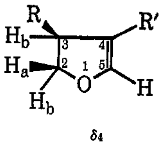
TABLE I

NMR PARAMETERS OF 3- AND 4-ALKYL-2,3-DIHYDROFURANS



R	R′	δ_{2a}	δ_{2b}	δ_3	δ_4	δ_5	J_{2a2b}	J_{2a3}	J_{2b3}	J_{34}	J_{35}	J_{45}
H	H	4.20	4.20	2.53	4.82	6.22		8.3	10.7	2.5	2.6	2.6
t-Bu	H	4.08	4.24	2.74	4.86	6.30	−9.1	7.4	9.6	2.4	2.0	2.8
(*S*)-*s*-Bu	H	3.96,[a] 3.97[b]	4.22,[a] 4.26[b]	2.86	4.86,[a] 4.87[b]	6.30	−8.7	6.9	9.8	2.3	2.2	2.5
Me	H	3.81	4.33	3.00	4.88	6.25	−8.6	6.6	9.8	2.3	1.8	2.6
H	Me	4.24	4.24	2.47		5.94	−8.8	7.0	9.6		1.7	
H	*i*-Pr	4.32	4.32	2.53		6.03	−9.0		9.8		1.7	
H	(*S*)-*s*-Bu	4.30	4.30	2.50		6.05	−9.0		9.0		2.1	

[a] *R,S* configuration. [b] *S,S* configuration.

amine (44 ml) was shaken in a high-pressure autoclave with a 1:1 mixture of carbon monoxide and hydrogen (80 atm) at a temperature of 80°. The reaction stopped when the theoretical amount of gas was absorbed. After removal of the solvents under reduced pressure (~100 mm), fractional distillation of the crude product gave **4** in 80–90% yield. Glpc of each product, using a 16 m × 0.5 mm Carbowax 20M support coated column, showed only one peak.

4a had bp 110° (0.3 mm); mass spectrum *m/e* (rel intensity) 70 (100), 41 (68), 57 (53), 55 (42), 69 (41), 56 (37), 29 (30), 42 (16.5), 83 (14.5), 43 (14).[22]

4b had bp 66° (12 mm); mass spectrum *m/e* (rel intensity) 56 (100), 41 (72), 57 (56), 72 (20), 29 (18.5), 27 (17), 43 (16), 39 (16), 58 (15.5), 55 (15).[22]

4c had bp 63° (0.1 mm); mp 35–37°; mass spectrum *m/e* (rel intensity) 70 (100), 57 (82), 41 (51), 55 (32), 83 (23), 29 (22), 43 (19.5), 42 (19), 81 (19), 69 (18).[22]

3-Alkyl-2,3-dihydrofurans (1a–c).—Each compound **4** (5 g) was placed in a distillation apparatus and heated at atmospheric pressure with an oil bath. The temperature was raised until a slow distillation of water and dihydrofuran was noticed; 160–230° were required according to the substituent (the presence of a trace of ammonium nitrate facilitates the dehydration). Heating was maintained until completion of the reaction. The distilled organic layer was dried (K_2CO_3) and redistilled over calcium hydride to afford pure **1** (70–80% yield). Glpc of each product, using a 2 m × 2.2 mm 15% polypropylene glycol column, showed only one peak.

1a had bp 90–91° (125 mm); $n^{25}\text{D}$ 1.4407; $[\alpha]^{25}\text{D}$ +21.50° (*c* 2.228, *n*-heptane); mass spectrum *m/e* (rel intensity) 69 (100), 41 (36), 68 (17), 126 (M^+, 13.5), 39 (9.5), 29 (9), 70 (7), 27 (6), 57 (5), 55 (4).

1b had bp 68°; $n^{25}\text{D}$ 1.4161 (lit.[6] bp 69–74°; $n^{25}\text{D}$ 1.4161); mass spectrum *m/e* (rel intensity) 69 (100), 41 (67), 84 (M^+, 54), 39 (39), 27 (21), 55 (20.5), 29 (17), 53 (13), 28 (10), 83 (6.5).

1c had bp 136°; $n^{25}\text{D}$ 1.4362; mass spectrum *m/e* (rel intensity) 69 (100), 41 (37), 57 (27), 68 (21), 126 (M^+, 13.5), 39 (13), 29 (12), 43 (11), 70 (10), 27 (6).

