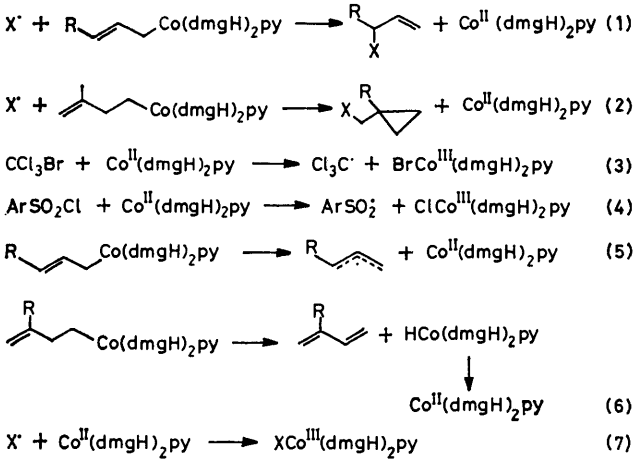
Homolytic Displacements at Carbon. Part 8. Synthesis of 1-Cyano-2-(trichloroethyl)cyclopropanes from Allylcobaloximes *via* But-3-enylcobaloximes and 1-Bromo-1-cyanobut-3-enes

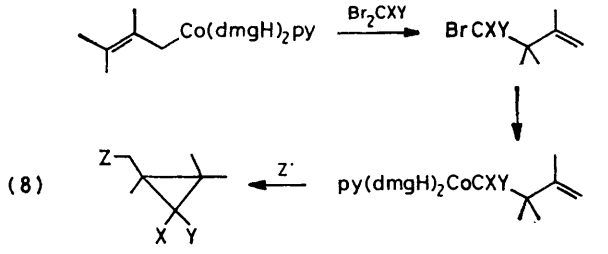
By **Adrian Bury**, **Stephen T. Corker**, and **Michael D. Johnson**,* Department of Chemistry, University College, 20 Gordon Street, London WC1H OAJ

Several 1-cyano-2-(trichloroethyl)cyclopropanes have been synthesised by a sequence of reactions involving homolytic displacement of cobaloxime(II) from allylcobaloxime(III) complexes by bromocyanomethyl radicals and homolytic displacement of cobaloxime(II) from but-3-enylcobaloxime(III) complexes by trichloromethyl radicals: the latter complexes being formed from the 1-bromo-1-cyanobut-3-enes formed in the reactions of the allylcobaloxime(III) complexes. In cases where the but-3-enylcobaloxime(III) complex could not be synthesised, alternative routes to 1-cyano-2-(trichloroethyl)cyclopropanes have been demonstrated, including the homolytic displacement of bromine atoms from 1-bromo-1-cyanobut-3-enes by trichloromethyl radicals.

Two types of regiospecific homolytic displacement reactions have been described in which cobaloxime(II) is displaced from allylcobaloxime(III) or from but-3-enylcobaloxime(III) by attack of an electrophilic radical at the γ- or δ-carbon of the allyl or but-3-enyl ligand, respectively [equations (1) and (2)].[1-3] In both cases it was proposed that the radical (X·) was generated *in situ* by further reaction of the displaced cobaloxime(II) complex with the appropriate free-radical precursor such as trichlorobromomethane [X = Cl_3C, equation (3)] [1,3] or toluenesulphonyl chloride [X = $ArSO_2$, equation (4)].[2,3] Thus a combination of equation (1) or equation (2) with equation (3) or equation (4) provided the propagation steps of a chain reaction. Initiation was readily provided by adventitious cobaloxime(II), frequently present in all but recently purified samples of organocobaloxime(III) complexes and particularly in allylcobaloxime(III) complexes,[4] or by cobaloxime(II) formed through thermolysis or photolysis of the carbon–cobalt bond [equation (5)], or by oxidation of hydridocobaloxime(III) formed in a β-elimination from an organocobaloxime(III) [*e.g.* equation (6)].[5] Termination, which is not achieved by dimerisation of the cobaloxime(II), almost certainly included capture of the radical X· by cobaloxime(II) [equation (7)]. In many of the above cases, very high yields of the regiospecific organic product were obtained merely on mixing the radical precursor with the organocobaloxime(III) in an inert solvent, though in some cases, slight warming or irradiation with tungsten lamps was necessary.



Since but-3-enylcobaloximes may be prepared from but-3-enyl halides, which may be prepared from allylcobaloximes by the above reactions, it was apparent that a sequence of reactions utilising reaction (1) to prepare novel substituted but-3-enyl halides, and subsequently reaction (2), might provide a route to some novel cyclopropanes of importance in pyrethroid chemistry [6] [*e.g.* sequence (8)].

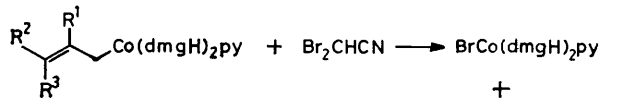


In this paper are described studies of the synthesis of cyano-substituted cyclopropanes by the above sequence and by some related paths from the novel but-3-enyl halides.

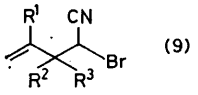
RESULTS

Preparation of 1-*Bromo*-1-*cyanobut*-3-*enes*.—Allyl-, 2-methylallyl-, 2-phenylallyl-, and 3-methylbut-2-enyl-bis(dimethylglyoximato)pyridinecobalt(III), compounds (1)—(4), respectively, reacted with a small excess of dibromoacetonitrile at ambient temperature in methylene chloride for periods in the range 1—6 h to give good yields of bromobis(dimethylglyoximato)pyridinecobalt(III) and the corresponding 1-bromo-1-cyanobut-3-ene [(5)—(8), equation (9)]. Similar reactions of 3-phenylallyl- (mainly *trans*), 2-methylbut-2-enyl-, and but-2-enyl-bis(dimethylglyoximato)pyridinecobalt(III) (9)—(11) gave mixtures of diastereoisomers of the cor-

responding 1-bromo-1-cyanobut-3-enes [(12)—(14), equation (9)].



