Thermal and Photochemical Reactions of Organocobaloximes with Diphenyl Disulphide and Diphenyl Diselenide

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Alkyl- and benzyl-bis(dimethylglyoximato)pyridinecobalt(III) complexes react with diphenyl disulphide or diphenyl diselenide, thermally and photochemically, to give good yields of alkyl or benzyl phenyl sulphides or selenides. Chiral alkylcobalt(III) complexes react to give racemic alkyl phenyl sulphides or selenides. Allyl- and propadienyl-bis(dimethylglyoximato)pyridinecobalt(III) complexes react similarly to give the thermodynamically more stable allyl, propadienyl, or propynyl phenyl sulphides or selenides. These reactions are interpreted in terms of free radical processes in which organic radicals formed as a result of thermal, photochemical, or chemically induced homolysis of the organocobalt complex, attack the diphenyl dichalcogenide to give the product organo phenyl chalcogenide. No evidence could be obtained for the direct attack of phenylthiyl or phenylselenyl radicals on the organic ligand of the organocobalt complexes, though this process cannot be exluded in the case of allylcobalt complexes.

In recent papers we described a novel series of reactions between organometallic complexes of cobalt,[1,2] rhodium,[3] and iridium[3] with polyhalogenomethanes that apparently involve, as a key step, the homolytic displacement of a low-valent metal complex by attack of a polyhalogenomethyl radical at unsaturated[2,3] or saturated[1] carbon of an organic ligand. The overall reaction sequence is (1)—(4).

Initiation $$\mathrm{RML}_n \rightleftharpoons \dot{\mathrm{R}} + \dot{\mathrm{M}}\mathrm{L}_n \qquad (1)$$

Propagation $$\dot{\mathrm{M}}\mathrm{L}_n + \mathrm{XCY}_3 \longrightarrow \mathrm{XML}_n + \dot{\mathrm{C}}\mathrm{Y}_3 \qquad (2)$$

$$\dot{\mathrm{C}}\mathrm{Y}_3 + \mathrm{RML}_n \longrightarrow \mathrm{RCY}_3 + \dot{\mathrm{M}}\mathrm{L}_n \qquad (3)$$

Termination $$\dot{\mathrm{C}}\mathrm{Y}_3 + \dot{\mathrm{M}}\mathrm{L}_n \rightleftharpoons \mathrm{Y_3CML}_n \qquad (4)$$

ML_n = $\mathrm{Ir(CO)P_2X_2}$, $\mathrm{Rh(CO)P_2X_2}$, $\mathrm{Co(dmgH)_2L'}$
X = Br, Cl
P = $\mathrm{PPh_3}$, $\mathrm{PMe_2Ph}$
L′ = pyridine, imidazole
R = allyl, 2- or 3-methylallyl, 3,3-dimethylallyl, benzyl
$\mathrm{CY_3}$ = $\mathrm{CCl_3}$, CHBrCN, $\mathrm{CCl_2CN}$, $\mathrm{CCl_2CHO}$, $\mathrm{CCl_2CO_2R}$. *etc.*

In principle, such chain reactions should also occur with a variety of other free radical precursors in place of $\mathrm{XCY_3}$, provided that the radical which is formed by attack of the metal complex on the precursor is sufficiently selective to attack the organic ligand of the substrate as in equation (3).

In the first of our studies of potential sulphur-centred radicals we demonstrated that arylsulphonyl and related organosulphonyl radicals are also able to displace cobaloxime(II) from allylcobaloxime(III)[4] and from but-3-enylcobaloxime(III)[5] complexes with regiospecific rearrangement of the allyl and but-3-enyl groups [equations (5) and (6)]. On the other hand, radical processes were not detected in the reaction between arenesulphenyl halides and allylcobaloximes because of the dominance of heterolytic electrophilic displacement processes [equation (7)].[6]

An alternative source of sulphur radicals is diphenyl disulphide and Gianotti and Merle[7] have shown that diphenyl disulphide does react with some simple alkylcobaloximes to give alkyl phenyl sulphides. It was proposed that the latter product was formed by combination of alkyl radicals and cobaloxime(II) species [equation (8)], though at the suggestion of a referee, a displacement reaction [equation (9)] similar to that shown in equation (3), was also considered briefly.[8]

This paper describes more detailed studies on the

$$\mathrm{Ar\dot{S}O_2} + \mathrm{RCH{:}CH{\cdot}CH_2Co(dmgH)_2py} \longrightarrow \mathrm{ArSO_2CHR{\cdot}CH{:}CH_2} + \mathrm{\dot{C}o^{II}(dmgH)_2py} \qquad (5)$$


