Rearrangements accompanying the Formation of Alkynyl- and Allylcobaloximes and Their Reactions with Sulphur Dioxide

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The bis(dimethylglyoximinato)pyridinecobaltate(I) ion reacts with allyl and alkynyl halides by both S_N2 and S_N2' mechanisms. In most cases only one of these reactions is apparent because of the major influence of steric effects. In the case of the relatively unhindered prop-2-ynyl bromide, the initial attack of the metal nucleophile is believed to be an S_N2 reaction, but this is followed by an S_N2' displacement of the first introduced cobalt by a second cobalt nucleophile. The products obtained therefore depend upon the concentration of the nucleophile, the reaction time, and the temperature. The absence of rearrangement of the organic group in the reaction of the metal nucleophile with 6-bromohex-1-ene also supports the nucleophilic displacement mechanism at saturated carbon. The alkenyl- and alkynyl-cobaloximes formed in the reactions react with sulphur dioxide to give insertion products, either with or without rearrangement of the organic group. The mechanism of these reactions is discussed, and the low yields of normal insertion products from the hex-5-enyl- and but-3-enyl-cobaloximes are interpreted in terms of an initial homolysis of the carbon–cobalt bond.

One of the interesting features of many d^8 transition-metal complexes is their ready reaction with even mildly electrophilic species. For example, the manganese(−I),[1] cobalt(I),[2] and iron(0) [3] anions, (I), (II), and (III), respectively, have been shown to be effective nucleophiles in the displacement of halide ion from saturated alkyl halides. The cobalt(I) anions have indeed been described as ' supernucleophiles '.[2] The evidence for the nucleophilic character comes largely from comparisons of the rates of their reactions with those for the more conventional nucleophiles in analogous S_N2 processes [2] and from the observation of inversion of configuration in their reactions with optically active alkyl halides.[4-6]

$Mn(CO)_5^-$	$Co(dmgH)_2py^-$	$(\pi\text{-}C_5H_5)Fe(CO)_2^-$
(I)	(II)	(III)

(dmgH = monoanion of dimethylglyoxime)

However, the same mechanism need not necessarily hold for each reagent at all centres, nor for the displacement of all leaving groups. We have recently shown, by a study of the stereochemistry of displacement of halide ion from β-halogenostyrenes,[7] that nucleophilic substitution is also the most probable mechanism for the reactions at olefinic carbon atoms. One other interesting group of compounds which have not been studied, other than superficially, are the allylic halides and similar unsaturated halides for which both S_N2 and S_N2' substitutions may occur.

In this paper we describe studies of the stereochemistry of displacement of halide ion from an allylic carbon atom by cobalt(I) species. Since alkylcobaloximes are known to react with sulphur dioxide to give alkylsulphonylcobaloximes,[8] we also describe the reactions of allyl and similar unsaturated cobaloximes with sulphur dioxide, and of some of the products formed thereby.

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RESULTS

Formation of Organocobaloximes.—(*a*) *Allylcobaloximes.* The products of reaction of several allyl halides with the bis(dimethylglyoximinato)pyridinecobaltate(I) ion are shown, together with their principal spectral characteristics, in Table 1. Only one cobaloxime was identified in the total product from each reaction, though the presence of traces of other organocobaloximes could not be ruled out completely. Products were identified primarily from the ^1H n.m.r. spectra of both crude and purified material. As stated earlier,[7] the presence of more than one sharp 12-proton singlet resonance, due to the dimethylglyoxime ligands of each product, is frequently an excellent indication of the presence of more than one cobaloxime in the crude product. The yields of cobaloximes were highest with the longer chain allyl halides and, though the characteristic orange colour of the β-methylallylcobaloxime was evident in the reaction mixture, this compound decomposed rapidly in solution and was not isolated.

TABLE 1

Products of reaction of organic halides with cobaloxime(I) ions in methanol

Halide	Product	Found (Calc.) (%) C	H	N	^1H N.m.r. $(CDCl_3)$[a] α-Py	C-1	C-2	C-3	C-4	dmgH[c]
$CH_2{:}CH{\cdot}CH_2Cl$	$\overset{3}{C}H_2{:}\overset{2}{C}H{\cdot}\overset{1}{C}H_2(Co)$[b]	46·4 (47·0)	5·9 (5·9)	17·1 (17·1)	1·66	6·28	4·27	4·65		7·60
$MeCH{:}CH{\cdot}CH_2Cl$[d] $CH_2{:}CH{\cdot}CHMeCl$[e]	$MeCH{:}CH{\cdot}\overset{1}{C}H_2(Co)$	48·1 (48·2)	5·9 (6·2)	16·2 (16·4)	1·43	7·60	4·5	4·5	8·77	7·77
$Me_2C{:}CH{\cdot}CH_2Cl$[f] $CH_2{:}CH{\cdot}CMe_2Cl$[g]	$Me_2C{:}CH{\cdot}\overset{1}{C}H_2(Co)$	48·8 (49·4)	6·4 (6·4)	15·5 (16·0)	1·40	7·64	4·99		8·81	7·87
$PhCH{:}CH{\cdot}CH_2Cl$[h]	$PhCH{:}CH{\cdot}\overset{1}{C}H_2(Co)$	54·4 (54·4)	6·0 (5·8)	14·0 (14·4)	1·40	7·47	4·00	3·81		7·87
$HC{\vdots}C{\cdot}CH_2Cl$ $H_2C{:}C{:}CHBr$ $HC{\vdots}C{\cdot}CH_2Br$	$HC{\vdots}C{\cdot}\overset{1}{C}H_2(Co)$[i]	46·6 (47·1)	5·8 (5·5)	17·3 (17·2)	1·35	7·7[j]		7·7[j]		7·78[k]
	$H_2C{:}C{:}\overset{1}{C}H(Co)$[i]	46·5 (47·1)	6·0 (5·5)	17·6 (17·2)	1·50	5·25[l]		5·60[l]		7·88 7·85
$HC{\vdots}C{\cdot}C(Me)(Et)Cl$	$MeC(Et){:}C{:}\overset{1}{C}H(Co)$	50·5 (50·4)	6·5 (6·1)	17·6 (17·2)	1·42	5·16			8·74[m,p] 8·54[n]	7·88[q]
$CH_2{:}CH{\cdot}[CH_2]_2Br$	$CH_2{:}CH{\cdot}[CH_2]_2(Co)$	48·0 (48·2)	6·2 (6·2)	16·2 (16·5)	1·35	8·86	*j*	*ca.* 4·3	*ca.* 8·5	7·87
$CH_2{:}CH{\cdot}[CH_2]_3Br$	$CH_2{:}CH{\cdot}[CH_2]_3(Co)$	48·6 (49·4)	6·4 (6·4)	15·8 (16·0)	1·33	*j*	*j*	*j*	*ca.* 4·3	7·87[r]
$CH_2{:}CH{\cdot}[CH_2]_4Br$	$CH_2{:}CH{\cdot}[CH_2]_4(Co)$	50·1 (50·0)	6·2 (6·6)	15·8 (15·5)	1·31	*j*	*j*	*j*	*j*	7·89[s]
$cyclo\text{-}C_6H_{11}Br$	$cyclo\text{-}C_6H_{11}(Co)$	49·9 (50·0)	6·3 (6·6)	15·2 (15·5)	1·43	*j*	*j*	*j*	*j*	7·90