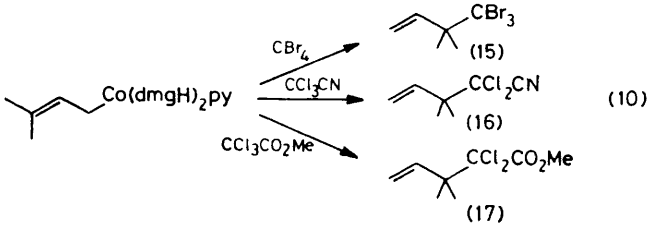
(1) $R^1 = R^2 = R^3 = H$
(2) R^1 = Me, $R^2 = R^3 = H$
(3) R^1 = Ph, $R^2 = R^3 = H$
(4) $R^1 = H$, $R^2 = R^3$ = Me
(9) $R^1 = R^2 = H$, R^3 = Ph
(10) $R^1 = R^2$ = Me, $R^3 = H$
(11) $R^1 = R^2 = H$, R^3 = Me



(9)

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

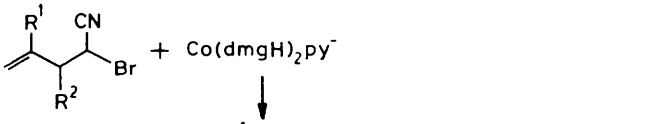
Cobaloxime (4) also reacted with tetrabromomethane, methyl trichloroacetate, and with trichloroacetonitrile in methylene chloride at ambient temperature to give 2,2-dimethyl-1,1,1-tribromobut-3-ene (15), methyl 1,1-dichloro-2,2-dimethylpent-4-enoate (16), and 1-cyano-1,1-dichloro-2,2-dimethylbut-3-ene (17), respectively [equation (10)]. No similar reaction was observed between compound (4) and methyl dichloroacetate or dichloroacetonitrile.



(10)

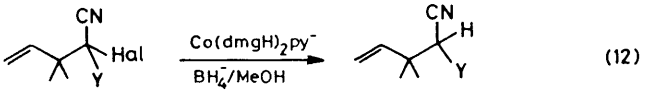
Preparation of 1-*Cyanobut*-3-*enylcobaloximes*.—1-Bromo-1-cyano-, 1-bromo-1-cyano-2-methyl-, 1-bromo-1-cyano-3-methyl-, and 1-bromo-1-cyano-3-phenyl-but-3-ene, (5), (14), (6), and (7), respectively, reacted with the bis(dimethylglyoximato)pyridinecobaltate(I) ion in aqueous methanol at ambient temperature for from 1—4 h to give the corresponding 1-cyano-, 1-cyano-2-methyl-, 1-cyano-3-methyl-, and 1-cyano-3-phenyl-but-3-enylbis-(dimethylglyoximato)pyridinecobalt(III) complexes, (18)—(21) respectively [equation (11)]. No but-3-enylcobaloximes could be isolated from the corresponding reactions of the bis(dimethylglyoximato)pyridinecobaltate(I) ion with the diastereoisomeric mixture of 1-bromo-1-cyano-2-phenylbut-3-ene or with the 2,2-dimethyl-substituted but-3-enyl halides (8) and (15)—(17). In the latter cases, reduction products of the but-3-enyl halides were formed [equation (12)] when borohydride ion was used in the preparation of the cobaltate(I) ion.

Preparation of Substituted Cyanocyclopropanes from 1-*Cyanobut*-3-*enylcobaloximes*.—Four 1-cyanobut-3-enylcobaloximes (18)—(21) were treated with trichloromethanesulphonyl chloride in methylene chloride at



(11)

(18) $R^1 = R^2 = H$
(19) $R^1 = H$, R^2 = Me
(20) R^1 = Me, $R^2 = H$
(21) R^1 = Ph, $R^2 = H$

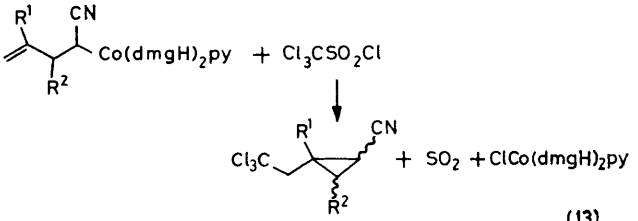


(12)

(Y = Halogen or H)

temperatures up to 55 °C for several hours to give chlorobis(dimethylglyoximato)pyridinecobalt(III) and isomeric mixtures of 1-cyano(β,β,β-trichloroethyl)cyclopropane (22), 1-cyano-2-methyl-3-(β,β,β-trichloroethyl)-cyclopropane (23), 1-cyano-2-methyl-2-(β,β,β-trichloroethyl)cyclopropane (24), and 1-cyano-2-phenyl-2-(β,β,β-trichloroethyl)cyclopropane (25), respectively [equation (13)].

The diastereoisomers of each of compounds (24) and (25) were formed in nearly equal yield, indicative of the nearly equal steric influence of the substituent R^1 and the incipient trichloroethyl group in the transition state for ring closure.[3] The diastereoisomers of compound (24) were separated by h.p.l.c. and separately characterised. The diastereoisomers of compound (25) were separated through their different solubilities in pentane



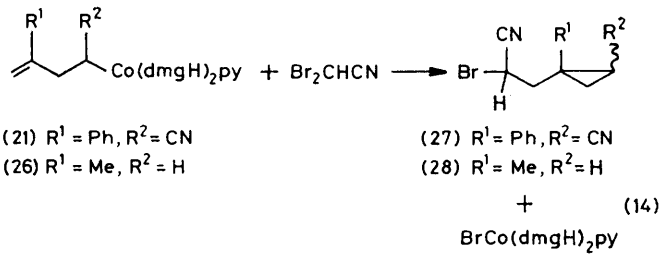
(13)

(22) $R^1 = R^2 = H$
(23) $R^1 = H$, R^2 = Me
(24) R^1 = Me, $R^2 = H$
(25) R^1 = Ph, $R^2 = H$

and separately characterised. A major feature of their ^1H n.m.r. spectra is the large difference in chemical shifts (0.92 and 0.80 p.p.m.) between the diastereotopic methylene protons of the trichloroethyl group. The several isomers of compound (23) were not separated.

