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FREE RADICAL REARRANGEMENTS OF ORGANOCOBALOXIMES: ALKYNYL TO CYCLOALKYLIDENE AND HEXENYL TO CYCLOPENTYLMETHYL

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Summary

Under irradiation by tungsten light in pyridine solution, several substituted alkylcobaloximes undergo rearrangement to more stable substituted alkyl- or alkenyl-cobaloximes. When the same reactions are carried out in the presence of carbon tetrachloride or chloroform, no rearranged organocobaloximes are obtained, but a variety of organic products are obtained derived from the interception of transient organic radicals by the halogenated solvent. The rearrangements are rationalised in terms of a reversible homolysis of the carbon–cobalt bond, rearrangement of the organic radical and recapture by the cobalt(II) fragment to give complexes that are more stable to irradiation than their precursors.

Two aspects of organocobalt chemistry which have been of particular concern in our understanding of the mechanism of biological rearrangements catalysed by coenzyme B_{12} [1] are, (i) the types of mechanism that can occur in the rearrangement of synthetic organocobalt(III) complexes and, because paramagnetic cobalt(II) species have been detected in the course of several in vivo rearrangements, (ii) the conditions under which radicals may be formed from both synthetic and naturally occurring organocobalt(III) complexes [2,3].

At least three different types of rearrangement mechanism have now been detected for synthetic organocobaloxime(III) complexes: (a) electrophilically induced rearrangements via η^2-alkene complexes [4]; (b) concerted unimolecular rearrangements via loss of axial ligand and formation of η^3-allyl or η^3-homoallyl intermediates [5,6]; and (c) bimolecular homolytic displacements in which attack of one cobalt(II) radical at a carbon atom of the organic ligand of an organocobaloxime(III) complex causes the displacement of another cobalt(II) radical from a different carbon atom of the same organic ligand [7,8].

Attempts to observe substantial rearrangement of an organocobalt(III) complex into an isomeric complex through simple homolysis of the carbon–cobalt bond,

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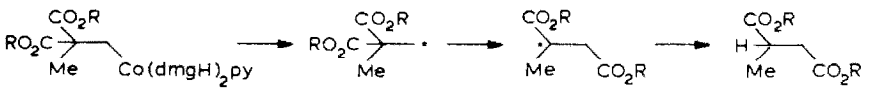
rearrangement of the organic radical and recapture of the rearranged organic radical by the cobalt(II) (eq. 1) have failed; because these experiments have either attempted to rearrange primary organocobalt(III) complexes into less stable secondary or tertiary complexes, or because the conditions have been too severe [9]. The conditions have been such as to decompose any rearranged organocobalt(III) complex that might have been formed. Rearranged organic products have indeed been detected in several such reactions (e.g. eq. 2), but this merely establishes that the rearrangement of the organic fragment has occurred. In some cases it is likely that the rearrangement did involve organic radicals, but in others, where inadvertently there was present an excess of a reducing agent such as borohydride ion has been present, carbanion intermediates.

In this paper we describe some free radical rearrangements of organocobaloxime(III) complexes in which stable alkenylcobaloxime(III) complexes are isolated from the rearrangement of less stable primary alkylcobaloxime(III) complexes and a primary alkylcobaloxime(III) is formed from a less stable secondary alkylcobaloxime(III) complex.

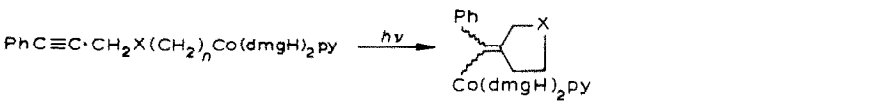
Results and discussion

On photolysis of 1-phenylhex-1-yn-6-ylbis(dimethylglyoximato)pyridinecobalt(III) (**2**; 100 mg) in pyridine (1 ml) at 0–10°C under irradiation by tungsten lamps in all-Pyrex apparatus, the ^{1}H NMR spectrum of the reagent, characterised by a sharp 12-proton singlet resonance at δ 2.10, a pyridine α-proton resonance at δ 8.62, and a broad singlet phenyl resonance at δ 7.29, changed smoothly to that of a new complex characterised by a sharp 12-proton singlet resonance at δ 1.92, a pyridine α-proton resonance at δ 8.48 and a well-separated relatively high field set of aromatic proton resonances in the region δ 7.05–6.76. Chromatography of the product did not provide a separation from traces of the reagent **2**, but gave

