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HOMOLYTIC DISPLACEMENT AT CARBON CENTRES

XII *. REGIOSPECIFIC FORMATION OF *N*-ALLYL AND *N*-CYCLOPROPYLCARBINYL SULPHONAMIDES AND OF ALLYL AND CYCLOPROPYL HALIDES IN THE REACTION OF *N*-HALOGENO COMPOUNDS WITH ORGANOCOBALOXIMES

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Summary

Several but-3-enyl and allylcobaloximes react regiospecifically with *N*-chloro-*N*-methyl sulphonamides to give *N*-cyclopropylcarbinyl- or rearranged *N*-allyl-*N*-methyl sulphonamides, by a process which is believed to take place by the attack of an *N*-centred radical at the terminal unsaturated carbon of the organic ligand, with displacement of cobaloxime(II). In contrast, *N*-bromoacetamide and several other *N*-halogenoimides react regiospecifically to give the cyclopropylcarbinyl halide or the rearranged allyl halide by a process in which a halogen-containing free radical species attacks the terminal unsaturated carbon of the organocobaloxime.

Organic *N*-halogeno compounds have been used as halogenating agents for many years [2]. Mechanistic studies have suggested several reaction paths including (a) the direct reaction of the *N*-halogeno compound acting as an electrophile, (b) the *N*-halogeno compound acting as a source of molecular halogen which then acts as an electrophile or as a free radical reagent, and (c) a free-radical chain process in which the *N*-halogeno compound is a direct participant.

* For part XI see ref. 1.

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Free radical chain [3] and electrophilic [4] processes have also been shown to vie with each other in the reactions of allyl-, but-3-enyl, benzyl, and other organocobaloximes, with a range of *C*-halogeno and *S*-halogeno compounds. In the majority of these reactions, the organic product is that derived by attack of a C- or S-centred free radical (eqs. 1 and 2) or of an S-centred electrophile (eq. 3) on the organic ligand of the cobaloxime in a regiospecific manner.

It seemed likely that a study of the reactions of some *N*-halogeno compounds with the same series of organocobaloximes might clarify the dichotomy of the free radical and electrophilic processes and provide a possible route to allyl and cyclopropylcarbinylamines.

Results

Reaction of N-chloro sulphonamides with alkenylcobaloximes

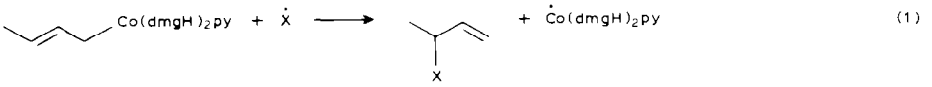
Allyl-, but-2-enyl-, 3-methylbut-2-enyl-, and cinnamyl-cobaloxime (**1**–**4**; each 1 mmol) reacted regiospecifically with *N*-chloro-*N*-methylmethane sulphonamide (**5**; 2 mmol) and with *N*-chloro-*N*-methyl-4-toluene sulphonamide (**6**; 2 mmol) in methylene chloride at ambient temperature to give good yields of the corresponding substituted *N*-allyl-*N*-methyl sulphonamide (**7**–**10** and **15**; eq. 4) in each case accompanied by the isomerically pure rearranged substituted allyl chloride (**11**–**14**). The corresponding reaction of 3-methylbut-3-enylcobaloxime (**16**) with reagents **5** and **6** gave predominantly the *N*-(cyclopropylcarbinyl)-*N*-methyl sulphonamides (**18** and **19**; eq. 5) together with the chloromethylcyclopropane **20**. But-3-enylcobaloxime (**17**) reacted under similar conditions to give chloromethylcyclopropane (**21**); the *N*-(cyclopropylcarbinyl)-*N*-methyl sulphonamide could not be detected. In the corresponding reaction of buta-1,2-dienylcobaloxime (**22**) with reagent **5**, the only sulphonamide that could be obtained was the *N*-(1-methylprop-2-ynyl)-*N*-methyl sulphonamide (**23**; eq. 6), contaminated with a variety of other products.

