β-Styrylcobaloximes: Mechanism of Formation from β-Styryl Halides and Mechanism of Cleavage by Electrophiles

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The ease of reaction of *cis*-β-halogenostyrenes (PhCH:CHX) with the nucleophilic bis(dimethylglyoximato)-pyridinecobaltate(I) ion decreases in the order (X =) I ⩾ Br ⩾ Cl > F. This order, together with the absence of isomerism of either reagent halogenostyrene or product *cis*-styrylcobaloxime during the reaction indicates that the displacement of halide ion and the attack of the nucleophile at the β-carbon are synchronous processes occurring with retention of configuration. The absence of incorporation of deuterium in the vinylcobaloxime formed from the corresponding reaction between vinyl chloride and the same cobaltate(I) ion in deuteriated methanol is in accord with this mechanism. Reactions of both *cis*- and *trans*-β-styrylcobaloxime with bromine, chlorine, and iodine and with mercury(II) acetate in pure acetic acid are also stereospecific substitutions; since *cis*-β-styryl-cobaloxime can be formed in good yield (⩾60%) from phenylacetylene, this reaction provides a useful route to pure *cis*-β-bromo-, -chloro-, and -iodo-styrene and to *cis*-β-styrylmercury(II) derivatives, but the method is of limited utility for the formation of other *cis*-vinyl derivatives.

THE bis(dimethylglyoximato)cobaltate(I) ions are remarkably effective nucleophiles, reacting even with vinyl chloride to give vinylbis(dimethylglyoximato)cobalt(III) complexes,[1] though the mechanism of this reaction has not been investigated. The corresponding reaction of the bis(dimethylglyoximato)pyridinecobaltate(I) ion with *cis*- (I; X = Br) and *trans*-β-bromostyrene (II; X = Br) is stereospecific,[2,3] giving good yields of *cis*- (III) and *trans*-β-styrylbis(dimethylglyoximato)pyridine-cobalt(III) (IV). *cis*-β-Styrylbis(dimethylglyoximato)-cobalt(III) complexes are also formed by the stereo-specific *trans*-addition [2-4] [equation (2)] of the bis(di-methylglyoximato)cobaltate(I) ion and a proton to phenylacetylene in methanolic solution at pH ⩾ 12. In contrast, in methanolic solution at pH ⩽ 8 the cobaltate(I) ion is converted into its conjugate acid, hydridobis(dimethylglyoximato)cobalt(III), and this adds stereospecifically [4] *cis* to phenylacetylene to give α-styrylbis(dimethylglyoximato)cobalt(III) complexes [*e.g.* (V), equation (3)].

$$\begin{matrix}\text{PhCH:CHX} + \text{Co(dmgH)}_2\text{py}^- \xrightarrow{\text{MeOH}} \\ \text{(I) } cis \qquad\qquad \text{PhCH:CH·Co(dmgH)}_2\text{py} + \text{X}^- \\ \text{(II) } trans \qquad\qquad \text{(III) } cis \\ \qquad\qquad\qquad\quad \text{(IV) } trans\end{matrix} \quad (1)$$

$$\begin{matrix}\text{PhC≡CH} + \text{Co(dmgH)}_2\text{py}^- \xrightarrow{\text{MeOH}} \\ \qquad\qquad \text{PhCH:CH·Co(dmgH)}_2\text{py} + \text{OMe}^- \\ \qquad\qquad\quad \text{(III)}\end{matrix} \quad (2)$$

$$\begin{matrix}\text{PhC≡CH} + \text{HCo(dmgH)}_2\text{py} \xrightarrow{\text{MeOH}} \\ \qquad\qquad \text{CH}_2\text{:CPh·Co(dmgH)}_2\text{py} \\ \qquad\qquad\quad \text{(V)}\end{matrix} \quad (3)$$

Besides the mechanistic interest of these reactions, the good yields and excellent stereospecificity indicated that they might also be of preparative value in the formation of other *cis*- and *trans*-styryl derivatives, particularly by the reaction of electrophiles with (III)—(V), and possibly also for the stereospecific conversion of other acetylenes to useful vinyl derivatives.

In this paper are described further studies of (i) the mechanism of formation of styrylcobaloximes from *cis*-β-halogenostyrenes and of vinylcobaloxime from vinyl chloride; (ii) the cleavage of styryl- and some related vinyl-cobaloximes by electrophiles; (iii) the scope and character of corresponding reactions starting from acetylenic compounds.

RESULTS

Reaction of Halogenostyrenes with Bis(dimethylglyoximato)-cobaltate(I) Ions.—The products of reaction of *cis*-β-iodo-, -bromo-, -chloro-, and -fluoro-styrene with the bis(di-methylglyoximato)pyridinecobaltate(I) ion in methanolic solution at various temperatures are shown in Table 1. The products were identified by their ^{1}H n.m.r. spectra [2,3] since it has not yet proved possible to separate isomeric cobaloximes. The reactions with β-iodo- and -bromo-styrene were appreciably faster than that with β-chloro-styrene, whereas no reaction could be detected with β-fluorostyrene. It is not possible to continue such reactions for very long periods because of the slow decomposition of the cobaltate(I) ion.

