h. The ketene frequency at 2137 cm^{-1} was observed in the GC–FTIR spectra of **2c** or **2d** when the light pipe was at 200 °C.

2-Methyl-3-oxo-2-propenoic Acid Methyl Ester, 6i.[6w] The ketene frequency at 2137 cm^{-1} was observed in the GC–FTIR spectra of **2b** or **2d** when the light pipe was at 280 °C.

2-Methylpropanedioic Acid Dimethyl Ester, 9a.[15] The compound was produced when **2d** or **2a** and methanol in 1:2 mol ratio of ester to alcohol were injected into the GC–FTIR or GC–MS. MS m/z: 43 (15), 55 (14), 56 (11), 59 (100), 87 (19), 115 (65), 146 (10) M^+. FTIR (vapor): 3002, 2961, 1764, 1443, 1326, 1253, 1210, 1159, 1092 cm^{-1}. The data are in good agreement with mass and FTIR (vapor) spectra of an authentic sample (see **9b**).

2-Methylpropanedioic Acid Ethyl Methyl Ester, 9b.[6w,16] The compound was produced when **2a** and methanol or **2d** and ethanol in 1:2 mol ratio of ester to alcohol were injected into the GC–FTIR or GC–MS. MS m/z: 41 (17), 43 (23), 45 (26), 55 (40), 56 (65), 57 (74), 59 (100), 87 (37), 88 (78), 115 (77), 129 (26), 133 (27), 160 (6) M^+. FTIR (vapor): 2994, 2959, 1759, 1462, 1322, 1249, 1206, 1157, 1093, 1048 cm^{-1}. The data are in good agreement with mass and FTIR (vapor) spectra of an authentic sample of **9b** made by heating **2a** with an excess of methanol at 106 °C, decarbonylating the mixture at 140–160 °C, and separating the products **9a–c** by preparative GC. The ^1H NMR spectrum agreed with literature values.[16]

2-Methylpropanedioic Acid Diethyl Ester, 9c.[1t] The compound was produced when a 1:2 mol ratio of ester to ethanol of **2a** or **2d** was injected into the GC–FTIR or the GC–MS. MS m/z: 45 (29), 55 (22), 56 (54), 57 (44), 73 (37), 74 (95), 75 (11), 101 (20), 102 (37), 128 (14), 129 (100), 147 (17), 174 (8) M^+. The FTIR (vapor) spectrum was in agreement with literature values.[17] For synthesis of an authentic sample, see **9b**.

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Registry No. **1a**, 13395-36-3; **1b**, 5396-14-5; **1c**, 58199-07-8; **1d**, 42957-17-5; **1e**, 5334-00-9; **1f**, 57763-56-1; **2a**, 759-65-9; **2b**, 99380-59-3; **2c**, 99380-58-2; **2d**, 63921-06-2; **3a**, 17094-34-7; **3b**, 1655-07-8; **3c**, 6742-26-3; **3d**, 609-14-3; **3e**, 141-97-9; **3f**, 597-04-6; **3g**, 55107-14-7; **3h**, 41302-34-5; **3i**, 7442-52-6; **3j**, 105-45-3; **3k**,

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17094-21-2; **4a**, 64165-15-7; **4b**, 771-12-0; **4c**, 135147-54-5; **6a**, 132723-19-4; **6b**, 132723-22-9; **6c**, 57558-70-0; **6d**, 132723-21-8; **6e**, 691-45-2; **6f**, 135147-55-6; **6g**, 36277-50-6; **6h**, 135147-56-7; **6i**, 36832-93-6; **9a**, 609-02-9; **9b**, 6065-52-7; **9c**, 609-08-5; diethyl oxalate, 95-92-1; dimethyl oxalate, 553-90-2; pinacolone, 75-97-8; cyclohexanone, 108-94-1; tetrahydronaphthalen-1-one, 529-34-0; ethyl propionate, 105-37-3; methyl propionate, 554-12-1.

Supplementary Material Available: Experimental procedures for preparation of **1a-c**, **3d**, **3j**, and **3k**; ^{1}H NMR (60-MHz) spectra of **1d-f**, **3g**, **3h**, **3j**, **3k**, **4c**, and **9a**; ^{1}H NMR (300-MHz) and ^{13}C spectral data for **1a-c** and **3a-d**; mass spectral data for keto and enol forms of **3g**; FTIR spectral data (neat) for authentic samples of **1a**, **1b**, **1d**, **1e**, **3d**, **3g**, **3h**, **3j**, **3k**, **9a**, and **9b** (7 pages). Ordering information is given on any current masthead page.