Reaction of alkenylcobaloximes with N-bromoacetamide

In the reaction of allylcobaloxime (1 mmol) with *N*-bromoacetamide (**23**; 1 mmol) in methylene chloride at ambient temperature, it was evident from the proton NMR spectrum of the mixture that not all of the allylcobaloxime was consumed. Using a two-fold excess of *N*-bromoacetamide, decomposition of the allylcobaloxime was complete within a few seconds and the main organic product was allyl bromide (**24**; eq. 7). Using a four-fold excess of the *N*-bromoacetamide the main product was 1,2,3-tribromopropane (**25**). Under similar conditions with a two-fold excess of *N*-bromoacetamide, but-2-enyl-, 3-methylbut-3-enyl, and but-3-enylcobaloximes gave isomerically pure 3-bromobutene (**26**; eq. 7), 1-methylbromomethylcyclopropane (**27**) and bromomethylcyclopropanes (**28**; eq. 8), respectively. Some 3,4-dibromobutylcobaloxime was also isolated from the latter reaction. In the reaction of 4-methylpent-4-enylcobaloxime (**30**) with a two-fold excess of *N*-bromoacetamide, the main product isolated was 4,5-dibromo-4-methylpentylcobaloxime (**31**).

Reaction of organocobaloximes with N-halogenoimides

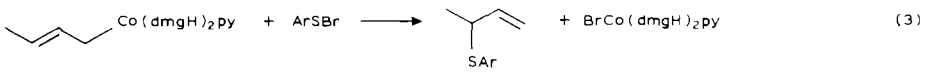
An investigation of the reaction of several *N*-halogenoimides with the above organocobaloximes showed that no *N*-allyl- or *N*-cyclopropylcarbinylimides were



(1)

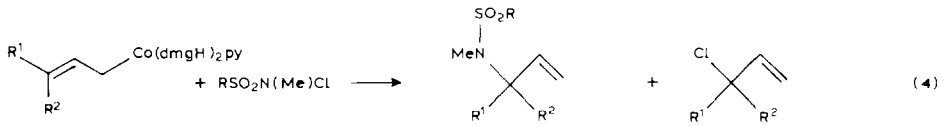
(2)

(X = Cl_3C CHBrCN , $ArSO_2$, RSO_2 , etc.)



(3)

(Ar = 2.4-dinitrophenyl)

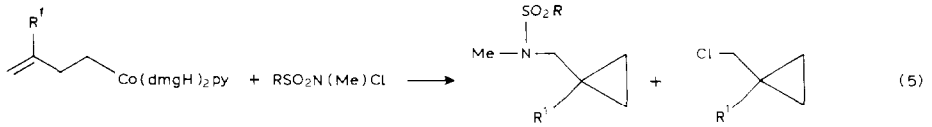


(4)

(**1** , $R^1 = R^2 = H$;
2 , $R^1 = Me$, $R^2 = H$;
3 , $R^1 = R^2 = Me$;
4 , $R^1 = Ph$, $R^2 = H$;
5 , R = Me ;
6 , R = Ph)

(**7** , $R^1 = R^2 = H$, R = Me ;
8 , $R^1 = R = Me$, $R^2 = H$;
9 , $R^1 = R^2 = R = Me$;
10 , $R^1 = Ph$, $R^2 = H$, R = Me ;
15 , $R^1 = R^2 = H$, R = Ph)

(**11** , $R^1 = R^2 = H$;
12 , $R^1 = Me$, $R^2 = H$;
13 , $R^1 = R^2 = Me$;
14 , $R^1 = Ph$, $R^2 = H$)

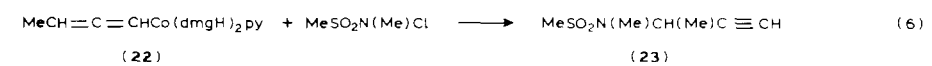


(5)

(**16** , $R^1 = Me$;
17 , $R^1 = H$)

