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HOMOLYTIC DISPLACEMENT AT CARBON

XI *. INTRAMOLECULAR HOMOLYTIC DISPLACEMENT AS A ROUTE TO CYCLOPENTANE AND TETRAHYDROFURAN DERIVATIVES FROM HEX-5-ENYL- AND HEX-3-OXO-5-ENYLCOBALOXIMES

CHRISTOPHE BONGARS, PETER BOUGEARD, ADRIAN BURY, CHRISTOPHER J. COOKSEY, MICHAEL D. JOHNSON*, STEWART MITCHELL, PAUL A. OWENS, and FAMIDA RAJAH

Department of Chemistry, University College, 20 Gordon Street, London WC1H OAJ (Great Britain)

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Summary

5-Methylhex-5-enylcobaloxime reacts with carbon tetrachloride and with fluorotrichloromethane at 80–100°C to give substantially pure 1-methyl-1-(β,β,β-trichloroethyl)- and 1-methyl-1-(β-fluoro-β,β-dichloroethyl)-cyclopentane. Hex-5-enylcobaloxime also gives trichloroethylcyclopentane from carbon tetrachloride, but the yield is dependent on the concentration of carbon tetrachloride. Similar cyclisation to give trichloroethyl- or fluorodichloroethyltetrahydrofuran is observed in the reactions of hex-3-oxo-5-enylcobaloxime with carbon tetrachloride and fluorotrichloromethane. However, no cyclisation was observed in the reactions of the ester, hex-2-one-3-oxo-5-enylcobaloxime, with carbon tetrachloride. These reactions are believed to take place by attack of a polyhalogenomethyl radical at the terminal unsaturated carbon of the organic ligand, followed either by an intramolecular homolytic displacement in which the carbon radical at position-5 attacks carbon-1 with displacement of cobaloxime(II), or by a halogen atom abstraction.

Introduction

Homolytic displacement at saturated carbon is rare; not because it is not possible, but because other processes usually take precedence [1]. The d^7 low-spin cobaloxime(II) complex has, however, been shown to be a good leaving group and several examples of such reactions have been postulated as being key steps in the reactions of diamagnetic organocobaloximes with free radical precursors. These include the attack of trichloromethyl radicals [2], arenesulphonyl radicals [3] and hydroxyalkyl

* For part X see ref. 3.

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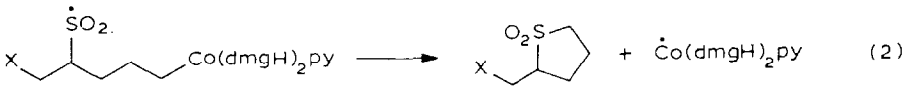
radicals [4] at the α-carbon of benzylcobalozime (eq. 1), and the formation of sulpholanes by the intramolecular attack of remote sulphonyl radical centres on the α-carbon of a substituted alkylcobaloxime (eq. 2) [5]. With some reservations * we may also consider that the more common formation of cyclopropane derivatives from but-3-enyl compounds is a further example of a homolytic substitution at saturated carbon (equation 3) [6].

$$\dot{X} + PhCH_2Co(dmgH)_2py \longrightarrow PhCH_2X + \dot{C}o(dmgH)_2py \qquad (1)$$



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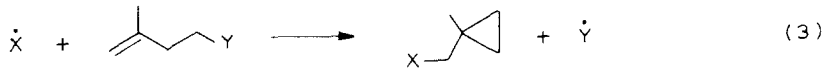


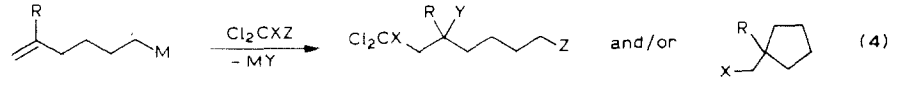
(3)

(X = Cl_3C, $ArSO_2$, $ArSO_2NMe$, etc.;
Y = $Co(dmgH)_2py$, Br, I etc.)

We now describe a series of reactions related to that shown in eq. 2 in which a key step is the intramolecular attack of a carbon centred radical on the α-carbon of the substituted alkyl ligand.