(6)

$$\mathrm{ArSCl} + \mathrm{RCH{:}CH{\cdot}CH_2Co(dmgH)py} \longrightarrow \mathrm{ArSCHR{\cdot}CH{:}CH_2} + \mathrm{ClCo^{III}(dmgH)_2py} \qquad (7)$$

$$\mathrm{Ar\dot{S}} + \dot{\mathrm{R}} \longrightarrow \mathrm{ArSR} \qquad (8)$$

$$\mathrm{Ar\dot{S}} + \mathrm{RCo(dmgH)_2py} \longrightarrow \mathrm{ArSR} + \mathrm{\dot{C}o^{II}(dmgH)_2py} \qquad (9)$$

TABLE 1

Products of reaction of alkyl- and arylalkyl-cobaloximes [RCo(dmgH)$_2$py] with diphenyl disulphide and with diphenyl diselenide

R	Reagent	T/°C	Solvent	t/h	Conditions	Product (yield)	Chemical shifts (δ)[e] 1-H[b]	2-H[b]	3-H[b]	Other H	J/Hz
Methyl[a]	PhSSPh	Ambient	Benzene	?	$h\nu$	MeSP (?)	2.35 (s)				
Ethyl[a]	PhSSPh	Ambient	Benzene	?	$h\nu$	EtSPh (?)	2.95 (q)	1.4 (t)			
Isopropyl[a]	PhSSPh	Ambient	Benzene	?	$h\nu$	Pr^{i}SPh (?)	3.25 (se)	2.25 (d)			
n-Butyl	PhSSPh	105	Toluene	14	Δ	Bu^{n}SPh (65)	2.90 (m)			0.91 (CH$_3$)	
n-Butyl	PhSSPh	18	MeOH	3	$h\nu$[c]	Bu^{n}SPh (50)					
s-Butyl	PhSSPh	18	MeOH	0.3	$h\nu$[c]	Bu^{s}SPh (85)	3.17 (m)	1.53 (m)	1.03 (t)	1.28 (d, CH$_3$)	
s-Octyl	PhSSPh	18	MeOH	0.3	$h\nu$[c]	s-OctSPh (45)[d]	3.20 (m)			1.26 (d, CH$_3$)	6.5
s-Octyl	PhSSPh	105	Toluene	2.5	Δ	s-OctSPh (39)[d]					
(*R*)-s-Octyl	PhSSPh	18	MeOH	0.3	$h\nu$[c]	s-OctSPh[d]					
(*S*)-s-Octyl	PhSSPh	18	MeOH	0.3	$h\nu$[c]	s-OctSPh[d]					
(*S*)-s-Octyl	PhSSPh	105	Toluene	2.5	Δ	s-OctSPh[d]					
(*R*)-s-Octyl	PhSeSePh	18	CH$_2$Cl$_2$	0.5	$h\nu$[c]	s-OctSePh (62)	3.27 (m)			1.38 (d, CH$_3$)	6.4
PhCH(CO$_2$Et)	PhSSPh	55	Toluene	1	Δ	PhCH(CO$_2$Et)SPh (60)	4.89 (s)			4.10 (q), 1.13 (t, Et)	
PhCH(CO$_2$Et)	PhSSPh	13	CH$_2$Cl$_3$	0.5	$h\nu$[c]	PhCH(CO$_2$Et)SPh (71)					
PhCHCH$_3$	PhSeSePh	28	CH$_2$Cl$_2$	0.8	Δ	PhCH(CH$_3$)SePh (28)	4.41 (q)	1.74 (d)		7.21 (Ph)	6.0
PhCHCH$_3$	PhSeSePh	12	CH$_2$Cl$_2$	0.5	$h\nu$[c]	PhCH(CH$_3$)SePh (70)					
4-BrC$_6$H$_4$CH$_2$	PhSSPh	95	Toluene	18	Δ	4-BrC$_6$H$_4$CH$_2$SePh (71)	3.98 (s)			7.93, 7.69 (Ar)	
PhCH$_2$	PhSeSePh	47	CHCl$_3$	2.5	Δ	PhCH$_2$SePh (47)	4.09 (s)			7.50	
PhCH$_2$CH$_2$	PhSSPh	18	CH$_2$Cl$_2$	4.5	$h\nu$[c]	PhCH$_2$CH$_2$SPh	3.22 (t)	2.80 (t)		7.26	
PhCHDCHD	PhSSPh	18	CDCl$_3$	4.5	$h\nu$[c]	PhCHDCHDSPh	3.22 (du)	2.80 (du)		7.26	

[a] From ref. 7. [b] Numbering from PhS or PhSe. [c] Tungsten lamps (2 × 250 W at 10 cm) through all-Pyrex apparatus. [d] Racemic complex, yield before final purification *ca.* 75%. [e] d = doublet, m = multiplet, q = quartet, se = septet, s = singlet, t = triplet; u, with deuterium decoupling.

reaction of diphenyl disulphide with a number of alkyl-; allyl-, and propadienyl-cobaloximes, with a particular view to establishing the validity of reaction (9), and the further extension of the reaction to diphenyl diselenide.