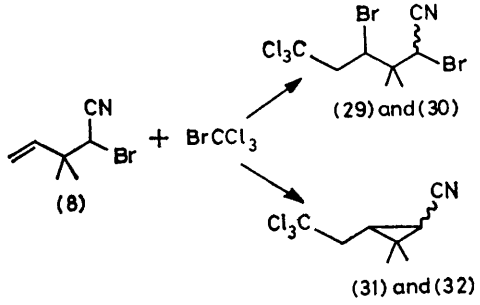
Two related cyclopropane derivatives (27) and (28) were similarly formed in the reaction of compound (21) and of 3-methylbut-3-enylcobaloxime (26)[3] with dibromoacetonitrile [equation (14)]. The diastereoisomers of (27) were not separated but recrystallisation of

the crude product gave a crystalline material apparently composed of a single diastereoisomer.



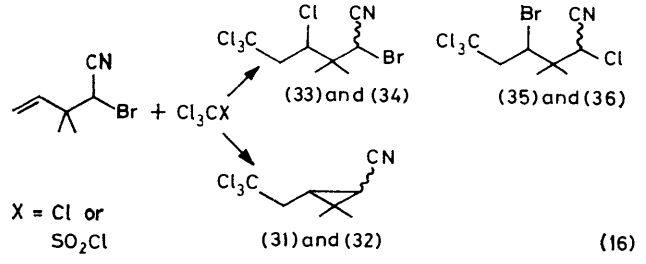
(14)

Reaction of But-3-enyl Halides with Polyhalogenomethanes.—1-Bromo-1-cyano-2,2-dimethylbut-3-ene (8) reacted with bromotrichloromethane at 110 °C in the presence of ferric chloride and n-butylamine to give predominantly two isomeric addition products, 1,3-dibromo-5,5,5-trichloro-1-cyano-2,2-dimethylpent-3-ene (29) and (3), and a low yields of the two isomeric 1-cyano-2,2-dimethyl-3-(β,β,β-trichloroethyl)cyclopropanes (31) and (32) [equation (15)]. The corresponding re-



(15)

actions of compound (8) with carbon tetrachloride at 150 °C in the presence of catalysts, or with trichloromethanesulphonyl chloride, gave four addition products which could not be completely separated from several minor unidentified products, but are believed, from their ^{1}H n.m.r. spectra, to be (33)—(36), together with higher yields of the cyclopropanes (31) and (32) [equation (16)]. The isomeric mixture of (31) and (32) was also

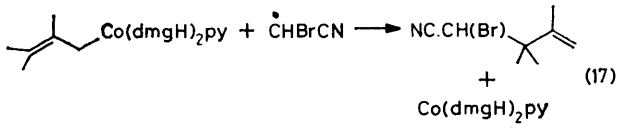


(16)

prepared by zinc-catalysed debromination of the diastereoisomeric mixture of (29) and (30). The components of this mixture were also separated by h.p.l.c. and separately characterised.

DISCUSSION

The reactions of the allylcobaloximes with the halogenomethanes conformed to those described earlier.[1] The proposed pathway [equation (17)] is supported by the additional observation that the reaction of 2 mol equiv. of dibromoacetonitrile with preformed bis(dimethylglyoximato)pyridinecobalt(II) gave 1-bromo-1-cyanomethylbis(dimethylglyoximato)pyridinecobalt(III) and bromobis(dimethylglyoximato)pyridinecobalt(III) in good yield, indicating the formation and capture of bromocyanomethyl radicals as in equations (18) and (19). In the presence of the allylcobaloxime, the bromocyanomethyl radicals react preferentially at the γ-carbon of the allyl ligand to give the observed bromocyanobutenes.



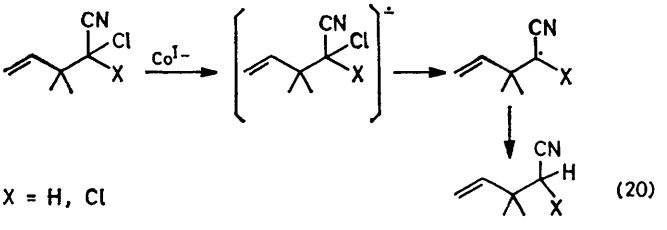
(17)

$$CHBr_2CN + Co(dmgH)_2py \longrightarrow BrCo(dmgH)_2py + {}^{\bullet}CHBrCN \quad (18)$$

$$^{\bullet}CHBrCN + Co(dmgH)_2py \longrightarrow NC.CH(Br)Co(dmgH)_2py \quad (19)$$

Similar production and reaction of tribromomethyl, cyanodichloromethyl, and methyl dichloroacetate radicals with (4) account for the formation of the products (15)—(17). The lack of reaction of methyl dichloroacetate and of dichloroacetonitrile with (4) is almost certainly a result of the reluctance of the cobaloxime(II) to abstract a chlorine atom from these two substrates [8] and of the propensity of the organic radical, if formed, to react with (4) preferentially by abstraction of a hydrogen atom from the dioximato-ligands.