Results

The main product of reaction of hex-5-enylcobaloxime (**1**) with carbon tetrachloride in the absence of any other solvent at 80–100°C was 1,5,7,7,7-pentachloroheptane (**3**). However, as the concentration of carbon tetrachloride in the reaction mixture was decreased by addition of methylene chloride, the main product changed to β,β,β-trichloroethylcyclopentane (**4**). The corresponding reaction of 5-methylhex-5-enylcobaloxime (**2**) with neat carbon tetrachloride gave almost exclusively the cyclic product 1-(β,β,β-trichloroethyl)-1-methylcyclopentane (**5**). Similar reaction of **2** with fluorotrichloromethane or with trichloroacetonitrile also gave substantially pure cyclic products (**6** and **7**, respectively). However, the reaction of complex **2** with trichloromethanesulphonyl chloride or with bromotrichloromethane gave only the open chain addition products (**8** and **9**, respectively).



(4)

(**1**, R = H, M = $Co(dmgH)_2py$;
2, R = Me, M = $Co(dmgH)_2py$)

(**3**, R = H, X = Y = Z = Cl ;
8, R = Me, X = Cl, Z = SO_2Cl ;
9, R = Me, X = Cl, Z = Br)

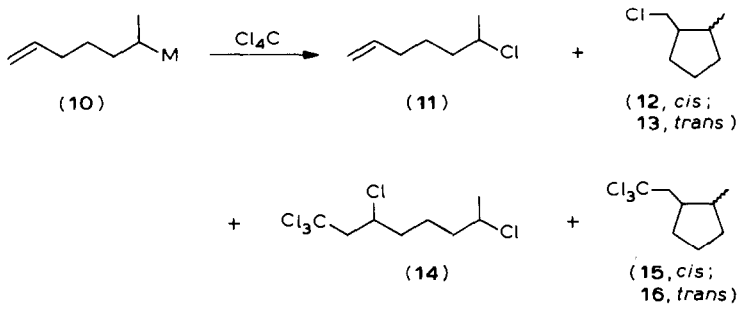
(**4**, X = CCl_3 , R = H ;
5, X = CCl_3 , R = Me ;
6, X = CCl_2F, R = Me ;
7, X = CCl_2CN, R = Me)

The thermal reaction of the secondary alkenylcobaloxime **10** with carbon tetrachloride gave at least 7 products which were shown by GLC/mass spectrometry to

* The main reservation concerns the fact that the radical centre is not remote from the α-carbon; indeed, there may be a permanent interaction between the radical centre and the carbon–metal bond, which makes the consequent displacement a special case.

be predominantly one-chlorine products $C_7H_{13}Cl$ (**11–13**), addition products containing four-chlorine atoms, and only about 15% of trichloroethyl(methyl)cyclopentanes (**15, 16**). The yields of the latter were however, slightly increased by dilution of the reaction mixture with dichloromethane. In view of the complexity of this reaction, detailed studies on the individual reaction products were not carried out.

The reactions of hex-3-oxo-5-enyl- and 5-methylhex-3-oxo-5-enyl-cobaloximes (**17** and **18**) with carbon tetrachloride also gave almost quantitative yields of the cyclic 3-(trichloroethyl)tetrahydrofurans **19** and **20** (eq. 6). Reaction of cobaloximes **17** and **18** with fluorotrichloromethane likewise gave exclusively the fluorodichloroethyltetrahydrolfuran derivatives **21** and **22**. However, in the reactions of carbon tetrachloride with the corresponding esters hex-2-one-3-oxo-5-enyl- and 5-methylhex-2-one-3-



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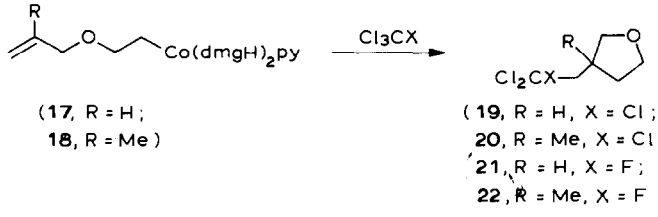