2-Alkyl-γ-hydroxyaldehyde Diethyl Acetals (7a–c).—The hydroformylation of **5** (0.4 mol) was carried out under the same conditions used for the preparation of **4**. The crude reaction mixture containing **6**[11] was added to a suspension of lithium aluminium hydride (5.0 g) in dry ether (300 ml) and stirred overnight at room temperature. The reaction mixture was worked up by the procedure described by Hill and Schearer;[23] distillation *in vacuo* afforded **7** in 80–85% yield.

7a had bp 98–99° (0.5 mm); $n^{25}\text{D}$ 1.4386–1.4390; $[\alpha]^{25}\text{D}$ −4.81° (*c* 1.061, *n*-heptane). *Anal.* Calcd for $C_{12}H_{26}O_3$: C, 66.01; H, 12.00. Found: C, 66.22; H, 12.18.

7b had bp 112–113° (14 mm); $n^{25}\text{D}$ 1.4292. *Anal.* Calcd for $C_9H_{20}O_3$: C, 61.33; H, 11.44. Found: C, 61.64; H, 11.74.

7c had bp 80–82° (0.9 mm); $n^{25}\text{D}$ 1.4400–1.4401. *Anal.* Calcd for $C_{11}H_{24}O_3$: C, 64.66; H, 11.84. Found: C, 64.60; H, 12.00.

2-Ethoxy-3-alkyl Tetrahydrofurans (8a–c).—Each compound **7** (5 g) was placed in a distillation apparatus in the presence of a trace of ammonium nitrate and heated with an oil bath at 140–150°; slow distillation of the theoretical amount of ethanol occurred; the residue, distilled *in vacuo*, afforded **8** in 80–85% yield.

8a had bp 85–95° (14 mm); **8b** had bp 52–54° (14 mm); **8c** had bp 62–68° (14 mm).

4-Alkyl-2,3-dihydrofurans (2a–c).—Each compound **8** (5 g) was placed in a distillation apparatus in the presence of a catalytic amount of phosphorus pentoxide and heated with an oil bath at 160–180°. Ethanol and dihydrofuran distilled as soon as they were formed; complete dealkoxylation was achieved in a matter of hours. Crude **2a** and **2c** were washed with water and distilled over calcium hydride to give the pure products in 75–80% yield. A pure sample of **2b** was obtained by preparative glpc on a Perkin-Elmer F 21 gas chromatograph, using a 3 m × 8 mm column packed with 20% polypropylene glycol on Chromosorb A at 80°. Glpc of each product, using a 2 m × 2.2 mm 15% polypropylene glycol column, showed only one peak.

2a had bp 145°; $n^{20}\text{D}$ 1.4450; $[\alpha]^{25}\text{D}$ +21.18° (*c* 2.762, *n*-heptane); mass spectrum *m/e* (rel intensity) 97 (100), 41 (48), 43 (31), 126 (M^+, 22), 39 (14), 55 (13), 69 (11.5), 27 (10.5), 29 (10), 111 (6).

2b had bp 63–64°; $n^{20}\text{D}$ 1.4425; mass spectrum *m/e* (rel intensity) 84 (M^+, 100), 55 (97), 83 (48), 41 (45), 39 (44), 29 (36), 27 (31), 53 (21), 56 (19), 69 (14).

2c had bp 124°; $n^{25}\text{D}$ 1.4492; mass spectrum *m/e* (rel intensity) 41 (100), 97 (93), 43 (56), 55 (42), 112 (M^+, 38), 39 (31), 27 (30.5), 67 (29), 71 (22.5), 69 (22).

Registry No.—**1a** (*R,S*), 34314-80-2; **1a** (*S,S*), 34368-07-5; **1b**, 1708-27-6; **1c**, 34314-82-4; **2a**, 34379-54-9; **2b**, 34314-83-5; **2c**, 34314-84-6; **4a**, 34379-55-0; **4b**, 34314-85-7; **4c**, 34314-86-8; **7a**, 34314-87-9; **7b**, 34314-88-0; **7c**, 34314-89-1; **8a**, 34314-90-4; **8b**, 34314-91-5; **8c**, 34314-92-6; 2,3-dihydrofuran, 1191-99-7.

Synthesis and Reactions of γ-Alkylthio-β-butyrolactones

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Diketene undergoes a variety of ring opening reactions to afford acetoacetate derivatives.[1] In contrast, the integrity of the β-lactone linkage may be maintained by a free-radical reaction at the olefinic linkage.