Reaction of Vinyl Chloride with the Bis(dimethylglyoximato)-pyridinecobaltate(I) Ion in Deuteriated Methanol.—Vinyl chloride reacts slowly with the bis(dimethylglyoximato)-pyridinecobaltate(I) ion in alkaline methanolic solution to give vinylbis(dimethylglyoximato)pyridinecobalt(III). When the reaction was carried out in CH_3OD–H_2O (20 : 3 v/v ≡ 10D : 6.5H) the ^{1}H n.m.r. spectrum of the product showed no incorporation of deuterium.

Reactions of Monosubstituted Acetylenes with the Bis-(dimethylglyoximato)cobaltate(I) Ion and with Hydridobis-(dimethylglyoximato)cobalt(III).—The products of reactions of bis(dimethylglyoximato)cobaltate(I)–hydridobis(dimethyl-glyoximato)cobalt(III) mixtures with ethyl propiolate, propargyl acetate, propargyl alcohol, but-3-yn-2-ol, propyne,

[1] G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, 1967, **89**, 1999.
[2] M. D. Johnson and B. S. Meeks, *J. Chem. Soc.* (*B*), 1971, 185.
[3] K. N. V. Duong and A. Gaudemer, *J. Organometallic Chem.*, 1970, **22**, 473.
[4] M. Naumberg, K. N. V. Duong, and A. Gaudemer, *J. Organometallic Chem.*, 1970, **25**, 231.

TABLE 1

Products of reaction of the bis(dimethylglyoximato)pyridinecobaltate(I) ion with halogenostyrenes PhCH:CHX

X	Configuration	Reduction [a] method	[OH⁻] [b]/M	T/°C	t/h	Products	Total yield (%)	Isomeric purity (%)[c]
I	*cis*	1	0.23	45	2	PhCH:CHCo(dmgH)$_2$py	53	100 *cis*
Br	*cis*	1	0.23	45	12	PhCH:CHCo(dmgH)$_2$py	67	100 *cis*
Br	*cis* [d]	2	0	Ambient	3	PhCH:CHCo(dmgH)$_2$py	47	100 *cis*
Br	*trans*	1	0.23	25	4	PhCH:CHCo(dmgH)$_2$py	54	100 *trans* [e]
Br	*trans*	2	0	Ambient	3	PhCH:CHCo(dmgH)$_2$py	49	100 *trans*
Cl	*cis*	1	0.23	45	12	PhCH:CHCo(dmgH)$_2$py	5	40 *cis*, 60 *trans*
F	*cis*	1	0.23	45	12	None		100 *cis* [g]
F	*cis*	1	0.23	70	5	None		100 *cis* [g]
F	*cis*	3	0	45	12	None		100 *cis* [g]

[a] Method 1 = alkaline disproportionation of Co^{II}(dmgH)$_2$py; method 2 = reduction of ClCo^{III}(dmgH)$_2$py by borohydride ion; method 3 = reduction of Co^{II}(dmgH)$_2$py by borohydride ion. [b] Excess of alkali over that required for stoicheiometric formation of cobalt(I). [c] Based on analysis of ^{1}H n.m.r. spectrum; see ref. 1 for details. [d] From ref. 2. [e] *ca.* ⩽3% Isomerisation of starting halide detected in recovered halide; see ref. 1. [f] Assignment of the 3% *trans*-isomer is based solely on observation of the dimethylglyoximato-resonance which might be of that isomer; recovered halide is 100% *cis*; some styrene (*ca.* 10%) also formed. [g] Purity of recovered unchanged halide.

TABLE 2

Products of reaction of acetylenes R^{1}C≡CR^2 (0.01 mol) with the bis(dimethylglyoximato)pyridinecobaltate(I) ion in aqueous methanol (*ca.* 200 ml)

R^1	R^2	[OH⁻]/10^{-2}M	T/°C	t/h	Overall yield (%)	Product composition (% of total) *cis*-RCH:CH(Co) [a]	CH_2:CR(Co) [a]	Other
EtO·CO	H	2.5	0	0.1	60	100 [b,c]	*d*	*d*
$HOCH_2$	H	0 [e]	Ambient	18		50 [b]	50 [b]	*d*
$HOCH_2$	H	2.5 [f]	40	4	50	60	40	*d*
$HOCH_2$	H	3.4 [g]	40	3.5	45	70	30	*d*
$HOCH_2$	H	5.0 [h]	40	2.5	30	85	15	*d*
$AcOCH_2$	H	2.5	40	4	42	70 [i]	30 [i]	*d*
HOCH(Me)	H	2.5	40	4	30	90	*d*	*d*
Me	H [k]	2.5	20	24	10	*d*	100 [l]	*d*
Ph	Br	2.5	0	0.3	60	*d*	*d*	PhC≡C·Co(dmgH)py [m]
EtO·CO	Me	3.0 [f]	Ambient	0.6—24	~35	*n*	*d*	EtOCOCH$_2$C(=CH$_2$)(Co) [n,p]

[a] (Co) = Co(dmgH)$_2$py. [b] Previously prepared and analysed but not characterised.[1] [c] In ethanol; methyl ester in methanol gives similar result.[2] [d] None evident in ^{1}H n.m.r. of crude product. [e] In the presence of an excess of BH_4^-. [f] *ca.* pH 9. [h] *ca.* pH 10. [h] *ca.* pH 11. [i] Hydrolysis of AcO to HO takes place totally. [j] Found; C, 46.4; H, 6.1; N, 15.8. $C_{17}H_{26}N_5O_5Co$ requires C, 46.5; H, 6.0; N, 15.9%. [k] Using an excess of MeC≡CH gas, yield based on cobalt. [l] Also formed, in 60% yield, from allene (Found: C, 46.8; H, 6.0; N, 17.3 $C_{16}H_{24}N_5O_4Co$ requires C, 46.9; H, 5.9; N, 17.1%). [m] Characterised as the cyano-derivative (tetraphenylarsonium salt).[17] [n] Formed with low reaction times in ethanol. [p] Formed with longer reaction times in ethanol; previously analysed as mixture with other isomer;[4] methyl esters formed in methanol.

