Homolytic Displacements at Carbon Centres. Part 1.[1] Reaction of Allyl- and Allenyl-cobaloximes with Polyhalogenomethanes

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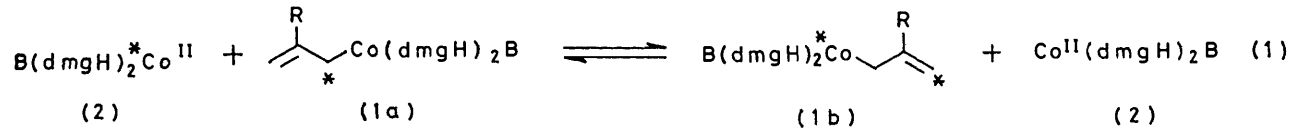
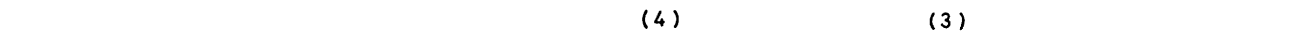
Allyl- and allenyl-cobaloximes react with bromotrichloromethane to give 4,4,4-trichlorobutene and 4,4,4-trichlorobutynes, respectively, and bromocobaloxime(III). The reactions of the allylcobaloximes, carried out at room temperature, are nearly quantitative, but those of the allenylcobaloximes, performed at higher temperatures, are dependent upon the nature of the allenyl group and of the other axial ligand; the yield of trichlorobutyne is appreciably higher with imidazole than with pyridine as the axial ligand, and decreases with increasing substitution on the allenyl ligand. The reactions are believed to involve novel chain processes in which the chain-carrying trichloromethyl radical, formed by the reaction of cobaloxime(II) with the bromotrichloromethane, attacks regiospecifically at the γ-carbon of the allyl or allenyl ligand to displace the other chain propagating species, cobaloxime(II), and give the observed organic product. Since cobaloxime(II) neither dimerises nor disproportionates under these conditions, two important chain terminating steps are eliminated. The main side reaction with allenylcobaloximes involves the formation of the corresponding acetylenic hydrocarbon, the additional hydrogen atom being derived from the dimethylglyoximato hydroxy group, probably as a consequence of attack of the trichloromethyl radical on the metal. The application of the reaction to other polyhalogenomethanes and related radical precursors is also demonstrated.

In a previous paper [2] we described the dynamic character of certain allylcobaloximes in solution; in $CDCl_3$ solution a rapid interchange between two σ-bonded species, *e.g.* (1a and b) takes place, in some cases at a rate sufficient to cause coalescence in the ^1H n.m.r. spectra at room temperature. One of the mechanisms involved was shown to be bimolecular homolytic displacement of a paramagnetic bis(dioximato)cobalt(II) species by attack



of a similar bis(dioximato)cobalt(II) species on the γ-carbon of the σ-allyl group [*e.g.* equation (1)].

In principle, therefore, the removal of all traces of cobalt(II) from the system should eliminate or greatly reduce the dynamic character, depending upon the importance of this mechanism. A common method for the removal of cobaloxime(II) has involved the addition of bromotrichloromethane which reacts with cobaloxime(II) according to equation (2) to give the diamagnetic products (3) and (4), and we have frequently utilised this method successfully to improve the resolution of ^1H n.m.r. spectra of alkyl- and vinyl-cobaloximes. However, on addition of bromotrichloromethane to solutions of allylcobaloximes, we obtained erratic behaviour. In a typical experiment, there would be a preliminary improvement in resolution, lasting for from a few seconds to a few minutes, and then the spectrum would rapidly change and precipitation of bromocobaloxime(III) (3) would occur with the formation, in solution, of 4,4,4-trichlorobutenes. Since it seemed likely that trichloromethyl radicals were involved in the formation of the trichlorobutenes, and there are very few examples in the literature of homolytic displacements at carbon,[3] it was of interest to study this reaction in more detail.

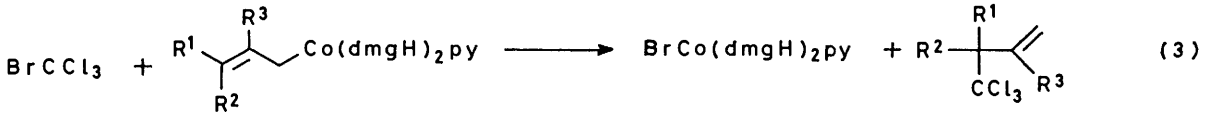


In this paper are described studies of the reaction of a number of allyl- and allenyl-cobaloximes with bromotrichloromethane. A mechanism is suggested and the extension of the reaction to other polyhalogenomethanes is also described.

RESULTS AND DISCUSSION

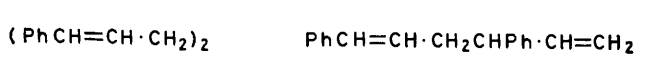
The reaction between allylbis(dimethylglyoximato)-pyridinecobalt(III) (1) (*ca.* 0.5M) and bromotrichloromethane (*ca.* 0.75M) in chloroform or dichloromethane at room temperature under aerobic or anaerobic conditions is subject to an induction period, the length of which depends upon the conditions, including the purity of the substrate. In some cases the reaction starts immediately but in nearly all cases reaction is complete within 20—30 min and bromobis(dimethylglyoximato)-pyridinecobalt(III) (3; B = py) usually precipitates. Pentane extraction of the mother liquor causes further precipitation of (3) but on working up gives 4,4,4-trichlorobut-1-ene (5) as the sole monomeric organic product, in some cases with traces of polymeric material. Similar reactions of 2-methylallyl-, 3-methylallyl-, 3,3-dimethylallyl-, and cinnamyl-bis(dimethylglyoximato)pyridinecobalt(III) (6)—(9) with bromotrichloromethane at room temperature for periods of up to an hour each give bromobis(dimethylglyoximato)pyridinecobalt(III) and the corresponding 4,4,4-trichlorobut-1-ene derivatives (10)—(13), respectively.

