are found at $\Delta\delta$ values of only 0.20–0.25 ppm; that for (C6)CH_3, however, was at $\Delta\delta$ = 1.20 ppm. From the latter peaks (at δ 12.8 and 14.0) the ratio of diastereomers (14 and its 6*R* epimer) was determined accurately[13b] to be 1:2.5; i.e., the ee is 43%.

(1*R*,2*S*)-2-Methylcyclobutanol (15). A solution of (*S*)-2-methylcyclobutanone (11; $[\alpha]_{578}$ −12.3°; 168 mg, 2.0 mmol) in THF (1 mL) was added to 2.8 mL of a solution of lithium tri-*sec*-butylborohydride[15] (L-Selectride, Aldrich; 1 M in THF, 2.8 mmol) at −80 °C under N_2. After the mixture was stirred for 2 h at −80 °C, the temperature was raised to room temperature (1 h). To the mixture were added water (0.4 mL), EtOH (1.5 mL), 6 M NaOH (1 mL), and, carefully, 30% H_2O_2 (1.5 mL), and stirring was continued for 2 h at room temperature. The organic layer was separated, the water layer was extracted twice with ether, the combined organic layers were washed with brine and dried (Na_2SO_4), and the ether was removed through a Vigreux column. The residue was purified twice by GLC (12-ft LAC-3-R-728 column, 80 °C) to give the cis alcohol **15**: $[\alpha]_{578}$ +13.7° (*c* 0.39, $CHCl_3$); IR (neat) 3450 cm^{-1} (OH); ^1H NMR (CCl_4) δ 1.05 (d, *J* = 8 Hz, 3), 2.00 (s, 1), 1.2–2.7 (m, 6), 4.29 (q, *J* = 8 Hz, 1).

The cis alcohol **15** was reacted with 1 equiv of the acid chloride of optically pure α-methoxy-α-(trifluoromethyl)benzeneacetic acid (Aldrich), according to Mosher et al.[14] in pyridine overnight at room temperature, followed by extraction with ether, washing with aqueous $NaHCO_3$, and drying, to give the acetate **16** as an oil; ^1H NMR (CCl_4) δ 0.98 and 1.07 (2 d, *J* = 7 Hz, 3, ratio ca. 1:4), 1.0–3.0 (m, 5), 3.48 (d, *J* = 1 Hz, 3), 5.15 (br q, *J* = 7 Hz, 1), 7.3 (br, 5); ^{19}F NMR (C_6D_6–CCl_4, 1:1) δ −76.54 and −76.69 in a ratio of 36:152, i.e., 62% ee.

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Registry No. **1**, 36635-61-7; **2**, 2216-51-5; **3**, 2230-82-2; **4**, 79357-06-5; **5**, 53273-24-8; **6**, 79357-07-6; **7**, 79357-08-7; **8**, 79357-09-8; **9**, 79357-10-1; **10**, 79390-62-8; **11**, 79390-63-9; **12**, 79390-64-0; **13** (6*S* epimer), 79357-11-2; **13** (6*R* epimer), 79433-79-7; **14**, 79390-65-1; **15**, 79390-66-2; **16**, 79357-12-3; ethyl xanthate, 151-01-9; *N*-(tosylmethyl)formamide, 36635-56-0; (±)-1,3-dibromobutane, 79390-67-3; (±)-2-methylcyclobutanone, 74528-79-3; (*S*)-(+)-1,3-dibromobutane, 79357-13-4; (*R*,*R*)-(−)-butane-2,3-diol, 24347-58-8; (*S*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride, 20445-33-4.

Hard Acid and Soft Nucleophile Systems. 5.[1] Ring-Opening Reaction of Lactones to ω-Alkylthio or ω-Arylthio Carboxylic Acids with Aluminum Halide and Thiol

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Lactones were converted into ω-alkylthio carboxylic acids in high yields through ω-carbon–oxygen bond cleavage when they were treated with aluminum halide and alkanethiol. The aluminum halide and arenethiol system has also been found to be useful for the preparation of the synthetically valuable ω-arylthio carboxylic acids from lactones.