RESULTS

Reactions of Diphenyl Disulphide and Diphenyl Diselenide.—(a) *With alkylcobaloximes.* When diphenyl disulphide (1) (10^{-2}M) was treated with n-butylbis(dimethylglyoximato)-pyridinecobalt(III) (2) (10^{-2}M) in toluene at 105 °C, or in methanol at 18 °C under irradiation by tungsten light through all-Pyrex water-cooled apparatus,[8] only one new organic product, n-butyl phenyl sulphide (3) was isolated in significant yield (30—80%; Table 1), together with unchanged or re-formed (1) and phenylthiobis(dimethylglyoximato)pyridinecobalt(III) (4). Similar reactions of s-butyl-, 2-phenylethyl-, and racemic s-octyl-cobaloximes (5)—(7), and of the substituted benzylcobaloximes (8) and (9), with equimolar amounts of (1) (1—5 × 10^{-2} mol dm^{-3}), either thermally or photochemically, gave similar yields of the corresponding organo phenyl sulphides (10)—(14), respectively, and of (4) [equation (10)].

$$\underset{(1)}{\mathrm{RCo(dmgH)_2py + PhSSPh}} \longrightarrow \mathrm{RSPh} + \underset{(4)}{\mathrm{PhSCo(dmgH)_2py}} \qquad (10)$$

(2) R = Bu^n	(3) R = Bu^n
(5) R = Bu^s	(10) R = Bu^s
(6) R = PhCH$_2$CH$_2$	(11) R = PhCH$_2$CH$_2$
(7) R = s-octyl	(12) R = s-octyl
(8) R = PhCH(CO$_2$Et)	(13) R = PhCH(CO$_2$Et)
(9) R = 4-BrC$_6$H$_4$CH$_2$	(14) R = 4-Br(C$_6$H$_4$)CH$_2$
(23) R = CH$_2$:CMeCH$_2$	(26) R = CH$_2$:CMeCH$_2$
(24) R = Me$_2$C:CHCH$_2$	(27) R = Me$_2$C:CHCH$_2$
(25) R = PhCH:CHCH$_2$	(28) R = PhCH:CHCH$_2$

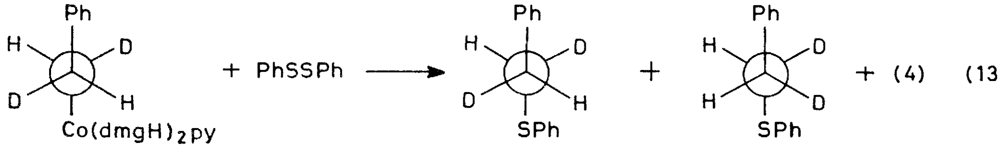
The corresponding photochemical reaction of (*S*)-2-octylcobaloxime (7a) {$[\alpha]_{546}^{20}$(EtOH) +53°, prepared from

$$[\mathrm{Co(dmgH)_2py}]^- + \text{s-octyl tosylate} \longrightarrow \text{s-octylCo(dmgH)}_2\text{py} + \mathrm{OTs}^- \qquad (11)$$

(15a) (−)-(*R*) (7a) (+)-(*S*)
(15b) (+)-(*S*) (7b) (−)-(*R*)

$$\text{s-octylCo(dmgH)}_2\text{py} + \mathrm{PhSSPh} \xrightarrow[10\,^\circ\mathrm{C}]{h\nu} \text{s-octylSPh} + (4) \qquad (12)$$

(7a) (+)-(*S*) (1) (12) racemic
(7b) (−)-(*R*)



(6a) (11a) (11b)

TABLE 2

Products of reaction of allyl- and propadienyl-cobaloximes [RCo(dmgH)$_2$py] with diphenyl disulphide and diselenide