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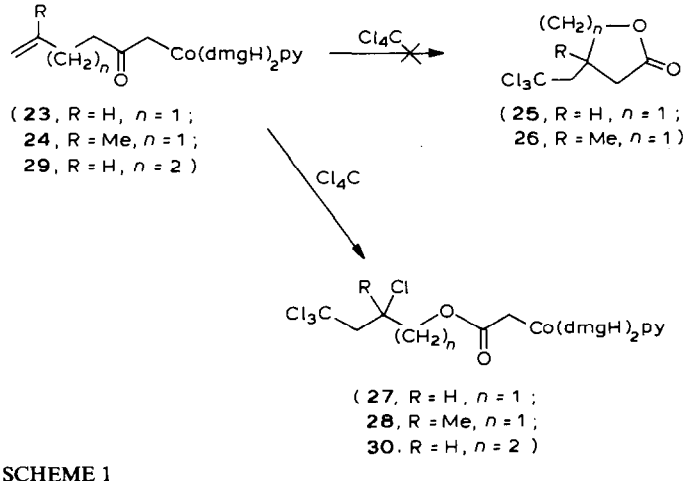
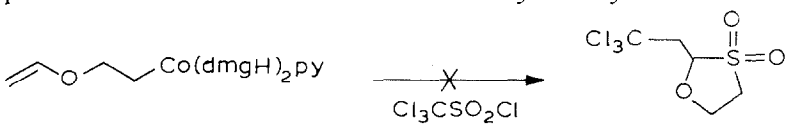


(7)

SCHEME 1

oxo-5-enyl-cobaloxime (**23** and **24**), not only could no trace of the cyclic lactone **25** or **26** be detected, but the carbon–cobalt bond in each case remained intact even though addition of the elements of carbon tetrachloride to the double bond occurred and the reactions were continued for several days at 100°C. Good yields of the addition products **27** and **28** were isolated. The stability of the carbon–cobalt bond was also evident in the reaction of hept-2-one-3-oxo-6-enylcobaloxime with carbon tetrachloride, from which the six-membered lactone could not be obtained, but the addition product **30** was isolated in high yield (Scheme 1).

Attempts to prepare the heterocycle **32** by reaction of pent-3-oxo-5-enylcobaloxime (**31**) with trichloromethanesulphonyl chloride were unsuccessful; the decomposition of the enol-ether occurred before any such cyclisation could occur.



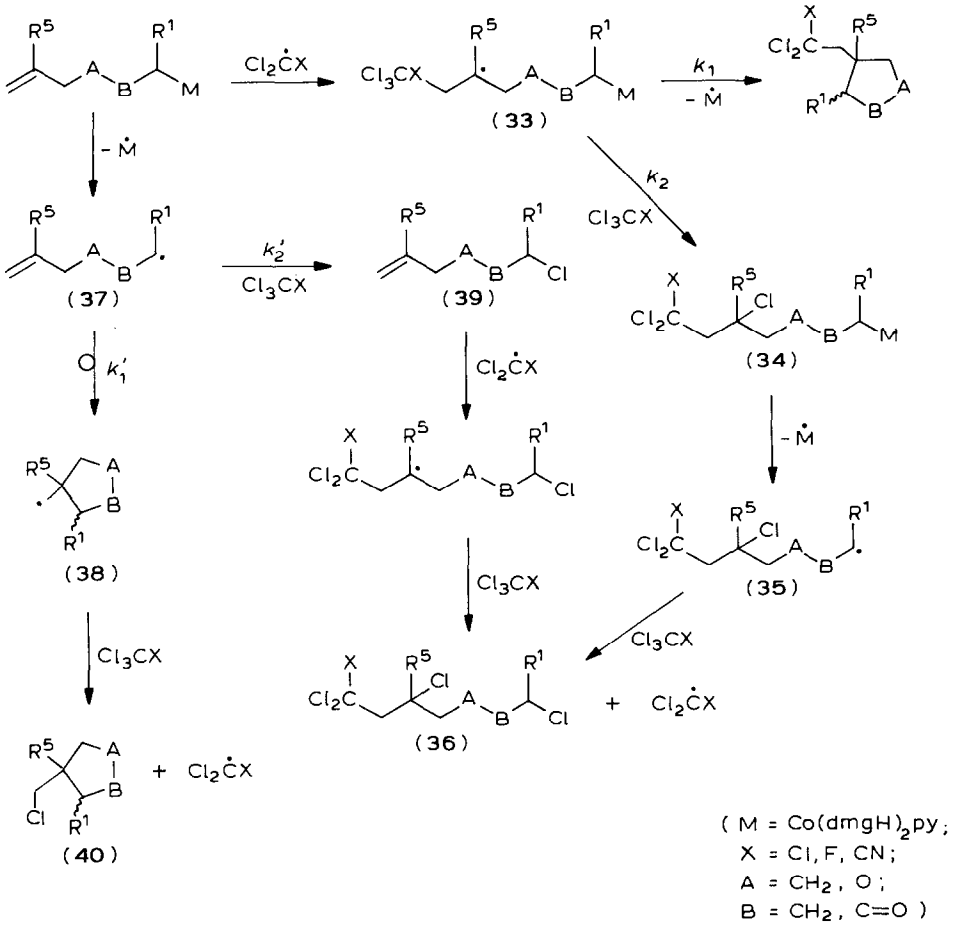
(31) (32) (8)