Lactones are important synthetic intermediates. The ring opening of lactones through the alkyl–oxygen bond cleavage with sulfur containing nucleophile, e.g., alkanethiol or arenethiol, is an interesting process because it produces synthetically valuable ω-alkyl(or aryl)thio carboxylic acids: for instance, 4-(phenylthio)butanoic acid and 5-(phenylthio)pentanoic acid can be recyclized to 4-(phenylthio)-γ-butyrolactone and 5-(phenylthio)-δ-valerolactone, respectively, and they can easily be transformed into the corresponding enol lactones.[2]

Excellent syntheses which have not involved a lactone opening procedure have not been reported.[3] Smith,[4] Liotta,[5] and their co-workers reported the conversion of lactones into ω-phenylseleno carboxylic acids by using a powerful nucleophile, phenylselenide anion. ω-Olefinic carboxylic acids were then synthesized. Cleavage of the alkyl–oxygen bond of γ-lactones using lithium thiomethoxide[6] or sodium thioethoxide[3d] has been reported. However, benzyl thiolate has been shown to attack the lactone carbonyl group.[7]

Scheme I

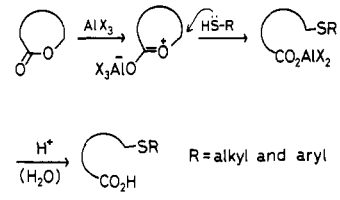
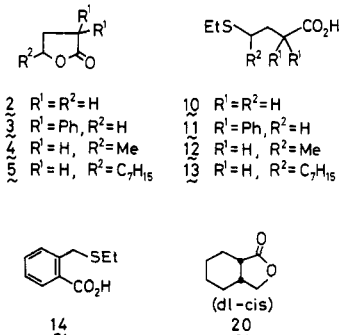


Chart I



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We have developed carbon–oxygen cleavage reactions of ethers,[8] methylenedioxy groups,[8] and esters[9] with a "hard acid and soft nucleophile system". In our method, the nonactivated thiol or sulfide itself is used as the nucleophile, while the substrate is activated by coordination of a Lewis acid to the oxygen atom.

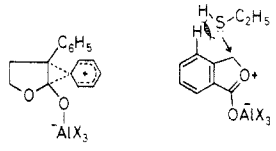
We report here a combination of an aluminum halide and a thiol as a very effective reagent system for the synthesis of ω-alkylthio carboxylic acids from lactones through ω-carbon–oxygen bond cleavage.[10]

Results and Discussion

As reported in our previous paper, the aluminum halide–ethanethiol system has been shown to be effective for deesterification of methyl and benzyl esters.[9] We tried to apply this reagent system for lactone ring opening.

The reaction proceeds as shown in Scheme I, which can be explained by "hard and soft acids and bases principles",[11] and gives the expected ring-opened product, ω-(alkyl(or aryl)thio)alkanoic acid, in good yield. Table I shows several examples of the reaction.

β-Propiolactone (1) was so reactive that its reaction was carried out under much milder conditions than the other reactions. γ-Butyrolactone (2, Chart I) on treatment with aluminum bromide in ethanethiol for a short time gave 4-(ethylthio)butyric acid in high yield (87.7–94.5%), showing superiority to Kresze's[3d] and Kelly's methods[6] (63% and 67%). On the other hand α,α-diphenyl-γ-butyrolactone (3) required a much longer time for completion of the ring opening, probably due to inactivation of the oxonium ion based on the formation of a phenonium ion (A), although a good yield of the desired product was



A B

obtained. The reactions with γ-lactones 4 and 5 bearing γ substituents also took rather long times because of their steric hindrance for the nucleophilic attack of thiol. The difference of the rates between 4 and 5 is attributed to the difference of the steric hindrance at their γ-carbon atoms. Phthalide (6) was shown to be almost inactive for this reaction; this may be attributed to the steric hindrance of the hydrogen atom at C-4 for the S_N2-type nucleophilic attack of ethanethiol, as shown in formula B. δ-Valerolactone (7) and especially ε-caprolactone (8) are more inactive than γ-lactones. A seven-membered-ring lactone has been known to be less suitable for the S_N2-type displacement than six- and five-membered-ring lactones.[4,5]

Next, we examined ring cleavage of γ-butyrolactone using aluminum bromide and several alkanethiols. The results are shown in Table II.

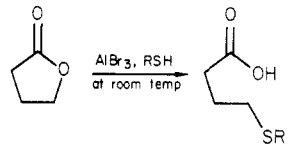
The primary and secondary alkanethiols gave the corresponding γ-(alkylthio)butyric acids in 83.0–94.5% yields.