$$RCo(dmgH)_2L \rightleftharpoons \dot{R} + \dot{C}o(dmgH)_2L \rightleftharpoons \dot{R}' + \dot{C}o(dmgH)_2L \rightleftharpoons R'Co(dmgH)_2L \qquad (1)$$



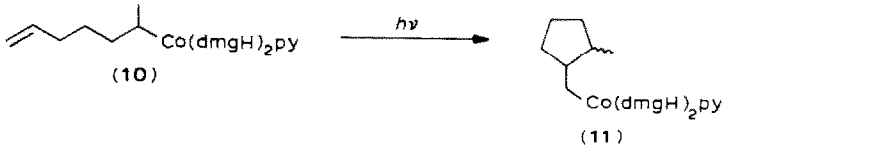
(2)



(3)

(**1**, X = CH_2; n = 1;
2, X = CH_2; n = 2;
3, X = CH_2; n = 3;
4, X = O; n = 2;
5, X = O; n = 3)

(**6**, X = CH_2; n = 2;
7, X = CH_2; n = 3;
8, X = O; n = 2;
9, X = O; n = 3)



(**10**) (**11**) (4)

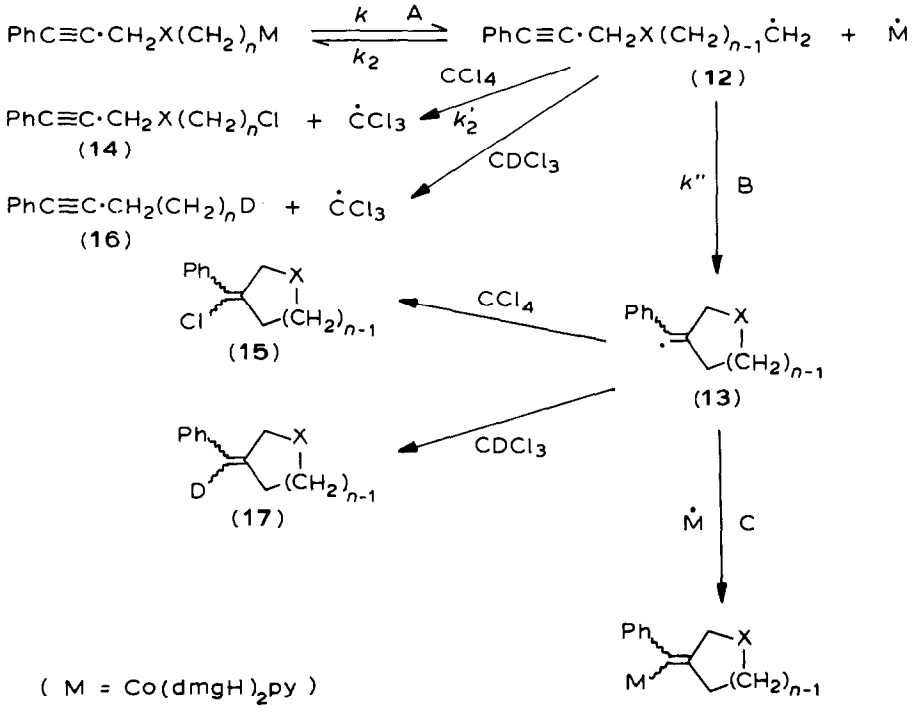
substantially pure α-(benzylidenecyclopentane)bis(dimethylglyoximato)pyridinecobalt(III) (**6**; eq. 5) and several organic products, in combined yield of ⩽ 20%, which were not examined in detail.