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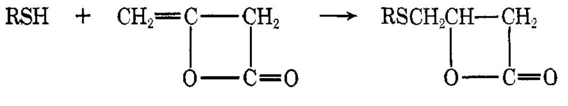
[22] The molecular ion (M^+) is not recognizable, as expected for compounds of this type, but peaks at *m/e* M + 1 (<1%) are easily identifiable.

[23] R. K. Hill and W. R. Schearer, *J. Org. Chem.*, **27**, 921 (1962).

[1] D. Borrman, "Methoden der Organischen Chemie," 2nd ed, Vol. 4-II, Houben-Weyl-Müller, Ed., Georg Thieme Verlag, Stuttgart, 1968, pp 226–259.

For example, the free-radical copolymerization of diketene with ethylene or vinyl chloride has been claimed to yield products containing the unopened lactone ring.[2] Similarly, the homolytic addition of mercaptans to diketene has been reported to give γ-alkylthio-β-butyrolactones in moderate yields.[3] Prompted by interest in another area, we examined the preparation of some of these β-butyrolactone derivatives formed from linear chain mercaptans. In the course of this synthetic work we found that these β-lactone derivatives undergo a novel rearrangement and polymerization.

The reaction of *n*-hexadecyl or *n*-octadecyl mercaptan with diketene in the presence of a catalytic amount of azobisisobutyronitrile (AIBN) gave 88–90% yields of crystalline 1:1 adducts, Ia,b. The presence of the β-lactone function in the product was indicated by a carbonyl band at 5.5 μ.[4] In the nmr spectra of the adducts the methylene protons adjacent to the carbonyl function are nonequivalent and spin coupled with the methine proton of the β-lactone ring. This latter proton is further spin coupled with the nonequivalent methylene protons adjacent to the ring connected to sulfur. This pattern is consistent with the proposed structure.



Ia, R = $C_{16}H_{33}$
b, R = $C_{18}H_{37}$

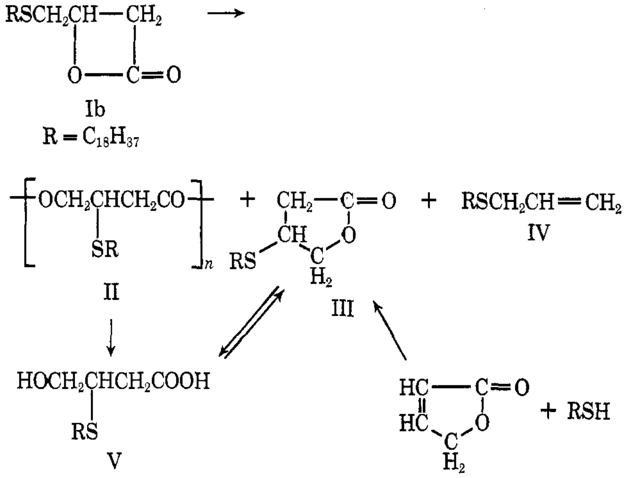
Further confirmation of the structure was obtained *via* ring opening with dimethylamine to give a 95% yield of the β-hydroxy-*N*,*N*-dimethylamide derivative.[5] In addition to AIBN, a sun lamp or normal interior lighting could also be used with equal effectiveness to catalyze the addition reaction. Hydrocarbons such as hexane or cyclohexane were the preferred solvents, since the adducts crystallized nearly quantitatively from the reaction mixture.

Heating Ib above its melting point resulted in the replacement of the β-lactone carbonyl ir absorption at 5.5 μ by new absorptions at 5.60, 5.75, and 6.1 μ. The reaction is shown in Scheme I.

Fractional crystallization gave a solid in 37% yield with the 5.75-μ absorption. This material was shown to be a polyester (II) with a molecular weight of 2160. Alkaline hydrolysis gave the monomeric γ-hydroxyl acid V. Structure V is supported by analytical and spectral data. The most structurally significant feature in the nmr spectrum of V is a doublet at δ 3.65. This is assigned to the methylene group adjacent to the hydroxyl function. The methylene group α to the carbonyl is present as an AB system at δ 2.51 and 2.75. The methine adjacent to sulfur appears as a multiplet at 3.17. These data are consistent with the rearrangement product and not with the anticipated 3-hydroxy-4-(*n*-octadecylthio)butyric acid.