R	Reagent	T/°C	Solvent	t/h	Conditions	Product (yield %)	Chemical shifts (δ) ^{c}				Other H	J/Hz
							1-H	2-H	3-H	4-H		
CH$_2$:CMeCH$_2$	PhSSPh	105	Toluene	24	Δ	CH$_2$:CMeCH$_2$SPh (25)	3.47 (s)		4.77 (m)		1.83 (s, Me)	
MeCH:CHCH$_2$	PhSSPh	100	Toluene	23	Δ	Me·CH:CHCH$_2$SPh (12) ^{a}	~3.5 (d)	~5.5 (m)	~5.5 (m)	1.6 (d)		
						CH$_2$:CHCH(Me)SPh	3.7 (m)	~5.8 (m)	4.87 (b)		1.35 (d, Me)	
Me$_2$C:CHCH$_2$	PhSSPh	50	MeOH	7	Δ	Me$_2$C:CHCH$_2$SPh (50)	3.57 (d)	5.36 (m)		1.70 (s) 1.58 (s)		7.7
Me$_2$C:CHCH$_2$	PhSeSePh	17	CH$_2$Cl$_2$	0.3	$h\nu$	Me$_2$C:CHCH$_2$SePh (41)	3.53 (d)	5.39 (m)		1.69 (s) 1.49 (s)		7.5
Me$_2$C:CHCH$_2$	PhSeSePh	60	CHCl$_3$	0.5	Δ	Me$_2$C:CHCH$_2$SePh (68)						
PhCH:CHCH$_2$	PhSSPh	80	Dioxan	18	Δ	PhCH:CH$_2$SPh (57)	3.68 (d)	6.22 (m)	6.43 (d)		7.27 (Ph)	$J_{1,2}$ 6
PhCH:CHCH$_2$	PhSSPh	18	MeOH	2	$h\nu$	PhCH:CH$_2$SPh (85)						
PhCH:CHCH$_2$	PhSeSePh	60	CHCl$_3$	0.5	Δ	PCH:CHCH$_2$SePh (72)	3.65 (d)	6.21 (d)	6.35 (d)		7.25 (Ph)	
PhCH:CHCH$_2$	PhSeSePh	17	CH$_2$Cl$_2$	0.3	$h\nu$	PhCH:CHCH$_2$SePh (>90)						
Me$_2$C:C:CH	PhSSPh	105	Toluene	22	Δ	Me$_2$C:C:CHSPh (12)	5.79 (sp)			1.70 (d)		
						HC≡CCMe$_2$SPh(13)			2.36 (s)		1.54 (s, Me)	
Me$_2$C:C:CH	PhSSPh	18	MeOH	0.7	$h\nu$	Me$_2$C:C:CHSPh (13) HC≡CCMe$_2$SPh (37)						
Me$_2$C:C:CH	PhSeSePh	17	CH$_2$Cl$_2$	0.5	$h\nu$	Me$_2$C:C:CHSePh (23)	5.87 (sp)			1.67 (d)		
						HC≡CCMe$_2$SePh (11)			2.42 (s)		1.62 (s, Me)	
(CH$_2$)$_5$C:C:CH	PhSSPh	105	Toluene	31	Δ	(CH$_2$)$_5$C:C:CHSPh (7)	5.86 (m)					
						HC≡CC(CH$_2$)$_5$SPh (7)			2.38 (s)			
(CH$_2$)$_5$C:C:CH	PhSSPh	18	MeOH	2.5	$h\nu$	(CH$_2$)$_5$C:C:CHSPh (14) HC≡CC(CH$_2$)$_5$SPh (15)						

^{a} Yield of mixed isomers, near equal proportions. ^{b} Other 3-H, δ 4.94. ^{c} d = doublet, s = singlet, m = multiplet, se = sept.

(R)-s-octyl tosylate (15a), $[\alpha]_{546}^{20}$(EtOH) $-10°$}, and of the R-isomer (7b) {$[\alpha]_{546}^{20}$(EtOH) $-53°$ prepared from (S)-2-octyl tosylate (15b), $[\alpha]_{546}^{20}$(EtOH) $+10°$} with (1) gave racemic s-octyl phenyl sulphide (12) in 75% yield. The thermal reaction of (7a) with (1) in refluxing toluene also gave racemic (12). Similarly, the product of the photochemical reaction of (1) with racemic *erythro*-[1,2-^{2}H$_2$]-2-phenylethylcobaloxime (6a) gave an equimolar mixture of racemic *erythro*- and *threo*-[1,2-^{2}H$_2$]-2-phenylethyl phenyl sulphide (11a and b) [equation (13)].

Under comparable conditions, diphenyl diselenide (16) reacted with (7b) to give phenylselenylbis(dimethylglyoximato)pyridinecobalt(III) (17) and racemic s-octyl phenyl selenide (18). Good yields of (17) and of the corresponding substituted benzyl phenyl selenides (21) and (22) were also obtained from the photochemical and thermal reactions of diphenyl diselenide with the substituted benzylcobaloximes (19) and (20) [equation (14) and Table 1].