When carbon tetrachloride is used as reagent, the reaction is appreciably slower and when the temperature is raised to facilitate reaction, some by-products are formed. For example, with cinnamylcobaloxime (9), some dicinnamyls [4] (14) and (15) are formed in the ratio 1 : 1. The reactions in carbon tetrachloride are accelerated by added dibenzoyl peroxide at the higher temperatures.



(3)

(1)	$R^1 = R^2 = R^3 = H$	(5)
(6)	$R^1 = R^2 = H, R^3 = Me$	(10)
(7)	$R^2 = R^3 = H, R^1 = Me$	(11)
(8)	$R^1 = R^2 = Me, R^3 = H$	(12)
(9)	$R^2 = R^3 = H, R^1 = Ph$	(13)



(14)

(15)

Trichloroacetonitrile and carbon tetrabromide react with the same allylcobaloximes almost as rapidly as bromotrichloromethane giving products (16) and (17), respectively, whereas dibromoacetonitrile, methyl trichloroacetate, and bromoform are successively less reactive, giving predominantly products (18)—(20). Only in the case of the reaction of cinnamylcobaloxime with bromoform is there an appreciable side reaction; the formation of *ca.* 25% cinnamyl bromide. In Table 1 are shown the products with their ^{1}H n.m.r. spectra and other characteristics. Several of these products were fully characterised, but others, isolated in almost pure form by a single pentane extraction from the reaction mixtures, were identified by comparison of the ^{1}H n.m.r. spectra with those of the more fully characterised materials.

TABLE 1

Products of reaction of allylcobaloximes, $RCo(dmgH)_2py$, with polyhalogenomethane reagents

