Photolyses of Organocobaloxime Having Aralkyl and (Alkylthio)carbonyl Groups on the β-Position. A Radical Reaction Involving the Thioester Group†

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Abstract: [2-[(Alkylthio)carbonyl]-4-mesityl-2-methylbutyl]cobaloxime (**1**), [2-[(alkylthio)carbonyl]-2-(ethoxycarbonyl)-5-phenylpentyl]cobaloxime (**2**), and [2-[(alkylthio)carbonyl]-2-(ethoxycarbonyl)-4-mesitylbutyl]cobaloxime (**3**) were photolyzed to produce pairs of organo radicals and cobaloxime(II) radicals by the rupture of a carbon–cobalt σ-bond. The organo radicals collapsed into hydrogen abstraction products **4**, **7**, and **10**, a thioester rearranged product, **5**, an intramolecular 1,5-hydrogen shift product, **8**, a thioester elimination product, **11**, and β-thiolactones **6**, **9**, and **12**. The β-thiolactones resulted by the radical substitution on sulfur of the thioester and are the major products from the cobaloximes that have a (*tert*-butylthio)carbonyl group. For the thioester rearrangement a stepwise mechanism is proposed, which involves an internal radical attack on sulfur followed by the bond switching from alkylthio to alkylcarbonyl (Scheme V). Last, the possible involvement of cobaloxime(II) in this thioester rearrangement is discussed. The cobalt complex is considered to facilitate the rearrangement by the interaction between sulfur and cobalt(II) radical species.

We have been concerned with model studies on the coenzyme B_{12} mediated rearrangement of a thioester group.[1] This type of rearrangement plays a central role in the isomerization of methylmalonyl-CoA into succinyl-CoA,[2-5] which is caused by the catalysis of coenzyme B_{12}/mutase system and is important to animal metabolism. In these model studies we have clarified that phenyl and (alkylthio)carbonyl groups rearrange competitively to a neighboring radical center. In the absence of a cobalt complex, a phenyl group rearranges in preference to an (alkylthio)-carbonyl group,[1d,e] and the intrinsic properties of the two groups have also been shown by recent kinetic studies.[6-8] In the presence of cobaloxime, however, the rearrangement preference is reversed, and the (alkylthio)carbonyl group rearranges preferentially.[1d,e]

Organocobaloxime, organobis(dimethylglyoximato)(pyridine)cobalt(III), has been widely used as a model of organocobalamin[9] since both the cobalt complexes have carbon–cobalt σ-bond as a sixth ligand, and their chemical properties are very alike. Photolysis of organocobaloximes gives a pair of organo-radicals and a cobaloxime(II) radical as the nearest neighbor,[10-12] and this radical pair must provide a good model for the pair of substrate radical and cobalamin, coenzyme B_{12}, radical constrained in an enzyme cavity.

These circumstances prompted us to investigate the radical rearrangement of (alkylthio)carbonyl groups in more detail, and we carried out photolysis of the organocobaloximes that have an (alkylthio)carbonyl group on the β-position to the cobalt–carbon bond. In most of the cases organocobaloximes were substituted with aralkyl groups for experimental convenience.

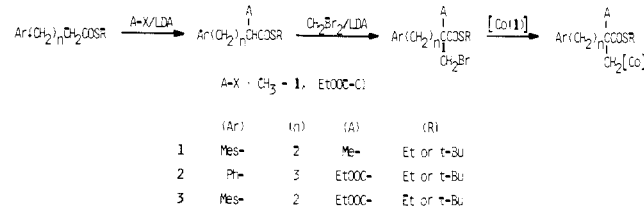
Results

[2-[(Alkylthio)carbonyl]-4-mesityl-2-methylbutyl]cobaloxime (**1**), [2-[(alkylthio)carbonyl]-2-(ethoxycarbonyl)-5-phenylpentyl]cobaloxime (**2**), and [2-[(alkylthio)carbonyl]-2-(ethoxycarbonyl)-4-mesitylbutyl]cobaloxime (**3**) were prepared from cobaloxime(I) anion (Figure 1) and the corresponding bromides, which were prepared by methylation or ethoxycarbonylation followed by bromomethylation of the corresponding *S*-alkyl 4- or 5-arylalkanethioate (Scheme I).

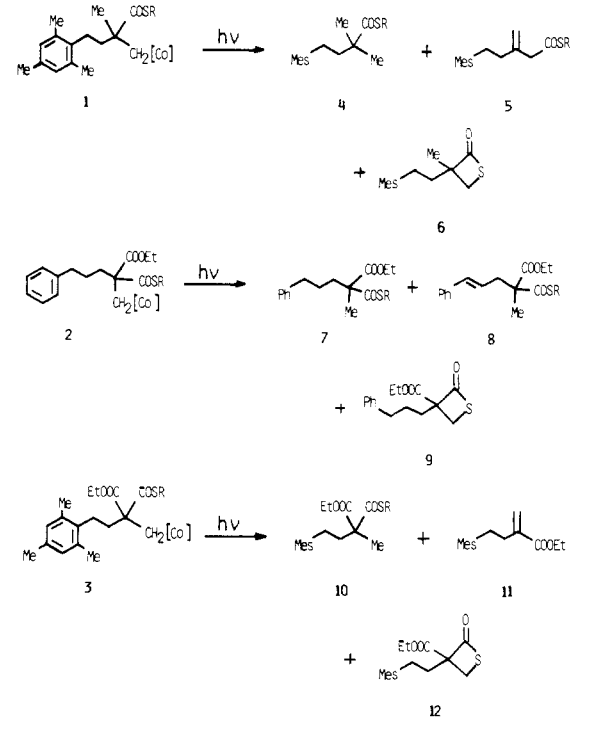
Photolyses of the cobaloximes with a high-pressure mercury lamp (Pyrex filter) and a fluorescent lamp gave similar results except for reaction time. The irradiations, therefore, were carried out with the mercury lamp for experimental convenience (short irradiation time).

The photolysis of cobaloxime **1** gave a reduction product **4**, a thioester-rearranged product **5**, and a β-thiolactone derivative **6** (Scheme II). The product **4** was identified with the authentic sample prepared by α-methylation of *S*-alkyl 4-mesityl-2-methylbutanethioate. The structure of **5** was deduced from the

Scheme I



Scheme II



† Dedicated to Professor E. J. Corey on the occasion of his 60th birthday.

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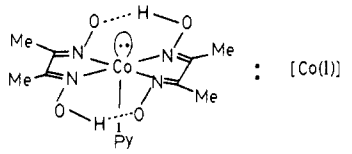


Figure 1. Structure of cobaloxime (I).