TABLE 3

Products of reaction of vinylmetal complexes (RCH:CHM and CH_2:CRM) with electrophiles in acetic acid

R	M	Configuration	Electrophile	Products [yield (%)]	
(a) RCH:CHM					
Ph	Co(dmgH)$_2$py	*cis*	Cl_2	*cis*-PhCH:CHCl [Q] [a]	
Ph	Co(dmgH)$_2$py	*cis*	Br_2	*cis*-PhCH:CHBr [Q]	
Ph	Co(dmgH)$_2$py	*cis*	I_2	*cis*-PhCH:CHI [Q] [b]	
Ph	Co(dmgH)$_2$py	*cis*	$Hg(OAc)_2$	*cis*-PhCH:CHHgOAc [81] [c,d]	
Ph	Co(dmgH)$_2$py	*trans*	Cl_2		*trans*-PhCH:CHCl [Q]
Ph	Co(dmgH)$_2$py	*trans*	Br_2		*trans*-PhCH:CHBr [Q]
Ph	Co(dmgH)$_2$py	*trans*	I_2		*trans*-PhCH:CHI [Q]
Ph	Co(dmgH)$_2$py	*trans*	$Hg(OAc)_2$		*trans*-PhCH:CH·HgOAc [78] [c,e]
EtOCO	Co(dmgH)$_2$py	*cis*	Br_2	*cis*-RCH:CHBr [30]	*trans*-RCH:CHBr [70] [f]
EtOCO	Co(dmgH)$_2$py	*cis*	I_2	*cis*-RCH:CHI [50]	*trans*-RCH:CHI [50] [f]
Ph	HgCl	*cis*	Cl_2	*cis*-PhCH:CHCl [95]	*trans*-PhCH:CHCl [5]
Ph	HgCl	*cis*	Br_2	*cis*-PhCH:CHBr [98]	*trans*-PhCH:CHBr [2]
Ph	HgCl	*cis*	I_2	*cis*-PhCH:CHI [99]	*trans*-PhCH:CHI [1]
Ph	HgCl	*trans*	Cl_2	*cis*-PhCH:CHCl [10]	*trans*-PhCH:CHCl [90]
Ph	HgCl	*trans*	Br_2	*cis*-PhCH:CHBr [12]	*trans*-PhCH:CHBr [88]
Ph	HgCl	*trans*	I_2	*cis*-PhCH:CHI [10]	*trans*-PhCH:CHI [90]
(b) CH_2:CRM					
Ph	Co(dmgH)$_2$py		Cl_2	RCCl:CH_2 [f,h]	
Ph	Co(dmgH)$_2$py		Br_2	RCBr:CH_2 (47) [g]	
Ph	Co(dmgH)$_2$py		I_2	RCI:CH_2 (50) [g]	

[a] Q = only one product detected in crude product. [b] Unstable in light. [c] Isolated as chloro-derivative. [d] Found: C, 28.7 H, 2.3. C_8H_7ClHg requires C, 28.3; H, 2.1. [e] Found; C, 28.6; H, 2.2%. [f] Identified from ^{1}H n.m.r., not isolated. [g] Low yield, starting material recovered partially. [h] Some acetophenone also formed.

and allene in aqueous alcoholic solution are shown in Table 2. Some related reactions of propargyl alcohol have already been reported [3] and are included in Table 2. Two disubstituted acetylenes were also studied, namely 1-bromo-2-phenylacetylene and ethyl but-2-ynoate.

The product from the last reaction in ethanol solvent varied with the time allowed for the reaction. At pH 8—9, the initial product was mainly that of a *trans*-addition of cobalt(I) to C-2 and a proton to C-3; but increasing amounts of the rearranged product, bis(dimethylglyoximato)-(1-ethoxycarbonylmethylvinyl)cobalt(III) were formed with longer reaction times. Similar mixtures were also formed in the corresponding reaction of the mixture of cobaltate(I) and hydridocobalt(III) species with ethyl 2-chlorocrotonate, but when the same reactions were carried out in methanolic solution, the main product was the corresponding mixture of methyl esters of normal and rearranged products. Hydrolysis of the ester function in the presence of the cobalt species also took place in the reaction of propargyl acetate in aqueous methanol.