Formation of Butenylcobaloximes.—A number of workers have observed that the yields of cobaloximes derived from α-cyano- and α-alkoxycarbonyl-alkyl halides are frequently low,[9] and this has been ascribed to effective competition between the normal displacement of halide ion and electron transfer from cobaloxime(I) to the halogenoester or nitrile leading, *inter alia*, to reduction [as in equation (20)] especially when the normal bimolecular displacement reaction is retarded, for example by β-methyl groups. Indeed, such retardation is undoubtedly responsible for the reduction of the 2,2-dimethylbut-3-enyl halides [equation (20)] which are comparable with, if not more hindered than, neo-

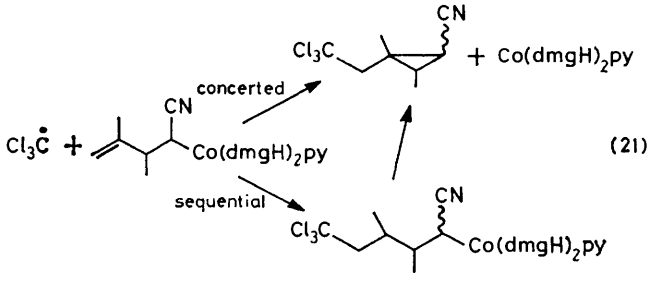


(20)

pentyl halides. However, we observed in other less hindered cases that the product cobaloxime was very slow to precipitate from aqueous methanolic solutions, but that surprisingly good yields could be obtained if the aqueous solutions were allowed to stand for several days, or if the organocobaloxime was efficiently extracted with

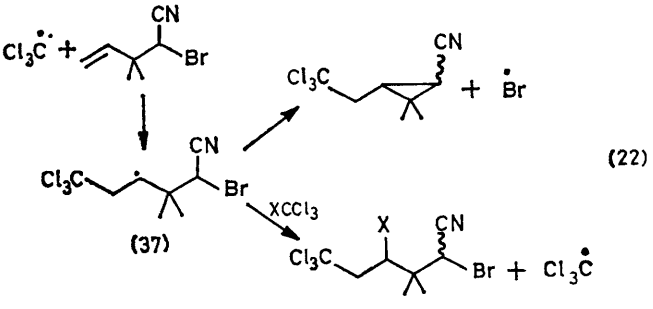
methylene chloride. 1-Cyanoalkyl- and 1-cyanobut-3-enyl-cobaloximes are among the more stable of organocobaloximes and survive such treatment without decomposition. The highest yield was obtained with the less soluble 1-cyano-3-phenylbut-3-enylcobaloxime (21).

Formation of Cyclopropanes.—The formation of trichloroethylcyclopropanes from the but-3-enylcobaloximes also proceeded in accord with the cyclisations described earlier.[3] The high yields obtained in most cases are indicative of an attack of the trichloromethyl radical at the δ-carbon of the but-3-enyl ligand with synchronous or subsequent expulsion of the cobaloxime(II) fragment and intramolecular cyclisation [equation (21)]. Neither in these reactions nor in the earlier



(21)

examples could a distinction be made between the concerted and sequential processes. However, we favour the sequential path because the corresponding reactions of the bromide (8) with bromotrichloromethane, carbon tetrachloride, and trichloromethanesulphonyl chloride gives yields of cyclisation products (31) and (32) which



(22)

clearly depend on the ease of atom transfer to the intermediate radical (37) from the organic radical precursor This ease of atom transfer decreases in the order $BrCCl_3 > ClSO_2CCl_3 > ClCCl_3$ and, as the concentration of the halogen atom donor decreases, so the yield of the cyclisation product from (37) also increases.*

The formation of four addition products in the reaction of compound (8) with carbon tetrachloride and trichloromethanesulphonyl chloride was unexpected. They show ^1H n.m.r. spectra (200 MHz) characteristic of 1,3-dihalogeno-2,2-dimethyl-5,5,5-trichloropentanes, but could not be completely separated from minor products and hence gave somewhat ambiguous analyses. We believe, however, that the major pair of these products are the normal 1,2-addition products, and that the others are formed through a 1,3-halogen shift or similar rearrangement.

* Since publishing a note on the homolytic displacement of bromine atoms from substituted bromopropyl radicals (A. Bury and M. D. Johnson, *J. Chem. Soc., Chem. Commun.*, 1980, 498) our attention has been drawn to a related study in which iodopropyl radicals derived from 1,3-di-iodopropane and perisobutyric anhydride underwent similar intramolecular cyclisation with loss of iodine atoms (R. F. Drury and L. Kaplan, *J. Am. Chem. Soc.*, 1973, **95**, 2217, and references cited therein).

EXPERIMENTAL

Materials.—2-Methylbut-2-enoic acid (Aldrich), lithium aluminium hydride (Hopkin and Williams), dimethylglyoxime (East Anglia Chemicals), pyridine, cobalt chloride hexahydrate, cobalt acetate tetrahydrate, trichloroacetic acid, iodoform, carbon tetrachloride (all B.D.H.), cinnamyl chloride, dibromoacetonitrile, trichloroacetonitrile, trichloromethanesulphenyl chloride, and bromotrichloromethane (all Aldrich) were commercial materials used without further purification. Allyl chloride, crotyl chloride, 2-methylallyl chloride (B.D.H.), and 2-methybut-2-enyl chloride (Aldrich) were redistilled prior to use. 2-Phenylallyl bromide was prepared as described earlier,[10] methyl trichloroacetate was prepared from trichloroacetic acid by standard methods, and trichloromethanesulphonyl chloride was prepared from trichloromethanesulphenyl chloride.[11]

Chromatography.—H.p.l.c. separations were carried out on a Waters ALC 100 Instrument with an M 6000 pump and a refractive index detector using a 3 × 25 cm Partisil ¼ ft in column with the particular eluants described below. Column chromatography was carried out using Mallinckrodt CC7 or CC4 silica gel.