(b) *Reaction with allyl- and propadienyl-cobaloximes*. The reactions of 2-methylallyl-, 3-methylbut-2-enyl-, and cinnamyl-cobaloximes (23)—(25) [equations (10) and (14)] with diphenyl disulphide and diphenyl diselenide were comparable with those of the alkylcobaloximes, giving only a single isomer (*i.e.* ⩽3% of the other isomer) of each allyl phenyl sulphide or selenide (26)—(28) and (29) and (30) (Table 2). However, but-2-enyl- and 3-methylbuta-1,2-dienyl-cobaloxime (31) and (32) and the exocyclic substituted dienylcobaloxime (33) each gave two isomeric organo phenyl sulphides or selenides [equations (15) and (16)] (Table 2).

RCo(dmgH)$_2$py + PhSeSePh (16) ⟶ PhSeCo(dmgH)$_2$py (17) + PhSeR (14)

(7b) R = (R)-s-octyl
(19) R = PhCHCH$_3$
(20) R = PhCH$_2$
(24) R = Me$_2$C:CHCH$_2$
(25) R = PhCH:CHCH$_2$

(18) R = racemic s-octyl
(21) R = PhCHCH$_3$
(22) R = PhCH$_2$
(29) R = Me$_2$C:CHCH$_2$
(30) R = PhCH:CHCH$_2$

MeCH:CHCH$_2$Co(dmgH)$_2$py (31) + (1) [or (16)] ⟶ (4) [or (17)] + MeCH:CHCH$_2$XPh + CH$_2$:CHCHMeXPh (15)

(34) X = S
(35) X = Se
(36) X = S
(37) X = Se

R^{1}R^{2}C:C:CHCo(dmgH)$_2$py + (1) [or (16)] ⟶ (4) [or (17)] + HC≡CCR^{1}R^{2}SPh + R^{1}R^{2}C=C=CHSPh (16)

(32) R^1 = R^2 = Me
(33) R^1, R^2 = (CH$_2$)$_5$

(38) X = S, R^1 = R^2 = Me (42)
(39) X = Se, R^1 = R^2 = Me (43)
(40) X = S, R^1, R^2 = (CH$_2$)$_5$ (44)
(41) X = Se, R^1, R^2 = (CH$_2$)$_5$ (45)

The 3-methylbuta-1,2-dienylcobaloxime (32) was also converted into the corresponding trimethyl phosphite complex (32a) [equation (17)] and then treated with diphenyl disulphide in the dark at ambient temperature, well below that required for the above reactions. Studies of the ^{1}H n.m.r. spectrum during the reaction showed that, over several hours, the phosphite ligand was displaced by the disulphide to give the new complex (32b).

$$\mathrm{Me_2C{:}C{:}CHCo(dmgH)_2py} \overset{\mathrm{(POMe)_3}}{\rightleftharpoons} \underset{(32a)}{\mathrm{Me_2C{:}C{:}CHCo(dmgH)_2P(OMe)_3}} \xrightarrow{(1)} \underset{(32b)}{\mathrm{Me_2C{:}C{:}CHCo(dmgH)_2S(Ph)SPh}} \quad (17)$$

DISCUSSION

It is well established that the photolysis of alkyl-, benzyl-, and allyl-cobaloximes gives rise to the formation of the corresponding alkyl, benzyl, or allyl radicals.[9] The formation of the same radicals in thermolysis reactions is less well established, though the thermolysis of some allylcobaloximes has been shown to be an efficient method of preparation of the inorganic product of homolysis, namely cobaloxime(II).[10] The close similarity between the thermal and photochemical reactions in this work, including the relative rates of reaction, s-benzyl > primary allyl > benzyl > s-alkyl > primary alkyl, suggest strongly that the same radical processes are involved under both sets of conditions. In the presence of diphenyl disulphide or diphenyl diselenide the organic radical from the cobaloxime [equation (18)] would be expected to react primarily to give the phenylthiyl or phenylselenyl radical [equation (19)]. However, it is clear from the formation of racemic s-octyl phenyl sulphide and selenide from both (*R*)- and (*S*)-s-octylcobaloxime and from the formation of *threo-* and *erythro-*[1,2-^{2}H$_2$]-2-phenylethyl phenyl sulphide from *erythro-*[1,2-^{2}H$_2$]-2-phenylethylcobaloxime, that the direct attack of the phenylchalcogenyl radical on the α-carbon of the organic ligand of the cobaloxime is at most a very minor pathway.[11] The main route to the products must involve processes in which the organic radical loses its stereochemical integrity, *i.e.*, through the combination reaction [equation (20)] or the attack of the organic radical on the disulphide or diselenide [equation (19)].