Table I. Photolyses of Organocobaloxime **1**

R	solvent	product composition, % 4	5	6	total yield, %
Et	benzene	48	50	2	57
Et	acetonitrile	66	30	4	
Et	methanol	80	16	4	
Et	chloroform	100	0	0	90
t-Bu	benzene	4	4	92	61
t-Bu	acetonitrile	18	13	69	
t-Bu	methanol	12	4	84	
t-Bu	chloroform	84	0	16	78

related compounds, *S*-alkyl 3-methyl-3-butanethioate and *S*-alkyl 3-phenyl-3-butanethioate,[1d,e] through a comparison of spectral data. The product **5** showed ^{1}H NMR signals due to the terminal methylene at δ 5.02 and 5.07 (both diffuse singlets) and the methylene next to carbonyl at δ 3.31 as a doublet (J = 0.7 Hz). The β-thiolactone structure of **6** was deduced from an IR absorption at 1755 cm^{-1} [13-15] and ^{1}H NMR signals due to the methyl at δ 1.47 as a singlet and an AB qurtet at δ 2.78 and 3.00 (J = 8.5) due to the ring methylene. The chemical shift of the quartet is typical for the methylene adjacent to the sulfur in the β-thiolactone ring.[13-15] β-Propiothiolactone and 2,2-dimethyl-β-propiothiolactone have signals at δ 3.05 and 2.78, respectively, due to the ring methylene next to the sulfur, whereas β-propiothiolactone and its 3,3-disubstituted derivatives have signals at around δ 4 due to the methylene next to the carbonyl group.[13-15] An alternative structure for **6**, 3,3-disubstituted β-thiolactone, was eliminated from these spectral features. The structure **6** was further supported by mass fragmentation: m/z 248 (M^+), 187 (M^+ - HCOS), 173 (M^+ - $HCOSCH_2$), 147 ($MesCH_2CH_2^+$), and 133 ($MesCH_2^+$). The second and third fragments must have been generated by McLafferty shift of the benzylic hydrogen to the carbonyl followed by ring rupture.

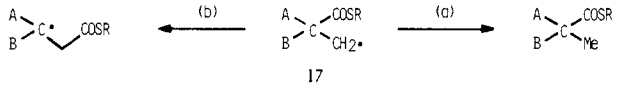
Table II. Photolyses of Organocobaloxime **2**

R	solvent	product composition, % 7	8	9	total yield, %
Et	benzene	11	89	0	80
Et	methanol	10	90	0	79
Et	dichloromethane	16	84	0	91
Et	chloroform	35	65	0	96
t-Bu	benzene	12	73	15	40
t-Bu	methanol	11	80	9	74
t-Bu	dichloromethane	17	68	15	65
t-Bu	chloroform	33	53	14	80

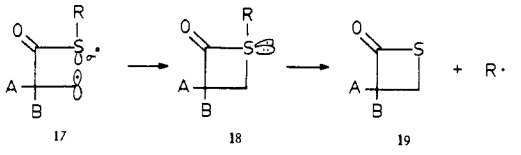
Table III. Photolyses of Organocobaloxime **3**

R	solvent	product composition, % 10	11	12	total yield, %
Et	benzene	31	52	17	45
Et	acetonitrile	29	60	11	
Et	methanol	47	41	12	
Et	chloroform	98	2	0	89
t-Bu	benzene	3	15	82	61
t-Bu	acetonitrile	5	44	51	
t-Bu	methanol	17	9	74	
t-Bu	chloroform	46	4	50	78

Scheme III



Scheme IV



The photolysis of cobaloxime **2** gave a reduction product **7**, a 1,5-hydrogen shift product **8**, and a β-thiolactone derivative **9**. Similarly, the photolysis of cobaloxime **3** gave a reduction product **10**, a thioester elimination product **11**, and a β-thiolactone derivative **12** (Scheme II). Products **7** and **10** were identified with the authentic samples prepared by α-methylation of the corresponding *S*-alkyl *O*-ethyl 2-aralkylmonothiomalonate. Structures **8** and **11** were deduced from spectral data. Product **8** (R = Et) had IR absorptions at 1720 and 1660 cm^{-1} due to the ester and thioester groups and ^{1}H NMR signals at 2.80 (d, J = 7 Hz), 6.06 (double t, J = 16 and 7 Hz), and 6.46 (d, J = 16 Hz) due to $CH{=}CHCH_2$ system. Product **11** had an IR absorption at 1715 cm^{-1} and ^{1}H NMR signals at δ 5.58 and 6.18 due to the 2-substituted α,β-unsaturated ester. The structures **9** and **12** were deduced by analogy to **6**. Product **9** had IR absorptions at 1770 and 1730 cm^{-1} and ^{1}H NMR signals at δ 2.85 and 3.58 (AB q, J = 9 Hz) due to the ring methylene. The lower half of the AB quartet for **6** at δ 3.00 shifted to δ 3.58 in **9** due to the neighboring effect of the ethoxycarbonyl group. An alternative structure, a 3,3-disubstituted β-thiolactone, was eliminated by the same reason discussed for **6**. A mesitylene counterpart **12** had similar spectral characteristics to those of **9**.[16] The formations of β-thiolactones from cobaloximes **1-3** were further supported by the photolyses

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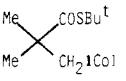
(16) Thermal instability of the β-thiolactones **6**, **9**, and **12** and the practical scale of the photolyses did not allow us to purify those liquid products for combustion analyses. Those products used for spectral measurements, however, were pure from gas chromatographic analyses.

of [2-[(*tert*-butylthio)carbonyl]-2-methylpropyl]cobaloxime (**13**) and [2-[(*tert*-butylthio)carbonyl]-2-(ethoxycarbonyl)propyl]cobaloxime (**14**). These cobaloximes gave 2,2-dimethyl-β-propiothiolactone (**15**) and 2-(ethoxycarbonyl)-2-methyl-β-propiothiolactone (**16**), which were identified with authentic samples synthesized unequivocally[13-15] by the comparison of ^{1}H NMR and MS spectral data. These results of photolyses of the cobaloximes are summarized in Tables I–III.



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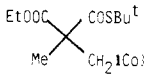

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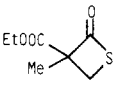


16

The bromides corresponding to the cobaloximes (Br instead of [Co] in structures **1–3**) gave reduction products **4**, **7**, and **10** on the reaction with tributylstannane (10^{-3}–10^{-1}/mol/L). The bromide corresponding to cobaloxime **2**, having the (*tert*-butylthio)carbonyl group (R = *t*-Bu, Br instead of [Co] in structure **2**), however, gave β-thiolactone derivative **9** in low yield beside the reduction product.