Table I. Ring-Opening Reaction of Lactone to ω-Ethylthio Carboxylic Acid

compd (amt, mmol)	Lewis acid (amt, molar equiv)	amt EtSH, mL	time, h[a]	product	yield, %
1 (6.0)	$AlCl_3$ (1.2)	2.3[b]	1.5	9	60.4
2 (2.0)	$AlBr_3$ (1.1)	3	0.2	10	87.7
2 (12.9)	$AlBr_3$ (2.2)	15	1.3	10	94.5
3 (1.0)	$AlBr_3$ (1.3)	1.5	43.5	11	88.0
3 (7.8)	$AlBr_3$ (3.0)	12	21	11	84.0
4 (3.1)	$AlCl_3$ (1.1)	3	23	12	84.6
4 (3.0)	$AlBr_3$ (1.1)	3	2	12	80.5
5 (1.0)	$AlCl_3$ (3.0)	2	37	13	91.3
5 (1.0)	$AlBr_3$ (3.0)	2	13	13	91.2
6 (1.5)	$AlBr_3$ (3.0)	2	23	14	9.5[c]
7 (2.0)	$AlBr_3$ (1.2)	3	3.5	15	53.0
8 (4.0)	$AlBr_3$ (1.2)	3	13	16	45.3

[a] All reactions were carried out in ethanethiol under stirring at room temperature. In only the case of 1, the reaction was carried out in nitrogen at 0 °C. [b] Dichloromethane (30 mL) was used as a cosolvent. [c] Starting material was recovered in 85.5% yield.

Table II. Conversion of γ-Butyrolactone into γ-(Alkylthio)butyric Acid with Aluminum Bromide and Alkanethiol

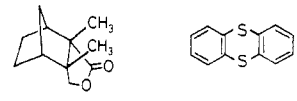


run	compd amt, mmol	alkanethiol R (amt, mL)	$AlBr_3$, molar equiv	time, h	product	yield, %
1	12.9	Et (15)	2.2	1.3	10	94.5
2	3.1	*n*-Pr (4)	2.1	1.0	17	92.0
3	13.1	*i*-Pr (9)	1.9	1.2	18	93.4
4	2.5	*i*-Bu (3)	1.8	3.0	19	83.0

The tertiary butanethiol could not be used, because aluminum bromide and *tert*-butanethiol gave a solid compound probably due to the formation of the stable *tert*-butyl cation.

Arenethiols can also be used as the nucleophiles for ring opening of lactones; the results from the use of benzenethiol are shown in Table III.

β-Propiolactone (1), a highly strained ring compound, has a high reactivity; hence it reacted readily with benzenethiol, in spite of its lesser nucleophilicity than that of an alkanethiol, to give a high yield of 3-(phenylthio)-propionic acid (22).[12] Reactions of γ-butyrolactones and δ-valerolactones with benzenethiol gave the corresponding ω-phenylthio carboxylic acids. The reactions, however, did not proceed so easily as compared with those with alkanethiols (Tables I–III); they required longer reaction times or more vigorous conditions and gave lower yields. A similar result was reported in the ring opening of lactone C with lithium thiophenoxide in HMPA.[6] The lower nucleophilicity of benzenethiol may result in these facts. But a more careful experiment showed that benzenethiol was



C D

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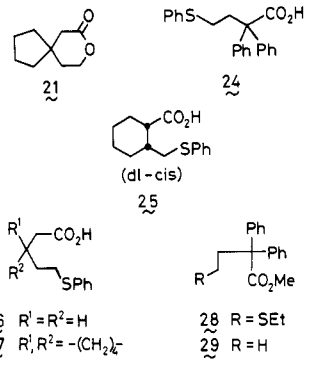
Table III. Conversion of Lactone into ω-Phenylthio Carboxylic Acid with Aluminum Bromide and Benzenethiol

compd (amt, mmol)	amt $AlBr_3$, molar equiv	amt PHSH, mL	temp,[d] °C	time	product	yield, %
1 (2.8)	1.3[a]	1.5	0-rt	2 h[b]	22	81.0
2 (1.6)	2.0	2.5	rt	7 h	23	53.9
3 (1.12)	4.8	2.0	rt	50 h	24	29.5
20 (7.0)	2.9	5.5	30	11 h	25	48.6
7 (30)	3.0	10.0	reflux	0.5 h	26	31.4
21 (1.5)	3.5	4.0	rt	10 days[b]	27	45.0[c]

[a] $AlCl_3$ was used. Dichloromethane (14 mL) was used as a cosolvent. [b] The reaction was carried out in nitrogen. [c] A small amount of impurity was contaminated. [d] rt = room temperature.