$$\mathrm{RCO^{III}(dmgH)_2py \rightleftharpoons \dot{R} + Co^{II}(dmgH)_2py} \quad (18)$$

$$\mathrm{\dot{R} + PhXXPh \longrightarrow RXPh + Ph\dot{X}} \quad (19)$$

$$\mathrm{\dot{R} + Ph\dot{X} \longrightarrow RXPh} \quad (20)$$

We are unable to estimate the proportions of reaction through the two pathways, because the phenylthiyl and phenylselenyl radicals can also be formed by the direct reaction of the cobaloxime(II) fragment with the disulphide or diselenide. Indeed, when pre-formed cobaloxime(II) is allowed to react with diphenyl disulphide or diphenyl diselenide, two molecules of the phenylthiocobaloxime or phenylselenocobaloxime are formed [equation (21)] through a combination of equations (22) and (23).

Though the above reactions are probably the main processes taking place, we cannot rule out some ancillary processes in which the phenylthiyl and phenylselenyl radicals either directly attack the metal or attack a disulphide or diselenide ligand that is co-ordinated to the metal. Such a reversible attack of a radical on the metal is effectively a reversible one-electron oxidation and would be followed, under the conditions used here, by the homolysis of the carbon–cobalt bond [equation (24)].[12] However, in view of the high formation constants and low rates of dissociation of the axial ligand in organocobaloximes, such a direct attack on a 'bare' cobalt would be unlikely, but the same intermediate could be readily formed by the attack of the same radical

$$\mathrm{PhXXPh + 2CO^{II}(dmgH)_2py \longrightarrow 2PhXCo(dmgH)_2py} \quad (21)$$

$$\mathrm{PhXXPh + Co^{II}(dmgH)_2py \longrightarrow PhXCo^{III}(dmgH)_2py + Ph\dot{X}} \quad (22)$$

$$\mathrm{Ph\dot{X} + Co^{II}(dmgH)_2py \longrightarrow PhXCo^{III}(dmgH)_2py} \quad (23)$$

on a pre-co-ordinated disulphide or diselenide [equations (25) and (26)].

Reactions of Allyl- and Propadienyl-cobaloximes.—The reactions of allyl- and propadienyl-cobaloximes with diphenyl disulphide and diphenyl diselenide proved to be less informative than the corresponding reactions with

$$\mathrm{RCo^{III}(dmgH)_2 + Ph\dot{X} \longrightarrow RCo^{IV}(dmgH)_2XPh \longrightarrow \dot{R} + Co^{III}(dmgH)_2XPh} \quad (24)$$

$$\mathrm{RCo^{III}(dmgH)_2py + PhXXP \longrightarrow RCo^{III}(dmgH)_2X(Ph)XPh + py} \quad (25)$$

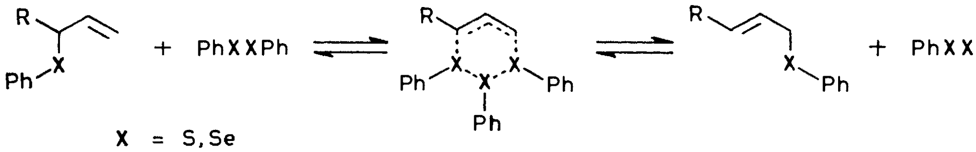
$$\mathrm{RCo^{III}(dmgH)_2X(Ph)XPh + Ph\dot{X} \longrightarrow RCo^{IV}(dmgH)_2XPh + PhXXPh} \quad (26)$$

polyhalogenomethanes,[2] diethyl bromomalonate,[13] or organosulphonyl chlorides,[4] because the products obtained in this case are thermodynamically controlled and do not give any indication of the regiospecificity of the kinetically controlled process. The isomerisation of allyl phenyl sulphides takes place both thermally and photochemically even in the absence of organocobalt complexes and is known to be catalysed by diphenyl disulphide [14,15] [equation (27; X = S)] under conditions almost identical to our own. A similar isomerisation also takes place with allyl phenyl selenides [16] and seems likely for the corresponding propadienyl (or propargyl) phenyl sulphides and selenides. Further discussion of the product proportions is not relevant to the possibility of homolytic attack of the phenylthiyl or phenylselenyl radicals at the γ-carbon of the allyl or propadienyl ligand, and it is therefore impossible at this stage to state whether the products are formed by attack on the organic ligand [equation (28)] or by attack of the organic radical on the disulphide or diselenide [equation (19)].