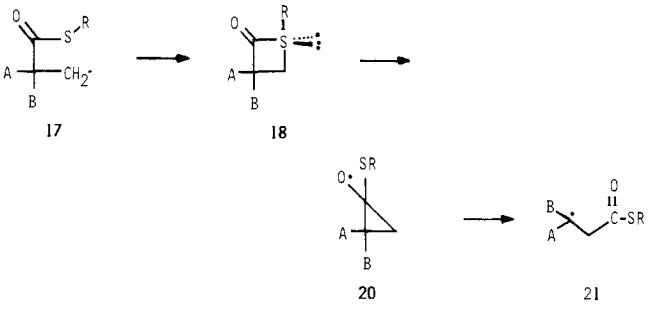
Discussion

From results of earlier studies, we anticipated two decay processes for the radical **17** from the cobaloxime and the corresponding bromide (Scheme III). Process a is the sole or major decay route for the radical **17** in the presence of tributylstannane and the major route for the photolyses of cobaloximes in chloroform, a strongly hydrogen donating solvent. The photolysis of cobaloxime **1** (R = Et) in poor hydrogen donating solvents gave product **5** in a reasonable ratio. The photolysis of cobaloxime **1** (R = *t*-Bu) in most of the solvents, however, gave **6** as a major product. Stability of the *tert*-butyl radical must stimulate the bond cleavage of *tert*-butylthio and an intramolecular radical substitution on sulfur takes place (Scheme IV).

Examples of intramolecular radical substitution on the sulfur atom of sulfide,[17-23] or disulfide[24-26] have been accumulating but substitution on the sulfur atom of thioester and formation of thiolactone by radical mechanism have no precedent. Alkyl radical has been recognized to have nucleophilic character in the reaction with olefins[27,28] and heteroaromatics,[27,29] and we propose a radical substitution mechanism for the formation of β-thiolactone as shown in Scheme IV. A nucleophilic type attack of the radical center to the $^*\sigma$ orbital of R–S bond gives the intermediate **18**, which has an apical CH_2SR bond. Facile rupture of *tert*-butyl radical from **18** furnishes the radical substitution to result in the formation of β-thiolactone **19**.

Cobaloxime **2** was hoped to be a closer model for methylmalonyl-CoA mutation. The photolysis of **2**, however, gave a

Scheme V



styrene derivative **8** as a major product in any solvent, since 1,5-hydrogen shift of the benzylic hydrogen followed by the hydrogen elimination by cobaloxime(II) radical is predominant in this system. Another result worthy of note is that the radical generated from the bromide corresponding to **2** (R = *t*-Bu, Br instead of [Co]) by tributylstannane furnishes a β-thiolactone even without the existence of cobalt species.

The photolysis of cobaloxime **3** is characterized by product **11**, an α,β-unsaturated ester, formed by the elimination of a (alkylthio)carbonyl group. Presently we have no definite explanation for this process. Other features of the photolysis of cobaloxime **3** are similar to those of cobaloxime **2**, and the β-thiolactone is the major product from the *tert*-butyl thioester derivative.

These experimental results and discussion show the existence of two major modes of the intramolecular radical attack on an alkyl thioester group: an attack on carbonyl to give a thioester-rearranged product and an attack on sulfur to give a β-thiolactone. In the present study, we found that those two processes are competitive with other decay processes of the radical intermediate, including inter- and intramolecular hydrogen abstraction. In the enzyme system of methylmalonyl-CoA mutase, the latter processes must be prohibited by the nature of the enzyme system or the structure of the substrate itself. The former two modes of radical attack, however, share rather similar stereochemical requirements, and the allotment of the attacking site, carbonyl or sulfur, must depend on a delicate consequence of stereoelectronic effect.

We would like to reserve the mechanistic possibility that the radical **17** attacks initially sulfur to give the intermediate **18**, which transforms into a three-membered intermediate, **20**, by bond switching. The intermediate **18** has a singly occupied orbital in an equatorial orientation, which can interact with Co(II) species having a singly occupied frontier orbital.[30] The intermediate **18** has also a weakened apical methylene–sulfur bond. This character of **18** may stimulate the bond switching to give **20** (Scheme V). This is a mechanistic possibility of the radical rearrangement of (alkylthio)carbonyl groups in the presence of cobalt(II) species.

As described in the introduction, the radical rearrangement of an alkyl thioester is assisted by cobaloxime. Thus it is highly possible that the radical rearrangement of the thioester in the presence of cobalt complex takes some other mechanism than a direct attack of the radical center on the carbonyl group to give an intermediate **20**.

This hop–skip–jump mechanism (**17** → **18** → **20** → **21**) may require lower activation energy than the direct attack. Of course the mechanism including the cobalt participation can be applied only to the model system of methylmalonyl-CoA → succinyl-CoA. Isomerization of 2-methyleneglutaric acid → 3-methylitaconic acid[9,31] is a similar process to the isomerization of methylmalonyl-CoA, but the rearrangement of an olefinic group to an adjacent radical center is intrinsically fast and is considered not to require a cobalt participation.[6] Radical rearrangement of ester or free acid is a slow process,[1,7] and the rearrangement is realized

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in the form of thioester acyl-CoA. Other coenzyme B_{12} assisted processes involving the migration of hydroxy or amino groups belong to different types of enzymatic processes, and rather elaborate mechanisms have been proposed.[4,5,32,33]

The present proposal, a stepwise mechanism and the participation of cobalt(II) species for the radical rearrangement of a thioester group, must be justified by further evidence from theoretical and experimental studies.

Conclusion

An organocobaloxime having an (alkylthio)carbonyl group at the β-position gave a pair of organo radicals and cobaloxime(II) radicals. The organo radical thus generated collapses in several competitive modes: inter- and intramolecular hydrogen abstraction, attack on sulfur, and attack on carbonyl group. The attack on sulfur and the elimination of alkyl radical gives a β-thiolactone, and this mode of decay is prominent with (*tert*-butylthio)carbonyl derivatives. The radical attack on the carbonyl group causes the 1,2-rearrangement of thioester group, which constitutes a biomimetic process. This rearrangement is assisted by cobaloxime(II) as shown in the present and earlier studies, and a hop–skip–jump mechanism (Scheme V) containing a bond switching of **18** → **20** is proposed. This mechanism accounts for the possible involvement of the cobalt(II) complex in the radical rearrangement of the thioester group, although more experimental evidence is required before any conclusions may be drawn.

Experimental Section

Spectroscopic Data. IR and NMR spectra were made in CCl_4 and $CDCl_3$ solutions, respectively. Chemical shifts and coupling constants are recorded in δ values and hertz. MS spectra were made by electron impact ionization method at 70 eV.

Syntheses of *S*-Alkyl 2-(Bromomethyl)-4-mesityl-2-methylbutanethioate and *S*-*tert*-Butyl 2-(Bromomethyl)-2-methylpropanethioate. The titled thioesters were synthesized from *S*-alkyl 4-mesitylbutanethioate by successive methylation and bromomethylation or by bromomethylation of *S*-*tert*-butyl 2-methylpropanethioate. All the manipulations were carried out in the same manner under nitrogen. The synthesis of the former thioester, therefore, is described in detail.