[a] τ Values. [b] (Co) = $Co(dmgH)_2py$. [c] dmgH = Monoanion of dimethylglyoxime. [d] 80% *trans*-20% *cis* by g.l.c. [e] 99% by g.l.c. [f,g] Mixture, 88 and 12%. [h] Mainly *trans*. [i] See Table 2 for details. [j] Resonances obscured. [k] dmgH Resonance as two singlets. [l] $J_{1,3}$ 7·0 Hz. [m] CH_2CH_3. [n] CH_2CH_3. [p] J_{Et} 6 Hz. [q] *Me*CEt τ 9·08. [r] C-5 Resonance *ca.* τ 5·1. [s] C-5 Resonance *ca.* τ 4·3, C-6 resonance *ca.* 5·1.

(*b*) *Alkenylcobaloximes.* Alkenylcobaloximes were the only organometallic products obtained from the reaction of the cobalt(I) ion with 6-bromohex-1-ene, 5-bromopent-1-ene, and 4-bromobut-1-ene. Their spectral characteristics are included in Table 1.

(*c*) *Allenyl- and alkynyl-cobaloximes.* A single cobaloxime was obtained from the reaction of 3-chloro-3-methylpent-1-yne, but the product of the reaction of 3-halogenoprop-1-yne depended upon the conditions used. The products of the reaction of 3-chloro- and 3-bromo-prop-1-yne with preformed bis(dimethylglyoximinato)pyridinecobalt(II) with and without reduction by sodium borohydride in neutral, acidic, and alkaline solution and with reduced chlorobis(dimethylglyoximinato)pyridinecobalt(III) are shown in Table 2. Most of those reaction conditions which led to mixed products have been excluded from the Table.

(*d*) *Related saturated alkylcobaloximes.* Bromocyclohexane and cyclopentylmethyl chloride reacted with the cobalt(I) species without rearrangement of the alkyl group to give the corresponding cyclohexyl- and cyclopentylmethylcobaloximes, respectively. The latter was not isolated, but was identified from its ^1H n.m.r. spectrum and its reactions, which are described later.

Rearrangement of Prop-2-ynylcobaloxime in the Presence of an Excess of Cobalt(I).—The reaction of prop-2-ynylbis(dimethylglyoximinato)pyridinecobalt(III) with the bis(cyclohexanedione dioximinato)pyridinecobalt(I) ion gave predominantly allenylbis(cyclohexanedione dioximinato)pyridinecobalt(III).

Displacement of Cobalt(I) *from γ-Methylallylcobaloxime.*—The reaction of γ-methylallylbis(dimethylglyoximinato)-pyridinecobalt(III) with an equivalent concentration of the bis(cyclohexanedione dioximinato)pyridinecobalt(I) ion gave an equilibrium mixture of the reagent cobaloxime and γ-methylallylbis(cyclohexanedione dioximinato)pyridinecobalt(III) within 10 min at 0° in methanolic solution.

Reaction of Organocobaloximes with Sulphur Dioxide.—(*a*) *Allylcobaloximes.* All the allylcobaloximes described here reacted rapidly with liquid sulphur dioxide in sealed tubes. The tubes were sealed at *ca.* −70°, and by the time they had warmed sufficiently for the ^1H n.m.r. spectrum to be measured at room temperature, the reactions were effectively complete. The products, which were identified from their ^1H n.m.r. spectra, both in solution in the reagent, sulphur dioxide, and, following their isolation, in deuteriochloroform, are shown in Table 3. In no case was more than one organometallic product containing sulphur dioxide identified. However, if undried sulphur dioxide was used, or if the product was heated in sulphur dioxide for several h, the corresponding alkene was obtained in good yield, as shown in Table 4. Treatment of the isolated insertion products with wet sulphur dioxide or with mineral acid also gave the corresponding alkene(s) (Table 4). Owing to their instability poor elemental analyses were obtained for several of the insertion products. In all cases the discrepancies in these analyses correspond with the partial loss of the organic group.

(*b*) *Prop-2-ynyl- and allenyl-cobaloximes.* No stable insertion products were isolated from the reaction of the allenyl- and prop-2-ynyl-cobaloximes with sulphur dioxide. It was apparent from the ^1H n.m.r. spectra of the reaction mixtures that several products were formed, but the presence of paramagnetic material reduced the resolution such that accurate analysis by this method was precluded. In moist sulphur dioxide, or when water was added to the reaction

TABLE 2

Products of reaction of prop-2-ynyl and allenyl halides with cobalt(I) and cobalt(II) species