Novel Template Effects of Distannoxane Catalysts in Highly Efficient Transesterification and Esterification

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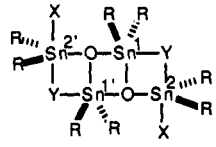
The transesterification of carboxylic esters and the esterification of carboxylic acids are effected under mild conditions under catalysis by 1,3-disubstituted tetraalkyldistannoxanes **1**. Various functional groups remain unaffected and otherwise difficult to obtain esters are accessible. An ester bearing a tertiary butyl group in the carboxylic acid moiety remained unchanged in competition experiments with a less bulky ester, which undergoes transesterification quantitatively. The unique features of the reactions are attributable to the template effects of the dimeric structure of **1**. The facility with which compounds **1** can be converted into alkoxydistannoxanes **2** and the synergistic effect of the proximate tin atoms of **2** play key roles in permitting smooth reactions and high selectivity. Another notable feature of compounds **1** is their unusually high solubility in organic solvents, even though the compounds have a metaloxane core as a major skeletal part. The double-layered structure of **1**, in which the inorganic moiety is surrounded by eight alkyl groups, permits esterification to be driven to completion simply by heating a mixture of the carboxylic acid and the alcohol. The distannoxane-catalyzed esterification is irreversible, and thus, no hydrolysis of the product esters occurs when compounds **1** are used as catalysts.

Introduction

The partial hydrolysis of diorganotin dihalides under alkaline conditions gives 1,3-disubstituted tetraorganodistannoxanes **1**.[1] In striking contrast, hydrolysis of the



1a: R = Bu, X = Y = -NCS; **1b**: R = Bu, X = -NCS, Y = OH; **1c**: R = Bu, X = Y = Cl

1d: R = Bu, X = Cl, Y = OH; **1e**: R = Me, X = Y = -NCS

analogous diorganodihalosilanes gives polydiorganosiloxanes, even in the presence of only a catalytic amount of base. What differentiates the two hydrolyses is that the hydrolysis of the organotin compounds leads to the formation of a stable rigid ladder structure.[2] This unusual structure, which exists both in the solid state[3] and in solution,[4] gives rise to various properties. Two kinds of pentacoordinate tin atoms exist in compounds **1**. Sn(1) is bonded to two alkyl groups, two oxygen atoms, and one Y group, whereas Sn(2) is bonded to two alkyl groups, one oxygen atom, and one X and one Y group. Because the two types of tin atom are in close proximity, it is possible that a chemical transformation occurring in the vicinity of one tin atom can be influenced by the presence of the other tin atom or that substrates that are bonded to, or coordinated with, the tin atoms can interact with each other. Such synergistic effects exerted by proximate metal centers are extremely interesting and are one of the features of metal cluster chemistry. Another unique property of compounds **1** is their high solubility in organic solvents. Although they possess a metaloxane core as a major component of their molecular skeleton, distannoxanes are soluble in most organic solvents, including aliphatic hydrocarbons. The exceptions are the tetramethyldistannoxanes, which are soluble in such solvents only under reflux. This unusual solubility arises from the double-layered structure of compounds **1**, in which surface

Table I. Effects of the Structure and Concentration of the Distannoxane Catalyst 1 on Transesterification[a]

$$n\text{-}C_3H_7COOMe + PhCH_2OH \xrightarrow{1} n\text{-}C_3H_7COOCH_2Ph + MeOH$$

1 (concn)[b]	reactn time (h)	yield of n-$C_3H_7COOCH_2Ph$[c] (%)
1a (0.005)	3	100
1b (0.005)	4	100
1c (0.005)	3	100
1e (0.005)	10	100
1b (0.0005)	20	77
1c (0.0005)	20	100
1d (0.0005)	20	100
1e (0.0005)	20	83

[a] Reaction conditions: n-C_3H_7COOMe:$PhCH_2OH$ = 1:2, toluene reflux. [b] Molar ratio catalyst to n-C_3H_7COOMe. [c] Determined by GLC analysis.

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