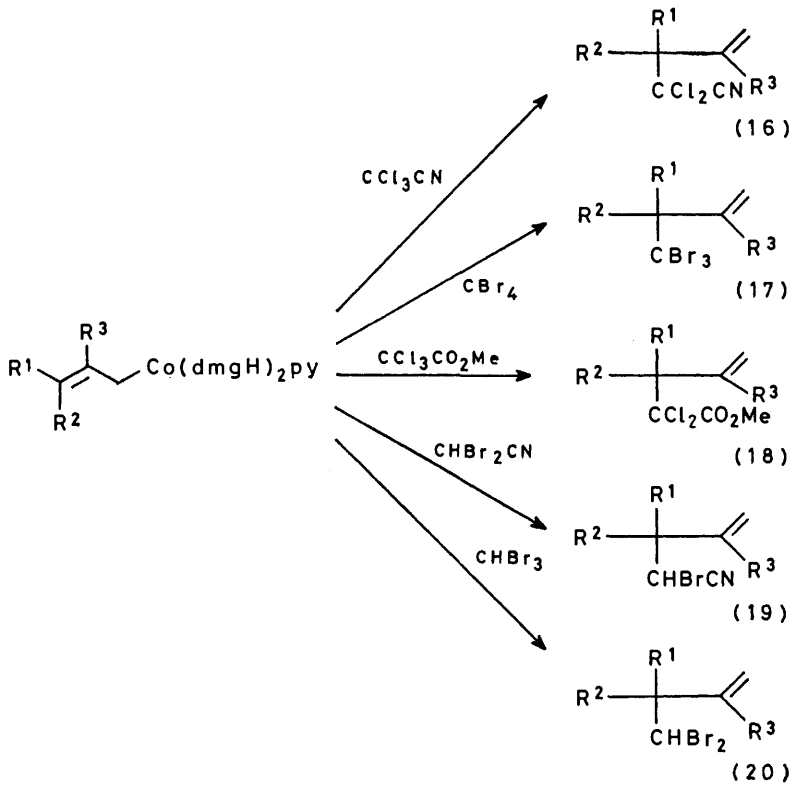
R	Reagent	Product (%) [a]	Found (%) [calc. (%)]	Chemical shift (δ) 1-H	2-H	3-H	Other	J/Hz
$CH_2{:}CH{\cdot}CH_2$	$CBrCl_3$	$Cl_3C{\cdot}CH_2CH{:}CH_2$ (100)	[b]	5.32, 5.37	5.99	3.40		J_{12} 11.0, 16.0; J_{23} 7.9
	CCl_4	$Cl_3C{\cdot}CH_2CH{:}CH_2$ (100)						
	$CHBr_2CN$	$NCCHBr{\cdot}CH_2CH{:}CH_2$ (100)		5.32, 5.38	5.85	2.81	4.32 (4-H)	J_{23} 7.4; J_{34} 7.6
$CH_2{:}CMe{\cdot}CH_2$	$CBrCl_3$	$Cl_3C{\cdot}CH_2CMe{:}CH_2$ (100)	[c]	5.14, 5.20		3.45	2.00 (3′-H)	
	CCl_4	$Cl_3C{\cdot}CH_2CHMe{:}CH_2$ (100)						
$MeCH{:}CH{\cdot}CH_2$	$CBrCl_3$	$Cl_3C{\cdot}CHMe{\cdot}CH{:}CH_2$ (100) [d]	C, 34.6 [34.6]; H, 4.0 [4.1]; Cl, 61.7 [61.3]	5.27, 5.28	5.95	3.21	1.44 (4-H)	J_{12} 9.3, 17.3; J_{23} 7.6; J_{34} 7.0
	CCl_3CN	$NC{\cdot}CCl_2CHMe{\cdot}CH{:}CH_2$ (100) [e]	C, 44.2 [43.9]; H, 4.5 [4.3]; Cl, 43.3 [43.2] [f]	5.36, 5.38	5.86	3.10	1.42 (4-H)	J_{12} 9.1, 17.6; J_{23} 7.5; J_{34} 6.9
$Me_2C{:}CH{\cdot}CH_2$	$CBrCl_3$	$Cl_3C{\cdot}CMe_2{\cdot}CH{:}CH_2$ (100)	C, 38.5 [38.4]; H, 4.25 [4.8]; Cl, 55.5 [56.7]	5.26, 5.27	6.21		1.44 (4-H)	J_{12} 10.5, 17.5
	CCl_3CN	$NC{\cdot}CCl_2CMe_2CH{:}CH_2$ (100)		5.26, 5.32	6.05		1.37 (4-H)	
	$CHBr_3$	$Br_2CH{\cdot}CMe_2CH{:}CH_2$ (>80)		5.15, 5.20	5.96		1.30 (4-H) [g]	
	$CHBr_2CN$	$NCCHBr{\cdot}CMe_2CH{:}CH_2$ (>90)	C, 45.1 [44.7]; H, 5.6 [5.4]; Cl, 41.4 [42.5] [h]	5.23, 5.27	5.88		1.32 (4-H) [i]	J_{12} 9.8, 17.6
$PhCH{:}CH{\cdot}CH_2$	$CBrCl_3$	$Cl_3C{\cdot}CHPh{\cdot}CH{:}CH_2$ (100) [j]	C, 51.2 [50.9]; H, 3.9 [3.85]; Cl, 42.3 [45.2]	5.28, 5.38	6.42	4.29	7.33 (Ph)	J_{12} 9.8, 16.6; J_{23} 8.2
	CCl_4	$Cl_3C{\cdot}CHPh{\cdot}CH{:}CH_2$ (100) [k]						
	CCl_3CN	$NC{\cdot}CCl_2CHPhCH{:}CH_2$ (>90) [k,l]	C, 60.1 [58.4]; H, 4.4 [4.4]; Cl, 31.2 [45.5] [m]	5.60, 5.50	6.46	4.15		
	$CHBr_3$	$Br_2CH{\cdot}CHPh{\cdot}CH{:}CH_2$ (70) [n,p]		5.23, 5.30	6.16	4.01	5.81 (4-H)	J_{12} 10.3, 17.0; J_{23} 8.0; J_{34} 5.8
	CBr_4	$Br_3C{\cdot}CHPh{\cdot}CH{:}CH_2$ (100) [q]	C, 35.2 [32.6]; H, 2.7 [2.5]; Br, 63.1 [65.0]	5.42, 5.56	6.57	4.56		

[a] % Organic product. [b] In refs. 3*c*, 5, and 7. [c] In refs 3*c* and 6. [d] B.p. 38.5 °C at 22 Torr. [e] B.p. 45 °C at 17 Torr. [f] N, 8.6 (8.5). [g] 5-H, δ 5.58 (s). [h] N, 6.4 (7.5). [i] 5-H, δ 4.21 (s). [j] B.p. 120 °C at 16 Torr. [k] Trace dicinnamyl [l] B.p. 70 °C at 0.1 Torr. [m] N, 6.1 (6.2). [n] 30% dicinnamyl. [p] B.p. 80 °C at 0.1 Torr. [q] B.p. 104 °C at 0.1 Torr.

Mechanism.—The nature of the organic products clearly points to a regiospecific attack of trichloromethyl and related polyhalogenomethyl radicals at the γ-carbon of the allyl group, with displacement, either synchronous or subsequent, of the metal as cobaloxime(II) [equation (6)]. Such radicals are known to be formed in the reaction between cobaloxime(II) and polyhalogenomethanes [equation (2)] [8] by the atom abstraction step of equation (5). The nature of the rate enhancement by benzoyl peroxide and the reactivity order $BrCCl_3 \geqslant CBr_4 > CCl_3CCN > CCl_4 \geqslant CCl_3CO_2Me \geqslant CHBr_2CN > CHBr_3$ is also in accord with reaction (5), for it is not only the expected order for atom abstraction, but also the order found in preparative reactions such as those of equations (2) and (10). A combination of equations (5) and (6) thus provides a chain reaction of rather unique character; for one of the chain propagating species, namely $Co^{II}(dmgH)_2B$, is stable in solution under the reaction conditions, undergoing neither dimerisation to any significant degree,[9] nor disproportionation. Two important termination steps are therefore lost and this allows the propagation steps to be of significantly different rates [*i.e.* reaction (5) slow and reaction (6) fast]. The main termination process is therefore the capture of halogenomethyl radicals by cobaloxime(II) [equation (7)],[10] the alternative process of equation (9) being unimportant if the concentration of halogenomethyl radicals is always small. Since the cobaloxime(II) species can be prepared and isolated independently,[11] it may be added to the reaction as a catalyst, though high concentrations of catalyst are not advisable since termination through equation (7) becomes appreciable and the catalyst and halogenomethane are largely diverted to the halogenomethylcobaloxime such as (4).