Substrate	Solvent (ml)	Temp. (°C)	[Co(dmgH)$_2$py] (mmol)	Excess of [NaOH] (mmol)	[NaBH$_4$] (mmol)	Time (min)	Total yield (%)	Product[a] (% of material isolated) (I)	(II)	(III)
$BrCH_2{\cdot}C{\equiv}CH$	H_2O (60)–THF (100)	−10	20			2	21	$\geqslant 95$		
	95% Methanol (160)	0	20			2	30	$\geqslant 95$		
	H_2O (100)–Dioxan (200)	0	60	60	25	5[b]	41	$\geqslant 95$		
$ClCH_2{\cdot}C{\equiv}CH$	95% Methanol (160)	0	20			2	30	$\geqslant 95$		
$BrCH_2{\cdot}C{\equiv}CH$	H_2O (30)–Dioxan (50)	−10	20	40		1	21		$\geqslant 90$	
	H_2O (30)–Dioxan (50)	−10	20	40	25	1	29		$\geqslant 90$	
	95% Methanol (80)	0	20	20	12·5	120	53		$\geqslant 90$	
	H_2O (60)–THF (100)	0	20	20	25	5[c]	10		$\geqslant 90$	
	95% Methanol (160)	50	20			10	30		$\geqslant 90$	
	95% Methanol (160)	40	20		12·5	10	30		$\geqslant 90$	
	95% Methanol (160)	20	20			2[d]	*ca.* 25			$\geqslant 90$
$ClCH_2{\cdot}C{\equiv}CH$	95% Methanol (160)	20	20[e]		25	5	*ca.* 25		$\geqslant 90$	
$H_2C{:}C{:}CHBr$[f]	95% Methanol (160)	0	20		1·3	15	*ca.* 25	17	83	
	95% Methanol (160)	40	20		1·3	40	*ca.* 25		$\geqslant 90$	

[a] (I) = Prop-2-ynylcobaloxime, (II) = allenylcobaloxime, (III) = acetonylcobaloxime. [b] Brought to pH 8 before addition of substrate. [c] Brought to pH 9—10 before addition of substrate. [d] Acetic acid (1 g) added before substrate. [d] Preformed ClCo(dmgH)$_2$py. Containing 5% prop-2-ynyl bromide.

TABLE 3

Products of reaction of cobaloximes with liquid sulphur dioxide

Reagent	Product	^{1}H N.m.r. (τ)						Solvent	$\lambda_{max.}$ nm[a]
		α-Py	C-1	C-2	C-3	C-4	dmgH		
$CH_2{:}CH{\cdot}CH_2(Co)$	$CH_2{:}CH{\cdot}CH_2(SO_2)(Co)$	1·76	6·44	*b*	*b*		7·73	SO_2	323
		1·66	6·28	4·27	4·77		7·60	$CDCl_3$	
$MeCH{:}CH{\cdot}CH_2(Co)$	$CH_2{:}CH{\cdot}CHMe(SO_2)(Co)$[c]	1·80	6·22	4·27	4·77	8·88[d]	7·73	SO_2	340
		1·63	6·14	4·14	4·82	8·80[d]	7·65	$CDCl_3$	
$Me_2C{:}CH{\cdot}CH_2(Co)$	$Me_2C{:}CH{\cdot}CH_2(SO_2)(Co)$[e]	1·77	6·36	4·86		8·30 8·45	7·65	SO_2	340
		1·47	6·32	4·74		8·38 8·47	7·63	$CDCl_3$	
$PhCH{:}CH{\cdot}CH_2(Co)$	$PhCH{:}CH{\cdot}CH_2(SO_2)(Co)$	1·76	6·24	3·89	3·41		7·71	SO_2	345sh
		1·62	6·22	3·73	3·47		7·76	$CDCl_3$	
$CH_2{:}CH{\cdot}[CH_2]_2(Co)$	$CH_2{:}CH[CH_2]_2(SO_2)(Co)$[h]	1·66	7·10	*g*	*ca.* 4·5	*ca.* 5·1	7·70	$CDCl_3$	
$CH_2{:}CH{\cdot}[CH_2]_4(Co)$	$CH_2{:}CH{\cdot}[CH_2]_4(SO_2)(Co)$[i]	1·71	7·12	*g*	*g*	*g*	7·71[j]	SO_2	331
		1·64	7·11	*g*	*g*	*g*	7·77[j]	$CDCl_3$	
cyclo-$C_6H_{11}(Co)$	cyclo-$C_6H_{11}(SO_2)(Co)$	1·77	7·03	*g*	*g*	*g*	7·72	SO_2	
cyclo-$C_5H_9CH_2(Co)$	cyclo-$C_5H_9CH_2(SO_2)(Co)$	1·70	7·04	*g*	*g*	*g*	7·70	SO_2	

[a] In methanol. [b] *ca.* τ 4·6. [c] C, 41·3 (41·9); H, 5·3 (5·3); N, 14·3 (14·4) %. [d] CH*Me*, *J* 6 Hz. [e] C, 42·3 (43·1); H, 5·7 (5·6); N, 13·2 (13·7) %. [f] C, 48·0 (48·1); H, 5·5 (5·1); N, 12·8 (12·7). [g] Resonances obscured $7{\cdot}7 \leqslant \tau \leqslant 9$. [h] Low yield (see text); C, 41·5 (41·9); H, 5·4 (5·3); N, 13·7 (14·4) %. [i] Low yield (see text); C, 44·6 (44·2); H, 6·0 (5·9); N 13·4 (13·6) %. [j] CH_2 Resonance τ 5·1.

TABLE 4

Products of reaction of cobaloximes (0·2 g) with an excess of sulphur dioxide (2 ml) and water

Substrate	H_2O (g)	Products
$MeCH{:}CH{\cdot}CH_2(Co)$	0·02	$MeCH{:}CHMe$ *cis* (30%), *trans* (70%)[a]
$MeCH{:}CH{\cdot}CH_2(Co)$	0·1	$MeCH{:}CHMe$ *cis* (30%), *trans* (70%)[a]
$CH_2{:}CH{\cdot}CH(Me)SO_2(Co)$	0·1	$MeCH{:}CHMe$ *cis* (30%), *trans* (70%)[a]
$CH_2{:}CH{\cdot}CH(Me)SO_2(Co)$	*b*	$MeCH{:}CHMe$ *cis* (25%), *trans* (75%)[a,c]
$CH_2{:}CH{\cdot}CH_2(Co)$	0·07	$CH_2{:}CHMe$
$PhCH{:}CH{\cdot}CH_2(Co)$	0·1	$PhCH{:}CHMe$ (mainly *trans*)[c]
$PhCH{:}CH{\cdot}CH_2SO_2(Co)$	0·1	$PhCH{:}CHMe$ (mainly *trans*)[c]
$Me_2C{:}CH{\cdot}CH_2(Co)$	0·1	$Me_2C{:}CHMe \geqslant 90\%$[c]
$HC{\vdots}C{\cdot}CH_2(Co)$	0·5	$Me_2CO \geqslant 90\%$[c]
$HC{\vdots}C{\cdot}CH_2(Co)$	0·07	$CH_2{:}C{:}CH_2$ (40%), $HC{\vdots}CMe$ (60%), Me_2CO (trace)[a,c]
$H_2C{:}C{\cdot}CH(Co)$	0·02	$CH_2{:}C{:}CH_2$ (50%), $HC{\vdots}CMe$ (50%)[c]
$H_2C{:}C{:}CH(Co)$	0·05	$CH_2{:}C{:}CH_2$ (50%), $HC{\vdots}CMe$ (50%)[c]
$H_2C{:}C{:}CH(Co)$	0·08	$CH_2{:}C{:}CH_2$ (50%), $HC{\vdots}CMe$ (50%)[c]

[a] By g.l.c. [b] Added to 18M-H_2SO_4, product extracted into chloroform. [c] By ^{1}H n.m.r.

mixture after the initial reaction had occurred, allene, propyne, and acetone were formed in good yield (Table 4).