Similar irradiation of 1-phenylhept-1-yn-7-ylbis(dimethylglyoximato)pyridinecobalt(III) (**3**) resulted in a slower rearrangement, accompanied by more decomposition, to α-(benzylidenecyclohexane)bis(dimethylglyoximato)pyridinecobalt(III) (**7**). Studies by NMR spectroscopy also showed that the complexes **4** and **5** on irradiation under similar conditions each rearranged to equal proportions of two isomers of each of the benzylideneoxolane complexes **8** and **9**, respectively (eq. 5). No rearrangement of the complex **1** to the potential benzylidenecyclobutane could be detected even after much more extensive irradiation over several days; after which complex **1** could still be recovered.

The irradiation of hept-6-enylbis(dimethylglyoximato)pyridinecobalt(III) (**10**; characterised by a methyl proton resonance at δ 0.36 and vinylic proton resonances in the region δ 4.5–5.0) caused marked decomposition, but the main organometallic complexes isolated by thin layer chromatography from the reaction mixture was a mixture of the two isomers (in the ratio 5/1) of 2-methylcyclopentylmethylbis(dimethylglyoximato)pyridinecobalt(III) (**11**; characterised by methyl doublet resonances at δ 0.59 and 0.73 respectively, and the complete absence of vinylic proton resonances).

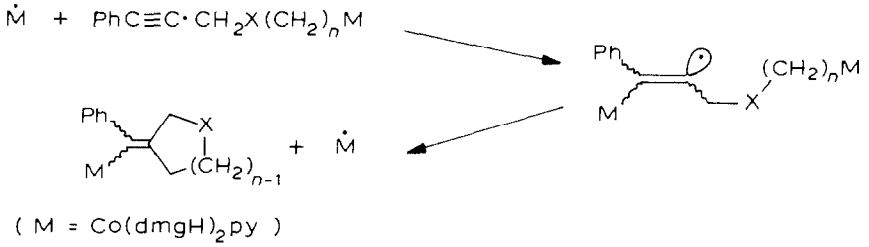
In view of the fact that irradiation of organocobaloximes with tungsten light promotes homolysis of the carbon–cobalt bond [10,11], there is no doubt that

SCHEME 1



organic radicals and paramagnetic cobaloxime(II) species are formed to a significant extent under these conditions. However, at least two distinct free radical processes need to be considered; namely (i) a unimolecular process in which rearrangement takes place stoichiometrically through the free organic radical (Scheme 1, path ABC) and (ii) a bimolecular process in which a small amount of cobaloxime(II) formed in the homolysis adds to the terminal unsaturated carbon, thereby generating a new radical which can, by intramolecular homolytic attack, create the observed rearranged organocobaloxime(III) product and regenerate a further molecule of cobaloxime(II) (Scheme 2); a trace of cobaloxime(II) thus acts as a catalyst for the

SCHEME 2

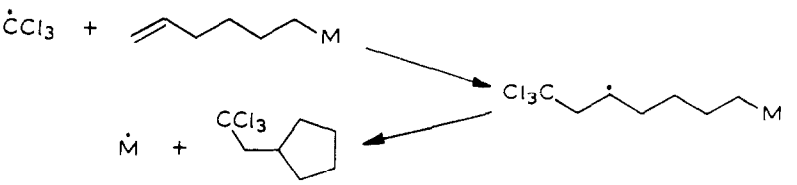


cyclisation. There is good evidence for a related cyclisation by the latter process in that trichloromethyl radicals can attack carbon-5 of hex-5-enylcobaloxime to give trichloroethylcyclopentane (Scheme 3) [12], and cobalt(II)-for-cobalt(II) displacements are known to take place in alkyl- [13], allyl- [7], and possibly but-3-enyl- [8] cobaloximes.