Compound III was isolated in 14% yield by crystallization from the mother liquors of II. The γ-lactone assignment is based upon elemental analysis, molecular weight determination, and spectral properties. The ir spectrum contains a 5.6-μ carbonyl absorption consistent with the γ-lactone structure.[6] In the nmr spectrum of III the methylene protons adjacent to the carbonyl are nonequivalent and spin coupled with the methine hydrogen on the ring adjacent to sulfur. The spin pattern of these methylene hydrogens overlapped with the triplet associated with the methylene adjacent to sulfur on the octadecyl chain. The use of the europium shift reagent[7] clarified the pattern, moving the signals downfield into clear view. The methine hydrogen on the ring is further spin coupled with the nonequivalent methylene hydrogen adjacent to the oxygen of the lactone linkage.

SCHEME I
REARRANGEMENT OF β-LACTONE Ib



Further confirmation for the structure of compound III was obtained by independent synthesis. γ-Crotonolactone[8] was treated with *n*-octadecyl mercaptan under alkaline conditions to give III. The alkaline hydrolysis of III also gave V. This was readily reconverted to III with *p*-toluenesulfonic acid in refluxing benzene. Lactonization was also observed in hot chloroform.

The product with the 6.1-μ absorption was purified by distillation and found to be *n*-octadecyl allyl sulfide (IV). This product is formed in 33% yield.

The rearrangement of the β-lactone has a number of unusual features. Normally, β-lactones undergo polymerization to form 3-hydroxypropionic acid polyesters.[9] In this instance the rearrangement during polymerization is due to the presence of the sulfur atom in the alkyl chain (Scheme II). The electron pair on sulfur is capable of assisting in the opening of the lactone ring[10] to give intermediate VI.

The reaction of VI along path a, *i.e.*, attack by the carboxylate anion on the secondary carbon of the episulfonium ion, would be fruitless, yielding starting material. Reaction along path b, *i.e.*, opening of the episulfonium ion on the primary carbon, yields the rearranged lactone III. The repetitive intermolecular

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[2] D. D. Coffman, U. S. Patent 2,585,537 (Feb 12, 1952).

[3] C. W. Theobald, U. S. Patent 2,675,392 (April 13, 1954).

[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1966, p 188.

[5] T. L. Gresham, *et al.*, *J. Amer. Chem. Soc.*, **73**, 3168 (1951).

[6] Reference 4, p 186.

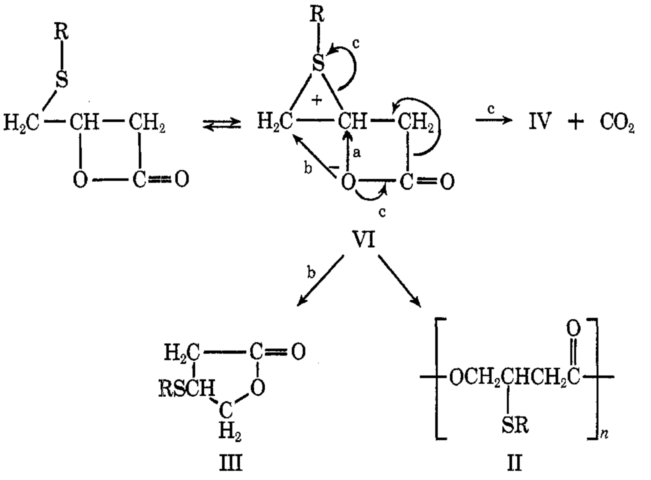
[7] J. K. M. Sanders and D. H. Williams, *J. Chem. Soc. D*, 422 (1970).

[8] C. C. Price and J. M. Judge, *Org. Syn.*, **45**, 22 (1965).

[9] H. E. Zaugg in "Organic Reactions," Vol. VIII, R. Adams, Ed., Wiley, New York, N. Y., 1954, p 327.

[10] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Company, New York, N. Y., 1959, p 572.

SCHEME II



opening of the episulfonium ion at the primary carbon yields the polyester II.

Decomposition of VI along path c yields the octadecyl allyl sulfide IV and carbon dioxide. This latter mode of reaction is very similar to a decarboxylative elimination.

The γ-lactone III was not a precursor of the polyester. Attempts to convert III to II were unsuccessful.