Chart II



subject to oxidation by aluminum bromide, a one-electron oxidizing reagent.[13] The reaction of lactone **3** with aluminum bromide in benzenethiol in nitrogen gave a considerable amount of thianthrene (D) together with the desired carboxylic acid. After 5 days, consumption of almost all of the benzenethiol was observed by GLC analysis of the reaction mixture.

It has been known that the β-propiolactone has a curious dichotomy of reactivity; diethylaluminum ethanethiolate[14] has been reported to cause both *O*-alkyl and *O*-acyl cleavages of the propiolactone at the same time. On the other hand, bis(dimethylaluminum) 1,2-ethanedithiolate[15] has been shown to give only *O*-acyl-cleaved product for the γ-butyro- and δ-valerolactones. Our new reagent system, AlX_3–thiol, is characteristic of only a selective *O*-alkyl cleavage for all of the β-, γ-, δ-, and ε-lactones.

As an example of the effective utilization of the lactone ring opening product, 4-(ethylthio)-2,2-diphenylbutyric acid (**11**) was subjected to methylation with diazomethane and reduction with Raney nickel to give methyl 2,2-diphenylbutyrate (**29**) via the methyl ester **28** (Chart II). An additional example consists in the aforementioned transformation of ω-phenylthio carboxylic acids into enol lactones.[2]

In conclusion, our synthetic method for the ω-(alkylthio)- or ω-(arylthio)alkanoic acids from lactones by their treatment with the aluminum halide–thiol system is recognized as an improved one on the basis of the following reasons. (i) The desired product can be obtained in a one-step reaction from the corresponding lactones. (ii) As compared with the already published methods of the lactone opening, activation of the nucleophile is not necessary, and the reaction proceeds smoothly under milder conditions (at room temperature or 0 °C). (iii) The procedure and operation for the reaction are simple and convenient. (iv) Especially, the ω-(alkylthio)alkanoic acid is obtained in a higher yield than that in the other methods.

Experimental Section

Melting points were determined on a micro hot stage. Boiling points were determined on a microdistillation apparatus. IR spectra were recorded with a JASCO A-202 diffraction grating infrared spectrophotometer, and ^1H NMR spectra were obtained with a JEOL JNM-FX100 spectrometer or a Varian T-60 spectrometer. Mass spectra were determined on a JEOL JMS-O1SG double-focusing mas spectrometer.

Materials. Lactones 1–8 were commercially available. *cis*-Hexahydrophthalide (**20**) and [1-(2-hydroxyethyl)cyclopentyl]-acetic acid δ-lactone (**21**) were prepared from the parent dicarboxylic anhydrides.[16]

General Procedure for Ring Opening of Lactones. To a stirred solution of aluminum halide in a thiol was added the substrate under the conditions described in Tables I–III. The reaction was monitored by TLC (aluminum halide was quenched by methanol in the capillary). The reaction mixture was poured into water, which, after addition of dilute HCl, was extracted with dichloromethane or ethyl acetate. The organic layer was shaken with brine, dried (Na_2SO_4), filtered, and then evaporated to leave a crude material, which was purified by chromatography over a silica gel column. The yields are given in Tables I–III.

3-(Ethylthio)propionic acid (9): colorless oil; bp 90–92 °C (1.0 mm) [lit.[3d] bp 152.5 °C (13 mm)]; IR ($CHCl_3$) 3600–2300, 1700 cm^{-1}; NMR ($CDCl_3$) δ 1.26 (t, *J* = 7.3 Hz, 3 H), 2.46–2.83 (m, 6 H), 7.81 (br s, 1 H, CO_2H); mass spectrum, *m/e* 134 (M^+).

4-(Ethylthio)butyric acid (10): colorless oil; bp 106 °C (1.0 mm); IR ($CHCl_3$) 3600–2400, 1705, 1295, 1235 cm^{-1}; NMR ($CDCl_3$) δ 1.26 (t, *J* = 7.5 Hz, 3 H), 1.92 (quintet, *J* = 7.5 Hz, 2 H), 2.51 (t, *J* = 7.5 Hz, 2 H), 2.55 (q, *J* = 7.5 Hz, 2 H), 2.58 (t, *J* = 7.5 Hz, 2 H), 10.49 (br s, 1 H). Anal. Calcd for $C_6H_{12}O_2S$: C, 48.62; H, 8.16. Found: C, 48.69; H, 8.25.