Reaction of Substituted Vinylbis(dimethylglyoximato)-pyridinecobalt(III) *Complexes with Mercury*(II) *and Thallium*-(III) *Complexes*.—The products of reaction of *cis*- and of *trans*-β-styrylbis(dimethylglyoximato)pyridinecobalt(III) with mercury(II) acetate in pure acetic acid at room temperature in the dark, isolated after addition of an excess of chloride ion, are shown in Table 3. In view of the insolubility of *trans*-β-styrylchloromercury(II) in most solvents, its stereochemistry was deduced from (a) the formation of predominantly *trans*-β-iodostyrene by reaction with iodine and (b) the isolation of the corresponding *cis*-isomer which gave *cis*-β-iodostyrene. No styrylmercury(II) derivative could be obtained from the corresponding reaction of 1-methylvinyl- or α-styryl-bis(dimethylglyoximato)pyridinecobalt(III), during which reactions metallic mercury was deposited. Similarly, no organothallium(III) complexes could be obtained from the corresponding reactions of either α- or β-styrylcobaloximes with thallium(III) acetate in acetic acid; however, the reduced yellow species, presumed to be Tl_2Cl_4, was obtained from the products of these reactions after addition of an excess of chloride ion.[5]

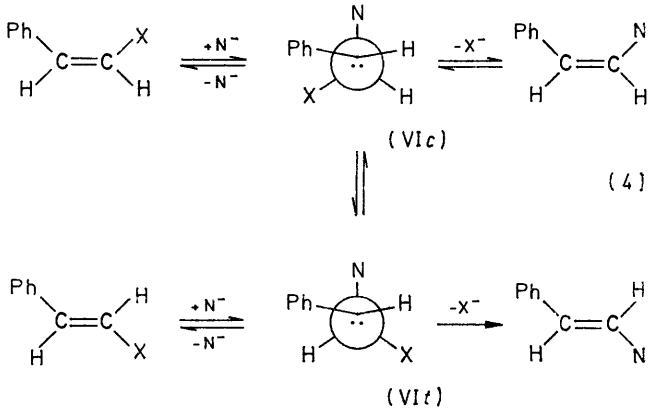
Reactions of Substituted Vinylmetallic Complexes with Halogens.—(a) *Styrylbis(dimethylglyoximato)pyridinecobalt*-(III) *complexes*. The organic products from the reaction of styrylbis(dimethylglyoximato)pyridinecobalt(III) complexes with bromine, chlorine, and iodine in the dark at room temperature are shown in Table 3. The green (hal = Cl or Br) or brown (hal = I) inorganic products, believed to be the corresponding halogenodimethylglyoximatodimethylglyoximecobalt(III) complexes [6] $(hal)_2(dmgH)(dmgH_2)Co$, where $dmgH_2$ represents dimethylglyoxime and dmgH is its conjugate base, were not investigated in detail. Several of the organic products, particularly β-iodostyrene, were unstable in light.

(b) *Styrylchloromercury*(II) *complexes*. The organic products of reaction of *cis*- and *trans*-β-styrylchloromercury-(II) with chlorine, bromine, and iodine, in the dark at room temperature, in acetic acid solution, are shown in Table 3.

(c) *(2-Ethoxycarbonylvinyl)bis(dimethylglyoximato)pyridinecobalt*(III). The organic products of reaction of (2-ethoxycarbonylvinyl)bis(dimethylglyoximato)cobalt(III) with bromine and with iodine are shown in Table 3.

DISCUSSION

Mechanism of Formation of Styrylbis(dimethylglyoximato)pyridinecobalt(III) *Complexes from* cis-*Halogenostyrenes*.—β-Halogenostyrenes are normally very resistant to substitution by nucleophiles [7] and prefer to react by routes other than direct substitution. The more reactive weakly basic nucleophiles, such as the benzenethiolate ion, react with activated halogenostyrenes, such as 4-nitro-β-halogenostyrenes, at elevated temperatures by an addition–elimination mechanism in which the addition of the nucleophile to the β-carbon precedes, or is almost synchronous with, the loss of the halide ion from that carbon atom [8] [equation (4)]. Where loss of halide



ion is synchronous with attack of the nucleophile or takes place prior to rotation about the carbon–carbon bond in an intermediate carbanion (VI*c* or *t*), then the reaction is stereospecific, but if rotation can occur either prior to the loss of the halide ion or of the attacking nucleophile, then the product formation is not stereospecific and isomerisation of the starting styryl halide may also be observed.[7] The reactions of the bis(dimethylglyoximato)cobaltate(I) ion with *cis*-β-iodo- or -bromo-styrene in methanol at 45° are several orders of magnitude faster than those of the reactive conventional nucleophiles and are also completely stereospecific; no isomerisation is observed in either reagent or product. However, whereas the rate of reaction of the benzenethiolate and other similar nucleophiles with *cis*-4-nitro-β-halogenostyrenes * decreases in the order Br < Cl < F indicating that the transition state involves very little carbon–halogen bond cleavage, the rate of the reaction of the bis(dimethylglyoximato)cobaltate(I) ion with the halogenostyrenes decreases in the reverse order, *i.e.* I ⩾ Br ⩾ Cl > F, no reaction being observed with

* In the reaction of thiolate ion with *cis*-4-nitro-β-fluorostyrene [8] the main product is the corresponding *trans*-olefin, indicating that not only is little bond-breaking involved in the transition state, but that the intermediate adduct (VI*c*) has a significant lifetime during which rotation about C_α–C_β can occur.

[5] D. H. Ballard, D. Dodd, and M. D. Johnson, unpublished observations; J. H. Espenson, personal communication.