Lithium diisopropylamide (LDA) (18 mmol) in 20 mL of THF, prepared in situ from diisopropylamine and butyllithium, was added slowly (30 min) with *S*-ethyl 4-mesitylbutanethioate (3.8 g, 15 mmol). During the addition the reaction mixture was stirred and kept at −90 °C in a methanol–dry ice bath. After being stirred for 1 h at the same temperature, the mixture was treated with iodomethane (2.8 mL, 30 mmol) in 10 mL of THF, and the resulting mixture was stirred overnight to allow slow warm up to room temperature. The reaction mixture was extracted with dichloromethane (20 mL × 3) after acidification with 2 N hydrochloric acid. The extract was condensed under reduced pressure after being washed with water and dried over sodium sulfate, and the residue was passed through a column of silica gel (2.4 × 10 cm) with benzene–hexane (1:1) to remove polar materials. The eluate was then distilled to give *S*-ethyl 4-mesityl-2-methylbutanethioate (3.3 g, 75%), bp 121 °C (0.2 mmHg). The *S*-ethyl thioester (2.6 g, 10 mmol) thus obtained was slowly added (25 min) to LDA (12 mmol) in 15 mL of THF as in the case of methylation described above. After being stirred for 50 min at −90 °C, the mixture was treated with dibromomethane (2.1 mL, 30 mmo) during 20 min and allowed to warm up by standing overnight. The product was extracted with dichloromethane after acidification with 2 N hydrochloric acid. The extract was condensed after being washed with water and dried over sodium sulfate, and the residue was passed through a column of silica gel (2.4 × 8 cm) with benzene–hexane (1:1) to remove polar materials. Kugelrohr distillation of the eluate gave *S*-ethyl 2-(bromomethyl)-4-mesityl-2-methylbutanethioate (1.8 g, 50%): bp 126 °C (0.02 mmHg); IR 1670 cm^{-1}; ^1H NMR δ 1.30 (t, J = 7, 3 H), 1.41 (s, 3 H), 1.50–1.90 (m, 2 H), 2.20 (s, 3 H), 2.21 (s, 6 H), 2.30–2.70 (m, 2 H), 2.93 (q, J = 7, 2 H), 3.55 (s, 2 H), 6.62 (s, 2 H).

The same experimental procedure with *S*-*tert*-butyl-4-mesitylbutanethioate as the starting material gave *S*-*tert*-butyl 2-(bromomethyl)-4-mesityl-2-methylbutanethioate: bp 135 °C (0.02 mmHg); IR 1680 cm^{-1}; ^1H NMR δ 1.30 (s, 3 H), 1.45 (s, 9 H), 1.60–1.73 (m, 2 H), 2.17 (s, 3 H), 2.19 (s, 6 H), 2.30–2.75 (m, 2 H), 3.50 (s, 2 H), 6.62 (s, 2 H).

S-*tert*-butyl 2-(bromomethyl)-2-methylpropanethioate was synthesized by bromomethylation of *S*-*tert*-butyl 2-methylpropanethioate in the same procedure and shows the following properties: bp 95 °C (5 mmHg); IR 1670 cm^{-1}; ^1H NMR δ 1.21 (s, 6 H), 1.45 (s, 9 H), 3.43 (s, 2 H).

These bromomethyl derivatives were difficult to purify for satisfactory elemental analyses and were transformed into organocobaloximes without further purification.

Syntheses of *S*-Alkyl 2-(Bromomethyl)-2-(ethoxycarbonyl)-5-phenylpentanethioate, *S*-Alkyl 2-(Bromomethyl)-2-(ethoxycarbonyl)-4-mesitylbutanethioate, and *S*-*tert*-Butyl 2-(Bromomethyl)-2-(ethoxycarbonyl)propanethioate. All the titled monothiomalonates were synthesized essentially in the same method as described in the previous experimental section. The synthesis of *S*-ethyl 2-(bromomethyl)-2-(ethoxycarbonyl)-4-mesitylbutanethioate is described as a representative.

LDA (18 mmol) in 20 mL of THF was added with *S*-ethyl 4-mesitylbutanethioate (3.8 g, 15 mmol), and the mixture was stirred for 1 h at −90 °C in a dry ice–methanol bath under nitrogen atmosphere. The mixture was then treated with ethyl chloroformate (2.4 g, 22.5 mmol) by a syringe needle and was left in the bath overnight to allow warm up. The product was extracted with dichloromethane (20 mL × 3) after acidification with 2 N hydrochloric acid, and the extract was condensed under reduced pressure after being washed with water and dried over sodium sulfate. The residue was purified by fast passing through a silica gel column (2 × 15 cm) eluted with benzene–hexane (1:1) and Kugelrohr distillation to give *O*,*S*-diethyl 4-mesitylethylmonothiomalonate (1.6 g, 33%), bp 140 °C (0.02 mmHg).

The monothiomalonate derivative (3.2 g, 10 mmol) in 2 mL of THF was added to sodium hydride (60% oil dispersion) (0.24 g, 10 mmol) in 12 mL of THF, and the mixture was heated to gentle reflux for 30 min under nitrogen atmosphere. The mixture was then added to dibromomethane (2.6 g, 15 mmol) and refluxed for 4 h. The mixture was condensed after filtration to remove solid materials and extracted with ether after addition of water. The ether extract was condensed after being washed with water and dried over sodium sulfate, and the residue was purified by passing through a silica gel column (2.4 × 10 cm) with benzene. Kugelrohr distillation of the eluate gave *S*-ethyl 2-(bromomethyl)-2-(ethoxycarbonyl)-4-mesitylbutanethioate (2.3 g, 56%): bp 154 °C (0.05 mmHg); IR 1735 cm^{-1}; ^1H NMR δ 1.27 (t, J = 7.5), 1.29 (t, J = 7), 1.80–2.10 (m, 2 H), 2.19 (s, 3 H), 2.22 (s, 6 H), 2.40–2.75 (m, 2 H), 2.92 (q, J = 7.5), 3.91 (s, 2 H), 4.20 (q, J = 7, 2 H), 6.68 (s, 2 H).

S-Ethyl 2-(bromomethyl)-2-(ethoxycarbonyl)-5-phenylpentanethioate: bp 136–138 °C (0.07 mmHg); IR 1710, 1650 cm^{-1}; ^1H NMR δ 1.13 (t, J = 7, 6 H), 1.30–1.90 (m, 2 H), 2.09–2.31 (m, 2 H), 2.61 (t, J = 7, 2 H), 2.82 (q, J = 7, 2 H), 3.75 (s, 2 H), 4.11 q, J = 7, 2 H), 7.04 (diffuse s, 5 H).

S-*tert*-Butyl 2-(bromomethyl)-2-(ethoxycarbonyl)-5-phenylpentanethioate: bp 134–136 °C (0.05 mmHg); IR 1715, 1655 cm^{-1}; ^1H NMR δ 1.25 (t, J = 7, 3 H), 1.20–1.75 (m, 2 H), 1.46 (s, 9 H), 1.95–2.35 (m, 2 H), 2.65 (t, J = 7 2 H), 3.77 (s, 2 H), 4.16 (q, J = 7, 2 H), 7.16 (diffuse s, 5 H).