Discussion

The majority of the results described above may be rationalised on the basis that the consequences of attack of the polyhalogenomethyl radical on the terminal olefinic carbon of the organic ligand (Scheme 2) [5] may be two-fold. Either the radical **33**, so formed, may abstract a halogen atom from the polyhalogenomethane reagent to give the addition product **34** and liberate another polyhalogenomethyl radical, or the radical **33** may cyclise directly to the observed cyclic organic product by an intramolecular homolytic displacement of cobaloxime(II). In either case the liberated radical, polyhalogenomethyl or cobaloxime(II), then takes part in a further propagation step (e.g. eq. 9) [7] to ensure the chain character of the process.

The abstraction of a halogen atom from the polyhalogenomethane is a bimolecular process with a second order rate equation (rate $= k_2[CCl_3X][\mathbf{33}]$) whereas the cyclisation process is unimolecular with a first order rate equation (rate $= k_1[\mathbf{33}]$). The preference of the one over the other is thus a function of the concentration of the polyhalogenomethane reagent and of the relative magnitudes of k_1 and k_2. Clearly, for the hex-3-oxo-5-enylcobaloximes, $k_1 \gg k_2[CCl_3X]$, for the hex-5-enylcobaloximes $k_1 \approx k_2[CCl_3X]$, and for the unsaturated esters $k_1 \ll k_2[Cl_3CX]$. Only in the case of the hex-5-enylcobaloximes is the concentration of the polyhalogenomethane the critical factor. Once having added the elements of the polyhalogenomethane to the double bond, subsequent homolytic cleavage of the carbon–cobalt bond may occur, leading to the radical **35** and consequently to the polychloroalkane **36**. As noted below, some homolysis of the carbon–cobalt bond of the substrate may also be expected under the reaction conditions [8] (indeed, since no initiator is necessary in these reactions, the initiation requires at least partial homolysis of one or other of the substrates) leading to the formation of the radical **37** which may either cyclise to **38** or react with the polyhalogenomethane to give **39** and, subsequently, the observed product **36**. Indeed, when the cobaloxime **1** is irradiated at lower temperatures with tungsten light, in the presence of low concentrations of carbon tetrachloride, the cyclopentylmethyl chloride **40** ($R^1 = R^5 = H$; $A = B = CH_2$) is the main product.

The substitution of methyl for hydrogen at position-5 of the hex-5-enyl and other ligands clearly increases the proportion of cyclic product; probably because it decreases k_2 more than it decreases k_1; i.e. the selectivity of the radical for attack at saturated carbon relative to halogen abstraction appears to be greater for the tertiary than for the secondary carbon centre. For a given substituent at carbon-5 the value of k_2 will be little influenced by the nature of the more remote parts of the ligand backbone. The differences in reactivity of the hex-5-enyl-, hex-3-oxo-5-enyl-, and hex-2-one-3-oxo-5-enyl-cobaloximes must therefore be a result of differences in the flexibility of those chains and/or of the carbon–cobalt bond strengths. For the hex-5-enyl- and hex-3-oxo-5-enylcobaloximes, which both have the character $RCH_2CH_2Co(dmgH)_2py$, the carbon–cobalt bond strengths would be expected to be very similar and the greater extent of cyclisation observed with the hex-3-oxo-5-enylcobaloximes may therefore be ascribed to the greater flexibility of the monoxo-