Initiation may also be achieved by thermolysis or more favourably by photolysis using tungsten lamps,[12] but in many cases the chain length is sufficiently long that the small amount of cobaloxime(II) present as impurity in the reagent is sufficient to promote effectively complete reaction. This is supported by the absence of detectable allyl bromide and the small amounts of hexachloroethane found in the product.

Comparable conclusions involving trichloromethyl and tributyltin radicals as intermediates have recently been drawn by the Bordeaux group [3c] from some reactions of allyl- and substituted allyl-tributyltin compounds with carbon tetrachloride under more forcing conditions [*e.g.* equation (11)] and an earlier precedent is the formation of (5) in low yield from the photochemical reaction of allyl bromide and bromotrichloromethane.[7] However, it is not possible at this stage to establish whether reaction (6) is synchronous or involves a transient intermediate (21). Such an intermediate might react with bromotrichloromethane to give another intermediate (24) which could then eliminate the bromocobaloxime (3) to give the observed organic product [equations (12) and (13)]. However, in view of observations that benzylcobaloximes also react with bromotrichloromethane in an exactly analogous manner [equation (14)], and since no such intermediate can be postulated in that case, the more devious route involving equations (5), (6), (12), and (13) seems less likely than

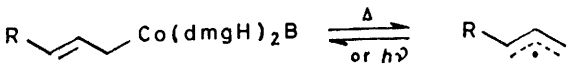


equations (5) and (6) alone. However, since no β-bromoethylcobaloximes comparable with (24) have been characterised, it is difficult to test this hypothesis with the allylcobaloximes.

The close similarity between these free radical reactions of such different allyl complexes, *i.e.* of cobalt and of tin, suggests that the general phenomenon of homolytic displacement of metals may be much more common than has previously been supposed. It is particularly likely to be found in transition metal chemistry under conditions where the substrate (25) is co-ordinatively saturated, where the *n* additional ligands L are such as to reduce the redox potential between M^m and M^{m-1} (where *m* and *m* − 1 are the oxidation states), and where the organic group R is accessible to attack by the radical. For the chain reaction to operate, there is the additional condition that the displaced metal complex must be sufficiently reactive to regenerate the appropriate organic radical X from XY [equation (16)]. A delicate balance between stability and reactivity of the intermediate metal complex $M^{m-1}L_n$ is thus an essential feature for such a process.

Reaction of Allenylcobaloximes with Polyhalogenomethanes.—The reactions of allenylbis(dimethylglyoximato)pyridinecobalt(III) (26) with carbon tetrachloride and bromotrichloromethane are similar to, but slower than, that of the corresponding allylcobaloxime. The two products, halogenobis(dimethylglyoximato)pyridinecobalt(III) and 4,4,4-trichlorobut-1-yne (27) [equation (17)] are consistent with a similar chain mechanism in which reaction (18) replaces reaction (6) in the sequence (4)—(10). As with the allylcobaloximes, the reaction is regiospecific, the organic radical showing no tendency to attack the α-carbon.

Allenylcobaloxime also reacts with carbon tetrabromide, trichloroacetonitrile, methyl trichloroacetate, and bromoform to give the organic products shown in equation (19). The characteristics of these products



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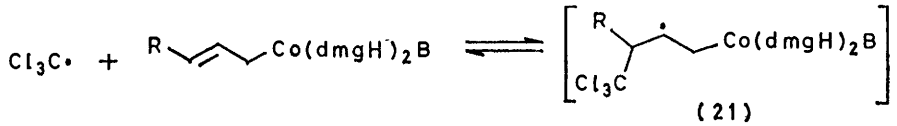

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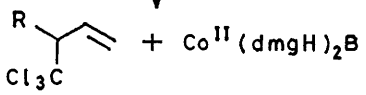

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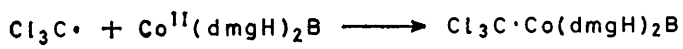

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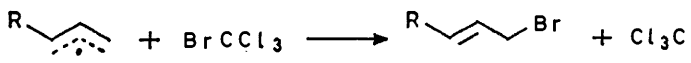

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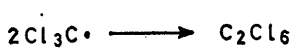

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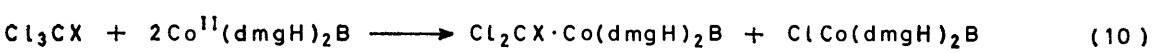
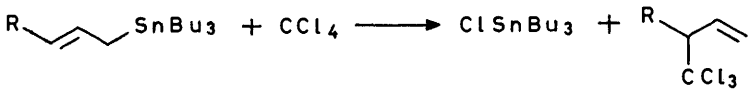


(10)

(22) X = CO_2Me

(23) X = CN

are listed in Tables 2 and 3. The reactions were appreciably slower than those of allylcobaloxime, but only one organic product was identified in each case. As outlined below, it is possible that some propyne was also



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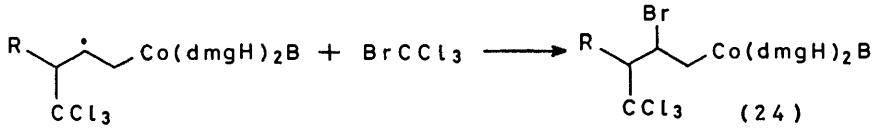