S-*tert*-Butyl 2-(bromomethyl)-2-(ethoxycarbonyl)-4-mesitylbutanethioate: bp 160 °C (0.04 mmHg); mp 42 °C; IR 1735, 1675 cm^{-1}; ^1H NMR δ 1.28 (t, J = 7, 3 H), 1.47 (s, 9 H), 1.80–2.00 (m, 2 H), 2.15 (s, 3 H), 2.22 (s, 6 H), 2.44–2.60 (m, 2 H), 3.85 (s, 2 H), 4.18 (q, J = 7, 2 H), 6.62 (s, 2 H).

S-*tert*-Butyl 2-(bromomethyl)-2-(ethoxycarbonyl)propanethioate was synthesized by bromomethylation of *S*-*tert*-butyl 2-(ethoxycarbonyl)-propanethioate, which was prepared by the partial hydrolysis of diethyl methylmalonate followed by thioesterification via acid chloride, and shows the following properties: bp 100 °C (0.05 mmHg); IR 1735, 1685 cm^{-1}; ^1H NMR δ 1.29 (t, J = 7, 3 H), 1.47 (s, 9 H), 1.51 (s, 3 H), 3.75 (s, 2 H), 4.20 (q, J = 7, 2 H).

These bromomethyl derivatives were difficult to purify for satisfactory combustion analyses, but all have reasonable spectral data and were used for the syntheses of cobaloximes without further purification.

Syntheses of Organocobaloximes. All the organocobaloximes were synthetized in a same method, and a general procedure is described. A mixture of cobalt(II) chloride (0.48 g, 2 mmol), dimethylglyoxime (0.46 g, 4 mmol), and sodium methoxide (4 mmol) in 5 mL of methanol was cooled in an ice bath under nitrogen atmosphere and treated with pyridine (0.16 mL, 2 mmol) and powdered zinc (1.3 g). The mixture was stirred for 30 min under cooling and treated with one of the bromides (2 mmol). Stirring was continued for 5 h with gradual warm up of the mixture to room temperature. The mixture was then added with 5 mL of chloroform, and solid materials were filtered off. The filtrate was condensed and eluted through a Florisil column (1.4 × 5 cm) with

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chloroform. The orange fraction of the eluate was condensed to give a crystalline product. Recrystallization from benzene containing small amount of pyridine gave pure organocobaloxime **1** (R = Et) in 45%, **1** (R = *t*-Bu) in 40%, **2** (R = Et) in 58%, **2** (R = *t*-Bu) in 48%, **3** (R = Et) in 40%, and **3** (R = *t*-Bu) in 35% yields.

Cobaloxime **1** (R = Et): mp 101–102 °C dec; IR 1665 cm^{-1}; ^1H NMR δ 1.00–1.80 (m, 4 H), 1.24 (t, J = 7, 3 H), 1.32 (s, 3 H). 2.05 (s, 6 H), 2.08 (s, 6 H), 2.11 (s, 9 H), 2.50 (t, J = 7, 2 H), 2.82 (q, J = 7, 2 H), 6.74 (s, 2 H), 7.10–7.35 (m, 2 H), 7.64 (t, J = 6, 1 H), 8.50 (d, J = 6, 2 H), 18.22 (br s, 2 H). Anal. Calcd for $C_{30}H_{44}N_5O_5SCo$: C, 55.80; H, 6.87; N, 10.85. Found: C, 55.99; H, 6.94; N, 10.99.

Cobaloxime **1** (R = *t*-Bu): mp 110–112 °C dec; IR 1660 cm^{-1}; ^1H NMR δ 1.01–1.67 (m, 4 H), 1.23 (s, 3 H), 1.45 (s, 9 H), 2.06 (s, 12 H), 2.20 (s, 9 H), 2.36 (t, J = 7, 2 H), 6.75 (s, 2 H), 7.18–7.35 (m, 2 H), 7.67 (t, J = 6, 1 H), 8.52 (d, J = 6, 2 H), 18.21 (br s, 2 H). Anal. Calcd for $C_{32}H_{48}N_5O_5SCo$: C, 57.05; H, 7.18; N, 10.39. Found: C, 57.10; H, 7.12; N, 10.20.

Cobaloxime **2** (R = Et): mp 134–135 °C dec; IR 1715, 1650 cm^{-1}; ^1H NMR δ 1.10–1.40 (m, 2 H), 1.16 (t, J = 7, 3 H), 1.19 (t, J = 7, 3 H), 1.69–2.90 (m, 6 H), 2.08 (s, 12 H), 2.77 (q, J = 7, 2 H), 4.06 (qq, J = 9 and 6.5, 2 H), 7.10–7.37 (m, 7 H), 7.68 (t, J = 6, 1 H), 8.49 (d, J = 6, 2 H), 18.17 (br s, 2 H). Anal. Calcd for $C_{30}H_{42}N_5O_7SCo$: C, 53.33; H, 6.27; N, 10.36. Found: C, 53.26; H, 6.18; N, 10.73.

Cobaloxime **2** (R = *t*-Bu): mp 160–161 °C dec; IR 1720, 1655 cm^{-1}; ^1H NMR δ 1.10–1.60 (m, 2 H), 1.19 (t, J = 7, 3 H), 1.37 (s, 9 H), 1.70–2.90 (m, 6 H), 2.08 (s, 12 H), 4.05 (qq, J = 9 and 6.5, 2 H), 7.21–7.40 (m, 7 H), 7.77 (t, J = 6, 1 H), 8.53 (d, J = 6, 2 H), 18.29 (br s, 2 H). Anal. Calcd for $C_{32}H_{46}N_5O_7SCo$: C, 54.60; H, 6.60; N, 9.95. Found: C, 54.84; H, 6.76; N, 9.85.

Cobaloxime **3** (R = Et): mp 130–132 °C dec; IR 1720, 1660 cm^{-1}; ^1H NMR δ 1.00–1.90 (m, 4 H), 1.22 (t, J = 7, 3 H), 1.30 (t, J = 7, 3 H), 1.95 (s, 6 H), 2.00 (s, 6 H), 2.17 (s, 3 H), 2.22 (s, 6 H), 2.46 (t, J = 7, 2 H), 2.83 (q, J = 7, 2 H), 4.22 (q, J = 7, 2 H), 6.68 (s, 2 H), 7.20 (m, 2 H), 7.60 (t, J = 6. 1 H), 8.36 (d, J = 6, 2 H), 18.15 (br s, 2 H). Anal. Calcd for $C_{32}H_{46}N_5O_7SCo$: C, 54.60; H, 6.60; N, 9.95. Found: C, 54.86; H, 6.76; N, 9.85.