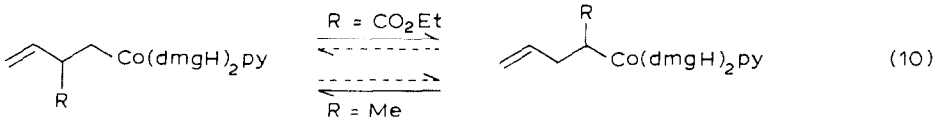


$$Cl_3CX + Co(dmgH)_2py \longrightarrow Cl_2\dot{C}X + ClCo(dmgH)_2py \qquad (9)$$

SCHEME 2

than of the all-carbon-chain. Whilst the lack of flexibility of the ester-containing chain of the hex-2-one-3-oxo-5-enylcobaloximes may inhibit the formation of cyclic lactones, the fact that the carbon–cobalt bonds of these complexes are not cleaved even over long reaction times in neat carbon tetrachloride suggests that the acyl carbon–cobalt bond is particularly strong and not susceptible to the homolytic displacement reaction. This view is supported by the lack of cyclisation and cleavage of the complex **29**, which might have given the corresponding six-membered lactone.

A similar conclusion about the strength of the acyl carbon–cobalt bond in such cobaloximes can be drawn from the fact that 2-carboxyethylbut-3-enylcobaloxime rearranges spontaneously into predominantly 1-carboxyethylbut-3-enylcobaloxime [9] (eq. 10), whereas it is 1-methylbut-3-enylcobaloxime which rearranges into 2-methylbut-3-enylcobaloxime [10].



(10)

The formation of substantial amounts of 1-chlorine products in the reaction of the secondary alkenylcobaloxime (**10**) is not inconsistent with Scheme 2. The secondary carbon–cobalt bond is certainly weaker than the primary carbon–cobalt bond of **1** and **2** [11], and, under the reaction conditions the extent of primary homolysis of **10** to give **37** (R^1 = Me, R^2 = H, A = B = CH_2) is substantial, and its cyclisation facile [12]. Since homolytic displacement at secondary carbon is likely to be less facile than at primary carbon, it is not surprising that the extent of formation of trichloroethylcyclopentanes in this case is small.

Experimental

^{1}H NMR spectra are 200 MHz except where stated.

Preparation of organic precursors

Allyl bromoacetate was prepared by the dropwise addition of bromoacetyl bromide (0.15 mol) to a well stirred solution of allyl alcohol (0.15 mol) in methylene chloride (50 ml). The mixture was allowed to stand overnight, washed with 10% aqueous sodium bicarbonate, with water, and dried (Na_2SO_4). (Yield 87%. ^{1}H NMR spectrum δ 3.62 (s, CH_2Br); 4.42 (d, CH_2O); 5.06 (m, :CH_2); 5.6 (m, :CH)). Similarly prepared were 2-methylallyl bromoacetate from 2-methylallyl alcohol and but-3-enyl bromoacetate from but-3-enol. 2-Hydroxyethyl vinyl ether was prepared by refluxing 2-bromomethyl-1,3-dioxolane with sodium in anhydrous ether (100 ml) under nitrogen for 6 h [13]. The suspension was filtered, the filtrate was poured into water and the product was extracted with ether. (Yield 70%. ^{1}H NMR spectrum δ 3.65 (m, 4H); 4.0 (m, :CH_2); 6.44 (q, :CH, J 15.2, 6.4 Hz)). Hex-3-oxo-5-enol was prepared by reaction of allyl bromide with the monosodium salt of ethan-1,2-diol prepared from sodium (0.4 mol) and ethandiol (0.8 mol). The mixture was heated under reflux for 2 h, filtered and distilled. The product was separated from final traces of ethandiol by chromatography on alumina with elution by carbon tetrachloride. (Yield 25%. ^{1}H NMR (60 MHz) δ 3.62 (m, 4H); 3.98 (d, CH_2); 5.2 (m, :CH_2); 5.8 (m, :CH)). Similarly prepared from 2-methylallyl chloride was 5-methylhex-3-oxo-5-enol (Yield 46%. ^{1}H NMR (60 MHz) δ 1.62 (s, CH_3); 3.43 (m, 4H); 3.80 (s,

CH_2); 4.8 (d, :CH_2)). 5-Methylhex-5-enol was prepared by the reaction of 2-methylallylmagnesium chloride with trimethylene oxide. Hept-6-en-2-ol was prepared by the reduction of hept-6-en-2-one with sodium borohydride.