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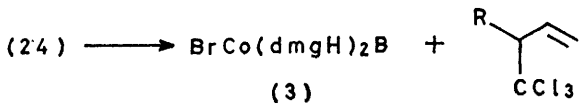

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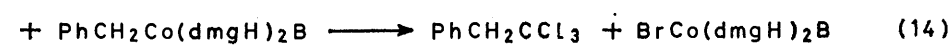

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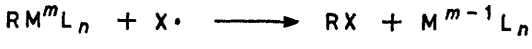

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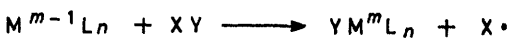
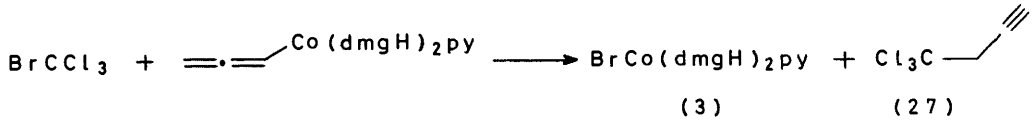


(16)

formed, but under the conditions of the reactions this would not have been retained.

In the reaction of 3,3-dimethylallenylbis(dimethylglyoximato)pyridinecobalt(III) (28) with bromotrichloromethane over a few hours at 50—60 °C, there are clearly two organic products, 4,4,4-trichloro-3,3-dimethylbut-1-yne (29) and 3-methylbut-1-yne (30) and the bromocobaloxime (3) is not the only inorganic product. The relative proportions of (29) and (30) vary considerably with the reaction conditions and with the nature of the reagent (CCl_4 or $BrCl_3$), but the ratio is greatly increased when the reaction is carried out in the presence of either an excess of pyridine or one mole of imidazole, when little of the hydrocarbon is formed.



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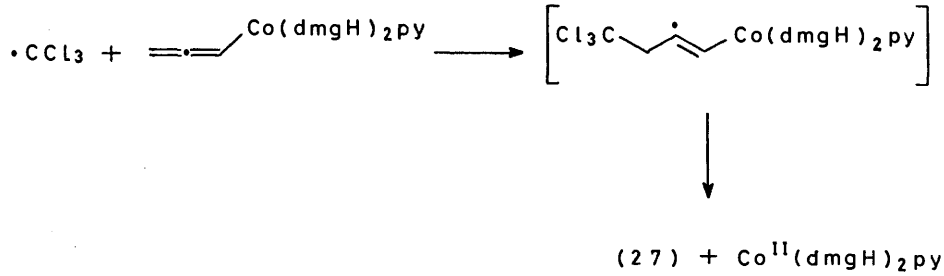


(18)

The reaction of 3,3-dimethylallenylbis([*O*-^{2}H]dimethylglyoximato)pyridinecobalt(III) (31) with bromotrichloromethane in methylene chloride containing traces of D_2O (to prevent exchange of the substrate deuterium)

gave exclusively 3-methyl[3-^{2}H]but-1-yne (32) and (29). Since the hydrocarbon (30) is not formed under the reaction conditions in the absence of bromotrichloromethane when dichloroacetic acid is the solvent, and decomposition of (28) in the absence of bromotrichloromethane in other solvents only occurs at temperatures greater than *ca.* 140°, neither an acidolysis nor a thermal decomposition is responsible for the formation of the hydrocarbon.

In view of the influence of the excess of pyridine and of imidazole which co-ordinates more strongly than pyridine to the cobalt,[13] on the extent of hydrocarbon formation, we propose that the hydrocarbon is formed as a result of the attack of trichloromethyl radicals on the metal of the transient five-co-ordinate complex [equation (21)]. Models of the allenyl cobaloximes show that the locus of the γ-carbon lies directly above the oxime hydrogens, and it seems likely that the cobalt(IV) intermediate (42) formed by attack of the trichloromethyl radicals on the metal undergoes a homolytic cleavage of the carbon–cobalt bond, with synchronous or subsequent abstraction of the oxime hydrogen. Whilst O–H bonds are normally strong, that in a dimethylglyoximato ligand is relatively weak because the radical so formed is a highly resonance-stabilised nitroxyl-oximato radical anion.

Formation of organocobaloxime(IV) complexes has been described,[14] and they are known to undergo homolysis under some conditions. Since displacement of the metal by attack of a nucleophile on the organic ligand of organocobaloxime(IV) complexes is facile and well established, it is most unlikely that the hydrocarbon formed under our conditions is a result of protonolysis at the γ-carbon of the allenyl ligand of (42). However,

TABLE 2

Products of reaction of allenylcobaloximes, RCo(dmgH)$_2$py, with polyhalogenomethane reagents