Further evidence of the relative reluctance of phenylthiyl and phenylselenyl radicals to attack the organic ligand of organocobaloximes comes from the fact that when the reaction of diphenyl disulphide with (24) was carried out in carbon tetrachloride, no dimethylallyl phenyl sulphide was formed; instead the propagation steps (2) and (3) (X = Y = Cl) were dominant and the product was exclusively the trichlorobutene derivative formed by attack of trichloromethyl radicals as in equation (29).

EXPERIMENTAL

Materials.—Diphenyl disulphide, diphenyl diselenide, toluene, cobalt chloride hexahydrate, dimethylglyoxime, pyridine, and carbon tetrachloride were commercial materials used without further purification. Methylene chloride and trimethyl phosphite were distilled before use and chloroform was washed with water, dried with a molecular sieve, and distilled immediately prior to use. Silica gel was Mallinckrodt Silicar CC4 or CC7 and t.l.c. plates were Merck 2mm GO–F254 silica gel.



(27)

(28)

(29)

Organocobaloximes.—The organocobalt complexes were prepared by standard methods [17] from the bis(dimethylglyoximato)pyridinecobaltate(I) ion and the appropriate organic bromide (for allyl-, propadienyl-, benzyl-, and some alkyl-cobaloximes) or organic tosylate (for alkylcobaloximes).

Thermal Reactions of Diphenyl Disulphide.—In a typical reaction, a solution of diphenyl disulphide (55 mg, 0.25 mmol) and α-ethoxycarbonylbenzylbis(dimethylglyoximato)pyridinecobalt(III) (265 mg, 0.5 mmol) in chloroform (15 cm^3) was degassed and heated under nitrogen at 55° for 1 h. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel using hexane–ether and pentane–ether mixtures for elution, to give α-ethoxycarbonylbenzyl phenyl sulphide (80 mg, 0.3 mmol, 60%). The other products, *i.e.* diphenyl disulphide and phenylthiobis(dimethylglyoximato)pyridinecobalt(III) were identified by n.m.r., but were not estimated. Thermal reactions of alkylcobaloximes required more forcing conditions (refluxing toluene), but those of some secondary benzylcobaloximes proceeded even at ambient temperature.

Photochemical Reactions of Diphenyl Disulphide.—In a typical reaction, a solution of n-butylbis(dimethylglyoximato)pyridinecobalt(III) (213 mg, 0.5 mmol) and diphenyl disulphide (109 mg, 0.5 mmol) in methylene chloride (50 cm^3) was degassed and then irradiated for 3 h at 18 °C under nitrogen in an all-Pyrex water-cooled apparatus with 2 × 250-W tungsten lamps 10 cm from the sample. The solvent was removed *in vacuo* and the residue was chromatographed as above and by t.l.c. to give n-butyl phenyl sulphide (68 mg, 0.4 mmol, 80%) and phenylthiobis(dimethylglyoximato)pyridinecobalt(III) (Found: C, 46.8; H, 4.9; N, 14.6. $C_{19}H_{24}CoN_5O_4S$ requires C, 47.8; H, 5.1; N, 14.7%).

Thermal Reactions of Diphenyl Diselenide.—In a typical reaction a solution of cinnamylbis(dimethylglyoximato)pyridinecobalt(III) (233 mg, 0.5 mmol) and diphenyl diselenide (156 mg, 0.5 mmol) in chloroform (10 cm^3) was degassed and refluxed under nitrogen for 25 min. The solvent was removed *in vacuo* and the residue was separated on silica gel CC7 or Kieselgel 60F using acetone–hexane or hexane–CH_2Cl_2 (98 : 2) mixtures to give cinnamyl phenyl selenide (86 mg, 0.31 mmol, 62%) (Found: C, 65.8; H, 5.2. $C_{15}H_{14}Se$ requires C, 65.7; H, 5.1%) and phenylselenobis(dimethylglyoximato)pyridinecobalt(III) (Found: C, 43.1; H, 4.7; N, 13.3. $C_{19}H_{24}CoN_5O_4Se$ requires C, 43.4; H, 4.6; N, 13.1%).

Photochemical Reactions of Diphenyl Diselenide.—In a typical reaction a nitrogen-degassed solution of (+)-*S*-s-octylbis(dimethylglyoximato)pyridinecobalt(III) (481 mg, 1 mmol) and diphenyl diselenide (312 mg, 1 mmol) in chloroform (40 cm^3) was irradiated as described above for 2.5 h at −3 °C. The product was isolated from the dark green solution as above to give s-octyl phenyl selenide (99 mg, 0.34 mmol, 34%), $[\alpha]_{546}^{25}$ 0°.