Preparation of Cobaloximes.—2-Methylbut-2-enoic acid (tiglic acid; 2.0 g, 20 mmol) in anhydrous ether (5 cm^3) was added dropwise to a suspension of lithium aluminium hydride (0.52 g, 15 mmol) in anhydrous diethyl ether (20 cm^3) and the mixture was refluxed for 2 h. Water (2 cm^3) and 15% aqueous sodium hydroxide were carefully added and the mixture was filtered. The precipitate was washed with diethyl ether (3 × 30 cm^3) and the combined ether fractions were evaporated to give 2-methylbut-2-enol (1.03 g, 11 mmol, 55%) [^1H n.m.r. δ 1.68 (d, Me), 1.62br (s, Me), 3.98 (s, CH_2), 5.5 (m, CH)] which was converted directly into *E*-1-bromo-2-methylbut-2-ene by reaction with PBr_3 in pyridine (yield 0.77 g, 33%) [^1H n.m.r. δ 1.77 (s, Me), 1.65 (d, Me) 4.04 (s, CH_2), and 5.76 (q, CH). The latter compound (0.75 g, 5 mmol) in methanol (10 cm^3) was degassed with N_2 and added dropwise to a solution of the bis(dimethylglyoximato)pyridinecobaltate(I) ion which had been prepared by the addition of sodium hydroxide (1.60 g, 40 mmol) in water (3 cm^3) to a degassed solution of cobalt chloride hexahydrate (2.38 g, 10 mmol), dimethylglyoxime (2.30 g, 20 mmol) and pyridine (0.79 g, 10 mmol) in methanol (100 cm^3). The mixture was stirred under N_2 for 10 min and poured into a large excess of water. The orange precipitate of *2-methylbut-2-enylbis(dimethylglyoximato)pyridinecobalt*(III) (0.87 g, 42%) was filtered off, washed copiously with water, and dried *in vacuo* (Found: C, 48.9; H, 6.5; N, 15.3. $C_{18}H_{28}CoN_5O_4$ requires C, 49.4; H, 6.45; N, 16.0%). This material almost certainly exists as an equilibrium mixture of *E*- and *Z*-isomers as a result of the dynamic equilibrium in solution,[4,12] which is evident from the time-dependent broadening of the ^1H n.m.r. spectrum.

[^{1}H n.m.r. (principal peaks only) δ 2.09 (s, dmgH Me's), 1.53br (s, Me), 1.01 (d, Me), 2.41 (s, CH_2), and 5.15br (quint, CH)]. All other allylcobaloximes were prepared as described earlier from the appropriate allyl halide.[4,10,13]

Preparation of Bromocyanomethylcobaloxime.—Cobalt acetate tetrahydrate (5.0 g, 20 mmol), dimethylglyoxime (4.6 g, 40 mmol), and pyridine (1.58 g, 20 mmol) were stirred under nitrogen in methanol (50 cm^3). To the homogeneous solution was added dibromoacetonitrile (1.99 g, 10 mmol). A brown precipitate formed immediately and the suspension was stirred for 10 min and poured into water. The solid was filtered off, dried *in vacuo*, and shown to be a mixture of bromobis(dimethylglyoximato)pyridinecobalt(III) and bromocyanomethylbis(dimethylglyoximato)pyridinecobalt(III) by ^{1}H n.m.r. spectroscopy and t.l.c. The filtrate was allowed to stand overnight after which the additional orange precipitate of *bromocyanomethylbis(dimethylglyoximato)pyridinecobalt*(III) was filtered off and dried *in vacuo* (Found: C, 36.7; H, 4.25; Br, 15.4; N, 17.0. $C_{15}H_{20}BrCoN_6O_4$ requires C, 37.0; H, 4.1; Br, 15.8; N, 17.25%), δ 4.07 (s, CHBrCN), 2.22 and 2.24 (both s, 2 diastereotopic pairs of dmgH Me's).[14] Similarly prepared from trichloroacetonitrile and purified by extraction with ethyl acetate was *cyanodichloromethylbis(dimethylglyoximato)pyridinecobalt*(III) (Found: C, 37.6; H, 4.2; Cl, 14.5; N, 17.9. $C_{15}H_9Cl_2CoN_6O_4$ requires C, 36.8; H, 4.0; Cl, 14.9; N, 17.6%), δ 2.35 (s, dmgH Me's). Similarly prepared from iodoform was *di-iodomethylbis(dimethylglyoximato)pyridinecobalt*(III) (Found: C, 26.8; H, 3.1; I, 39.6; N, 11.0. $C_{14}H_{20}CoI_2N_5O_4$ requires C, 26.5; H, 3.1; I, 40.0; N, 11.0%), δ 5.23 (s, CHI_2) and 2.28 (s, dmgH Me's). Several attempts to isolate trichloromethylbis(dimethylglyoximato)pyridinecobalt(III) [15] from the reaction of bis(dimethylglyoximato)-pyridinecobalt(II) with either carbon tetrachloride or trichloromethanesulphonyl chloride failed because of decomposition of the product, though a 1 : 1 mixture with chlorobis(dimethylglyoximato)pyridinecobalt(III) was precipitated at the end of each reaction.