(*c*) *Cyclohexyl- and cyclopentylmethyl-cobaloximes.* The reactions of the cyclohexyl- and cyclopentylmethyl-cobaloximes with sulphur dioxide were much slower than those just described. After several days, the unrearranged cyclohexyl- and cyclopentylmethyl-sulphonylcobaloximes were obtained (Table 3). These products were not isolated, but their behaviour on t.l.c. was determined for the purpose of comparison with products described later.

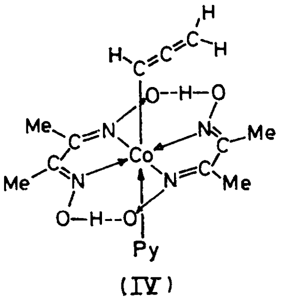
(*d*) *Other alkenylcobaloximes.* The reaction of hex-5-enylcobaloxime with sulphur dioxide was also slow at room temperature. After several days, complete reaction had occurred, but only *ca.* 40% of the product was the unrearranged hexenylsulphonylcobaloxime. The major product could not be identified (see Discussion section) and cobalt(II) material was also formed. The same products were also formed when the reaction was carried out in the dark at 0° and in bright sunlight. Even lower yields of the butenylsulphonylcobaloxime were formed from the but-3-enylcobaloxime in sulphur dioxide, and the other products from this reaction were unstable.

(*e*) *Vinylcobaloximes*. No reaction was observed between vinyl-, *cis*- and *trans*-β-styryl-, or α-styryl-cobaloxime and liquid sulphur dioxide, even over several months in sealed tubes at room temperature.

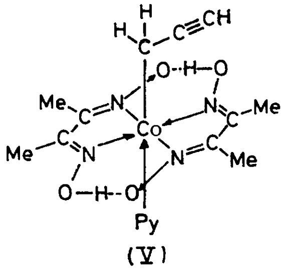
DISCUSSION

Formation of Organocobaloximes.—The most informative results on the formation of the cobaloximes were obtained from the reactions of the prop-2-ynyl and allenyl halides (Table 2).

It was originally reported[9,10] that only the allenylcobaloxime (IV) was obtained from the reaction of preformed cobalt(I) * with prop-2-ynyl bromide or chloride. Our work confirms that, when the reaction is carried out with preformed cobalt(I) at relatively high pH (*e.g.* 10) with a relatively long reaction time, the allenylcobaloxime is the sole isolable organometallic product. The same product is also obtained from the reaction with preformed cobalt(II) in alkaline solutions in the absence of a reducing agent, where disproportionation of the cobalt(II) to cobalt(I) and cobalt(III) is appreciable.



(IV)



(V)

However, when the reaction is carried out with preformed cobalt(II) in approximately neutral solution, in which the disproportionation is much less marked, the prop-2-ynylcobaloxime (V) may be the only isolable product, provided the reaction time is short and the temperature is low.

Prop-2-ynyl halides are known to react with nucleophiles by a variety of mechanisms. In view of the high nucleophilic power of cobalt(I) species[2] and of their low basicity, we anticipated that these displacements might involve S_N2 and/or S_N2' processes. Indeed, the formation of the prop-2-ynylcobaloxime from prop-2-ynyl halides in the presence of low concentrations of cobalt(I) species over short reaction times is consistent with the primary reaction being a very fast S_N2 displacement of the halide ion by the cobalt(I) species [equation (1)]. The formation of the allenylcobaloxime over longer reaction times, in the presence of higher concentrations of cobalt(I) species, and at higher temperature would therefor indicate that the more stable allenylcobaloxime is is formed by an S_N2' displacement of cobalt(I) from the first formed prop-2-ynylcobaloxime by another cobalt(I) species, in a slower, but still fairly rapid reaction [equation (2)]. This latter process was confirmed by our observation that prop-2-ynylbis(dimethylglyoximinato)-pyridinecobalt(III) (V) reacts with bis(cyclohexanedione dioximinato)pyridinecobaltate(I) ion [(Co′)$^-$] to give largely allenylbis(cyclohexanedione dioximinato)pyridinecobalt(III) (VI) [equation (3)].

$$\mathrm{BrCH_2{\cdot}C{\equiv}CH + (Co)^- \xrightarrow{fast} Br^- + \underset{(V)}{(Co)CH_2{\cdot}C{\equiv}CH}} \qquad (1)$$

$$\mathrm{(Co)CH_2{\cdot}C{\equiv}CH + (Co)^- \xrightarrow{slow} (Co)^- + \underset{(IV)}{CH_2{:}C{:}CH(Co)}} \qquad (2)$$

$$\mathrm{\underset{(V)}{(Co)CH_2{\cdot}C{\equiv}CH} + (Co')^- \longrightarrow (Co)^- + \underset{(VI)}{CH_2{:}C{:}CH(Co')}} \qquad (3)$$

Support for the initial S_N2 displacement reaction comes also from the observation that the less nucleophilic pentacarbonylmanganese(—I) ion reacts with prop-2-ynyl bromide to give[11] pentacarbonylprop-2-ynylmanganese(I) [equation (4)].

$$\mathrm{Mn(CO)_5^- + BrCH_2{\cdot}C{\equiv}CH \longrightarrow (CO)_5MnCH_2{\cdot}C{\equiv}CH + Br^-} \qquad (4)$$

We may eliminate the carbenoid mechanism[12] [equations (5) and (6)] from further consideration, because of our observation that, when the allenylcobaloxime is formed from prop-2-ynyl bromide in alkaline deuterium oxide–tetrahydrofuran solution, the product contains no significant amounts of deuterium.