R	Reagent	Product (%) [a]	Found (%) [calc. (%)]	Chemical shift (δ) [b] 1-H	3-H	4-H	J/Hz [c] Coupling constants	B.p./(°C) [p/Torr]
CH_2=C=CH	$CBrCl_3$	$Cl_3C{\cdot}CH_2C{\equiv}CH$ (100)	C, 30.1 [30.5]; H, 2.05 [1.9]; Cl, 66.5 [67.6]	2.37	3.64		J_{13} 2.6	42 [21]
CH_2=C=CH	CBr_4	$Br_3C{\cdot}CH_2C{\equiv}CH$ (100)		2.52	4.04		J_{13} 2.7	
CH_2=C=CH	CCl_3CO_2Me	$MeOCO{\cdot}CCl_2CH_2C{\equiv}CH$ (>80)		2.17	3.40		J_{13} 2.6	
CH_2=C=CH	CCl_3CN	$NC{\cdot}CCl_2CH_2C{\equiv}CH$ (>90)		2.40	3.42			
CH_2=C=CH	$CHBr_3$	$Br_2CH{\cdot}CH_2C{\equiv}CH$ (>60)		2.30	3.37	5.62		
Me_2C=C=CH	$CBrCl_3$	$Cl_3C{\cdot}CMe_2C{\equiv}CH$ (70)	C, 38.4 [38.8]; H, 3.8 [3.8]; Cl, 57.6 [57.3]	2.60		1.88		60
		$HCMe_2C{\equiv}CH$ (30)		1.98	*ca.* 1.48	1.12	J_{34} 6.7, J_{13} 2.7	[20]
Me_2C=C=CH	$CBrCl_3$ [b]	$Cl_3C{\cdot}CMe_2C{\equiv}CH$ (>95)						
Me_2C=C=CH	CCl_4	$Cl_3C{\cdot}CMe_2C{\equiv}CH$ (80); $HCMe_2C{\equiv}CH$ (20)						
Me_2C=C=CH	$CBrCl_3$ [c]	$Cl_3C{\cdot}CMe_2C{\equiv}CH$ (96); $HCMe_2C{\equiv}CH$ (4)						
Me_2C=C=CH	$CBrCl_3$	$Cl_3C{\cdot}CMe_2C{\equiv}CH$ (70); $DCMe_2C{\equiv}CH$ (30)		1.98		1.12	J_{34} 1.0	
Me(Et)C=C=CH	$CBrCl_3$	$Cl_3C{\cdot}CMe(Et)C{\equiv}CH$ (65); $HCMe(Et)C{\equiv}CH$ (35)	C, 42.2 [42.1]; H, 4.6 [4.35]; Cl, 53.5 [53.3]	2.43; 1.98		1.60 (Me) [d]	$J_{4'5'}$ 7.5; J_{13} 2.5	86 [18]
Me(Et)C=C=CH	$CBrCl_3$ [b,c]	$Cl_3C{\cdot}CMe(Et)C{\equiv}CH$ (>90)						
cyclo-$[CH_2]_4$C=C=CH	$CBrCl_3$	cyclo-$[CH_2]_4C(CCl_3)C{\equiv}CH$ (~30); cyclo-$[CH_2]_4CH{\cdot}C{\equiv}CH$ (~70)	C, 43.3 [45.4]; H, 4.2 [4.3]; Cl, 53.5 [53.3]	2.47; 1.96		*ca.* 2.2 [e]		50 [0.2]
cyclo-$[CH_2]_4$C=C=CH	$CBrCl_3$ [b,c]	cyclo-$[CH_2]_4C(CCl_3)C{\equiv}CH$ (>70)						
cyclo-$[CH_2]_5$C=C=CH	$CBrCl_3$	cyclo-$[CH_2]_5C(CCl_3)C{\equiv}CH$ (~25); cyclo-$[CH_2]_5CH{\cdot}C{\equiv}CH$ (~75)	C, 47.4 [47.9]; H, 4.9 [4.9]; Cl, 48.1 [47.7]	2.52; 2.00	2.37	*ca.* 2 [f]; *g*	J_{13} 2.4	70 [0.3]
cyclo-$[CH_2]_5$C=C=CH	$CBrCl_3$ [b,c]	cylo-$[CH_2]_5C(CCl)C{\equiv}CH$ (>70)						

[a] % Organic product' [b] In the presence of 1 mol pyridine. [c] In the presence of 1 mol imidazole. [d] CH_2 protons (4-H), diastereotopic, δ 2.23 and 1.85 ($J_{4'4'}$ 14 Hz); 5-H, δ 1.17. [e] 4'-H, 5'-H, 5-H, δ *ca.* 1.9. [f] 4'-H, 5'-H, 5-H, δ *ca.* 1.78; 6-H, 6'-H, δ *ca.* 1.26 [g] Broad resonance, 4-H, 4'-H, 5-H, 5'-H, 6-H, 6'-H δ 1—2.2.

TABLE 3

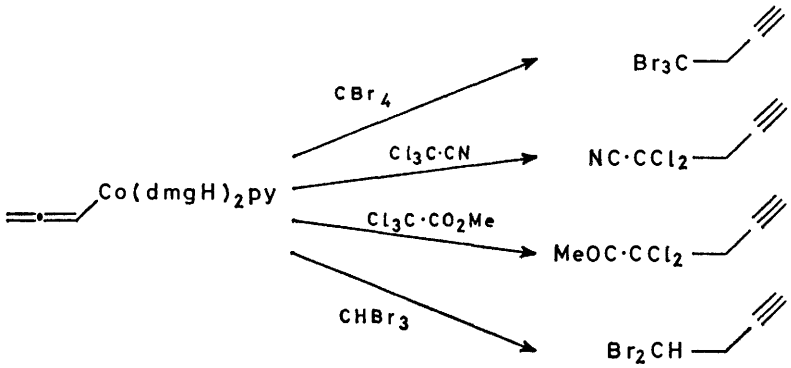
Carbon-13 n.m.r. spectra of acetylenic products