(**18** , $R = R^1 = Me$;
19 , R = Ph , $R^1 = Me$)

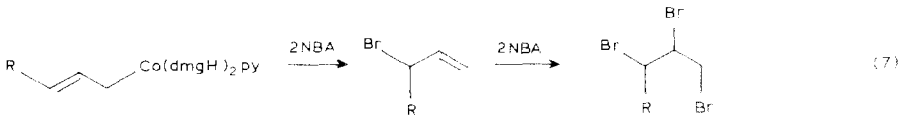
(**20** , $R^1 = Me$;
21 , $R^1 = H$)



(6)

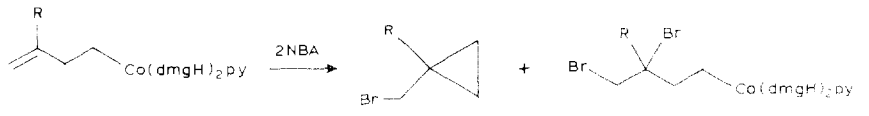
(**22**) (**23**)

formed. The following reactions were thus studied in less detail. The reaction of cobaloxime **16** with *N*-bromosuccinimide, *N*-chlorosuccinimide, or *N*-chlorosaccharin (**32**) at 0 °C in methylene chloride was exothermic and gave substantial yields of the halogenomethylcyclopropane. Benzylcobaloximes reacted similarly to give the benzyl halide.



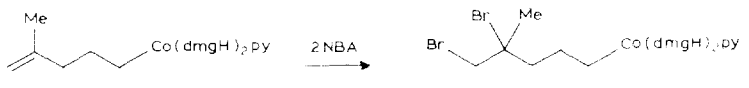
(7)

(1, R = H; 2, R = Me) (24, R = H; 26, R = Me) (25, R = H)



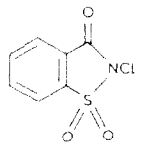
(8)

(16, R = H; 17, R = Me) (27, R = Me; 28, R = H) (29, R = H)



(9)

(30) (31)



(32)

Reaction of oct-1-ene with N-bromoacetamide

In the absence of light oct-1-ene (0.5 *M*) reacted very slowly during 72 h with *N*-bromoacetamide (1 *M*) to give a good yield of 1,2-dibromooctane. When the same reaction was carried out in the presence of a trace of s-butylcobaloxime (0.3 mol%) the reaction was 30% complete within 5 min, and 1,2-dibromooctane was isolated in 92% yield after only 1 h.