$$\mathrm{HC{\equiv}C{\cdot}CH_2Br + OH^- \longrightarrow H_2O + {:}C{:}C{:}CH_2 + Br^-} \qquad (5)$$

$$\mathrm{{:}C{:}C{:}CH_2 + (Co)^- \longrightarrow H_2C{:}C{:}C(Co)^- \xrightarrow{H_2O} (Co)CH{:}C{:}CH_2 + OH^-} \qquad (6)$$

However, it is more difficult to rule out completely a free radical reaction [equations (7) and (8)] for those solutions in which cobalt(II) is the predominant species. Such a reaction would be expected to give rise to the prop-2-ynyl/allenyl radical (VII), which is known to react with a number of radical trapping reagents[13] to give mixtures of prop-2-ynyl and allenyl products, in which the former usually predominates. Nevertheless, we have shown that prop-2-ynyl bromide is inert to attack by the same cobalt(II) species in non-polar solvents over several h at room temperature.

$$\mathrm{BrCH_2{\cdot}C{\equiv}CH + {\bullet}(Co) \longrightarrow \underset{(VII)}{{\bullet}CH_2{\cdot}C{\equiv}CH \longleftrightarrow CH_2{:}C{:}CH{\bullet}} + Br(Co)} \qquad (7)$$

$$\mathrm{\underset{(VII)}{{\bullet}CH_2{\cdot}C{\equiv}CH \longleftrightarrow CH_2{:}C{:}CH{\bullet}} + {\bullet}(Co) \longrightarrow (Co)CH_2{\cdot}C{\equiv}CH + CH_2{:}C{:}CH(Co)} \qquad (8)$$

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* The abbreviations cobalt(I) and cobalt(II) refer to the bis(dimethylglyoximinato)pyridinecobaltate(I) and the bis(dimethylglyoximinato)pyridinecobalt(II) species, respectively. These are also referred to as (Co)$^-$ and (Co)•, respectively, in the equations.

[9] M. D. Johnson and C. Mayle, *Chem. Comm.*, 1969, 192.

[10] J. P. Collman, J. N. Cawse, and J. W. Kang, *Inorg. Chem.*, 1969, **8**, 2574.

[11] J. E. Thomasson and A. Wojcicki, *J. Amer. Chem. Soc.*, 1968, **90**, 2709.

[12] H. D. Hartzler, *J. Amer. Chem. Soc.*, 1961, **83**, 4990; V. J. Shiner and J. S. Humphrey, *ibid.*, 1967, **89**, 622.

[13] M. M. Martin and E. B. Saunders, *J. Amer. Chem. Soc.*, 1967, **89**, 3777; R. M. Fantazier and M. L. Poutsma, *ibid.*, 1968, **90**, 5490.

From the results it is apparent that the formation of some prop-2-ynylcobaloxime in the reaction of allenyl bromide with the cobalt(I) ion may well be a result of a direct S_N2' displacement of the bromide ion by the metal ion. However, we have not studied this reaction in the same detail as that of the prop-2-ynyl bromide.

The ^1H n.m.r. spectrum of the prop-2-ynylcobaloxime is also of interest because the methyl resonance of the dimethylglyoxime appears as a doublet. This suggests that there is restricted rotation about the carbon–cobalt bond, due possibly to some interaction between the triple bond and the equatorial ligands.

The reactions of the substituted prop-2-ynyl halides with the cobalt species are more straightforward. Only the rearranged product was obtained from the reaction of the cobalt species with 3-chloro-3-methylpent-1-yne [equation (9)] and a previous report[10] showed that the same is true for the reactions with 3-chloro-3-methylbut-1-yne and 1-chloro-1-ethynylcyclohexane. It is probable that these reactions proceed by a direct S_N2' displacement, because it is well established that the displacement of halide ion by cobalt(I) from a secondary carbon atom by an S_N2 process is very much slower than that from a primary carbon atom[2] and it would be expected that the displacement from a tertiary carbon atom would be slower still. Under these circumstances the S_N2' reaction at the unhindered unsaturated carbon atom should predominate.

$$\mathrm{EtC(Me)Cl{\cdot}C{\equiv}CH} + \mathrm{(Co)^-} \longrightarrow \mathrm{EtC(Me){:}C{:}CH(Co)} + \mathrm{Cl^-} \qquad (9)$$

Similar conclusions may be drawn from the reactions of the allyl halides with the cobalt species. Under a variety of conditions, similar to those used for the reactions of prop-2-ynyl halides, only the γ-methylallylcobaloxime (VIII) could be obtained from both α- and γ-methylallyl halides [equation (10)].

$$\underset{\text{(IX)}}{\mathrm{MeCH{:}CH{\cdot}CH_2Cl}} + \mathrm{(Co)^-} \longrightarrow$$

$$\underset{\text{(VII)}}{\mathrm{MeCH{:}CH{\cdot}CH_2(Co)}} + \mathrm{Cl^-} \longleftarrow \underset{\text{(X)}}{\mathrm{MeCHCl{\cdot}CH{:}CH_2}} + \mathrm{(Co)^-} \qquad (10)$$

In the corresponding reactions of the same two halides with moderately reactive conventional nucleophiles, such as alkoxide ions, the ratio of the rates of the S_N2 and S_N2' reactions is much greater than unity.[14] The slightly higher ratio in the case of the γ-methylallyl halide (IX) has been ascribed to the small but significant steric influence of the methyl groups on the S_N2 reaction of the α-methylallyl halide and on the S_N2' reaction of the γ-methylallyl halide. The same steric influence is apparent in the reactions with the cobalt(I) species, but is of such a magnitude that, whereas the S_N2 reaction still predominates with the γ-methylallyl halide, the S_N2' reaction now predominates with the α-methylallyl halide (X). Indeed, the discrimination of the cobalt(I) species for the primary or unhindered unsaturated carbon atom appears to be sufficiently great that the rapid displacement of the bis(dimethylglyoximinato)-pyridinecobalt(I) ion [(Co)$^-$] by the bis(cyclohexanedione dioximinato)pyridinecobaltate(I) ion [(Co')$^-$] from γ-methylallylbis(dimethylglyoximinato)pyridinecobalt-(III) (VIII), takes place exclusively by the S_N2 mechanism [equation (11)].