Reactions of Allylcobaloximes.—In a typical reaction, a solution of dibromoacetonitrile (1.99 g, 10 mmol) in methylene chloride (75 cm^3) was added directly to solid 3-methylbut-2-enylbis(dimethylglyoximato)pyridinecobalt(III) (4.37 g, 10 mmol). The mixture was stirred for a period in the range 30 min to 24 h during which time bromobis(dimethylglyoximato)pyridinecobalt(III) was precipitated. Pentane (50 cm^3) was added and, after coagulation, the solid was filtered off and washed with pentane. The combined pentane extracts were evaporated and the residue was chromatographed on silica gel to give 1-bromo-1-cyano-2,2-dimethylbut-3-ene (1.54 g, 82%) [1] containing traces of 1,1-dibromo-1-cyano-2,2-dimethylbut-3-ene formed by reaction of traces of tribromoacetonitrile in the reagent. The product was therefore purified further by h.p.l.c. Similarly prepared were: 1-*bromo*-1-*cyanobut*-3-*ene* (66% yield) (Found: C, 37.9; H, 3.9; Br, 50.2; N, 8.9. C_5H_6BrN requires C, 37.5; H, 3.8; Br, 49.9; N, 8.8%), for ^{1}H n.m.r. details ree ref. 1. 1-*Bromo*-1-*cyano*-3-*phenylbut*-3-*ene* (83% yield) (Found: C, 55.8; H, 4.4; Br, 33.7; N, 5.9. $C_{11}H_{10}BrN$ requires C, 56.0; H, 4.3; Br, 33.8; N, 5.9%), δ 4.16 (t, CHBrCN, *J* 7.8 Hz), 3.27br (d, CH_2), 5.47 and 5.30br (both s, CH_2), and 7.37 (Ph). 1-*Bromo*-1-*cyano*-3-*methylbut*-3-*ene* (79% yield) (Found: C, 41.7; H, 4.6; N, 8.1. C_6H_8BrN requires C, 41.4; H, 4.6; N, 8.0%), δ 4.41 (t, CHBrCN, *J* 7.6 Hz), 2.82br (d, CH_2), 5.0br (m, :CH_2), and 1.82 (s, Me). Mixed diastereoisomers of 1-*bromo*-1-*cyano*-2-*phenylbut*-3-*ene* (31% yield), δ 4.50 and 4.47 (both d, CHBrCN of diastereoisomers), 3.47 (t, CHPh), 5.8—6.5 (:CH), 5.1—5.4 (:CH_2), and 7.33 (Ph). Mixed diastereoisomers of 1-*bromo*-1-*cyano*-2,3-*dimethylbut*-3-*ene*, δ 4.37 (d, CHBrCN *J* 7.6 Hz), 2.5—3.0 (m's, CHMe), 4.99 (m, :CH_2), 1.30 (d, *J* 7.0 Hz) and 1.38 (d, *J* 7.3 Hz) (diastereoisomeric CH_3CH), and 1.78 (s, CH_3C:). Mixed diastereoisomers of 1-*bromo*-1-*cyano*-2-*methylbut*-3-*ene* (yield 74%) (Found: C, 41.4; H, 4.4; Br, 47.0. C_6H_8BrN requires C, 41.4; H, 4.6; Br, 45.9; N, 7.0%), δ 4.28 and 4.30 (both d, *J* 5.3 Hz, CHBrCN), 2.73 (m, CHMe), 5.3—5.6 (m, CH), *ca.* 5.1 (m, CH_2), and 1.28 and 1.30 (d's *J* 6.7 Hz, diastereoisomeric CH_3). Similarly prepared from other polyhalogenomethanes were: 1,1,1-*tribromo*-2,2-*dimethylbut*-3-*ene* (yield 88%) (Found: C, 21.4; H, 2.8; Br, 74.2. $C_6H_9Br_3$ requires C, 22.4; H, 2.8; Br, 74.7%), δ 6.24 (q, CH *J* 10.0 and 18.0 Hz), 5.2—5.5 (m, CH_2), 1.53 (s, CH_3); *methyl* 2,2-*dichloro*-3,3-*dimethylpent*-4-*enoate* (yield 23%) (Found: C, 45.0; H, 2.8; Cl, 74.2. $C_6H_{12}Cl_2O_2$ requires C, 46.0; H, 2.8; Cl, 74.7%), δ 6.17 (q, CH, *J* 10.1 and 18.1 Hz), 5.0—5.3 (m, CH_2), 1.38 (s, Me), 3.51 (s, CO_2Me)], and 2,2-dichloro-3,3-dimethylpent-4-enonitrile.[1]

Preparation of 1-*Cyanobut*-3-*enylcobaloximes.*—In a typical reaction, 1-bromo-1-cyano-3-methylbut-3-ene (1.25 g, 7.2 mmol) in methanol (5 cm^3) was degassed with N_2 and added to bis(dimethylglyoximato)pyridinecobaltate(I) (7.2 mmol) prepared as above. The mixture was stirred vigorously for 2.5 h, poured into a large excess of water, and extracted with methylene chloride. The extract was dried (Na_2SO_4), evaporated to *ca.* 15 cm^3, and mixed with pentane (100 cm^3). The precipitate of 1-*cyano*-3-*methylbut*-3-*enylbis(dimethylglyoximato)pyridinecobalt*(III) was filtered off, dried *in vacuo*, and purified by chromatography on silica gel with elution by methylene chloride containing 5% (v/v) ethyl acetate (yield 1.39 g, 42%) (Found: C, 48.95; H, 6.0; N, 18.3. $C_{19}H_{27}CoN_6O_4$ requires C, 49.35; H, 5.9; N, 18.2%) δ 2.24 (s, dmgH Me's), 1.62 (s, Me), and 4.7 (m, CH_2).

Similarly prepared were: 1-*cyanobut*-3-*enylbis(dimethylglyoximato)pyridinecobalt*(III) (yield 39%) (Found: C, 47.9; H, 5.7; N, 18.5. $C_{18}H_{25}CoN_6O_4$ requires C, 48.2; H, 5.6; N, 18.8%), δ 2.23 (s, dmgH Me's), 1.7 (t, CHCN), 5.0 (m, :CH_2). 1-*Cyano*-3-*phenylbut*-3-*enylbis(dimethylglyoximato)pyridinecobalt*(III) (yield 75%) (Found: C, 54.9; H, 5.8; N, 15.8. $C_{24}H_{30}CoN_6O_4$ requires C, 55.0; H, 5.6; N, 16.0%), δ 2.27 (d, dmgH Me's), 7.25br (s, Ph), and 5.2 (m, :CH_2); and mixed diastereoisomers of 1-*cyano*-2-*methylbut*-3-*enylbis(dimethylglyoximato)pyridinecobalt*(III) (yield 74%) (Found: C, 49.0; H, 5.8; N, 18.0. $C_{19}H_{27}CoN_6O_4$ requires C, 49.3; H, 5.9; N, 18.2%), δ 2.20 (s, dmgH Me's), 0.99 and 0.97 (both d, 2 × CH_3 of diastereoisomers), and 4.8 (m, CH_2).