That the rearrangement takes place by the stoichiometric rather than the catalytic path is shown as follows. First, neither is the reaction accelerated by the presence of traces of cobaloxime(II) nor is there any sign of autocatalysis which would have been expected if there was a build up of cobaloxime(II) during the course of photolysis. Secondly, the formation of the rearrangement product is not significantly affected by the presence of a small molar percentage of radical traps such as nitrones and nitroxyl radicals. Thirdly, and most significantly, the organic radical can be trapped by carrying out the photolysis in the presence of reagents such as carbon tetrachloride or chloroform.

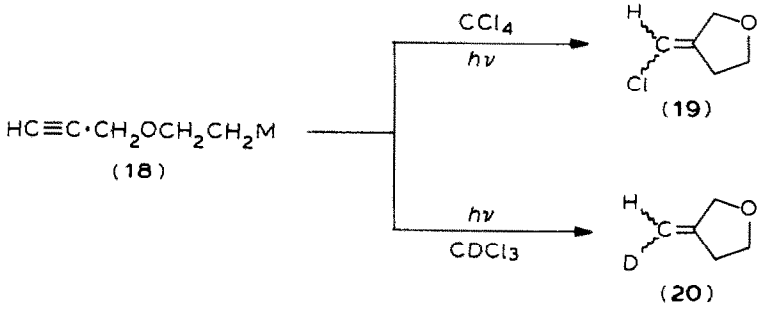
Thus on photolysis of the trimethylene complex **1** in pyridine containing carbon tetrachloride, the main organic product was the open-chain chloride **14** ($X = CH_2$; $n = 1$). Under identical conditions and at virtually the same rate the tetramethylene complex **2** and the trimethylene complex **3** gave mixtures of the open-chain chloride **14** ($X = CH_2$; $n = 2$ or 3) and the closed-chain chloride **15** ($X = CH_2$; $n = 2$ or 3);

SCHEME 3

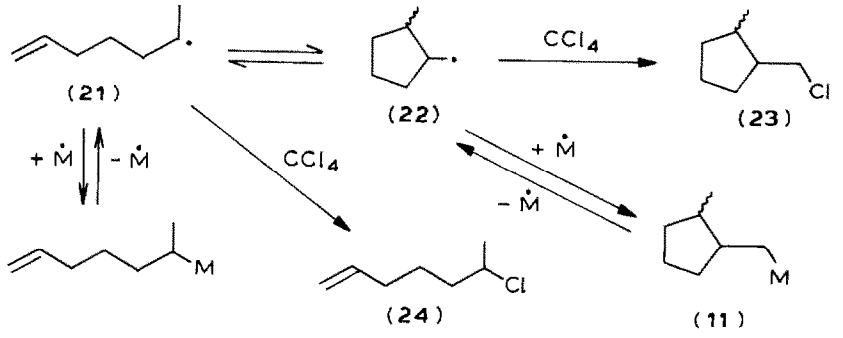


the rate of each reaction being at least as high as that for the rearrangement of **2** in

SCHEME 4



SCHEME 5



pyridine. The proportion of the cyclic chloride derived from **2** and **3** decreased as the concentration of carbon tetrachloride was increased. However, irradiation of each of the two complexes **4** and **5** in neat carbon tetrachloride gave only the cyclic chlorides **15** (X = O; $n = 2$ or 3); in each case there being an equimolar mixture of the two possible isomers of product. No open-chain chlorides could be detected. The irradiation of complexes **4** and **5** in deuteriochloroform also led to rapid decomposition giving equimolar mixtures of the two isomers of **17** (X = O; $n = 2$ or 3, respectively). The open-chain isomer **16** could not be detected. Irradiation of the alkynylcobaloxime **18** in pyridine/carbon tetrachloride (Scheme 4) and in deuteriochloroform gave the closed chain chloride **19** or deuteriated product **20**, but surprisingly no rearranged alkylidene complex could be detected in the absence of carbon tetrachloride or chloroform.