Tosylates. The following tosylates were prepared from the above alcohols, but not purified, by the method of Golding [14]. 5-Methylhex-5-enyl tosylate (87%); hept-6-en-2-yl tosylate (67%); hex-3-oxo-5-enyl tosylate (69%). ^{1}H NMR (60 MHz) δ 2.43 (s, CH_2); 3.60 (t, CH_2); 3.93 (m, CH_2); 4.17 (t, CH_2); 5.1 (m, :CH_2); 5.7 (m, :CH); 7.3 and 7.75 (2d, C_6H_4)); 5-methylhex-3-oxo-5-enyl tosylate (70% yield. ^{1}H NMR (60 MHz) δ 1.70 (s, CH_3); 2.45 (s, CH_3); 3.50 (t, CH_2); 3.86 (s, CH_2); 4.40 (t, CH_2): 4.95 (m, :CH_2); 7.3 and 7.75 (2d, C_6H_4)); pent-3-oxo-4-enyl tosylate (66% yield. ^{1}H NMR 2.38 (s, CH_3); 3.84 (t, CH_2); 3.99 and 4.12 (m, :CH_2); 4.24 (t, CH_2); 6.83 (q, :CH); 7.30 and 7.81 (2d, C_6H_4)).

Cobaloximes. Cobaloximes were prepared either (i) from the bromide by the method of Widdowson [15], except that the final toluene solution of the organocobaloxime was filtered hot, evaporated until crystals began to appear and mixed with petroleum ether to complete precipitation of the crude organocobaloxime, or (ii) by reaction of the tosylate with the bis(dimethylglyoximato)pyridinecobaltate(I) ion formed by alkaline disproportionation of bis(dimethylglyoximato)pyridinecobalt(II) in aqueous methanol [16]. The following cobaloximes were prepared: hex-5-enylbis(dimethylglyoximato)pyridinecobalt(III) [17]; *5-methylhex-5-enylbis(dimethylglyoximato)pyridinecobalt(III)* (92%. Found: C, 51.4; H, 6.8; N, 14.9. $C_{20}H_{32}CoN_5O_4$ calcd.: C, 51.6; H, 6.9; N, 15.05%. ^{1}H NMR spectrum δ 0.88 (m, CH_2); 1.30 (q, CH_2); 1.60 (t, CH_2); 1.61 (s, CH_3); 1.90 (t, CH_2); 2.09 (s, dmg); 4.54 and 4.58 (2m, :CH_2)); *hept-6-en-2-ylbis(dimethylglyoximato)pyridinecobalt (III)* (56%. Found: C, 51.1; H, 6.7; N, 14.9. $C_{20}H_{32}CoN_5O_4$ calcd.: C, 51.6; H, 6.9; N, 15.05%); *hex-3-oxo-5-enylbis(dimethylglyoximato)pyridinecobalt(III)* (56%. Found: C, 47.6; H, 6.2; N, 15.5. $C_{18}H_{28}CoN_5O_5$ calcd.: C, 47.7; H, 6.2; N, 15.45%. ^{1}H NMR spectrum δ 1.60 (t, CH_2); 2.12 (s, dmg); 3.15 (t, CH_2O); 3.87 (d, CH_2O); 5.13 (m, :CH_2); 5.85 (m, :CH)); *5-methylhex-3-oxo-5-enylbis(dimethylglyoximato)pyridinecobalt(III)* (63%. Found: C, 48.3; H, 6.45; N, 14.85. $C_{19}H_{30}CoN_5O_5$ calcd.: C, 48.8; H, 6.5; N, 15.0%. ^{1}H NMR spectrum δ 1.57 (t, CH_2); 1.63 (s, CH_3); 2.07 (s, dmg); 3.09 (t, CH_2O); 3.73 (s, CH_2O); 4.76 and 4.83 (m, :CH_2); pyridine resonances at δ 7.25, 7.69 and 8.53)); *pent-3-oxo-4-enylbis(dimethylglyoximato)pyridinecobalt(III)* (22% Found: C, 46.1; H, 6.0; N, 15.9. $C_{17}H_{26}CoN_5O_5$ calcd.: C, 46.5; H, 6.0; N, 15.9%. ^{1}H NMR spectrum δ 1.59 (t, CH_2); 2.14 (s, dmg); 3.41 (t, CH_2O); 3.85 and 4.05 (2d, :CH_2, J 6.6, 14.2 Hz); 6.31 (q, :CH); pyridine resonances at δ 7.31, 7.72 and 8.55)); *hept-2-one-3-oxo-6-enylbis(dimethylglyoximato)pyridinecobalt(III)* (42%. Found: C, 46.8; H, 5.8; N, 14.2. $C_{19}H_{25}CoN_5O_6$ calcd.: C, 47.3; H, 5.85; N, 14.5%. ^{1}H NMR spectrum δ 1.67 (s, CH_2Co); 2.20 (s, dmg); 2.42 (m, CH_2); 3.84 (t, CH_2); 5.12 and 5.18 (m, :CH_2); 5.82 (m, :CH)); *hex-2-one-3-oxo-5-enylbis(dimethylglyoximato)pyridinecobalt(III)* (39%. ^{1}H NMR spectrum δ 1.68 (s, CH_2Co); 2.18 (s, dmg); 4.29 (d, CH_2O); 5.4 (m, CH_2); 5.90 (m, :CH); pyridine resonances at δ 7.29; 7.72 and 8.51); *5-methylhex-3-oxo-2-one-5-enylbis(dimethylglyoximato)-pyridinecobalt(III)* (51%. ^{1}H NMR δ 1.71 (s, CH_2Co); 1.76 (s, CH_3); 2.20 (s, dmg); 4.22 (s, CH_2O); 4.86 and 4.94 (2m, CH_2); pyridine resonances at δ 7.31, 7.73 and 8.54).