[6] 'Gmelins Handbuch', Verlag-Chemie, Syst. No. 58, Part B2, 1964, pp. 713—716.

[7] Z. Rappoport, *Adv. Phys. Org. Chem.*, 1969, **7**, 1.

[8] G. Marchese, F. Naso, and G. Modena, *J. Chem. Soc.* (*B*), 1969, 290.

cis-β-fluorostyrene even under reflux over long periods. Such a reversal of the reactivity sequence is not uncommon in nucleophilic displacements of aromatic, particularly naphthyl,[9] halides and indicates that, in the sequence here in which the fluoride is the least reactive, the degree of carbon–halogen bond breaking in the transition state must be appreciable. Moreover, as no isomerisation of the recovered fluorostyrene is observed, a long lived intermediate similar to (VI*c*) is not formed reversibly, and the reaction must involve effectively synchronous cleavage of the carbon–halogen bond and formation of the carbon–cobalt bond.

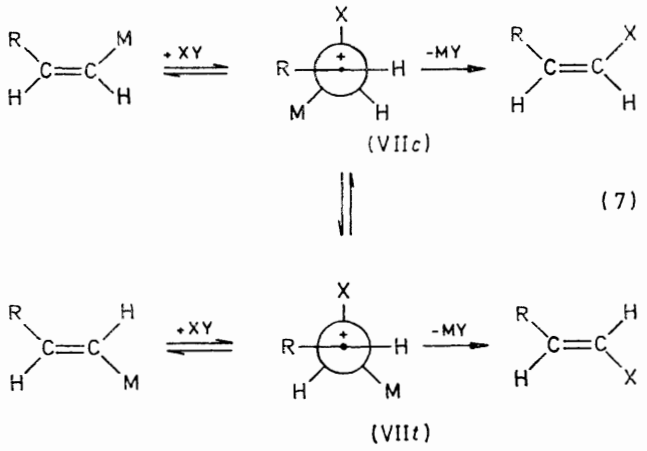
An initial co-ordination of the reagent olefin to the cobaltate(I) ion cannot be ruled out. Any such complex may be either irrelevant to the reaction path leading to products or an intermediate which rearranges to products with synchronous loss of halide ion, not *via* intermediates of comparable 'open' structure to (VI). Such co-ordination is, however, not inconsistent with the observed retention of configuration.[10]

The low yield of *cis*-styrylbis(dimethylglyoximato)-pyridinecobalt(III) from *cis*-chlorostyrene was confirmed by t.l.c., but, since we have not yet been able to separate isomeric organocobaloximes by chromatography we cannot rule out that there may also have been traces of the *trans*-isomer in this product (Table 1). However, since appreciable quantities of styrene were also recovered from the reaction mixture, it seems likely that this result is an artifact of the long reaction time and elevated temperature allowing the incursion of other, possible free radical, reactions [*e.g.* reactions (5) and (6)]. Using shorter reaction times, only traces of styrylcobaloximes could be obtained.

$$PhCH{:}\dot{C}H\cdot + HCo(dmgH)_2py \longrightarrow PhCH{:}CH_2 + Co(dmgH)_2py \quad (5)$$

$$PhCH{:}\dot{C}H\cdot + Co(dmgH)_2py \longrightarrow PhCH{:}CH\cdot Co(dmgH)_2py \quad (6)$$
(III) and (IV)

Stereochemistry of the Reaction of β-*Styrylbis(dimethylglyoximato)pyridinecobalt*(III) *with Electrophiles.*—(a) *Halogenation.* The reactions of both *cis*- and *trans*-β-styrylbis(dimethylglyoximato)pyridinecobalt(III) with chlorine, bromine, and iodine in pure acetic acid are completely stereospecific and proceed in quantitative yield. This contrasts with the corresponding reactions of the primary alkylcobaloximes which not only give poor yields of the alkyl halide, but probably proceed by a mechanism which does not involve a direct electrophilic attack at the α-carbon atom.[5] The high yield and stereospecificity in the case of the styryl derivatives indicates that these reactions do involve a direct addition–elimination displacement of cobalt by attack of the halogen at the β-carbon atom (β to the phenyl group) and that no effective rotation takes place in the two conformations of any intermediate adduct that may be formed [(VII*c* and *t*; X = Y = Cl, Br, or I, R = Ph) equation (7)]. In view of the high yield in these reactions and the ready synthesis of the *cis*-β-styryl complex from phenylacetylene, these pair of reactions provide the best available method for the synthesis of *cis*-β-chloro-, -bromo-, and -iodo-styrene, of which only the latter had not been described.



Unfortunately, the reaction is limited in scope; not only do the reactions of several other acetylenes with cobaltate(I) ions give more than one organocobalt(III) product (see below) or even rearranged organocobalt(III) products, but in some of those cases where a single stereochemically pure vinylcobalt(III) complex is formed, the halogenation step is not stereospecific. For example, though only *cis*-(2-alkoxycarbonylvinyl)cobaloxime is formed from alkyl esters of propiolic acid, the former reacts with bromine and iodine to give almost equal yields of *cis*- and *trans*-1-alkoxycarbonyl-2-halogenoethylene. Either rotation of an intermediate addition product (VII*c*; R = EtOCO, X = Y = Br or I) takes place very readily or, more likely, a free radical halogen addition readily intrudes.