4-(Ethylthio)-2,2-diphenylbutyric acid (11): colorless needles (from petroleum ether–benzene); mp 102.0–103.0 °C; IR ($CHCl_3$) 3600–2400, 1700, 1260 cm^{-1}; NMR ($CDCl_3$) δ 1.13 (t, *J* = 7.3 Hz, 3 H), 2.08–2.72 (m, 6 H) 7.30 (s, 10 H, aromatic). Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.96; H, 6.71. Found: C, 72.09; H, 6.75.

4-(Ethylthio)valeric acid (12): colorless oil; bp 108 °C (0.7 mm); IR ($CHCl_3$) 3600–2400, 1705, 1280, 1230 cm^{-1}; NMR ($CDCl_3$) δ 1.25 (t, *J* = 7.3 Hz, 3 H), 1.30 (d, *J* = 6.7 Hz, 3 H), 1.86 (q, *J* = 6.7 Hz, 2 H), 2.54 (t, *J* = 6.7 Hz, 2 H), 2.55 (q, *J* = 7.3 Hz, 2 H), 2.83 (sextet, *J* = 6.7 Hz, 1 H), 10.92 (br s, 1 H). Anal. Calcd for $C_7H_{14}O_2S$: C, 51.82; H, 8.70. Found: C, 52.00; H, 8.89.

4-(Ethylthio)undecanoic acid (13): colorless oil; bp 156 °C (0.5 mm); IR ($CHCl_3$) 3600–2400, 1710 cm^{-1}; NMR ($CDCl_3$) δ 0.92 (br t, *J* = 7.5 Hz, 3 H), 1.24 (t, *J* = 7.5 Hz, 3 H), 1.20–2.00 (m, 14 H), 2.16–2.62 (m, 5 H), 10.32 (br s, 1 H). Anal. Calcd for $C_{13}H_{26}O_2S$: C, 63.36; H, 10.64. Found: C, 63.42; H, 10.98.

2-[(Ethylthio)methyl]benzoic acid (14): colorless needles (from petroleum ether); mp 109–111 °C; IR ($CHCl_3$) 3600–2400, 1695, 1295, 1265 cm^{-1}; NMR ($CDCl_3$) δ 1.26 (t, *J* = 8.0 Hz, 3 H), 2.72 (q, *J* = 8.0 Hz, 2 H), 4.20 (s, 2 H), 7.24–7.60 (3 H, aromatic), 8.04 (d, *J* = 8.0 Hz, 1 H, aromatic), 11.60 (br s, 1 H). Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.16. Found: C, 61.05; H, 6.16.

5-(Ethylthio)valeric acid (15): colorless oil; bp 124.5–125.5 °C (1.2 mm); IR ($CHCl_3$) 3600–2400, 1710, 1280, 1230 cm^{-1}; NMR

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($CDCl_3$) δ 1.25 (t, J = 7.3 Hz, 3 H), 1.66–1.73 (m, 4 H), 2.32–2.65 (m, 6 H), 9.08 (br s, 1 H). Anal. Calcd for $C_7H_{14}O_2S$: C, 51.82; H, 8.70. Found: C, 51.40; H, 8.81.

6-(Ethylthio)hexanoic acid (16): colorless oil; bp 124 °C (1.8 mm); IR ($CHCl_3$) 3600–2400, 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.25 (t, J = 7.3 Hz, 3 H), 1.30–1.88 (m, 6 H), 2.32–2.64 (m, 6 H), 10.10 (br s, 1 H). Anal. Calcd for $C_8H_{16}O_2S$: C, 54.51; H, 9.15. Found: C, 54.35; H, 8.93.

4-(n-Propylthio)butyric acid (17): colorless oil; bp 115–116 °C (1.5 mm); IR ($CHCl_3$) 3600–2400, 1710, 1290, 1235 cm^{-1}; NMR ($CDCl_3$) δ 0.99 (t, J = 6.8 Hz, 3 H), 1.60 (sextet, J = 6.8 Hz, 2 H), 1.91 (quintet, J = 6.8 Hz, 2 H), 2.50 (t, J = 6.8 Hz, 4 H), 2.57 (t, J = 6.8 Hz, 2 H), 11.08 (br s, 1 H). Anal. Calcd for $C_7H_{14}O_2S$: C, 51.82; H, 8.70. Found: C, 52.06; H, 8.90.