Reactions of organocobaloximes. The organocobaloxime (usually 0.1 mmol) was treated either with the polyhalogenomethane reagent or with that reagent (CCl_4,

$BrCCl_3$, Cl_3CSO_2Cl, Cl_3CF, Cl_3CCN) diluted with methylene chloride, in a sealed tube at 80–100°C for from 1 to 4 days. The product was chromatographed on silica gel (Mallinkcrodt CC4) eluting with successively pentane, methylene chloride, ethyl acetate, and mixtures thereof to give, in order, organic products, organocobaloximes and halogenocobaloximes. The organic products were further separated by GLC or by HPLC as described earlier [5]. Products isolated were as follows: (in each case expressed as organocobaloxime/reagent; product). From 5-methylhex-5-enylcobaloxime/CCl_4; *1-(β,β,β-trichloroethyl)-1-methylcyclopentane* (Found: C, 44.3; H, 5.8; Cl, 49.8. $C_8H_{13}Cl_3$ calcd.: C, 44.6; H, 6.0; Cl, 49.3%. ^1H NMR spectrum δ 1.18 (s, CH_3); 1.67 (m, 8H); 2.90 (s, CH_2CCl_3)). From 5-methylhex-5-enylcobaloxime/Cl_3CF; *1-(β,β-dichloro-β-fluoroethyl)-1-methylcyclopentane* (^1H NMR δ 1.12 (d, CH_3, *J* 2.3 Hz); 1.4–1.9 (m, 8H); 2.69 (d, CH_2CCl_2F, *J* 18.7 Hz)). From 5-methylhex-5-enylcobaloxime/ Cl_3CCN; *1-(β-cyano-β,β-dichloroethyl)-1-methylcyclopentane* (Found: C, 34.6; H, 3.7; N, 5.8; Cl, 29.0. $C_9H_{11}Cl_2N$ calcd.: C, 34.7; H, 3.7; N, 6.2; Cl, 29.3%. ^1H NMR spectrum δ 1.23 (s, CH_3); ~ 1.7 (m, 8H); 2.70 (s, CH_2CCN)). From 5-methylhex-5-enylcobaloxime/trichloromethanesulphonyl chloride/CH_2Cl_2; 3-methyl-1,1,1,3-tetrachloroheptanesulphonyl chloride [8]. From 5-methylhex-5-enylcobaloxime/ bromotrichloromethane/ CH_2Cl_2; 3-methyl-3,7-dibromo-1,1,1-trichloroheptane (not isolated: ^1H NMR spectrum δ 1.6–2.6 (m, 6H); 2.11 (s, CH_3); 3.42 (t, CH_2Br, *J* 6.4 Hz); 3.58 (s, CH_2CCl_3)). From hex-5-enylcobaloxime/carbon tetrachloride/CH_2Cl_2; β,β,β-trichloroethylcyclopentane [18] (Mass spectrum, *m/e* 198.9843, 200.9811, 202.9740. $C_7H_{10}Cl_3$ calcd.: 198.983, 200.979, 202.964). From hex-3-oxo-5-enylcobaloxime/carbon tetrachloride; 