Compound	Chemical shift (δ) [a] C-1 [b]	C-2 [b]	C-3	C-4	C-4'	C-4''	C-5'	C-5''	C-6
$Cl_3C{\cdot}CH_2C{\equiv}CH$	73.8	76.4	46.5	96.9					
$Cl_3C{\cdot}C(CH_3)_2C{\equiv}CH$	72.5	85.1	51.3	106.8	26.3	26.3			
$Cl_3C{\cdot}CH(CH_3)(C_2H_5)C{\equiv}CH$	74.1	83.3	55.8	107.5	22.3 [c]	29.9 [c]		10.2 [c]	
cyclo-$Cl_3C{\cdot}C[CH_2]_4C{\equiv}CH$	72.7	77.5	63.1	105.5	38.9 [c]	38.9 [c]	25.8 [c]	25.8 [c]	
cyclo-$Cl_3C{\cdot}C[CH_2]_5C{\equiv}CH$	75.7	82.7	56.6	107.4	33.0 [c]	33.0 [c]	25.0 [c]	25.0 [c]	23.0
cyclo-$CH[CH_2]_5C{\equiv}CH$	68.3	77.3	32.7		33.7 [c]	33.7 [c]	25.0 [c]	25.0 [c]	29.0

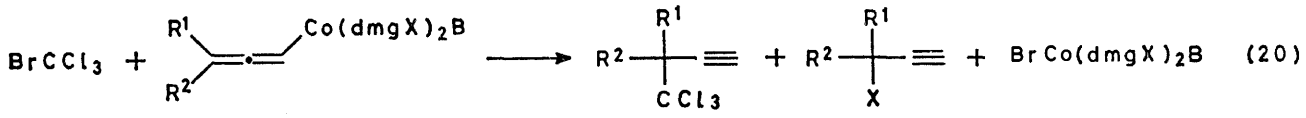
[a] From tetramethylsilane. [b] Some of these assignments may be reversed. [c] These assignments may be reversed.

in the mechanism of equation (21) the fate of the diradical organometallic fragment is far from clear; and formation of a diamagnetic trichloromethylcobaloxime(II) complex would require some distortion of the planar dioximato ligands in order to organise the appropriate orbital symmetry for electron pairing to take place.

Trichlorobut-1-yne products are also formed in the reactions of the more highly substituted allenylcobaloximes (32)—(35) with bromotrichloromethane [Table 2 and equation (20)] but the yield of the hydrocarbon product (39)—(41) is larger when the substituents are more bulky than in (28). In each case, the yield of the trichlorobutyne is greatly increased when the reaction is carried out in the presence of imidazole.



(19)



(20)

(28) $R^1 = R^2 = Me, X = H$	(29)	(30)
(31) $R^1 = R^2 = Me, X = D$		(32)
(33) $R^1 = Me, R^2 = Et, X = H$	(36)	(39)
(34) $R^1, R^2 = [CH_2]_4, X = H$	(37)	(40)
(35) $R^1, R^2 = [CH_2]_5, X = H$	(38)	(41)

In view of the ready formation of the allenylcobaloximes from the accessible and inexpensive 3-hydroxyalkynes,[15] these reactions provide a valuable and simple synthetic method for regiospecific replacement of OH by CCl_3 or related polyhalogenomethyl substituents [equation (22)].

EXPERIMENTAL

Materials.—Allyl- and allenyl-cobaloximes were prepared by the methods described previously from the corresponding allyl or propargyl halide and cobaloxime(I) formed by alkaline disproportionation of cobaloxime(II) in methanol under nitrogen.[16,17] For $[CH_2]_4C{:}C{:}CHCo(dmgH)_2py$: Found: C, 50.0; H, 5.9; N, 14.65. Calc. for $C_{20}H_{20}CoN_5O_4$: C, 52.0; H, 6.15; N, 15.2%.

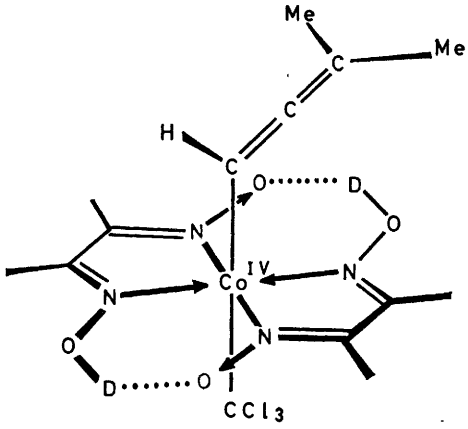
Reactions of Allylcobaloximes with Bromotrichloromethane.—Chloroform (20 ml) was degassed with nitrogen. Bromotrichloromethane (2 g, 10 mmol) was added, followed by the allylcobaloxime (5 mmol) and pyridine, imidazole, or dibenzoyl peroxide as required. When the reaction started (0—10 min) the solution darkened and green crystals of bromobis(dimethylglyoximato)pyridinecobalt(III) precipitated. When reaction was complete, light petroleum (b.p. 40—60°) was added; the bromocobaloxime was filtered off and the filtrate evaporated, extracted with light petroleum, and the excess of solvent removed *in vacuo* before final distillation of the organic product. For analyses see Table 1. In the reactions of all the allylcobaloximes only a single organic product, except for traces of hexachloroethane, was detected either by ^1H n.m.r. or g.l.c. Little difference was detected when the reaction was carried out without prior degassing by nitrogen.