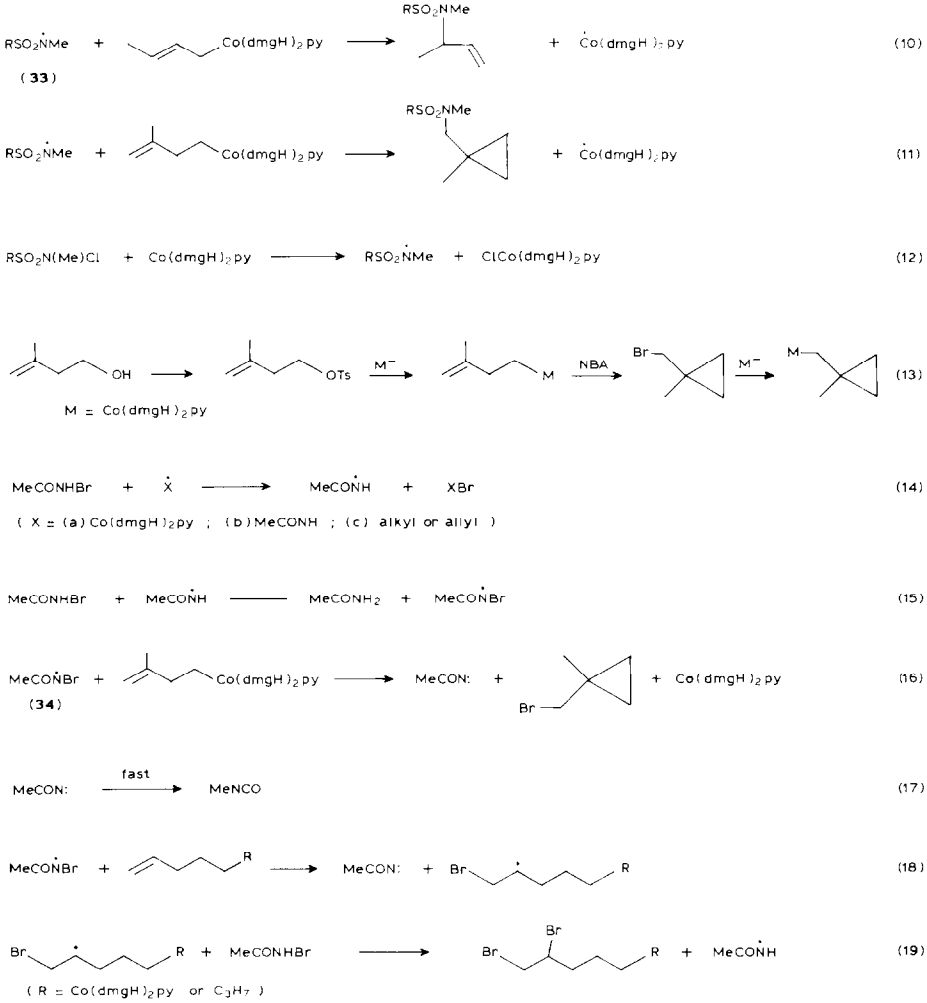
Discussion

The reactions of the *N*-chlorosulphonamides with allyl- and but-3-enyl-cobaloximes follow a pattern directly analogous to those shown in the corresponding reactions of *C*-halogeno and *S*-halogeno compounds [3]. The regiospecific formation of the *N*-allyl and *N*-cyclopropylcarbinyl sulphonamides **7**–**10**, **15**, **18** and **19**, is indicative of the direct attack of the *N*-centred free radical **33** on the terminal unsaturated carbon of the organic ligand (eqs. 10 or 11). Abstraction of the chlorine atom from the *N*-chloro sulphonamide by cobaloxime(II) (eq. 12) [5] thus regenerates the *N*-centred radical **33** and provides the second of two chain-propagating reactions. The process is probably readily initiated by adventitious cobaloxime(II), a free radical which neither dimerises nor disproportionates, which is usually present

in other than fresh solutions of very pure organocobaloximes, or which will be formed after a few moments by trace homolysis of the carbon–cobalt bond.

It is clear that the *N*-organo sulphonamides are not formed by the attack of organic radicals on the *N*-chloro sulphonamide. Such a process would undoubtedly give non-regiospecific organic chlorides which are not observed. It is also unlikely that the *N*-chloro sulphonamide can react as an *N*-centred electrophile, because the electrophilic centre of such species is generally the halogen atom. Indeed, the regiospecific formation, as by-products in some cases, and as the major product from but-3-enylcobaloxime, of regiospecific organic chlorides is indicative of a process in which the chlorine centre of the *N*-chloro sulphonamide, or some chlorine-containing species derived from it, attacks directly at the terminal unsaturated carbon of the organocobaloxime substrate; a process closely related to the bromination reactions described below.

The reactions of but-2-enyl and but-3-enylcobaloximes with *N*-bromoacetamide



(NBA), *N*-bromosuccinimide, *N*-chlorosuccinimide, and *N*-chlorosaccharin, provide convenient regiospecific syntheses of pure 1-methylallyl or cyclopropylcarbinyl halides; indeed, we have used this method as part of the sequence shown in eq. 13 to prepare isomerically pure 1-methylcyclopropylcarbinyl bromide for other stereochemical studies [6]. However, the mechanism of reaction of *N*-bromoacetamide is far from clear. Four features stand out: (i) that the formation of the allyl and cyclopropylcarbinyl halides is regiospecific; (ii) that the stoichiometry is 2NBA/1organocobaloxime; (iii) that the reactions of cobaloximes are far more rapid than those of NBA with terminal olefins; and (iv) that the latter reactions are markedly catalysed by even traces of secondary alkylcobaloximes.