(b) *Mercuriation.* The corresponding reactions of *cis*- and *trans*-styrylbis(dimethylglyoximato)pyridinecobalt(III) with an excess of diacetatomercury(II) in pure acetic acid are also stereospecific. However, under some conditions, notably in less pure acetic acid, appreciable loss of stereospecificity was observed and is attributed to the incursion of a free radical reaction. Attempts to prepare di-(*cis*-β-styryl)mercury(II) using one-half an equivalent of mercury(II) reagent were unsuccessful, probably because of the longer reaction time necessary. The mechanism of the stereospecific reaction is probably similar to that described for the halogens [equation (7; X = HgOAc, Y = OAc)].

Reaction of α-*Styrylcobaloxime with Electrophiles.*—Attempts at the preparation of α-styrylacetato- and -chloro-mercury(II) compounds by the reaction of diacetatomercury(II) with α-styrylbis(dimethylgly-

[9] S. D. Ross, *Progr. Phys. Org. Chem.*, 1963, **1**, 31.
[10] J. Rajaram, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1974, **96**, 2103.

oximato)pyridinecobalt(III) were unsuccessful. Even with long reaction times appreciable amounts of the unchanged organocobalt(III) complex could be recovered and some mercury metal was deposited. This deposition of mercury is typical of a reaction in which mercury(II) behaving as an oxidising agent to the organometallic complex forms mercury(I) in the presence of pyridine; the latter catalyses the disproportionation of the mercury(I) to mercury(II) and mercury(0) which precipitates.[11] Such oxidative reactions are not unexpected in view of the fact that electrophilic attack at the α-carbon is much more sterically hindered than that at the β-carbon of the β-styrylcobalt(III) complexes, and the alternative oxidation processes may well be favoured. A similar change from direct displacement of cobalt to an oxidative reaction at cobalt is also evident on changing from primary to secondary alkylbis(dimethylglyoximato)-cobalt(III) substrates with both mercury(II) reagents and halogens.[5] It is not surprising therefore that only poor yields of α-halogenostyrenes are formed in the corresponding reaction with halogens, and that no α-styrylthallium(III) complexes are observed when the more powerfully oxidising thallium(III) reagents are used. In the case of the reaction of chlorine with α-styrylbis(dimethylglyoximato)pyridinecobalt(III), the recovered styrylcobalt(III) complex contained traces of a second complex which, from its n.m.r. spectrum, may have been the chlorine adduct $ClCH_2CPh(Cl)Co(dmgH)_2$-py. Unfortunately we have been unable to separate these two organocobalt complexes.

Stereochemistry of the Reaction of β-Styrylchloromercury(II) with Halogens.—The reaction of *cis*-β-styrylchloromercury(II) with chlorine, bromine, and iodine in acetic acid is almost completely stereospecific, giving the corresponding *cis*-halogenostyrene in almost quantitative yield. However, the reaction of *trans*-β-styrylchloromercury(II) with these halogens is not only slower than that of the *cis*-isomer, but is markedly less stereospecific. Such loss of stereospecificity as a result of isomerisation to the *less* stable isomer is indicative of a process which involves an intermediate which does not discriminate significantly between the two possible products, and can be ascribed, as above, to the incursion of a free radical process in which the styryl radical is formed [equation (8)]. This provides further confirmation of the clean heterolytic character of the halogenation of the styrylcobaloximes but, in view of the known homolytic reactions of other organocobaloximes,[5,11] suggests that homolytic mechanisms may readily intrude with only slight modification of the reaction conditions.

$$PhCH{:}CH\cdot + X_2 \longrightarrow PhCH{:}CHX + X\cdot \quad (8)$$

The formation of both *cis*- and *trans*-halogenostyrenes in the free radical halogenation of styrylmercury(II) complexes has been observed previously [12] and would be expected to intrude in our case with the reaction of the less reactive *trans*-styrylchloromercury(II) isomer. However, even in this case, the main reaction clearly involves a direct electrophilic attack of the halogen molecule on the β-carbon in a manner similar to that shown in equation (7; R = Ph; X = Y = Halogen; M = HgCl) but without significant isomerisation of any intermediate corresponding to (VII*c* or *t*).

Stereochemistry of Reactions of Acetylenes with the Bis(dimethylglyoximato)cobaltate(I) ion and with Hydridobis(dimethylglyoximato)cobalt(III) Species.—Of the reactions studied in this and related work,[2-4] only two monosubstituted acetylenes, namely alkoxycarbonylacetylenes and 3,3,3-trifluoropropyne have given solely the *cis*-β-substituted vinylcobaloximes under the various conditions studied involving solutions of different pH. In contrast, using suitably alkaline or neutral solutions, the reaction of phenylacetylene has been shown to give pure *cis*-β- or pure α-styrylcobaloxime, respectively. With propargyl alcohol ($HOCH_2C{\equiv}CH$) both *cis*-β- and -α-substituted vinylcobaloximes were obtained under a variety of conditions and with propyne only the α-substituted product was obtained.