4-(Isopropylthio)butyric acid (18): colorless oil; bp 110–112 °C (1.8 mm); IR ($CHCl_3$) 3600–2400, 1710, 1290, 1230 cm^{-1}; NMR ($CDCl_3$) δ 1.26 (d, J = 6.7 Hz, 6 H), 1.91 (quintet, J = 7.5 Hz, 2 H), 2.52 (t, J = 7.5 Hz, 2 H), 2.60 (t, J = 7.5 Hz, 2 H), 2.93 (septet, J = 6.7 Hz, 1 H), 11.23 (br s, 1 H). Anal. Calcd for $C_7H_{14}O_2S$: C, 51.82; H, 8.70. Found: C, 51.98; H, 8.44.

4-(Isobutylthio)butyric acid (19): colorless oil; bp 120–121 °C (1.7 mm); IR ($CHCl_3$) 3600–2400, 1710, 1290, 1235 cm^{-1}; NMR ($CDCl_3$) δ 0.98 (d, J = 6.3 Hz, 6 H), 1.65–2.05 (m, 3 H), 2.36–2.63 (m, 6 H), 11.39 (br s, 1 H). Anal. Calcd for $C_8H_{16}O_2S$: C, 54.51; H, 9.15. Found: C, 54.57; H, 9.33.

3-(Phenylthio)propionic acid (22): colorless needles; mp 56.0–56.5 °C (from petroleum ether) (lit.[3d] mp 59–60 °C); IR ($CHCl_3$) 3600–2300, 1700 cm^{-1}; NMR ($CDCl_3$) δ 2.66 (AA', 2 H, CH_2Cl_2), 3.15 (BB', 2 H, SCH_2) 7.18–7.41 (m, 5 H), 8.50 (br s, 1 H, CO_2H), mass spectrum, m/e 182 (M^+).

4-(Phenylthio)butyric acid (23): colorless needles; mp 66.0–67.0 °C (from petroleum ether–dichloromethane); IR ($CHCl_3$) 3600–2400, 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.96 (quintet, J = 7.0 Hz, 2 H), 2.46 (t, J = 7.0 Hz, 2 H), 2.98 (t, J = 7.0 Hz, 2 H), 7.04–7.56 (5 H, aromatic). Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.16. Found: C, 61.35; H, 5.94.

4-(Phenylthio)-2,2-diphenylbutyric acid (24): colorless prisms; mp 173–174 °C (from petroleum ether–dichloromethane); IR ($CHCl_3$) 3600–2400, 1700 cm^{-1}; NMR ($CDCl_3$) δ 2.73 (s, A_2B_2, 4 H), 7.00–7.28 (m, 5 H, aromatic), 7.31 (s, 10 H, aromatic). Anal. Calcd for $C_{22}H_{20}O_2S$: C, 75.83; H, 5.79. Found: C, 75.52; H, 5.74.

***cis*-2-[(Phenylthio)methyl]cyclohexanecarboxylic acid (25)**: colorless prisms; mp 65–66 °C (from petroleum ether–dichloromethane; IR (NaCl, neat) 3600–2400, 1700 cm^{-1}; NMR ($CDCl_3$) δ 1.00–2.20 (9 H), 2.50–3.30 (3 H), 6.80–7.55 (m, 5 H, aromatic); high-resolution mass spectrum, calcd for $C_{14}H_{18}O_2S$ (M^+) m/e 250.103, found m/e 250.102.

5-(Phenylthio)valeric acid (26): mp 61–62 °C (from n-hexane–ether); IR ($CHCl_3$) 3600–2400, 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.61–1.81 (m, 4 H), 2.37 (br t, J = 7.5 Hz, 2 H), 2.93 (br t, J = 7.5 Hz 2 H), 7.00–7.50 (5 H, aromatic). Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.71. Found: C, 62.79; H, 6.81.