Features (iii) and (iv) together indicate a free radical process, but in each case the regiospecificity demands that the product-forming step takes place through attack of some bromine-containing species on the terminal unsaturated carbon of the organic ligand. As in the reactions of the *N*-chloro sulphonamides, we can rule out any attack by free organic radicals on the bromide-containing species, except as the final step where the reaction is the addition of the elements of bromine to a double bond. The 2/1 stoichiometry, which rules out a simple electrophilic displacement mechanism, appears to be the key to the mechanism, for this demands either the rapid formation of molecular bromine from the reagent or some alternative process in which two molecules of reagent are consumed. If indeed this is a free radical process, initiation, and probably chain propagation in those reactions which concern the cleavage of the carbon–cobalt bond, almost certainly takes place by abstraction of a bromine atom from NBA by, inter alia, cobaloxime(II) (eq. 14a): a reaction analogous to that shown in eq. 12. Though evidence for subsequent processes is limited, it is clear from the absence of *N*-allyl and *N*-cyclopropylcarbinylacetamides, that the acetamido radical is insufficiently electrophilic to attack the organic ligand (all previous examples of such attack have utilised electrophilic radicals) but is capable of reaction with another molecule of NBA, either by abstraction of a bromine atom, which creates no net chemical change (eq. 14b), or by abstraction of a hydrogen atom which, producing a net chemical change (eq. 15) will be evident, even if only by default. The abstraction of a hydrogen atom from NBA has been proposed previously as a key step in the free radical reaction of NBA with cyclohexene [7]. In our case, the *N*-bromo radical **34** may itself be the active brominating reagent, as in eq. 16, or it may merely be a precursor of the true brominating agent. In any event, it is likely that methylisocyanate will be a by-product which would rapidly be consumed by any of several species, acetamide, complexes containing dioximato ligands, etc., which have acidic hydrogen atoms. In cases where the carbon–carbon double bond is remote from any cobaloxime moiety, as in the pentenylcobaloxime or oct-1-ene, the radical **34** (or species derived from it) may add to the double bond and the chain will continue by further abstraction of a bromine atom from NBA by the carbon radical (eqs. 18 and 19).

However, it should be noted that, because of the absence of an abstractable hydrogen atom, the mechanism of reaction of the *N*-halogenoimides cannot be of an identical character to that described above.

Experimental

Materials

N-Methylmethane sulphonamide (^{1}H NMR spectrum δ 2.8 (s, CH_3), 2.9 (s,

CH_3), 4.6 (s, NH)) and *N*-methyl-4-toluene sulphonamide were prepared by the reaction of methanesulphonyl chloride and 4-toluenesulphonyl bromide with an excess of an aqueous solution of methylamine. *N*-Bromoacetamide, *N*-chlorosaccharin, *N*-chloro-*N*-methylmethane sulphonamide (^{1}H NMR spectrum δ 3.1 (s, CH_3), 3.2 (s, CH_3)) and *N*-chloro-*N*-methyl-4-toluene sulphonamide were prepared by reaction of the appropriate halogen with an aqueous solution of the sodium salt of the substituted parent amide or sulphonamide. Allyl- [8], but-2-enyl- [8], but-3-enyl- [9], 3-methylbut-3-enyl- [9], 3-methylbut-2-enyl- [8], buta-1,2-dienyl- [10], 4-methyl-pent-4-enyl- [10], and butyl-cobaloximes were prepared by methods described previously.