Cobaloxime **3** (R = *t*-Bu): mp 135–136 °C dec; IR 1722, 1660 cm^{-1}; ^1H NMR δ 1.05–1.85 (m, 4 H), 1.32 (t, J = 7, 3 H), 1.46 (s, 9 H), 1.93 (s, 6 H), 1.98 (s, 6 H), 2.00–2.50 (m, 2 H), 2.20 (s, 3 H), 2.31 (s, 6 H), 4.07–4.33 (m, 2 H), 6.75 (s, 2 H), 7.12–7.45 (m, 2 H), 7.63 (t, J = 6, 1 H), 8.44 (d, J = 6, 2 H), 18.15 (br s, 2 H). Anal. Calcd for $C_{34}H_{50}N_5O_7SCo$: C, 55.80; H, 6.89; N, 9.85. Found: C, 55.68; H. 6.76; N, 9.42.

Cobaloxime **13**: mp 196–197 °C dec; IR 1665 cm^{-1}; ^1H NMR δ 1.12 (s, 6 H), 1.42 (s, 9 H), 1.87 (s, 2 H), 2.15 (s, 12 H), 7.38 (m, 2 H), 7.80 (t, J = 6, 1 H), 8.68 (d, J = 6, 2 H), 18.20 (br s, 2 H). Anal. Calcd for $C_{22}H_{36}N_5O_5SCo$: C, 48.78; H, 6.71; N, 12.93. Found: C, 48.95; H, 6.97; N, 12.59.

Cobaloxime **14**: mp 142–143 °C dec; IR 1723, 1658 cm^{-1}; ^1H NMR δ 1.20 (t, J = 7, 3 H), 1.33 (s, 3 H), 1.38 (s, 9 H), 1.50–2.00 (m, 2 H), 2.09 (s, 12 H), 4.03 (m, 2 H), 7.25 (m, 2 H), 7.73 (t, J = 6, 1 H), 8.42 (d, J = 6, 2 H), 18.10 (br s, 2 H). Anal. Calcd for $C_{24}H_{38}N_5O_7SCo$: C, 48.08; H, 6.39; N, 11.68. Found: C, 47.71; H, 6.27; N, 11.96.

Photolyses of Organocobaloximes. All the photolyses of organocobaloximes **1–3** were carried out essentially in the same manner, and the photolysis of **1** (R = Et) in benzene is described as a representative. Photolyses in other solvents were done in less amount of the solvent due to the better solubility of cobaloximes and degradation products.

Organocobaloxime **1** (R = Et) (0.32 g, 0.5 mmol) in 150 mL of benzene was placed in a reaction vessel, and the solution was deaerated by bubbling argon under the irradiation of ultrasonic wave. The solution was then irradiated internally with a 450-W high-pressure mercury lamp through a Pyrex cooling jacket. After 4 h of irradiation the solution was condensed, and the residue was subjected to a preparative TLC (20 g of silica gel on a 20 × 20 cm glass plate) developed by benzene–hexane (1:1). The top, middle, and bottom bands gave products **4**, **5**, and **6** in 27%, 28%, and 1% yield, respectively.

Product **4** (R = Et): bp 120–121 °C (0.1 mmHg); IR 1675 cm^{-1}; ^1H NMR δ 1.27 (t, J = 7, 3 H), 1.28 (s, 6 H), 1.56–1.77 (m, 2 H), 2.17 (s, 3 H), 2.18 (s, 6 H), 2.30–2.65 (m, 2 H), 2.87 (q, J = 7, 2 H), 6.60 (s, 2 H); MS 278 (2.0%, M^+), 133 (100%, $MesCH_2^+$).

Product **4** (R = *t*-Bu): bp 115 °C (0.2 mmHg); IR 1670 cm^{-1}; ^1H NMR δ 1.24 (s, 6 H), 1.48 (s, 9 H), 1.50–1.80 (m, 2 H), 2.15 (s, 3 H), 2.20 (s, 6 H), 2.30–2.70 (m, 2 H), 6.62 (s, 2 H); MS 306 (1.5%, M^+), 133 (100%, $MesCH_2^+$).

The products **4** were identified with the authentic samples prepared by the double methylation of *S*-alkyl 4-mesitylbutanethioate in the similar procedure described in the previous Experimental Section.

Product **5** (R = Et): IR 1685 cm^{-1}; ^1H NMR δ 1.24 (t, J = 7, 3 H), 2.23 (s, 3 H), 2.28 (s, 6 H), 2.70–3.20 (m, 4 H), 2.85 (q, J = 7, 2 H), 3.31 (d, J = 0.7, 2 H), 5.02 (diffuse s, 1 H), 5.07 (diffuse s, 1 H), 6.82 (s, 2 H); MS 276 (3.5%, M^+), 215 (1.2%, $M^+ - C_2H_5S$), 187 (2.4%, $M^+ - COSC_2H_5$), 186 (6.9%, $M^+ - HCOSC_2H_5$), 133 (100%, $MesCH_2^+$).

Product **5** (R = *t*-Bu) was obtained only in small amount but shows a similar mass spectrum to that of **5** (R = Et): MS 304 (0.8%, M^+), 248 (6.0%, $M^+ - CH_2CMe_2$), 215 (1.0%, $M^+ - C_4H_9S$), 187 (1.5%, $M^+ - COSC_4H_9$), 186 (2.0%, $M^+ - HCOSC_4H_9$), 133 (100%, $MesCH_2^+$).

Product **6**: IR 1755 cm^{-1}; ^1H NMR δ 1.47 (s, 3 H), 1.73 (t, J = 8, 2 H), 2.24 (s, 3 H), 2.27 (s, 6 H), 2.45–2.80 (m, 2 H), 2.78 and 3.00 (AB q, J = 8.5, 2 H), 6.82 (s, 2 H); MS 248 (16%, M^+), 187 (6.2%, $M^+ - HCOS$), 173 (8.4%, $M^+ - CH_2COS - H$), 147 (11.6%, $MesCH_2CH_2^+$), 133 (100%, $MesCH_2^+$).

Product **7** (R = Et): bp 130 °C (0.2 mmHg); IR 1725, 1670 cm^{-1}; ^1H NMR δ 1.10 (t, J = 7, 6 H), 1.20–2.00 (m, 4 H), 1.28 (s, 3 H), 2.50 (t, J = 7. 2 H), 2.73 (q, J = 7, 2 H), 3.99 (q, J = 7, 2 H), 6.93 (diffuse s, 5 H); MS 308 (0.5%, M^+), 247 (35%, $M^+ - C_2H_5S$), 91 (100%, $PhCH_2^+$).

Product **7** (R = *t*-Bu): bp 122 °C (0.05 mmHg); IR 1730, 1670 cm^{-1}; ^1H NMR δ 1.20 (t, J = 7, 3 H), 1.30–2.10 (m, 4 H), 1.31 (s, 3 H), 1.40 (s, 9 H), 2.57 (t, J = 6.5, 2 H), 4.08 (q, J = 7, 2 H), 7.09 (diffuse s, 5 H); MS 336 (1%, M^+), 279 (1.6%, $M^+ - C_4H_9$), 247 (16%, $M^+ - C_4H_9S$), 91 (45%, $PhCH_2^+$), 57 (100%, $C_4H_9^+$).