These variations in product composition can be readily rationalised if the rate of reaction of the hydridobis(dimethylglyoximato)cobalt(III) species is relatively independent of the nature of the acetylenic substituent and the rate of reaction of the cobaltate(I) species is significantly influenced by that substituent. The former is a reasonable assumption in view of the detailed studies of the reaction of the closely related hydridopentacyanocobaltate(III) ion with various olefins,[13] and the latter is not only a reasonable assumption for the proposed two step addition of the cobaltate(I) ion [equation (2)], but is supported by the short reaction times needed for reaction with the ethoxycarbonylacetylene and 3,3,3-trifluoropropyne, and the slow reaction of propyne. The shift in favour of the *cis*-β-substituted product in the case of 3-hydroxybut-1-yne is probably a steric effect acting selectively on the addition of the hydridocobalt(III) species.

The rearrangement product observed in the reaction of methyl but-2-ynoate is also consistent with this general mechanism. Thus, the initial product formed on addition of the cobaltate(I) ion and a proton would be expected to be the vinylcobaloxime (VIII) [equation (9)]. Reversible loss of cobaltate(I) ion and a proton, or of hydridocobalt(III) directly, is a well established process [14] and in this case would either regenerate the starting acetylene or yield the new allene (IX) [equation (10)]. Further addition of the cobaltate(I) ion and a proton to this allene would be expected, from the stereochemistry of addition to allene itself (Table 2) to give the observed rearranged isomer (2) [equation (11)].

[11] M. D. Johnson and J. Z. Chrzastowski, unpublished observations.

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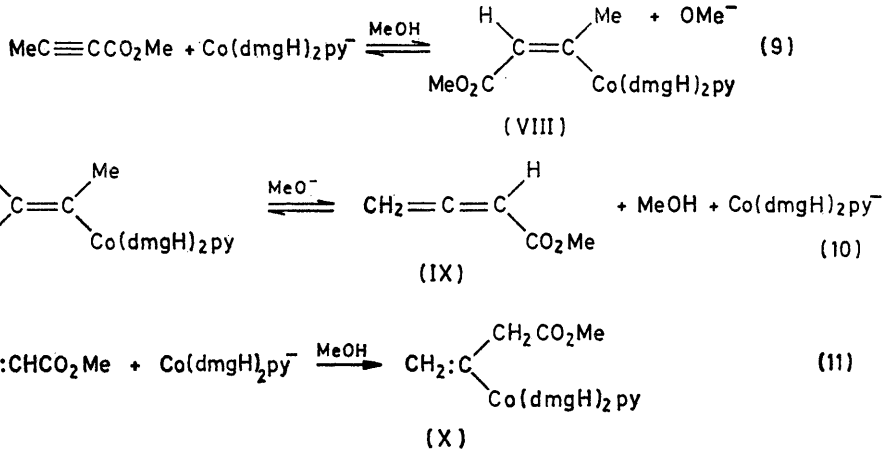

EXPERIMENTAL

Materials.—Methan[^{2}H]ol, cobalt chloride hexahydrate, dimethylglyoxime, acetic acid (B.D.H. AristaR), phenylacetylene, propargyl alcohol, ethyl propiolate, phenylpropiolic acid, ethyl but-2-ynoate, propargyl bromide, propyne, and allene were commercial materials shown to be sufficiently pure by ^{1}H n.m.r. and used without further purification. Fluoroacetamide was kindly supplied by Rentokil Ltd.; but-3-yn-2-ol was a 70% aqueous solution (Emanuel) used directly. *cis*-β-Iodo-, -β-bromo-, and -β-chloro-styrene were prepared from phenylacetylene *via* cis-β-styrylbis(dimethylglyoximato)pyridinecobalt(III) as described below. *cis*-β-Fluorostyrene was prepared from benzaldehyde and methyl fluoroacetate by the method of Elkik.[15] Methyl fluoroacetate was prepared by direct esterification of fluoroacetamide. Propargyl acetate was prepared by the esterification of propargyl alcohol. 1-Bromo-2-phenylacetylene was prepared by the bromination of phenylacetylene in alkaline solution.[16]

Formation of Organocobalt(III) *Complexes.*—The reaction of the bis(dimethylglyoximato)pyridinecobalt(I) ion with phenylacetylene, with halogenostyrenes, with other monosubstituted acetylenes, and with allene were carried out under conditions similar to those described previously,[2-4] using the concentrations, reaction times, and temperatures shown in Tables 1 and 2. The product solutions were evaporated to less than half their original volume and poured into water. The crude organocobalt(III) product was filtered off, washed with water, dried *in vacuo*, and investigated without further purification by ^{1}H n.m.r. In some cases extraction by ether or methylene chloride was also used to obtain the last traces of less soluble material. Where more than one isomer was present, the proportions of the isomers were determined from the spectra and elemental analyses, where relevant, were carried out on the mixture.

Mercuriation of Organocobalt(III) *Species.*—To a stirred suspension of the styrylcobalt(III) complex (0.01 mol) in acetic acid (20 ml; AristaR) was slowly added a solution of mercury(II) acetate in acetic acid (81 ml; 4%) over 20 min. After a further 10 min the solution was poured into saturated aqueous sodium chloride solution (100 ml). The precipitate was filtered off, washed with water, and dried *in vacuo*. The crude product was examined by ^{1}H n.m.r. and recrystallised from acetone–water. Yields are shown in Table 3. The absence of *cis*-styrylchloromercury(II) in the crude product from the reaction of the *trans*-β-styrylcobalt(III) complex was clearly shown by extracting the crude *trans*-β-styrylchloromercury(II) with deuteriochloroform in which the *cis*-isomer is much the more soluble. No *cis*-isomer could be detected in the extract. Reactions of α-styrylcobalt(III) with mercury(II) and with thallium(III) were carried out in a similar manner, but no organo-mercury(II) or -thallium(III) products could be detected.