$$\mathrm{MeCH{:}CH{\cdot}CH_2(Co)} + \mathrm{(Co')^-} \rightleftharpoons \mathrm{MeCH{:}CH{\cdot}CH_2(Co')} + \mathrm{(Co)^-} \qquad (11)$$

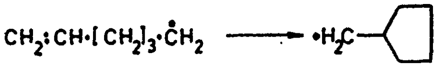
Similarly, 3-methylbut-2-enyl chloride (XI) and cinnamyl chloride (XII) react with the cobalt(I) ion by the less sterically hindered S_N2 mechanism without rearrangement [equations (12) and (13)].

$$\underset{\text{(XII)}}{\mathrm{PhCH{:}CH{\cdot}CH_2Cl}} + \mathrm{(Co)^-} \longrightarrow \mathrm{PhCH{:}CH{\cdot}CH_2(Co)} + \mathrm{Cl^-} \qquad (12)$$

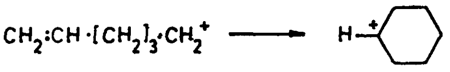
$$\underset{\text{(XI)}}{\mathrm{Me_2C{:}CH{\cdot}CH_2Cl}} + \mathrm{(Co)^-} \longrightarrow \mathrm{Me_2C{:}CH{\cdot}CH_2(Co)} + \mathrm{Cl^-} \qquad (13)$$

It is apparent that the reactions of several other strongly nucleophilic transition-metal anions [*e.g.*, (I) and (III)] follow these patterns in their reactions with allylic and propargylic halides. Where differences in behaviour do arise, they may be attributed to the ease with which the first formed organometallic product can undergo metal for metal exchange[4,15] by either an S_N2 or an S_N2' process, and to the steric requirements of the nucleophile.

Further confirmation of the dominant character of the nucleophilic displacement mechanism at a primary saturated carbon atom by the cobalt(I) species comes from the reactions of the higher alkenyl halides. It is well established that reactions of 6-bromohex-1-ene which proceed through intermediate hex-5-enyl radicals[16] or cations,[17] give rise to significant amounts of cyclopentylmethyl and cyclohexyl products, respectively. The clean reactions of 4-bromobut-1-ene, 5-bromopent-1-ene, and 6-bromohex-1-ene with the cobalt(I) nucleophile to give the corresponding unrearranged alkenylcobaloximes in good yield, rule out any significant route through carbonium ion or free radical intermediates [equation (16)].



(14)



(15)

$$\mathrm{CH_2{:}CH{\cdot}[CH_2]_{\mathit{n}}{\cdot}CH_2Br} + \mathrm{(Co)^-} \longrightarrow \underset{\text{(XIII)}}{\mathrm{CH_2{:}CH{\cdot}(CH_2)_{\mathit{n}}{\cdot}CH_2(Co)}} + \mathrm{Br^-} \qquad (16)$$

$$n = 0-3 \qquad\qquad n = 0-3$$

Sulphur Dioxide Insertion Reactions.—Only one insertion product was obtained from the reaction of each of the

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[14] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' 2nd edn., Cornell University Press, Ithaca, 1969, ch. XI, section 48c.

[15] D. Dodd and M. D. Johnson, *Chem. Comm.*, 1971, 1371.

[16] M. Julia, *Pure Appl. Chem.*, 1967, **15**, 167.

[17] P. D. Bartlett, W. D. Closson, and T. J. Cogdell, *J. Amer. Chem. Soc.*, 1965, **87**, 1308.

allylcobaloximes with liquid sulphur dioxide. Whereas the cinnamyl- and γ-methylbut-2-enyl-cobaloxime underwent rapid insertion under a variety of conditions to give only the unrearranged cinnamyl- and γ-methylbut-2-enyl-insertion products [equations (17) and (18); Table 3], the γ-methylallylcobaloxime (VIII) underwent insertion of sulphur dioxide to give the rearranged α-methylallyl insertion product (XIV) [equation (19); Table 3].

Similar rearrangements have been observed with other substituted allylmetal compounds and sulphur dioxide, but there is uncertainty as to the relative degree of kinetic and thermodynamic control of product formation. It has been suggested[18] that the normal course of insertion may give first the rearranged product and that the more stable unrearranged products are formed as a result of a further rearrangement of the allyl group. Whilst this is probably correct for a number of main group elements bonded to carbon,[19] evidence from the reactions of compounds containing bonds from carbon to transition metals suggests that the insertion products are formed as a result of kinetic control and that further rearrangement does not take place.[20] This is supported in the present case by the observation that rearrangement of the α-methylallyl insertion product (XIV) to the corresponding γ-methylallyl insertion product (XV) could not be achieved even on heating the former in liquid sulphur dioxide at 65° for several days. A similar but extremely rapid rearrangement of an intermediate α-methylbut-2-enyl insertion product to the observed γ-methylbut-2-enyl insertion product (XVI) therefore seems most unlikely.

Little evidence has been forthcoming on the mechanism of insertion reactions of sulphur dioxide. In general it has been assumed that the reactions are concerted with attack of the sulphur dioxide at the metal and at the organic group. However, there are a number of puzzling features of several of the reactions involving carbon–transition metal bonds and the present results appear to support a dissociative mechanism. In particular, the reactions of the hexenyl- and but-3-enyl-cobaloximes, though not completely elucidated, are not consistent with a concerted insertion reaction.

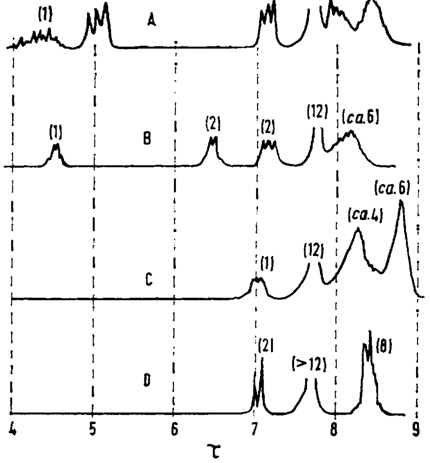
$$\mathrm{PhCH{:}CH{\cdot}CH_2(Co)} \xrightarrow{SO_2} \mathrm{PhCH{:}CH{\cdot}CH_2(SO_2)(Co)} \qquad (17)$$

$$\mathrm{Me_2C{:}CH{\cdot}CH_2(Co)} \xrightarrow{SO_2} \underset{\text{(XVI)}}{\mathrm{Me_2C{:}CH{\cdot}CH_2(SO_2)(Co)}} \qquad (18)$$

$$\underset{\text{(VIII)}}{\mathrm{MeCH{:}CH{\cdot}CH_2(Co)}} \xrightarrow{SO_2} \underset{\text{(XIV)}}{\mathrm{CH_2{:}CH{\cdot}CH(Me)(SO_2)(Co)}} \qquad (19)$$

$$\underset{\text{(XIV)}}{\mathrm{CH_2{:}CH{\cdot}CH(Me)(SO_2)(Co)}} \not\longrightarrow \underset{\text{(XV)}}{\mathrm{MeCH{:}CH{\cdot}CH_2(SO_2)(Co)}} \qquad (20)$$