Irradiation of the hept-6-en-2-yl complex **10** in the presence of carbon tetrachloride gave a variety of products only a few of which, i.e. isomers of 1-methyl-2-chloromethylcyclopentane (**23**) and 2-chlorohept-6-ene (**24**) were derived from capture of the transient radicals **21** and **22** (Scheme 5). The main products, which will be described elsewhere were derived from a reaction analogous to that shown in Scheme 3.

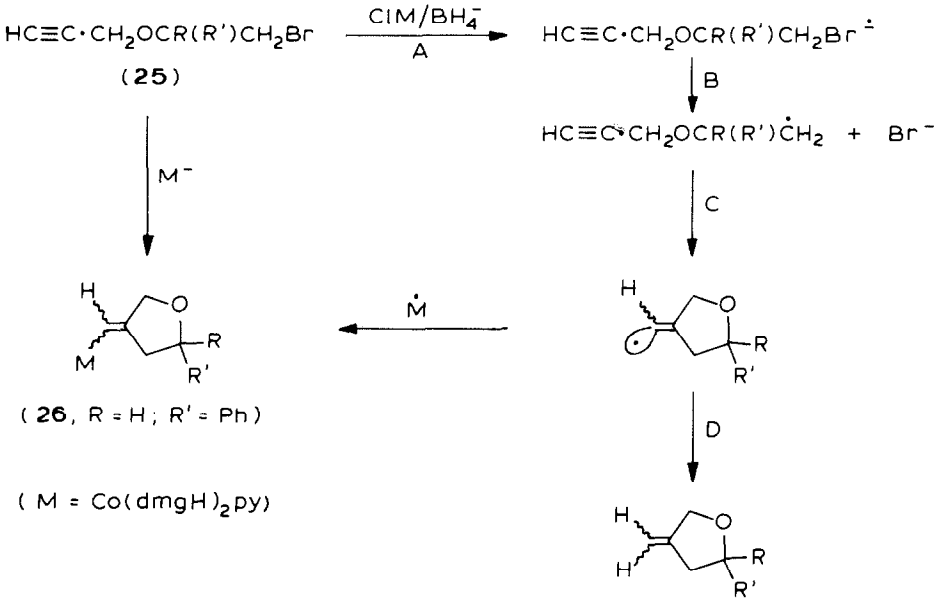
All of the above observations are consistent with the stoichiometric mechanism. We anticipated that the rates of homolysis of the carbon–cobalt bond in complexes **1**, **2** and **3** would be very similar because the carbon–cobalt bond strength and the

electronic excitation would be little influenced by the remote acetylenic group on the organic ligand. The differences in rates of rearrangement and the similarity in rates of reaction in carbon tetrachloride therefore indicate that the rates of rearrangement are a function of the relative rates of capture of the first formed organic radical **12** by cobaloxime(II) or by carbon tetrachloride (Rate = k_2[**12**][Co^{II}] or rate = k_2'[**12**][CCl_4]) and of its rearrangement to the cyclic organic radical **13** (Rate = k''[**12**]). Thus, radical **12** (X = CH_2; $n = 1$) shows no sign of rearrangement, whereas radicals **12** (X = CH_2; $n = 2$ and 3) have been prepared independently [14] and their rearrangement to **13** has been separately demonstrated. The present results also clearly indicate that the insertion of the oxygen atom in the methylene chain, as in the radicals **12** (X = O; $n = 2$ and 3) greatly facilitates the cyclisation of the radical and confirms that the vinylic radicals **13** are not configurationally stable.

The formation of the *cis*- and *trans*-isomers of the cyclic alkylcobaloxime **11** from the heptenylcobaloxime **10** is also completely consistent with the stoichiometric homolytic mechanism. It is already well established that the open-chain radical **21** cyclises with a rate constant of the order of 10^5 s^{-1} at 25°C to give a mixture of 5-membered cyclic radicals in the ratio *cis*-**22**/*trans*-**22** = 2.3, with only a trace of the corresponding 6-membered cyclic radical [15]. The observed ratio of products (presumably)*cis*-**11**/*trans*-**11** = 5 is in good accord with this ratio, bearing in mind the different media and the possibility that the rearrangement is reversible.