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrometer. Nuclear magnetic resonance spectra were recorded on a Varian Associates DA-100-15 spectrometer. Chemical shifts are expressed in δ units parts per million downfield from tetramethylsilane. Molecular weight determinations were conducted by Mr. D. R. Stevens using a Mechrolab vapor pressure osmometer, Model 301A. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Preparation of γ-(*n*-Hexadecylthio)-β-butyrolactone (Ia).—Diketene (31.8 g, 0.378 mol) was added dropwise over a 0.25-hr period to a stirred solution of *n*-hexadecylmercaptan (107.3 g, 0.415 mol) and 0.5 g of AIBN in 210 ml of cyclohexane at ambient temperature. An exothermic reaction occurred and the internal temperature was maintained at 35–40° by external cooling. A solid separated from solution during diketene addition. After addition was complete the mixture was stirred at 20–30° for 1.5 hr. The product was removed by filtration, washed with cyclohexane, and air dried to give 105.1 g of Ia, mp 61.5–62.5°. A second crop, mp 59–60°, was obtained from the mother liquor. The total yield of Ia was 111.3 g (86%). An analytical sample was prepared by recrystallization from petroleum ether (bp 30–60°) to give material of mp 62–63°: ir ($\mathrm{CHCl_3}$) 5.5, 8.85 μ; nmr ($\mathrm{CDCl_3}$) δ 0.86 [t, $J = 6.0$ Hz, 3 H, $-(\mathrm{CH_2})_{15}\mathrm{C}\mathbf{H}_3$], 1.24 [s, 26 H, $-(\mathrm{C}\mathbf{H}_2)_{13}\mathrm{CH_3}$], 1.52 [m, 2 H, $-\mathrm{SCH_2C}\mathbf{H}_2(\mathrm{CH_2})_{13}$], 2.59 (t, $J = 7.0$ Hz, 2 H, $-\mathrm{SCH_2C_{15}}$), 2.80 and 3.0 (AB, two d of d, $J_{AX} = 6.75$, $J_{BX} = 5.5$, $J_{AB} = 14.0$ Hz, 1 H each, $-\mathrm{SC}\mathbf{H}_2\mathrm{CH}-$), 3.24 and 3.56 (CD, two d of d, $J_{CX} = 5.5$, $J_{DX} = 4.5$, $J_{CD} = 16.25$ Hz, 1 H each, $-\mathrm{CH_2C{=}O}$), 4.64 (X of ABX, CDX, 11 lines, $J_{AX} = 6.75$, $J_{BX} = J_{CX} = 5.5$, $J_{DX} = 4.5$ Hz, 1 H, $-\mathrm{SC}\mathbf{H}\mathrm{CH_2}-$).

Anal. Calcd for $\mathrm{C_{20}H_{38}SO_2}$: C, 70.20; H, 11.11; S, 9.35. Found: C, 70.36; H, 11.04; S, 9.55.

In a similar manner Ib was prepared in 89% yield using *n*-octadecyl mercaptan. The ir and nmr spectra were identical with those of Ia with the exception of the integration of the methylene chain singlet at δ 1.24. The integral in this case indicated 30 H. The product has mp 68–69°.

Anal. Calcd for $\mathrm{C_{22}H_{42}SO_2}$: C, 71.29; H, 11.42; S, 8.65. Found: C, 71.35; H, 11.51; S, 8.70.

Preparation of *N*,*N*-Dimethyl-3-hydroxy-4-(*n*-hexadecylthio)-butyric Acid Amide.—A solution of Ia (5.00 g, 0.0146 mol) in 100 ml of ether was added dropwise to a stirred solution of dimethylamine (4.5 g, 0.1 mol) in 150 ml of ether at −5 to 0°. After addition was complete the solution was warmed to room temperature and stirred overnight. The product crystallized during concentration of the ether to give 5.6 g (99%) of material, mp 55–57°, ir ($\mathrm{CHCl_3}$) 2.95, 6.1 μ.

Anal. Calcd for $\mathrm{C_{22}H_{45}NSO_2}$: C, 68.13; H, 11.70; N, 3.64; S, 8.27. Found: C, 67.91; H, 11.42; N, 3.61; S, 8.37.

Thermal Rearrangement of Ib.—A melt of Ib (29.5 g, 0.08 mol) was heated at 100° for 1 hr. An ir indicated the complete disappearance of 5.5-μ absorption and the appearance of bands at 5.6, 5.75, and 6.1 μ. The mixture was dissolved in 100 ml of boiling acetone and allowed to cool slowly to room temperature overnight. The polyester II was removed by filtration to give 11.0 g of material, mp 48–53°, ir (film) 5.75 μ, mol wt (vpo), 2160 (THF).

Anal. Calcd for $(\mathrm{C_{22}H_{42}O_2S})_n$: C, 71.29; H, 11.42; O, 8.63; S, 8.65. Found: C, 70.44; H, 11.36; O, 9.10; S, 8.35.