Products **7** were identified with the authentic samples prepared by the methylation of *S*-alkyl 2-(ethoxycarbonyl)-5-phenylpentanethioate in the method described earlier in the Experimental Section.

Product **8** (R = Et): IR 1720, 1660 cm^{-1}; ^1H NMR δ 1.25 (t, J = 7, 6 H), 1.49 (s, 3 H), 2.80 (d, J = 7, 2 H), 2.82 (q, J = 7, 2 H), 4.20 (q, J = 7, 2 H), 6.06 (double t, J = 16 and 7, 1 H), 6.46 (d, J = 16, 1 H), 7.10–7.88 (m, 5 H); MS 306 (9.6%, M^+), 245 (8.6%, $M^+ - C_2H_5S$), 216 (54%, $M^+ - HCOSC_2H_5$), 171 (38%, $M^+ - HCOSC_2H_5 - C_2H_5O$), 170 (9.1%, $M^+ - HCOSC_2H_5 - C_2H_5OH$), 117 (100%, $PhCH{=}CHCH_2^+$).

Product **8** (R = *t*-Bu): IR 1725, 1670 cm^{-1}; ^1H NMR δ 1.26 (t, J = 7, 3 H), 1.45 (s, 3 H), 1.47 (s, 9 H), 2.78 (d, J = 7, 2 H), 4.20 (q, J = 7, 2 H), 6.05 (double t, J = 16 and 7, 1 H), 6.46 (d, J = 16, 1 H), 7.15–7.40 (m, 5 H); MS 334 (0.2%, M^+), 278 (25%, $M^+ - CH_2{=}CMe_2$), 245 (2.0%, $M^+ - C_4H_9S$), 216 (9.3%, $M^+ - HCOSC_4H_9$), 57 (100%, $C_4H_9^+$).

Product **9**: IR 1770, 1730 cm^{-1}; ^1H NMR δ 1.28 (t, J = 7, 3 H), 1.46–2.20 (m, 4 H), 2.65 (t, J = 7, 2 H), 2.85 and 3.58 (AB q, J = 9, 2 H), 4.24 (q, J = 7, 2 H), 7.25 (m, 5 H); MS 278 (0.5%, M^+), 232 (46%, $M^+ - CH_2S$), 204 (7.8%, $M^+ - HCOOC_2H_5$), 91 (100%, $PhCH_2^+$).

Product **10** (R = Et): bp 130 °C (0.05 mmHg); IR 1730. 1675 cm^{-1}; ^1H NMR δ 1.24 (t, J = 7, 3 H), 1.28 (t. J = 7, 3 H), 1.53 (s, 3 H), 1.60–2.10 (m, 2 H), 2.18 (s, 3 H), 2.22 (s, 6 H), 2.30–2.65 (m, 2 H), 2.85 (q, J = 7, 2 H), 4.15 (q, J = 7. 2 H), 6.65 (s, 2 H); MS 336 (1.0%, M^+), 133 (100%, $MesCH_2^+$).

Product **10** (R = *t*-Bu): bp 135 °C (0.03 mmHg); IR 1725, 1670 cm^{-1}; ^1H NMR δ 1.27 (t, J = 7, 3 H). 1.46 (s. 9 H), 1.50 (s, 3 H), 1.60–2.05 (m, 2 H), 2.16 (s, 3 H), 2.21 (s, 6 H), 2.30–2.70 (m, 2 H), 4.15 (q, J = 7, 2 H), 6.67 (s, 2 H); MS 364 (0.5%, M^+), 133 (100%, $MesCH_2^+$).

Products **10** were identified with the authentic samples prepared by methylation of *S*-alkyl 2-(etoxycarbonyl)-4-mesitylbutanethioate in the method described earlier.

Product **11**: IR 1715 cm^{-1}; ^1H NMR δ 1.32 (t, J = 7, 3 H), 2.24 (s, 3 H), 2.30–2.60 (m, 2 H), 2.31 (s, 6 H), 2.65–2.95 (m, 2 H), 4.24 (q, J = 7, 2 H), 5.58 (diffuse s, 1 H), 6.18 (diffuse s, 1 H), 6.83 (s, 2 H); MS 246 (0.2%, M^+), 201 (1.5%, $M^+ - C_2H_5O$), 133 (100%, $MesCH_2^+$).

Product **12**: IR 1770, 1730 cm^{-1}; ^1H NMR δ 1.34 (t, J = 7, 3 H), 3.12 (t, J = 6.5, 2 H), 2.24 (s, 3 H), 2.27 (s, 6 H), 2.69 (t, J = 6.5, 2 H), 2.99 and 3.68 (AB q, J = 9, 2 H), 4.30 (q, J = 7, 2 H), 6.83 (s, 2 H); MS 306 (9.3%, M^+), 246 (0.2%, $M^+ - COS$), 133 (100%, $MesCH_2^+$).

Photolysis of cobaloxime **13** gave 2,2-dimethyl-β-propiothiolactone (**15**) as a major product. The product **15** was collected by a bulb-to-bulb transfer under reduced pressure and dry ice cooling, and the yield varied within 20–40% due to high volatility. Structure **15** was determined by the comparison of the spectral data with those of the authentic sample.[13-15]

Product **15**: IR 1769 cm^{-1}; ^1H NMR δ 1.34 (s, 6 H). 2.73 (s, 2 H); MS 116 (5.0%, M^+), 73 (9.0%, $M^+ - CHMe_2$), 70 (13%, $M^+ - CH_2S$), 56 (100%, $M^+ - COS$).

Photolysis and similar workup of cobaloxime **14** to the case of cobaloxime **1** gave 2-(ethoxycarbonyl)-2-methyl-β-propiothiolactone (**16**) in low yield (ca. 15%) but as a major product. Structure **16** was determined by the comparison of the spectral data with those of the authentic sample prepared unequivocally from 2-(bromomethyl)-2-(ethoxycarbonyl)-propionyl chloride and sodium sulfide.[13-15]

Product **16**: IR 1770, 1731 cm^{-1}; ^1H NMR δ 1.31 (t, J = 7, 3 H), 1.63 (s, 3 H), 2.72 (d, J = 9, 1 H), 3.56 (d, J = 9, 1 H), 4.21 (q, J = 7, 2 H); MS 114 (65%, M^+ - COS), 99 (47%, M^+ - COS - CH_3), 86 (70%, M^+ - $COOC_2H_5$ - CH_3), 69 (100%, M^+ - COS - OC_2H_5), 45 (100%, $C_2H_5O^+$).