Preparation of Cyanocyclopropanes.—In a typical reaction, 1-cyanobut-3-enylbis(dimethylglyoximato)pyridinecobalt(III) (0.56 g, 1.25 mmol) and trichloromethanesulphonyl chloride (0.27 g, 1.25 mmol) were heated with deuteriochloroform (3 cm^3) in a sealed tube to 60 °C for 20 h. The ^{1}H n.m.r. spectrum of the mixture was taken and the mixture was chromatographed on silica gel using methylene chloride to elute the organic material and ethyl acetate to elute chlorobis(dimethylglyoximato)pyridinecobalt(III). The organic fraction was separated by h.p.l.c. using 10% ethyl acetate in light petroleum (b.p. 40—60 °C) to give trans-1-*cyano*-2-β,β,β-*trichloroethylcyclopropane* (0.06 g, 26%) [(Found: C, 36.5; H, 3.2; Cl, 53.5; N, 7.2. $C_6H_6Cl_3N$ requires C, 36.3; H, 3.1; Cl, 53.6; N, 7.1%), δ 3.0

(m, CH_2CCl_3), 0.97—1.85 (m's cyclopropane)], and *cis*-1-*cyano*-2-β,β,β-*trichloroethylcyclopropane* [δ 2.71 (2 d's, CH_2CCl_3), and 0.9—2.0 (m's, cyclopropane) ($J_{1\alpha}$ 7.2, $J_{1\alpha'}$ 6.8 Hz)].

Similarly prepared were: (*a*) the two isomers (66% total yield) of 2-*cyano*-1-*methyl*-1-β,β,β-*trichloroethylcyclopropane* [isomer A (Found: C, 40.0; H, 3.8; N, 6.4. $C_7H_8Cl_3N$ requires C, 39.7; H, 3.8; N, 6.6%), δ 2.63 and 2.77 (both d, diastereotopic CH_2CCl_3, J 15.2 Hz); 1.51 (s, Me), and 1.0—1.8 (three m's, cyclopropane); isomer B (Found: C, 39.3; H, 3.7; N, 6.6%), δ 2.77, 3.18 (both d, diastereotopic CH_2CCl_3, J 15.4 Hz), 1.34 (s, Me), and 1.1—1.5 (m, cyclopropane).

(b) E *and* Z-2-*Cyano*-1-*phenyl*-1-(β,β,β-*trichloroethyl*)-*cyclopropane* separated by extraction with pentane (insoluble isomer, 43% yield) (Found: C, 52.4; H, 3.8; Cl, 38.5; N, 5.0. $C_{12}H_{10}Cl_3N$ requires C, 52.7; H, 3.7; Cl, 38.7; N, 5.1%), δ 2.60 3.52 (both d's diastereotopic CH_2CCl_3, $J_{\alpha\alpha}$ 15.2 Hz), 7.37 (Ph), and 1.83 (m, cyclopropane); ^{13}C n.m.r. δ 59.5 (C_α), 11.0, 20.3, and 31.4 (cyclopropane), 118.0 (CCl_3), 197.5 (CN), 128.2, 128.6, 129.7, and 138.6 (Ph). Soluble isomer, 15% yield isolated, 40% yield in mixture (Found: C, 52.3; H, 3.7; Cl, 38.0; N, 5.0), δ 3.00 and 3.80 (both d's diastereotopic CH_2CCl_3, $J_{\alpha\alpha}$ 15.6 Hz), 7.37 (Ph), 1.5—2.0 (m, cyclopropane); ^{13}C n.m.r. δ 62.5 (C_α), 11.2, 20.3, and 32.4 (cyclopropane), 118.6 (CCl_3), 197.3 (CN); and 128.6, 128.8, 130.4, and 135.9 (Ph).

(c) A mixture of E- and Z-2-*cyano*-1-(β-*bromo*-β-*cyanoethyl*)-1-*phenylcyclopropane*, from the corresponding reaction of dibromoacetonitrile with 3-phenylbut-3-enylcobaloxime. Product recrystallised from pentane (yield 87%) (Found: C, 56.5; H, 4.2; Br, 29.1; N, 10.1. $C_{13}H_{11}BrN_2$ requires C, 56.8; H, 4.0; Br, 29.0; N, 10.2%), ^1H n.m.r. of main isomer δ 3.96 (m, α-CH_2), 2.8—3.0 (m, CHBrCN, $J_{\alpha\beta}$ 5.4 Hz), 7.34 (Ph), and 1.6—1.9 (cyclopropane).

(d) 1-*Methyl*-1-(β-*bromo*-β-*cyanoethyl*)*cyclopropane* from the reaction of dibromoacetonitrile with 3-methylbut-3-enylcobaloxime (yield 61%) δ 2.1 (m, α-CH_2), 4.41 (q, CHBrCN, $J_{\alpha\beta}$ 7.2 Hz $J_{\alpha'\beta}$ 9.2 Hz), 1.13 (s, Me), and 0.25—0.67 (m, cyclopropane).

(e) Mixture of isomers of 1-*cyano*-2-*methyl*-3-(β,β,β-*trichloroethyl*)*cyclopropane* (yield 73%) δ (principal resonances only) 2.0—3.3 (m, α-CH_2), 1.3—1.4 d's, Me's), and 1.3—1.8 (m, cyclopropane)).

Reactions of 2-*Bromo*-3,3-*dimethylpent*-4-*enonitrile* (8).—(*a*) *With bromotrichloromethane.* Compound (8) (4.7 g, mmol) and bromotrichloromethane (25 cm^3) were heated in a sealed tube with anhydrous ferric chloride (0.5 g) and butylamine (1.5 g) at 150 °C for 24 h. The product was chromatographed on silica gel to give a mixture of diastereoisomers of 2,4-dibromo-6,6,6-trichloro-3,3-dimethylhexanonitrile (Found: C, 24.3; H, 2.6; total halogen as Cl, 46.4; N, 3.3. $C_8H_{10}Br_2Cl_3N$ requires C, 24.9; H, 2.6; total halogen, 45.9; N, 3.6%). The diastereoisomers were separated on h.p.l.c. using 20% methylene chloride in light petroleum (b.p. 40—60 °C) to give: minor isomer (32% yield) (Found: C, 25.3; H, 2.9; total halogen 44.8; N, 3.6%) δ 4.87 (s, CHBrCN), 4.44 (q, CHBr), 3.45 (m, CH_2), 1.25 and 1.45 (both s, 2 × Me). Major isomer in 48% yield (Found: C, 25.1; H, 2.8; total halogen, 46.2; N, 3.6%), δ 4.83 (s, CHBrCN), 4.42 (q, CHBr), 3.30 (m, CH_2), and 1.34 and 1.44 (both s, 2 × CH_3). Traces of 2-cyano-3,3-dimethyl-1-(trichloroethyl)cyclopropanes were evident in the ^1H n.m.r. spectrum of the crude material, but they were not isolated (see below). No reaction took place under the same conditions in the absence of ferric chloride and butylamine.