Halogenation of Organo-cobalt(III) *and -mercury*(II) *Complexes.*—To a stirred solution or suspension of the organocobalt(III) or organomercury(II) complex (0.001 mol) in acetic acid (10 ml) was added a solution of the halogen (0.001 1 mol) in acetic acid (40 ml) over *ca.* 20 min. After a further 15 min the solution was filtered, any precipitate was washed with a little acetic acid, and the filtrate was poured into water (200 ml). This solution was extracted with light petroleum (b.p. 40°), which was washed with 5% aqueous sodium hydrogen carbonate and dried (Na_2SO_4). The solvent was partially evaporated and the final 1 ml of solution was examined by ^{1}H n.m.r. In the case of the halogenation of *cis*-β-styrylcobaloxime with chlorine and with iodine, the reaction was also carried out using five times the above volumes and twice the above concentrations without change in the products. The product halogenostyrenes were purified by distillation, though some decomposition of the *cis*-β-iodostyrene occurred during distillation (Found: C, 40.1; H, 3.1. C_8H_7I requires C, 41.8; H, 3.1%). In those cases where isomeric mixtures of halogenostyrenes were formed, the proportions and configuration were determined from the ^{1}H n.m.r. spectra and no further attempts were made at purification.

Formation of Vinylcobaloxime from Vinyl Chloride.—Cobalt chloride hexahydrate (474 mg, 2×10^{-3} mol) and dimethyl glyoxime (464 mg, 4×10^{-3} mol) were added to methan[^{2}H]ol (10 ml). The suspension was stirred under nitrogen and pyridine (0.15 ml) and sodium hydroxide (0.50 ml, 8M) were added. The solution was saturated with vinyl chloride and sodium hydroxide (1.2 ml, 4M) was added. The measured pH was *ca.* 10. After 30 min the solution was poured into water and the vinylcobaloxime was extracted with ether. The extract was dried (Na_2SO_4) and evaporated to dryness. The ^{1}H n.m.r. spectrum of the crude product showed only normal resonances of undeuteriated vinyl-cobaloxime.

^{1}H *N.m.r. Spectra.*—All were taken in $CDCl_3$ (chemical shifts in δ, *J* in Hz). For α-, *cis*-β and *trans*-β-styryl-

[15] E. Elkik, *Bull. Soc. chim. France*, 1964, 2258.
[16] F. Straus, L. Kollek, and W. Heyn, *Ber.*, 1930, **63**, 1868.
[17] D. Dodd and M. D. Johnson, *J.C.S. Dalton*, 1973, 1218.

cobaloximes, see refs. 2 and 3; 2-ethoxycarbonylvinylcobaloxime, ref. 2; α- and *cis*-2-(hydroxymethyl)vinylcobaloxime, ref. 2; *cis*- and *trans*-chloro-, -bromo-, and -iodostyrenes, ref. 18. *cis*-1-Bromo-2-ethoxycarbonylethene showed δ 8.29 and 5.61 (:CH, *J* 12.8); *trans*-1-bromo-2-ethoxycarbonylethene, δ 7.52 and 6.44 (:CH, *J* 14); *cis*-1-ethoxycarbonyl-2-iodoethene δ 7.46 and 6.89 (:CH, *J* 9.2); *trans*-1-ethoxycarbonyl-2-iodoethene, δ 7.87 and 6.89 (:CH, *J* 15.0); *cis*-β-fluorostyrene, δ 6.55 (α-CH) and 4.60 (β-CH) ($J_{\alpha,F}$ 44.4, $J_{\beta,F}$ 78.6); *cis*-β-styrylchloromercury(II) δ 7.63 (α-CH) and 6.15 (β-CH) (*J* 10.8); *trans*-β-styrylchloromercury(II) δ (DMSO) 7.04 (α-CH) and 6.97 (β-CH); *cis*-3-hydroxybut-1-enylcobaloxime δ 5.18 (1-H), 6.12 (2-H *J* 7.5), 4.6 (3-H, $J_{2,3}$ 7.5), 1.14 (4-H_3, $J_{3,4}$ 6), and 2.12 (dmgH); 2-ethoxycarbonylprop-1-enylcobaloxime, δ 6.39 (1-H), 8.3 (3-H, *J* 1.5), and 2.17 (dmgH); 2-ethoxycarbonylprop-2-enylcobaloxime, 4.91 (*J* 1) and 4.36 (q) (both 3-H_2), 2.97 (1-H_2, *J* 1.5), 1.95 (dmgH); 1-methylvinylcobaloxime, 4.62 and 4.28 (*J ca.* 1) (both CH_2), 1.60 (CH_3), and 2.08 (dmgH); α-chloro-, -bromo-, and -iodo-styrene, δ 5.64 and 5.40 (CH); 6.00 and 5.68 (CH); and 6.64 and 6.01 (CH), respectively.

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