Reaction of Allenylcobaloximes with Bromotrichloromethane.—The reactions of allenylcobaloximes were carried out as described above except that the solutions were heated at temperatures up to the b.p. of chloroform prior to the work-up procedure. In several cases, to retain the more volatile hydrocarbon products, the reactions were carried out in sealed tubes. Products and their characteristics are given in Tables 2 and 3.

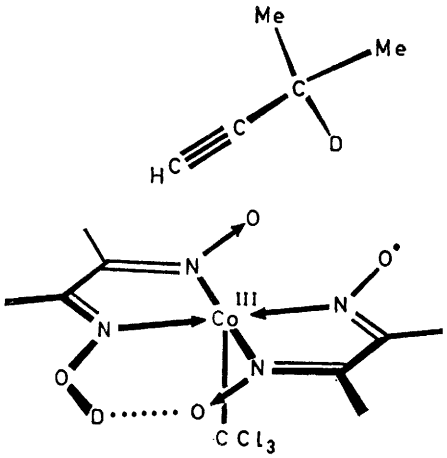
Reactions of Allyl- and Allenyl-cobaloximes with Other Polyhalogenohydrocarbons.—In a few cases the reactions were carried out by the above method, but using a 4—10 fold excess of the polyhalogenomethane reagent (CBr_4, $CHBr_3$, CCl_3CN, CCl_3CO_2Me). In other cases reactions were carried out in n.m.r. tubes and the products were identified both during the reaction and after pentane extraction (Tables 1 and 2).

Deuteriation Experiments.—3,3-Dimethylallenylbis[*O*-^2H]-dimethylglyoxime)pyridinecobalt(III) was prepared by stirring the non-deuteriated complex (1 g) in anhydrous tetrahydrofuran (20 ml) and D_2O (20 ml) for two days. The solvent was removed *in vacuo* and the solid product was reacted with bromotrichloromethane in anhydrous

chloroform (10 ml) containing D_2O (0.5 ml) at 50° for 4 h. The hydrocarbon product, 3-methyl[3-^{2}H]but-1-yne, b.p. 29°, was distilled off and identified by ^{1}H n.m.r. analysis.



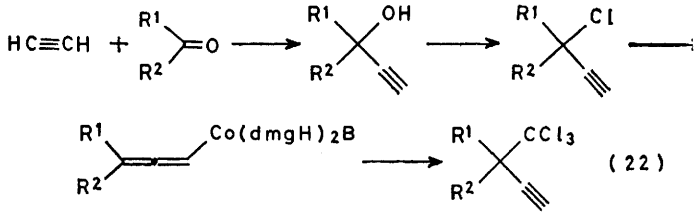
(42)



(21)

Acidolysis and Thermal Decomposition of 3,3-*Dimethylallenylcobaloxime*.—3,3-Dimethylallenylcobaloxime (2 g) was heated to up to 160° in three solvents (each 15 ml): mesitylene, dichloroacetic acid, and trifluoroacetic acid. In mesitylene and dichloroacetic acid no decomposition was evident over several minutes at temperatures below 130—140°, but at *ca.* 150 °C, a mixture of 3-methylbut-1-yne and 3-methylbuta-1,2-diene rapidly distilled off. In trifluoroacetic acid decomposition was rapid and at 40° 3-methylbut-1-yne distilled off. The hydrocarbon products were identified by ^{1}H n.m.r. and g.l.c.

Preparation of Halogenoalkylcobaloximes.—The polyhalogenomethane ($BrCCl_3$, $CHBr_3$, $CHCl_2CO_2Me$, CCl_3CN, or CCl_3CO_2Me) (1 mmol) was stirred with bis(dimethylglyoximato)pyridinecobalt(II) prepared from cobalt chloride hexahydrate (2 mmol), dimethylglyoxime (4 mmol), pyridine (2 mmol), and sodium hydroxide (4 mmol) in methanol (50 ml) under nitrogen. After a period of from 30 min at room temperature ($BrCCl_3$) to 3 h at 50° (Cl_2CHCO_2Me), the mixture was poured into water [500 ml, containing pyridine (0.5 ml)] and allowed to stand at −5° overnight. The yellow-orange crystals of the mixed organocobaloxime and halogenocobaloxime were filtered off,



(22)

washed with water, dried *in vacuo*, and separated by thin layer or column chromatography on silica gel. New cobaloximes: 1-*cyano*-1,1-*dichloromethylbis*(*dimethylglyoximato*)*pyridinecobalt*(III) (Found: C, 37.6; H, 4.2; N, 17.9; Cl, 14.4. $C_{15}H_{19}Cl_2CoN_6O_4$ requires C, 37.4; H, 4.0; N, 17.6; Cl, 14.9%); 1,1-*dichloro*-1-*methoxycarbonylmethylbis*(*dimethylglyoximato*)*pyridinecobalt*(III) (Found: C, 38.05; H, 4.55; N, 13.6; Cl, 13.4. $C_{16}H_{22}Cl_2CoN_5O_6$ requires C, 37.7; H, 4.75; N, 13.7; Cl, 13.9%); 1-*chloro*-1-*methoxycarbonylmethylbis*(*dimethylglyoximato*)*pyridinecobalt*(III) (Found: C, 40.15; H, 4.9; N, 14.8; Cl, 7.9. $C_{16}H_{23}ClCoN_5O_6$ requires C, 40.4; H, 4.9; N, 14.7; Cl, 7.45%).

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