Reaction of *S*-Alkyl 2-(Bromomethyl)-4-mesityl-2-methylbutanethioate and *S*-Alkyl ω-Aryl-2-(bromomethyl)-2-(ethoxycarbonyl)alkanethioate with Tributylstannane. All the experiments were carried out in a same way, and the reaction of *S*-ethyl 2-(bromomethyl)-4-mesityl-2-methylbutanethioate is described as a representative. For the bromide corresponding to cobaloxime **1** (Br instead of [Co] in structure **1**) (0.21 g, 0.5 mmol), tributylstannane (0.17 g, 0.6 mmol) and AIBN (1 mg) were dissolved in 10 mL of benzene to make the concentration of 50 mmol/L for the bromide and 60 mmol/L for tributylstannane. The mixture was refluxed for 4 h under nitrogen, and the condensate of the reaction solution was separated by silica gel chromatography (5 × 10 cm) into hexane eluate (tributylstannyl bromide) and benzene eluate. Kugelrohr distillation of the benzene eluate gave 0.15 g (89%) of product **4** (R = Et), which was identified with the product from cobaloxime **1**.

The reactions were also carried out in different concentration (0.1 mol/L and 1.0 mmol/L) by changing the volume of the solvent, but the results were essentially same except the yields of the products. The reaction of *S*-*tert*-butyl 2-(bromomethyl)-2-(ethoxycarbonyl)-5-phenylpentanethioate (Br instead of [Co] in structure **2**), however, gave a β-thiolactone derivative **9** as a minor product.

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Registry No. 1 (R = Et), 112312-33-1; **1** (R = *t*-Bu), 112312-34-2; **2** (R = Et), 114762-71-9; **2** (R = *t*-Bu), 114762-72-0; **3** (R = Et), 114762-73-1; **3** (R = *t*-Bu), 114762-74-2; **4** (R = Et), 112303-78-3; **4** (R = *t*-Bu), 112303-79-4; **5** (R = Et), 112303-81-8; **5** (R = *t*-Bu), 112303-82-9; **6**, 112303-85-2; **7** (R = Et), 114739-20-7; **7** (R = *t*-Bu), 114739-21-8; **8** (R = Et), 114739-22-9; **8** (R = *t*-Bu), 114739-23-0; **9**, 114739-24-1; **10** (R = Et), 114762-70-8; **10** (R = *t*-Bu), 114739-25-2; **11**, 114739-26-3; **12**, 114739-27-4; **13**, 114762-75-3; **14**, 114762-76-4; **15**, 16432-61-4; **16**, 114739-28-5; [Co(I)], 75699-52-4; $MeS(CH_2)_3COSEt$, 114739-05-8; CH_3-I, 74-88-4; $Mes(CH_2)_2CH(Me)COSEt$, 112303-88-5; $Mes(CH_2)_2C(Me)(CH_2Br)COSEt$, 112303-74-9; CH_2Br_2, 74-95-3; $Mes(CH_2)_3COS$-*t*-Bu, 114739-06-9; $Mes(CH_2)_2CH(Me)COS$-*t*-Bu, 112303-89-6; $Mes(CH_2)_2C(Me)(CH_2Br)COS$-*t*-Bu, 112303-75-0; $Mes(CH_2)_2CH(CO_2Et)COSEt$, 114739-08-1; EtOOC-Cl, 541-41-3; $Mes(CH_2)_2C(CO_2Et)(CH_2Br)COSEt$, 114739-09-2; $Ph(CH_2)_3C(CO_2Et)(CH_2Br)COSEt$, 114739-10-5; $Ph(CH_2)_3CH(CO_2Et)COSEt$, 114739-11-6; $Ph(CH_2)_4COSEt$, 114739-12-7; $Ph(CH_2)_3C(CO_2Et)(CH_2Br)COS$-*t*-Bu, 114739-13-8; $Ph(CH_2)_3CH(CO_2Et)COS$-*t*-Bu, 114739-14-9; $Ph(CH_2)_4COS$-*t*-Bu, 114739-15-0; $Mes(CH_2)_2C(CO_2Et)(CH_2Br)COS$-*t*-Bu, 114739-16-1; $Mes(CH_2)_2CH(CO_2Et)COS$-*t*-Bu, 114739-17-2; *S*-*tert*-butyl 2-(bromomethyl)-2-methylpropanethioate, 114739-07-0; *S*-*tert*-butyl 2-methylpropanethioate, 29786-94-5; *S*-*tert*-butyl 2-(bromomethyl)-2-(ethoxycarbonyl)propanethioate, 114739-18-3; *S*-*tert*-butyl 2-(ethoxycarbonyl)propanethioate, 114739-19-4; cobalt(II) chloride, 7646-79-9; dimethylglyoxime, 95-45-4; benzene, 71-43-2; acetonitrile, 75-05-8; methanol, 67-56-1; chloroform, 67-66-3; tributylstannane, 688-73-3.

Highly Diastereofacial Selective Chelation of a Phosphite-Containing α,β-Unsaturated Ketone System to the $Fe(CO)_2$ Group†,1

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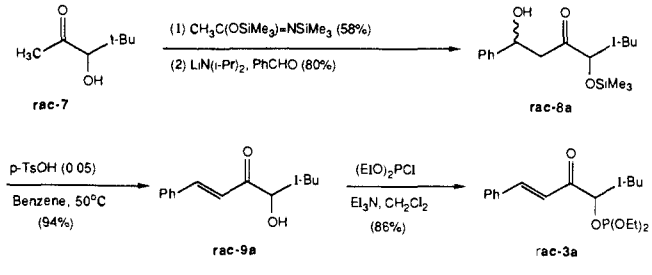
Abstract: Chiral, phosphite-containing α,β-unsaturated ketones of the general structure $RCH{=}CHC(=O)CH(t\text{-}Bu)OP(OEt)_2$ (**3**) have been synthesized as specially designed chelating ligands that permit the highly diastereofacial selective coordination of the conjugated enone moiety to transition metals. The coordination of these ligands with iron carbonyl units has been studied in detail, and the structures of three of the resulting complexes *rac*-**5a**, *rac*-**6a**, and (*S*)-**5b** have been determined by single-crystal X-ray diffraction. Conjugate addition to one of these complexes has demonstrated the potential utility of these systems in asymmetric synthesis.

Asymmetric synthesis is an intensively studied area of chemistry.[3,4] Of special interest to us are methods that permit the diastereofacial selective coordination of a prochiral face of an alkene or other π-systems to a transition metal.[5] Subsequent addition reactions of the coordinated double bond are then expected to proceed with control of the configurations of the resulting adducts. Our goal is to design systems that employ chelation effects[6] to induce diastereofacial selective coordination in a completely predictable fashion so that the overall products of coordination and then addition will possess predictable configurations. Various aspects of chelation and functional group directing effects have been studied by others,[7,8] but especially related to our studies is recent work of Collum.[6c,f]

Scheme I



† This paper is dedicated to Professor E. J. Corey on the occasion of his 60th birthday.

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