Thus, whereas good yields of insertion products are obtained from a wide range of both primary and secondary alkylcobaloximes and from allylcobaloximes, relatively low yields of the normal insertion product are obtained from the hexenyl- and but-3-enyl-cobaloximes. For example, four products were obtained from the reaction of the hexenylcobaloxime (XIII; $n = 3$) with sulphur dioxide. These were separated by t.l.c. The first fraction was the normal hexenyl insertion product (Figure, A) which was stable in sulphur dioxide and after isolation (Table 3). The second fraction was a minor unidentified organometallic product and the third fraction was the major component (Figure, B) which was unstable and unfortunately has defied complete characterisation. However, the variable results of elemental analyses and the ^{1}H n.m.r. spectrum show clearly that this is a sulphur-containing cobaloxime which has the elements of the hexenyl group, but not in the hexenyl form.



100 MHz N.m.r. spectrum of products of reaction of C_6-organocobaloximes with sulphur dioxide. Peak areas in parentheses, pyridine resonances omitted, and dimethylglyoxime proton resonances incomplete. A, Hex-5-enylsulphonylcobaloxime; B, unknown product from the reaction of hex-5-enylcobaloxime with sulphur dioxide (chromatographic fraction 3); C, cyclohexylsulphonylcobaloxime; D, cyclopentylmethylsulphonylcobaloxime

Almost certainly this compound is formed as a result of the ability of the hexenyl group to undergo cyclisation reactions, not only of the form shown in equations (14) and (15), but also after capture by sulphur dioxide. Cyclisation without prior dissociation of the carbon–cobalt bond seems unlikely.

The formation of such a product and the complete absence of cyclohexyl products is consistent with an initial homolysis of the carbon–cobalt bond. Whereas the capture of the hexenyl radical by sulphur dioxide would produce the relatively stable hexenylsulphonyl radical (XVII) which could be captured by the paramagnetic cobalt(II) fragment either before or after cyclisation, the hexenyl cation, if formed, would be solvated by the sulphur dioxide and would have sufficient lifetime for the solvated cyclohexyl cation to be formed. Moreover, the fourth fraction from the t.l.c. was largely

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[18] C. W. Fong and W. Kitching, *Organometallic Chem. Rev. A*, 1970, **5**, 281.

[19] C. W. Fong and W. Kitching, *J. Organometallic Chem.*, 1970, **22**, 107.

[20] R. L. Downs, *Diss. Abs.*, 1968, **29**, 1593.

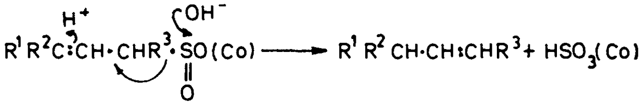
paramagnetic cobalt(II) compounds similar to those formed from the reaction of bis(dimethylglyoximinato)-pyridinecobalt(II) with liquid sulphur dioxide. Similar products were also formed from the butenylcobaloxime.

Further discussion of this reaction seems inappropriate without knowledge of the structure of the main product. However, a homolytic mechanism would also satisfactorily account for the reactions of the allylcobaloximes. For example, the greater stability of the allyl radical would be expected to facilitate the homolysis of the carbon–cobalt bond and thereby to explain the higher rates of these insertions. The stereochemistry of reaction of the allyl radical with sulphur dioxide and hence with the metal radical would then depend upon the selectivity of that radical and on the influence of product character on the transition state for its capture. Thus, with the cinnamyl radical, which is relatively stable, the cinnamyl product would be so much more stable than the alternative α-phenylallyl product,[21] that any reflection of this in the transition state would ensure a predominance of the observed cinnamyl product. On the other hand, though the methylbutenyl radical is less stable and the dominance of the influence of the γ-methylbutenyl insertion product is less marked,[21] the adverse steric effect of the tertiary reaction centre would tend to force the formation of the observed γ-methylbutenyl product. In contrast, the methylallyl radical is still less stable, the γ-methylallyl insertion product would be only slightly more favoured than the α-methylallyl product, and there is less steric hindrance to attack at the secondary carbon atom. Consequently, the methylallyl radical may be captured at the secondary carbon atom to give the observed α-methylallyl product; possibly such capture may take place while the homolysis of the carbon–cobalt bond is occurring. With other transition metals, for which the transition states may have less product character, the alternative products, or mixtures of products, may well be obtained.

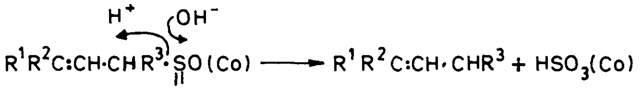
Hydrolysis of the Insertion Products.—Owing to the complexity of the cobaloxime molecules, the i.r. spectra are not definitive in the determination of the nature of the bonding of the sulphur dioxide in the insertion products. However, two facts are apparent; the chemical shifts of the α-protons are inconsistent with the organic group being bound through oxygen, and each of the insertion products from the allyl-, substituted allyl-, prop-2-ynyl-, and allenyl-cobaloximes have the sulphur dioxide bound in the same manner, for each is hydrolysed in wet sulphur dioxide to the corresponding unsaturated hydrocarbon. The formation of the hydrocarbon is novel, but the mechanism is uncertain. We have attempted a number of other electrophilic substitutions on the alkylsulphonylcobaloximes of the structure RS(=O)$_2$(Co), but no reactions could be observed. The contrasting ready hydrolysis of the alkenylsulphonylcobaloximes does suggest a different bonding, *e.g.*, allyl·S(=O)O(Co) which can allow both electrophilic attack at the α- or γ-positions of the allyl group and nucleophilic attack at the sulphur atom [compounds (XVIII) and (XIX)]. The inorganic products from such a reaction would be the known, labile [22] sulphitopyridinecobalt(III) compound (XX).