The acetone filtrate from above was evaporated to dryness and the residue was recrystallized from hexane to give 4.3 g (14%) of III, mp 52–54°. Recrystallization from ether gave an analytical sample: mp 55–56°; ir ($\mathrm{CHCl_3}$) 5.6, 8.55 μ; nmr ($\mathrm{CDCl_3}$) δ 0.86 [t, $J = 6.0$ Hz, 3 H, $-(\mathrm{CH_2})_{17}\mathrm{C}\mathbf{H}_3$], 1.24 [s, 30 H, $-(\mathrm{C}\mathbf{H}_2)_{15}\mathrm{CH_3}$], 1.52 [m, 2 H, $-\mathrm{SCH_2C}\mathbf{H}_2(\mathrm{CH_2})_{15}$], 2.42 and 2.87 (AB, two d of d, $J_{AX} = 7.5$, $J_{BX} = 8.0$, $J_{AB} = 18.5$ Hz, 1 H each, $-\mathrm{CH_2C{=}O}$), 2.56 [t, $J = 7.0$ Hz, 2 H, $-\mathrm{SC}\mathbf{H}_2(\mathrm{CH_2})_{16}-$], 3.59 (X of ABX, CDX multiplet, $-\mathrm{SCH}<$), 4.10 and 4.54 (CD, two d of d, $J_{CX} = 7.0$ $J_{DX} = 6.5$, $J_{CD} = 10.0$ Hz, 1 H each, $-\mathrm{OC}\mathbf{H}_2\mathrm{CH}<$). Addition of $\mathrm{Eu(thd)_3}$ shifted resonances at δ 2.42 and 2.87 to 3.25 and 3.70, respectively; 2.56 to 2.71; and 4.10 and 4.54 to 4.64 and 5.08, respectively.

Anal. Calcd for $\mathrm{C_{22}H_{42}O_2S}$: C, 71.29; H, 11.42; O, 8.63; S, 8.65. Found: C, 71.76; H, 11.49; O, 8.41; S, 8.62.

The hexane filtrate was evaporated to 9.1 g of an oil. Vacuum distillation gave 8.5 g (33%) of IV: bp 176–184° (0.4 mm); mol wt (vpo), 325. (calcd 326); ir (film) 6.13, 10.15, 10.9 μ; nmr ($\mathrm{CDCl_3}$) δ 0.95 [t, $J = 6.0$ Hz, 3 H, $-(\mathrm{CH_2})_{17}\mathrm{C}\mathbf{H}_3$], 1.29 [s, 32 H, $-(\mathrm{C}\mathbf{H}_2)_{16}\mathrm{CH_3}$], 2.52 [t, $J = 7.0$ Hz, 2 H, $-\mathrm{SC}\mathbf{H}_2(\mathrm{CH_2})_{16}$], 3.18 (apparent d with some traces of higher splitting, $J = 7.0$ Hz, 2 H, $-\mathrm{SC}\mathbf{H}_2\mathrm{CH{=}}$), allyl pattern with peaks centered at 5.20, 5.22, and 6.02 (5.20, $J = 9.5$, 2.0, and 1.0 Hz), 5.22 ($J = 17.5$, 2.0, and 1.0 Hz), 6.02 ($J = 17.5$, 9.5, and 7.0 Hz, total 3 H).

Anal. Calcd for $\mathrm{C_{21}H_{42}S}$: C, 77.21; H, 12.96. Found: C, 77.41; H, 12.86.

Preparation of V. Hydrolysis of Polyester II.—A solution of polyester II (20.0 g, 0.054 mol) and potassium hydroxide (13.2 g, 0.195 mol) in 60 ml of 50% aqueous ethanol was heated at reflux for 5 hr. The mixture was cooled and acidified to pH 2 with concentrated hydrochloric acid. The solid was filtered, washed with water, and air dried. The residue was recrystallized from chloroform to give V (6.9 g, 0.018 mol), 33%, mp 78–79°. Evaporation of the filtrate gave 8.0 g of solid, mp 43–61°. The ir spectra indicated that the material was a mixture of partially hydrolyzed polyester and lactone III: ir ($\mathrm{CHCl_3}$) 3.2–3.9 (broad), 5.95, 7.6, and 8.2 μ; nmr ($\mathrm{CDCl_3}$) δ 0.85 [t, $J = 6.0$ Hz, 3 H, $-(\mathrm{CH_2})_{17}\mathrm{C}\mathbf{H}_3$], 1.24 [s, 30 H, $-(\mathrm{C}\mathbf{H}_2)_{15}\mathrm{CH_3}$], 1.52 [m, 2 H, $-\mathrm{SCH_2C}\mathbf{H}_2(\mathrm{CH_2})_{15}$], 2.51 and 2.75 (AB, two d of d, $J_{AX} = 4.0$, $J_{BX} = 3.5$, $J_{AB} = 16.5$ Hz, 1 H each, $\mathrm{CH_2C{=}O}$), 2.54 [t, $J = 7.0$ Hz, $-\mathrm{SC}\mathbf{H}_2(\mathrm{CH_2})_{17}-$], 3.17 (m, 1 H, $>\mathrm{CHS}$), 3.65 (d, $J = 5.5$ Hz, 2 H, $-\mathrm{C}\mathbf{H}_2\mathrm{OH}$), 6.18 (b exchange H from OH and COOH, 2 H).