Reactions with N-chloro-N-methyl sulphonamides

In a typical reaction a solution of 3-methylbut-3-enylcobaloxime (440 mg, 1.01 mmol) and *N*-chloro-*N*-methylmethane sulphonamide (290 mg, 2.02 mmol) in methylene chloride (20 ml) was allowed to stand for 50 min. The solvent was partially evaporated and the residue was chromatographed on silica gel (Malinkcrodt CC4), eluting successively with pentane, methylene chloride and ethyl acetate mixtures to give sequentially 1-methylchloromethylcyclopropane, *N-(1-methylcyclopropylcarbinyl)-N-methylmethane sulphonamide* (65 mg, 36%; Mass spectrum *m/e* 177.0823. $C_7H_{15}NO_2S$ calc. 177.0823. ^{1}H NMR spectrum δ 0.39 (m, 4H), 1.12 (s, CH_3), 1.61 (s, CH_2), 2.78 (s, CH_3), 2.91 (s, CH_3). ^{13}C NMR spectrum δ 11.06 ($2CH_2$), 20.9, 34.9, 35.7, 58.2 (CH_2N)), and chlorocobaloxime. Similarly prepared were (in order: from parent cobaloxime/reagent; product) from 3-methylbut-3-enylcobaloxime/*N*-chloro-*N*-methyl-4-toluene sulphonamide; *N-(1-methylcyclopropylcarbinyl)-N-methyl-4-toluene sulphonamide* (53%; Mass spectrum *m/e* 253.1128. $C_{13}H_{19}NO_2S$ calc 253.1121. ^{1}H NMR spectrum δ 0.30 (m, 4H), 1.08 (s, 3H), 2.39 (s, 3H), 2.72 (s, 3H), 2.80 (s, 2H), 7.24 and 7.60 (m, C_6H_4). ^{13}C NMR spectrum δ 11.6 (2C), 13.7, 20.9 (CH_3), 31.5 (CH_3), 34.8 (CH_3), 58.2 (CH_2), 127.4, 129.6, 135.0, 143.1 (aromatics)). From allylcobaloxime/*N*-chloro-*N*-methylmethanesulphonyl chloride; *N*-allyl-*N*-methylmethane sulphonamide (57%; Mass spectrum *m/e* 149.0503. $C_5H_{11}NO_2S$ calc 149.0510. ^{1}H NMR spectrum δ 2.83 ($2 \times CH_3$), 3.78 (d, 2H), 5.28 (d, H_{cis} *J* 9.6 Hz), 5.30 (d, H_{trans}, *J* 16.8 Hz), 5.83 (m, 1H); ^{13}C NMR spectrum δ 34.2 (CH_3), 36.3 (CH_3), 52.8 (CH_2), 119.2 (:CH_2), 132.4 (:CH)). From allylcobaloxime/*N*-chloro-*N*-methyl-4-toluene sulphonamide; *N*-allyl-*N*-methyl-4-toluene sulphonamide, (60%. Mass spectrum 225.0823. $C_{11}H_{15}NO_2S$ calc 225.0823. ^{13}C NMR spectrum δ 21.4 (CH_3); 34.2 (CH_3), 53.0 (CH_2), 118.9 (:CH_2), 132.6 (:CH), 127.5, 129.6, 134.7, 143.3 (aromatics)). From but-2-enylcobaloxime/*N*-chloro-*N*-methylmethane sulphonamide, *N-(1-methylallyl)-N-methylmethane sulphonamide* (50%. Found: C, 43.7; H, 8.01; N, 8.8; S, 19.0. $C_6H_{13}NO_2S$ calc.: C, 44.15; H, 8.0; N, 8.6; S, 19.6%. ^{1}H NMR spectrum δ 1.32 (d, 3H), 2.72 (s, 3H), 2.82 (s, 3H), 5.23 (m, CH_2), 5.85 (m, 1H)). From cinnamylcobaloxime/*N*-chloro-*N*-methylmethane sulphonamide; *N-(1-phenylallyl)-N-methylmethane sulphonamide* (40%. Found: C, 58.4; H, 7.7; N, 6.1; S, 13.6. $C_{11}H_{15}NO_2S$ calc: C, 58.6; H, 6.7; N, 6.2; S, 14.2%. ^{1}H NMR spectrum δ 2.64 (s, 3H), 2.75 (s, 3H), 5.38 (m, 2H), 5.55 (d, 1H), 6.05 (m, 1H), ca. 7.3 (m, Ph)). From 3-methylbut-2-enylcobaloxime/*N*-chloro-*N*-methylmethanesulphonamide; *N-(1,1-dimethylallyl)-N-methylmethane sulphonamide* (^{1}H NMR spectrum δ 1.44 (s, 6H), 2.09 (s, 3H), 2.16 (s, 3H), 5.25 (m, 2H), 6.14 (q, 1H)). From buta-1,2-dienylcobaloxime/*N*-chloro-*N*-methylmethane sulphonamide; *N-(1-methylprop-2-ynyl)-N-methylmethane sulphonamide* (18%); Separated by HPLC