Some similar but less well defined (with respect to the cobaloxime) rearrangements have been put to very satisfactory use in the preparation of 3-methyleneoxolanes from a variety of 2-(2-propynyl)oxyethyl bromides and borohydride ion in the presence of catalytic quantities of chlorobis(dimethylglyoximato)pyridinecobalt(III) [16] (Scheme 6). It was suggested that electron transfer from a transient cobaloxime(I)

SCHEME 6



complex to the bromide led to the open-chain radical which was rapidly reduced

after rearrangement (Paths ABCD). When we treated the bromide **25** (R = H; R′ = Ph) with cobaloxime(I) in the absence of borohydride ion the sole organometallic product, obtained in 49% yield, was indeed the cyclic cobaloxime (**26**).

Experimental

Materials

Allyl bromide and pyridine were redistilled before use and dried over molecular sieves. 4-Toluenesulphonyl chloride was recrystallised and only used if on addition to dry pyridine there was a marked decrease in temperature. Paraformaldehyde, phosphorus tribromide, ethyl acetoacetate, sodium borohydride, methanol, propylene oxide, phenyl acetylene, ethyl iodide, lithium amide, 1,3-dibromopropane, 1,4-diiodobutane, 1,5-diiodopentane, cobalt chloride hexahydrate, dimethylglyoxime, ethyl acetate and dichloromethane were commercial materials used without further purification. Magnesium was dried in an oven at 80°C overnight and sodium ethoxide, the monosodium salts of ethylene glycol and propylene glycol were prepared directly using an excess of the parent alcohol. NMR spectra were measured on a Varian XL200 instrument and mass spectra were determined with a VG Micromass 7070 instrument.

Preparation of organic precursors

Alcohols. But-3-enol was prepared from allyl magnesium bromide and paraformaldehyde and converted by reaction with PBr_3 to 1-bromobut-3-ene. Reaction of the latter with ethyl acetoacetate in the presence of sodium ethoxide, followed by hydrolysis and decarboxylation of the product, gave hept-6-en-2-one which was reduced with sodium borohydride in aqueous methanol to hept-6-en-2-ol. Hex-5-en-2-ol was prepared by reaction of allyl magnesium bromide with trimethylene oxide. 3-Phenylprop-2-ynol was prepared by the reaction of paraformaldehyde with 2-phenylethynyl magnesium iodide obtained from ethylmagnesium iodide and phenylacetylene. 3-Phenylprop-2-ynol was converted into the chloride by reaction with thionyl chloride and reacted with the monosodium salt of ethylene glycol or trimethylene glycol to give, respectively, 6-phenyl-3-oxo-hex-5-ynol and 7-phenyl-4-oxohept-6-ynol.

Tosylates. Tosylates were prepared by the method of Golding [17]. They included hept-6-en-2-yl tosylate, 6-phenyl-3-oxohex-5-enyl tosylate (^{1}H NMR 7.80 and 7.38 (2 d, C_6H_4); 7.32 (s, phenyl); 4.36 (s, CH_2O); 4.24 (t,CH_2O); 3.80 (t, CH_2O); 2.40 (s, CH_3)) and 7-phenyl-4-oxohept-6-enyl tosylate (^{1}H NMR δ 7.80 and 7.36 (2 d, C_6H_4); 7.3 (m, Ph); 4.24 (s, CH_2O); 4.18 (t, CH_2OTos); 3.58 (t, CH_2O); 1.95 (m, CH_2); 2.35 (m, CH_3)), and 3-oxohex-5-ynyl tosylate.