For comparison, (+)-*S*-s-octyl phenyl selenide was prepared as follows. Sodium borohydride (800 mg, 24 mmol) was added under nitrogen to a solution of diphenyl diselenide (2.18 g, 7 mmol) in anhydrous tetrahydrofuran (35 cm^3). (−)-(*R*)-s-Octyl tosylate (3.9 g, 15 mmol) was then added dropwise and the mixture was stirred. After 4 h the solvent was removed *in vacuo* and the brown oily residue was chromatographed on silica gel (Mallinckrodt CC7) with hexane–CH_2Cl_2 (98 : 2) and then by thin layer (Kieselgel 60F) with the same solvent to give (+)-s-octyl phenyl selenide (1.46 g, 39%) as an oil, δ 0.9 (CH_3), 1.3br (10 H, s), 1.4 (d, CH_3), 3.3 (quintet, CHSe), 7.2 (3 H, m, aromatic), and 7.5 (2 H, m, aromatic), $\nu_{max.}$ ($CHCl_3$) 3 030, 2 950, 2 920, 2 840, 1 480, 1 570, 1 520, 1 470, 1450, 1 430, and 1 370 cm^{-1}, $\lambda_{max.}$ (EtOH) 215 (ε 9 000), 240 (2 300), and 270 nm (2 300), $[\alpha]_D^{25}$ +16.7° (EtOH), +15.5° (acetone), +17.4° ($CHCl_3$) +20.5° (C_6H_6), +20.8° (hexane) (all *c* 4), $[\alpha]^{25}$ (EtOH; *c* 1.9) +16.7° (589 nm), +17.8° (580 nm), +20.5 (546 nm), +40° (436 nm), and +75° (365 nm), *m/e* (50 eV) 264, 266, 267, 268, 270, and 272 (M^+); 250, 252, 253, 254, 256, and 258 ($M - CH_2$)$^+$ 152, 154, 155, 156, 158, and 160 ($PhSeH$)$^+$; corresponding to the selenium isotopes 74, 76, 77, 78, 80, and 82, respectively.

Ligand Exchange Reactions.—3-Methylbuta-1,2-dienylbis(dimethylglyoximato)pyridinecobalt(III) (1 g) was refluxed with an excess of trimethyl phosphite (3 g) in methanol for 24 h. The organocobalt complex was isolated and the procedure was repeated with further portions of trimethyl phosphite (3 g). After recrystallisation, 3-*methylbuta*-1,2-*dienylbis(dimethylglyoximato)(trimethyl phosphite)cobalt*(III) (0.4 g, 38%) was obtained (Found: C, 41.4; H, 6.5; N, 12.4; P, 6.5. $C_{16}H_{30}CoN_4O_7P$ requires C, 40.4; H, 6.2; N, 11.7; P, 6.45%), δ 1.35 (6 H, q, J_{HH} 2.2, J_{HP} 7.4 Hz), 4.98 (1 H, m), 2.18 (12 H, d), J_{HP} 3.4 Hz), and 3.60 (9 H, d, J_{HP} 10 Hz). The latter (59 mg, 0.13 mmol) was mixed with diphenyl disulphide (27 mg, 0.13 mmol) in $CDCl_3$ (0.8 cm^3) at ambient temperature and the ^{1}H n.m.r. spectrum was measured at intervals. Within a few minutes the doublet resonance (δ 3.81) of free trimethyl phosphite was apparent and after three hours at 50 °C formation of 3-methylbuta-1,2-dienylbis(dimethylglyoximato)(diphenyl sulphide)-cobalt(III) (28b), δ 1.15 (6 H, d, J_{HH} 2 Hz), 4.77 (1 H, septet), 1.97 (1 H, s), and *ca.* 7.3 (10 H, m), was nearly complete.

Reaction of Diphenyl Disulphide in Carbon Tetrachloride.—3-Methylbut-2-enylbis(dimethylglyoximato)pyridinecobalt(III) (67 mg, 0.2 mmol) was heated with diphenyl disulphide (54 mg, 0.25 mmol) in carbon tetrachloride (2 cm^3) at 55 °C for 4 h. The solvent was removed *in vacuo* and the organic product extracted with pentane was shown to be 3,3-dimethyl-4,4,4-trichlorobut-1-ene by comparison of its ^{1}H n.m.r. spectrum with that of the authentic material.[2]

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