Anal. Calcd for $\mathrm{C_{22}H_{44}SO_3}$: C, 67.98; H, 11.41; O, 12.35; S, 8.25. Found: C, 67.79; H, 11.50; O, 12.65; S, 8.44.

Cyclization of V to III.—A solution of V (1.0 g, 0.0026 mol) and *p*-toluenesulfonic acid (0.1 g) in 10 ml of benzene was heated at reflux for 15 hr using a water separator. The solvent was evaporated and the residue was recrystallized from petroleum ether to give III (0.9 g, 0.0026 mol), 95%, mp 53–54°. The mixture melting point with III was undepressed and the ir spectra were superimposable.

Preparation of III.—A solution of *n*-octadecyl mercaptan (3.44 g, 0.012 mol), γ-crotonolactone (0.94 g, 0.012 mol), and sodium methylate (0.054 g, 0.001 mol) in 10 ml of methanol was heated at 50° for 0.5 hr. An oily layer separated which was dissolved in chloroform and the chloroform was evaporated. The residue (3.5 g) was chromatographed over silica gel. Unreacted mercaptan was eluted with petroleum ether. Elution with 10% diethyl ether in petroleum ether gave III (0.60 g, 0.0016 mol), 13.5%, mp 54–57°. Recrystallization from ether gave material, mp 56–57°. A mixture melting point with III obtained from the rearrangement of Ib was undepressed. The ir spectra were superimposable.

Preparation of V *via* Hydrolysis of III.—A solution of III (2.0

g, 0.0074 mol) and 1.4 g of potassium hydroxide in 20 ml of 50% aqueous methanol was heated at reflux for 3.5 hr. The solution was cooled and acidified to pH 2 with concentrated hydrochloric acid. The solid material was filtered, washed with water, and dried to give 2.0 g of hydroxy acid V, mp 75–76°. A mixture melting point with the acid obtained from the hydrolysis of polyester II was not depressed and the ir spectra were superimposable.

Registry No.—Ia, 34289-54-8; Ib, 34289-55-9; polymer of Ib, 34287-66-6; II, 34268-90-1; III, 34289-56-0; IV, 34289-57-1; V, 34289-58-2; *N*,*N*-dimethyl-3-hydroxy-4-(*n*-hexadecylthio)butyric acid amide, 34289-59-3.

Hydrogenation of Cinnamic Acids with Iridium(I) Catalysts. Effect of Various Ligands

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Recent communications have described olefin hydrogenations using $Ir(olefin)_2L_n$ based systems as catalysts.[1–3] Green and coworkers have noted ligand and solvent effects on the rate of hydrogenation of 1,5-cyclooctadiene and 1-hexene with these systems.[2] Van der Ent *et al.*, have studied the rate of hydrogenation of 1-hexene in benzene as a function of the ligand-iridium ratio (R).[3] With L = Ph_3P the maximum rate was observed at R = 2 at which point the rate is approximately ten times the rate at R = 1. I now report that α,β-unsaturated acids can also be reduced with these iridium catalysts and note some important rate effects based on ligand type, ligand ratio, and the presence or absence of chloride ligand.

Cinnamic acid and α-methylcinnamic acid have been hydrogenated to β-phenylpropionic acid and α-methyl-β-phenylpropionic acid, respectively, with $[Ir(1,5\text{-cyclooctadiene})Cl]_2$ and various phosphines in MeOH solvent at 100° and 75 psig of H_2. Table I records the per cent reduction after 2 hr under these conditions with a substrate–catalyst ratio of 400. It is found that cinnamic acid is reduced faster than α-methylcinnamic acid for all three phosphines (catalyst system A).