on Partisil 5 silica, eluting with 15% EtOAc/petroleum. Mass spectrum *m/e* 161.0516. $C_6H_{11}NO_2S$ calc 161.0521. ^1H NMR spectrum δ 1.47 (d, 3H), 2.43 (d, 1H *J* 2.2 Hz), 2.87 (s, 3H), 2.89 (s, 3H), 4.83 (m, 1H)).

Reactions of N-bromoacetamide

In a typical reaction, *N*-bromoacetamide (0.95 g, 6.9 mmol) was slowly added to a stirred solution of but-3-enyl-cobaloxime (1.44 g, 3.44 mmol) in methylene chloride. After 5 min the mixture was chromatographed on silica gel, as described above, to give bromomethylcyclopropane (0.20 g, 44%, ^1H NMR spectrum (500 MHz) δ 0.36 (m, 2H), 0.75 (m, 2H), 1.29 (m, 1H), 3.28 (d, 2H)), 3,4-dibromobutylcobaloxime (0.6 g; 31%, ^1H NMR spectrum (500 MHz) 1.46–1.73 (m, 4H), 3.62 (dd, 1H, *J* 12.5 & 9.0 Hz), 3.74 (dd, 1H, *J* 12.5 & 6.5 Hz), 4.07 (m, 1H)) and bromocobaloxime. Identical treatment of 3-methylbut-3-enyl-cobaloxime gave 1-methylcyclopropylcarbinyl bromide (Yield 70%, ^1H NMR spectrum (500 MHz) δ 0.55–0.64 (m, 4H), 1.20 (s, 3H), 3.35 (s, 2H)) and of 4-methylpent-4-enylcobaloxime gave *4,5-dibromo-4-methylpentylcobaloxime* (Yield 88%. Found: C, 37.4; H, 5.1; N,11.2; Br, 25.9. $C_{19}H_{30}Br_2CoN_5O_4$ calc: C, 37.3; H, 4.95; N, 11.5; Br, 26.2%. ^1H NMR spectrum (500 MHz) δ 1.09 (m, 2H), 1.50 (m, 1H), 1.61 (m, 1H), 1.74 (s, 3H), 1.81 (m, 2H), 3.73 (d, 1H, *J* 12.0 Hz), 3.78 (d, 1H, *J* 12.0 Hz)). The product of the corresponding reaction of *N*-bromoacetamide with but-2-enylcobaloxime, namely 3-bromobutene, was isolated in 40% yield by careful fractionation of the methylene chloride extract of the reaction mixture at low temperature. In a separate reaction, 3-bromobutene isomerised to a mixture containing 1-bromobut-2-ene when fractionated at higher temperature. Oct-1-ene (0.69 g, 6.2 mmol), *N*-bromoacetamide (0.36 g, 2.6 mmol) and s-butylcobaloxime (0.9 g, 0.02 mmol) in methylene chloride (12 ml) were stirred at ambient temperature for 1 h. The mixture was chromatographed on silica gel as described above to give 1,2-dibromooctane (0.33 g, 1.2 mmol, 92%) identified by comparison with authentic material. The corresponding reaction in $CDCl_3$ in the absence of s-butylcobaloxime showed little change after 24 h, much of the *N*-bromoacetamide remaining undissolved. After 72 h however, 1,2-dibromooctane was isolated as the major product.

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