Halides. Lithium phenylacetylide was prepared by the addition of phenylacetylene (8 g, 78 mmol) to finely powdered lithium amide (2 g, 86 mmol) in dry tetrahydrofuran (100 ml) under nitrogen. When the reaction had subsided the mixture was refluxed for 10 h. To this solution was added 1,4-diiodobutane (24.2 g, 78 mmol) and the mixture was refluxed for 8 h. The cooled slurry was diluted with diethyl ether (100 ml), washed with water and dried (Na_2SO_4). The solvent was removed in vacuo to give a brown oil (30 g) which was distilled to give 6-iodo-1-phenylhex-1-yne (8.6 g, 35%). B.p. 91–96°C/0.01 mmHg (^{1}H NMR: δ 7.0-7.8 (m,

Ph); 3.25 (t, CH_2I); 2.45 (t, CH_2C); 1.83 (m, $2 \times CH_2$). ^{13}C NMR δ 6.7, 18.3, 29.4, 32.6 ($4 \times CH_2$); 81.1, 89.5 (C≡C); 123.8, 127.6, 128.2, 131.4 (Ph)). Similarly prepared from 1,3-dibromopropane was 5-bromo-1-phenylpent-1-yne b.p. 110–114°C/0.25 mmHg (^1H NMR: δ 7.1–7.5 (m, Ph); 3.56 (t, CH_2Br); 2.59 5t, CH_2C); 2.10 (m, CH_2). ^{13}C NMR: δ 18.2, 31.6, 32.5 ($3 \times CH_2$); 81.7, 88.0 (C≡C); 123.6, 127.8, 128.3, 131.6 (Ph)); and from 1,5-diiodopentane, 7-iodo-1-phenylhept-1-yne, b.p. 112–120°C/0.005 mmHg (^1H NMR spectrum δ 7.1–7.7 (m, Ph); 3.21 (t, CH_2I); 2.43 (t, CH_2C); ca. 1.6 (m, $3 \times CH_2$). ^{13}C NMR δ 6.3, 19.2, 27.6, 29.8, 33.1 ($5 \times CH_2$); 81.0, 90.6 (C≡C); 123.9, 127.5, 128.2, 131.6 (Ph)). 1-Bromo-2-phenyl-3-oxohex-5-yne was prepared from propargyl alcohol, styrene and *N*-bromosuccinimide by the method of Tada et al. [16].