$CH_2{:}CH{\cdot}[CH_2]_3{\cdot}CH_2(SO_2){\cdot}$

(XVII)



(XVIII) (XX)



(XIX) (XX)

EXPERIMENTAL

Materials.—Commercial materials used were as follows: allyl chloride, 2-methylallyl chloride, prop-2-ynyl chloride, and prop-2-ynyl bromide (B.D.H.); but-2-enyl chloride, 1-methylallyl chloride, 3-methylbut-2-enyl chloride, and 3-methylpent-1-yn-3-ol (Eastman Kodak). The purity of these products was determined by g.l.c. and ^{1}H n.m.r. spectra and the composition of mixtures is shown in Table 1. 3-Methylpent-1-yn-3-ol was converted into 3-chloro-3-methylpent-1-yne by treatment with phosphorus(V) chloride [23]. Prop-2-ynyl bromide was converted into a mixture of bromoallene (94%) and prop-2-ynyl bromide (6%) by treatment with copper(I) bromide.[24] 6-Bromohex-1-ene (Columbia), 5-bromopent-1-ene (Eastman Kodak), and 4-bromobut-1-ene (Koch–Light) were used without further purification. Cyclopentylmethanol (K and K) was converted into cyclopentylmethyl chloride by treatment with thionyl chloride. Sulphur dioxide was B.D.H. Laboratory Reagent Grade and was distilled into the reaction vessel at −70° either directly or after drying over phosphorus(V) oxide.

Reactions with Bis(dimethylglyoximinato)pyridinecobalt(I).—Cobalt chloride hexahydrate (*x* mol) was dissolved in methanol, aqueous dioxan, or aqueous tetrahydrofuran, under nitrogen, with dimethylglyoxime (2*x* mol). Sodium hydroxide (2*x* mol) and pyridine (*x* mol) were added and the mixture was brought to the required temperature (−10 to 50°). The halide (*x* mol) in the appropriate solvent was then added either directly or after the addition of sodium borohydride and further sodium hydroxide, and in some cases acetic acid (see Table 2 for details). The mixture was stirred for the appropriate time and was poured into water either directly or after rapid filtration. The cobaloxime that precipitated was filtered off, dried *in vacuo*, and studied directly and after chromatography on alumina. The filtrate was concentrated and further product was obtained in a few cases. The character of the product did not depend upon the conditions used except in the case of allenyl and prop-2-ynyl halides.

Reactions with Sulphur Dioxide.—An excess of sulphur

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[21] Ref. 14, p. 861.

[22] H. G. Tsiang and W. K. Wilmarth, *Inorg. Chem.*, 1968, **7**, 2535.

[23] G. F. Hennion and A. P. Boisselle, *J. Org. Chem.*, 1961, **26**, 725.

[24] T. L. Jacobs and W. F. Brill, *J. Amer. Chem. Soc.*, 1953, **75**, 1314.

dioxide was distilled on to the cobaloxime, with or without the addition of specified amounts of water (Table 4) in an n.m.r. sample tube, which was then sealed off. The ^{1}H n.m.r. spectrum of the solution was measured at intervals. When the reaction was complete the excess of sulphur dioxide and other volatile products was distilled off into a second sample tube, which was also sealed. The ^{1}H n.m.r. spectrum of this second sample was measured and the volatile products, other than sulphur dioxide, were analysed by g.l.c. following the absorption of the sulphur dioxide in aqueous sodium hydroxide solution. The involatile material from the reaction was extracted with chloroform, and reprecipitated with light petroleum (b.p. 40—60°). The precipitate was characterised directly (Table 3) or after further treatment with wet sulphur dioxide (Table 4). The chloroform–light petroleum filtrate was evaporated to dryness. In most cases little material was recovered, but in the case of cinnamylcobaloxime, various amounts of phenylpropene were obtained, depending upon the amount of water present in the sulphur dioxide.

The organometallic solids precipitated by light petroleum from the product of reaction of the hex-5-enyl- and but-3-enyl-cobaloximes with sulphur dioxide were separated by t.l.c. on silica gel. Elution with a mixture of chloroform (50%), light petroleum (45%), and ethanol (5%) gave four fractions; the insertion products from the unrearranged cobaloxime and other products (see Discussion section). The unknown organometallic product from the hexenylcobaloxime gave varying analytical figures (Found: C, 38·6, 38·5, 36·6, or 37·7; H, 4·9, 4·7, 4·7, or 4·8; N, 14·4, 14·4, 13·6, or 12·2; S, 6·4%).

Cobalt Exchange Experiments.—(a) *γ-Methylallylcobaloxime*. To a stirred suspension of chlorobis(cyclohexanedione dioximinato)pyridinecobalt(III) (0·456 g, 1 mmol) in nitrogen-flushed methanol (35 ml) at 0° was added sodium hydroxide (0·1 g) and sodium borohydride (0·038 g) in water (3·3 ml total) to give a dark blue solution of the bis(cyclohexanedione dioximinato)pyridinecobalt(I) ion. γ-Methylallylbis(dimethylglyoximinato)pyridinecobalt(III) (0·423 g, 1 mmol) in nitrogen-flushed methanol (60 ml) at 0° was added to the cobalt(I) solution and the mixture was stirred for 10 min at 0° before pouring into an excess of air-blown ice–water containing a little pyridine. After 30 min the brown solution was evaporated to low volume (*ca.* 100 ml) at 40° whence crystals of organocobaloxime separated. The product was filtered off, washed with water, and dried *in vacuo* (yield 0·320 g). The ^{1}H n.m.r. spectrum of the product in deuteriochloroform showed only the presence of γ-methylallylbis(dimethylglyoximinato)pyridinecobalt(III) (33%) and γ-methylallylbis(cyclohexanedione dioximinato)-pyridinecobalt(III) (67%).

(b) *Prop-2-ynylcobaloxime*. The experiment was performed similarly to reaction (a) except that prop-2-ynylbis(dimethylglyoximinato)pyridinecobalt(III) (0·407 g, 1 mmol) was used in place of the γ-methylallyl analogue. The ^{1}H n.m.r. and i.r. spectra showed that the product was essentially (>90%) allenylbis(cyclohexanedione dioximinato)-pyridinecobalt(III).

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