3-(β,β,β-trichloroethyl)tetrahydrofuran (Mass spectrum *m/e* 202, 204; 157, 159; 109, 111 (each pair in the ratio 1/1); base peak 67). From 5-methylhex-3-oxo-5-enylcobaloxime/carbon tetrachloride; *3-methyl-3-β,β,β-trichloroethyl)tetrahydrofuran* (Mass spectrum *m/e* 215.9847 and 217.9885, 186 and 188, 158 and 160. $C_7H_{11}OCl_3$ calcd.: 215.9864 and 217.994. ^1H NMR spectrum δ 1.35 (s, CH_3); 1.87 (m, CH_2); 2.94 and 3.02 (2d, CH_2CCl_3, *J* 15.2 Hz); 3.89 (m, CH_2O); 2.62 and 2.71 (2d, CH_2O, *J* 8.5 Hz)). From 5-methylhex-3-oxo-5-enylcobaloxime/fluorotrichloromethane; *3-methyl-3-(β,β-dichloro-β-fluoroethyl)tetrahydrofuran* (Found: C, 41.6; H, 5.3; $C_7H_{11}Cl_2FO$ calcd.: C, 41.8; H, 5.5%. Mass spectrum: *m/e* 200.0182 and 202.0125. $C_7H_{11}Cl_2FO$ calcd.: 200.0193 and 202.0108. ^1H NMR spectrum δ 1.22 (d, CH_3, *J*(HF) 2.5 Hz); 1.82 (m, CH_2); 2.67 (q, $CHCCl_3$, *J*(HH) 15.8, *J*(HF) 18.9 Hz); 2.77 (q, $CHCCL_3$, *J*(HH) 15.8, *J*(HF) 18.2 Hz); 3.56 and 3.62 (2d, CH_2O, *J*(HH) 8.5 Hz); 3.89 (t, CH_2O)). From hex-2-one-3-oxo-5-enylcobaloxime/carbon tetrachloride; *5,7,7,7-tetrachloro-2-one-3-oxoheptylcobaloxime* (Found: C, 37.4; H, 4.5; N, 10.8; Cl, 22.9. $C_{19}H_{26}Cl_4N_5OC_6Co$ calcd.: C, 36.6; H, 4.2; N, 11.2; Cl, 22.8%). From 5-methylhex-2-one-3-oxo-5-enylcobaloxime/carbon tetrachloride; 5-methyl-5,7,7,7-tetrachloro-hept-3-oxo-2-onylcobaloxime (^1H NMR spectrum δ 1.60 (m, CH_2); 1.84 (s, CH_3); 2.19 (s, dmg); 3.36 and 3.64 (2d, CH_2CCl_3, *J* 16 Hz); 3.97 (s, CH_2O); pyridine resonances at 7.33, 7.76 and 8.53). From hept-2-one-3-oxo-5-enylcobaloxime/carbon tetrachloride; *6,8,8,8-tetrachlorooct-3-oxo-2-onylcobaloxime* (Found: C, 37.8; H, 4.4; N, 11.1; Cl, 20.0. $C_{20}H_{28}CoCl_4N_5O_6$ calcd.: C, 37.8; H, 4.4; N, 11.0; Cl, 20.25%. ^1H NMR spectrum δ 1.67 (m, CH_2); 2.23 (s, dmg); 2.2 (m, CH_2 obscured); 3.26 (q, $CHCCl_3$, *J* 4, 16 hz); 3.36 (q, $CHCCl_3$, *J* 4, 16 Hz); 4.05 (m, CH_2); 4.57 (m, CH_2); pyridine resonances at δ 7.36, 7.78 and 8.58).

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