[1-[2-(Phenylthio)ethyl]cyclopentyl]acetic acid (27): colorless oil; IR (NaCl, neat) 3600–2400, 1705 cm^{-1}; NMR ($CDCl_3$) δ 1.20–2.00 (10 H), 2.33 (s, 2 H, CH_2CO_2H), 2.73–3.10 (m, 2 H, CH_2SPh), 7.00–7.40 (m, 5 H, aromatic), 11.2 (br s, 1 H, CO_2H); high-resolution mass spectrum, calcd for $C_{15}H_{20}O_2S$ (M^+) m/e 264.118, found m/e 264.121.

Thianthrene[17] (D): colorless needles; mp 153–156 °C (from acetone); IR (KBr) 1440, 760, 750 cm^{-1}; NMR ($CDCl_3$) δ 7.09–7.26 (m, 4 H), 7.36–7.53 (m, 4 H). Anal. Calcd for $C_{12}H_8S_2$: C, 66.68; H, 3.73. Found: C, 66.63; H, 3.66.

Methyl 4-(Ethylthio)-2,2-diphenylbutyrate (28). The acid 11 was methylated with diazomethane (in either solution) as usual to give the methyl ester **28** (98%, after purification by SiO_2 column chromatography): colorless prisms; mp 51.5–52.0 °C (from methanol); IR ($CHCl_3$) 1725 cm^{-1}; NMR ($CDCl_3$) δ 1.15 (t, J = 7.3 Hz, 3 H), 2.12–2.76 (m, 6 H), 3.69 (s, 3 H), 7.27 (br s, 10 H, aromatic). Anal. Calcd for $C_{19}H_{22}O_2S$: C, 72.57; H, 7.05. Found: C, 72.54; H, 6.99.

Methyl 2,2-Diphenylbutyrate (29). To a solution of the ester **28** (232 mg, 0.74 mmol) in 95% EtOH (10 mL) was added Raney nickel (3.24 g). After being refluxed for 15 h, the reaction mixture was treated as usual to give **29** (166 mg, 88.8%), which was purified by microdistillation: colorless oil; bp 126–128 °C (1.8 mm); IR ($CHCl_3$) 1725 cm^{-1}; NMR ($CDCl_3$) δ 0.75 (t, J = 7.3 Hz, 3 H), 2.43 (q, J = 7.3 Hz, 2 H), 3.67 (s, 3 H), 7.27 (br s, 10 H, aromatic). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.41; H, 6.88.

Registry No. 1, 57-57-8; 2, 616-45-5; 3, 956-89-8; 4, 108-29-2; 5, 104-67-6; 6, 87-41-2; 7, 542-28-9; 8, 502-44-3; 9, 7244-82-8; 10, 71057-15-3; 11, 71057-16-4; 12, 71057-17-5; 13, 71057-18-6; 14, 79313-52-3; 15, 71057-19-7; 16, 71057-20-0; 17, 79313-53-4; 18, 79313-54-5; 19, 79313-55-6; 20, 79389-25-6; 21, 27579-18-6; 22, 5219-65-8; 23, 17742-51-7; 24, 77734-57-7; 25, 79313-56-7; 26, 17742-53-9; 27, 77754-88-2; 28, 79313-57-8; 29, 79328-68-0; thianthrene, 92-85-3; EtSH, 75-08-1; n-PrSH, 107-03-9; i-PrSH, 75-33-2; i-BuSH, 513-44-0; PhSH, 108-98-5; $AlCl_3$, 7446-70-0; $AlBr_3$, 7727-15-3.

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Organometallic Complexes in Organic Synthesis. 15. Absolute Configurations of Some Simply Substituted Tricarbonyliron Complexes

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Unsymmetrically substituted tricarbonyl(η-cyclohexadiene)iron(0) complexes have a molecular center of chirality. Stereospecific reactions of the derived tricarbonyl(η-cyclohexadienyl)iron(1+) salts have been used to direct the formation of new chiral centers at carbon and so to define absolute configurations of key complexes by chemical correlation with the terpenes cryptone and phellandrene. Further interconversions in the series have determined the configurations of a number of simply substituted tricarbonyliron complexes which have potential for application in asymmetric organic synthesis.

Complexation by transition metals can confer on an organic compound reactivity properties which differ markedly from those expected for the functional groups of the free ligand. Stabilization[1] of cationic species in such cases activates the ligand toward nucleophilic attack in a fashion that is independent[2] of the need for classical cationoid substituents, though the position and nature of substituents is still of importance if regioselectivity is to

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