(*b*) *With carbon tetrachloride.* Compound (8) (3.76 g, 20 mmol), ferric chloride (0.3 g), and butylamine (1.2 g) were heated in a sealed tube with carbon tetrachloride (20 cm^3) at 120 °C for 48 h. The mixture was worked up as above to give recovered (8) (20%) *cis*- and *trans*-2-cyano-3,3-dimethyl-1-(trichloroethyl)cyclopropane (*ca.* 15% total) and addition products, separated by h.p.l.c. as follows: (i) major product (30%) identified as a diastereoisomer of 2-*bromo*-3,3-*dimethyl*-4,6,6,6-*tetrachlorohexanonitrile* (33) (Found: C, 29.1; H, 3.2; Br, 25.7; total halogen, 51.9. $C_8H_{10}BrCl_4N$ requires C, 28.1; H, 2.97, Br, 23.4; total halogen, 48.2; N, 4.2%), δ 4.87 (s, CHBrCN), 4.38 (q, CHCl, J 3.0 and 5.3 Hz), *ca.* 3.2 (m, CH_2), and 1.20 and 1.37 (both s, 2 × Me). (ii) Second diastereoisomer of 2-bromo-4,6,6,6-tetrachloro-3-3-dimethylhexanonitrile (34) (18%) (Found: C, 29.1; H, 3.15; Br, 23.5; total halogen as Cl, 49.5; N, 4.0), δ 4.74 (s, CHBrCN), 4.36 (q, CHCl, J 6.2 and 2.6 Hz), 3.2 (m, CH_2), 1.20 and 1.37 both s, 2 × Me). (iii) Unknown addition products possibly compound (35) or a tetrachloro-derivative (6%) δ 4.90 s, CHCNHal), 4.40 (q, CHHal, J 5.5 and 3.0 Hz), *ca.* 3.2 (m, CH_2), and 1.28 and 1.37 (both s, 2 × Me). (iv) Second unknown addition product (3%), δ 4.85 (s, CHCNHal), 4.33 (q, CHHal, J 6.2 and 2.5 Hz), 3.2 (m, diastereotopic CH_2, J 16.5 Hz), and 1.21 and 1.36 (both s, 2 × Me).

(*c*) *With trichloromethanesulphonyl chloride.* Compound (8) (0.94 g, 5 mmol) and trichloromethanesulphonyl chloride (2.18 g, 10 mmol) were heated in a sealed tube for 5 h at 150 °C. The product was chromatographed as above to give diastereoisomers of (33) and (34) (*ca.* 70% yield) and the cyclic products (31) and (32) (*ca.* 30% yield from the n.m.r. spectrum of the crude eluate). Similar reaction of Compound (8) (0.94 g, 5 mmol) with trichloromethanesulphonyl chloride (1.09 g, 5 mmol) in carbon tetrachloride (3 cm^3) at 180 °C for 5 h gave compounds (33) and (34) (*ca.* 60%) and (31) and (32) *ca.* 40% (see below). Substantial recovery of compound (8) was achieved when 0.94 g (5 mmol) of it and trichloromethanesulphonyl chloride (0.11 g, 0.05 mmol) were used in the above reaction. In the reaction of compound (8) (0.94 g, 5 mmol) with trichloromethanesulphonyl chloride (1.09 g, 5 mmol) and carbon tetrachloride (9 cm^3) at 150 °C for 10 h, the yield of addition products (33) and (34) was *ca.* 45% and that of the cyclisation products (31) and (32) was *ca.* 55%. When the latter reaction was carried out at 180 °C in pentane (9 cm^3) in place of carbon tetrachloride, the yield of cyclisation products rose to *ca.* 60% and the latter were isolated as a *cis*/*trans*-mixture in 46% yield (see below). When a mixture of compounds (33) and (34) was heated with trichloromethanesulphonyl chloride (5 mmol) in carbon tetrachloride (3 cm^3) for 24 h at 150 °C, no cyclic products (31) or (32) could be detected.

Preparation of cis- *and* trans-1-*Cyano*-2,2-*dimethyl*-3-(*trichloroethyl*)*cyclopropane*.—2,4-Dibromo-6,6,6-trichloro-3,3-dimethylhexanonitrile (1.93 g, 5 mmol) in dimethylformamide (1 cm^3) was added dropwise to a zinc–copper couple (0.66 g, Zn, 10 mmol) prepared as described earlier.[16] The mixture was maintained at 80 °C for 1 h, poured into water, and extracted with diethyl ether (3 × 10 cm^3). The organic phase was washed with water, dried (K_2CO_3), and the solvent evaporated off. The residue was separated by h.p.l.c. with 7% ethyl acetate in light petroleum (b.p. 40—60 °C) as eluant to give cis-1-*cyano*-2,2-*dimethyl*-3-

trichloromethylcyclopropane (0.34 g, 33%), [δ 1.30 and 1.25 (both s, 2 × Me), 0.88 and 1.55 (both m's cyclopropane), and 2.75—3.00 (m, CH_2CCl_3)], and trans-1-*cyano*-2,2-*dimethyl*-3-*trichloromethylcyclopropane* (0.5 g, 45%) [δ 1.15 and 1.32 (both s, 2 × CH_3), 1.2—1.7 (m, cyclopropane), and 2.60 (q, *J* 6.8 and 15.0 Hz) and 2.83 (q, *J* 5.9 and 15.0 Hz) (diastereotopic CH_2CCl_3)] [Found (for mixture of isomers): C, 42.4; H, 4.8; Cl, 47.1; N, 5.8. $C_8H_{10}Cl_3N$ requires C, 42.4; H, 3.45; Cl, 46.95; N, 6.2%].

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