The importance of a 2:1 phosphine–iridium ratio as against a 1:1 ratio in the reduction of α-methylcinnamic acid (catalyst system A *vs.* B) manifests itself with the less basic phosphines, Ph_3P and Ph_2PEt, but entirely disappears with $PhPEt_2$. In the latter case the rates of reduction are identical for both systems. Even with Ph_2PEt the rate differences are not nearly so pronounced as with Ph_3P.[4]

Hydrogenation of α-methylcinnamic acid in the absence of chloride ligand (system C) was achieved by use of isolated $[Ir(1,5\text{-cyclooctadiene})L_2]BF_4$ as the catalyst. In this case the reduction proceeds much more rapidly with all three phosphines than the same reduction in the presence of chloride (system A).

TABLE I
PER CENT REDUCTION AT 2 HR[a]

	Cinnamic acid	α-Methylcinnamic Acid		
Catalyst[b]	A	A	B	C
Ph_3P	82	38	1.5	92
Ph_2PEt	55	19	6	39
$PhPEt_2$	64	25	25	78

[a] Reaction cessation at 2 hr was chosen arbitrarily. All catalyst systems were still alive at this point with the possible exception of system B with Ph_3P and Ph_2PEt. In these cases partial loss of catalyst by iridium plate-out was observed early in the reaction. [b] A = PR_3/Ir = 2.0 $[Ir(1,5\text{-cyclooctadiene})Cl]_2$ and PR_3 mixed *in situ;* B = PR_3/Ir = 1.0 $[Ir(1,5\text{-cyclooctadiene})Cl]_2$ and PR_3 mixed *in situ;* C = Used isolated $[Ir(1,5\text{-cyclooctadiene})(PR_3)_2]BF_4$: Prepared by previously published general procedures for analogous rhodium and iridium complexes. *Cf.* ref 1 and 2 and R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc*, **93**, 2397 (1971).

One further observation of note is that the rate of hydrogenation of cinnamic acid with L = Ph_3P was considerably reduced when no effort was made to eliminate the presence of atmospheric oxygen. The inhibitory effect of oxygen with this iridium catalyst is exactly the opposite of the rate-enhancing effect of oxygen in the reduction of maleic acid in DMA catalyzed by $IrX(CO)(Ph_3P)_2$ reported by James and Memon.[5] I have repeated the effect reported by these authors in the reduction of cinnamic acid with $IrCl(CO)(Ph_3P)_2$ in both DMA and MeOH.

Experimental Section

All hydrogenations were conducted in glass Fischer–Porter aerosol compatibility tubes with 20 mmol of substrate and 0.05 mmol of catalyst dissolved in 25 ml of anhydrous MeOH. For systems A and B, $[Ir(1,5\text{-cyclooctadiene})Cl]_2$[6] and the phosphines were premixed in 5 ml of MeOH under N_2 for 15 min prior to the addition of substrate. All reaction mixtures were vigorously sparged with nitrogen prior to being pressured to 75 psig of H_2. Reaction timing commenced upon placement of a 100° oil bath under the reaction vessel and activation of a magnetic stirrer.

Analyses were performed by integrating the $CDCl_3$ nmr spectra of solvent-stripped reaction aliquots. The reported integrals for cinnamic acid are actually corrected from observed figures to allow for integral deviations observed from known values in standard mixtures. In the case of α-methylcinnamic acid and α-methyl-β-phenylpropionic acid, standard mixtures integrated correctly.

Registry No.—Cinnamic acid, 621-82-9; α-methylcinnamic acid, 1199-77-5.

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[1] J. R. Shapley, R. R. Schrock, and J. A. Osborn, *J. Amer. Chem. Soc.*, **91**, 2816 (1969).

[2] M. Green, T. A. Kuc, and S. N. Taylor, *J. Chem. Soc. D*, 1553 (1970).

[3] H. van Gaal, H. G. A. M. Cuppers, and A. van der Ent, *ibid.*, 1694 (1970).

[4] Van der Ent's work on phosphine–iridium ratios (ref 3) was confined to Ph_3P and the hydrogenation of 1-hexene. It is interesting to speculate whether the rate differences would also disappear in this case with use of $PhPEt_2$ instead of Ph_3P.

(5) B. R. James and N. A. Memon, *Can. J. Chem.*, **46**, 217 (1968).

(6) Strem Chemicals, Inc.

Reduction of α-Substituted Acetoacetate Enolates with Lithium Aluminum Hydride

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In connection with a current synthesis project we had occasion to examine the reduction of α-substituted ethyl acetoacetate enolates. A recent report concern-