Cobaloximes. The cobaloximes were prepared by the reaction of the appropriate organic halide or tosylate with cobaloxime(I) formed by alkaline disproportionation of cobaloxime(II) as described earlier. Purification by column chromatography on silica gel (Malinkrodt CC4 or CC7) gave *1-phenylhex-1-yn-6-ylbis(dimethylglyoximato)pyridinecobalt(III)* (**2**) (82%) (Found: C, 56.4; H, 6.1; N, 12.8. $C_{24}H_{32}CoN_5O_4$ calcd.: C, 57.1; H, 6.1; N, 13.3%). ^1H NMR δ 7.29 (m, Ph); 2.33 (t, CH_2C); 2.10 (s, dmg); 1.59 (m, $2 \times CH_2$); 1.08 (t, CH_2Co); pyridine resonances at δ 8.62, 7.72 and 7.37 ppm. *1-Phenylpent-1-yn-5-ylbis(dimethylglyoximato)pyridinecobalt(III)* (**1**) (Found: C, 56.0; H, 5.7; N, 13.7. $C_{23}H_{30}CoN_5O_4$ calcd.: C, 56.4; H, 5.9; N, 13.7%). ^1H NMR δ 7.31 (m, Ph); 2.29 (t, CH_2C) 2.15 (s, dmg); 1.58 (m, CH_2); 0.94 (t, CH_2Co); pyridine resonances at δ 8.66, 7.73 and 7.41 ppm. *1-Phenylhept-1-yn-7-ylbis(dimethylglyoximato)pyridinecobalt(III)* (**3**) (Found: C, 56.8; H, 6.6; N, 12.8. $C_{25}H_{34}CoN_5O_4$ calcd.: C, 57.9; H, 6.3; N, 13.0%) ^1H NMR δ 7.40 (m, Ph); 2.32 (t, CH_2C); 2.16 (s, dmg); 1.53 (m, $3 \times CH_2$); 0.88 (t, CH_2Co); pyridine resonances at δ 8.78, 7.85 and 7.51 ppm. *Hept-6-en-2-ylbis(dimethylglyoximato)pyridinecobalt(III)* (**10**) (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%) ^1H NMR δ 0.46 (d, CH_3); 0.85 (m, CH); 1.4–2.3 (m, $3 \times CH_2$); 2.13 (s, dmg); 4.85 (m, :CH_2); 4.45 (m, CH:); pyridine resonances at δ 8.60, 7.70, and 7.28 ppm. *6-Phenyl-3-oxohex-5-ynylbis(dimethylglyoximato)pyridinecobalt(III)* (**4**) (^1H NMR δ 7.22 (m, Ph); 4.16 (s, CH_2); 3.19 (t, OCH_2); 1.95 (s, dmg); 1.53 (t, CH_2Co); pyridine resonances at 8.49, 7.64, and 7.33 ppm. *7-Phenyl-4-oxohepta-6-ynylbis(dimethylglyoximato)-pyridinecobalt(III)* (**5**) (^1H NMR ($CDCl_3$) δ 7.32 (m, Ph); 4.29 (s, CH_2); 3.45 (t, CH_2O); 1.96 (s, dmg); 1.55 (t, CH_2Co); 1.26 (m, CH_2); pyridine resonances at δ 8.60, 7.72 and 7.44 ppm). *Hex-3-oxo-5-ynylbis(dimethylglyoximato)pyridinecobalt(III)* (**18**) (Found: C, 48.1; H, 5.9; N, 14.7. $C_{18}H_{25}CoN_5O_5$ calcd.: C, 47.9; H, 5.8; N, 15.5%; ^1H NMR δ 4.00 (d, CH_2 *J* 2.7 Hz); 3.17 (t, CH_2O); 2.32 (t, CH, *J* 2.7 Hz); 2.08 (s, dmg); 1.54 (t, CH_2Co); pyridine resonances at δ 8.54, 7.69; 7.29 ppm. An unequal mixture of the two isomers of cobaloxime **26** (Found: C, 59.2; H, 5.7; N, 11.7. $C_{30}H_{34}CoN_4O_5$ calcd.: C, 59.7; H, 5.7; N, 11.6%. ^1H NMR (*Isomer A*: δ 2.54, 3.00 (CH_2); 4.44, 4.29 ($2 \times$ Bd d, *J* 11.9 Hz); 4.92 (t, CH, *J* 7.1 Hz); 5.68 (m, :CH); 7.3 (m, Ph); pyridine resonances at δ 8.60, 7.70 and obsc 7.3. *Isomer B*: δ 2.63, 2.96 (CH_2); 4.30, 4.54 ($2 \times$ Bd d, *J* 13.7 Hz); 4.75 (q, CH, *J* 8.2, 6.1 Hz); 5.63 (:CH); 7.30 (Ph); py at δ 8.62, 7.70, obsc.)

Photolysis of cobaloximes

In a typical experiment 1-phenylhex-1-yn-6-ylbis(dimethylglyoximato)-pyridinecobalt(III) (**a**; ca. 40 mg) in pyridine or pyridine-d_5 was irradiated in an

NMR tube at 0–10°C by 4 × 150 watt tungsten spotlights through a water-cooled all-glass apparatus. The extent of the reaction was monitored by observation of the decrease of the 12-proton resonance at δ 2.10 and the growth of the new singlet resonance at δ 1.92. After 4 h the pyridine was removed in vacuo and the residue was chromatographed on silica gel eluting with ethyl acetate/methylene chloride mixtures. The main product was α-(benzylidenecyclopentane)bis(dimethylglyoximato)pyridinecobalt(III) (**6**; 28 mg; 70%. Found: C, 56.9; H, 6.1; N, 12.4. $C_{24}Hd3_2CoN_5O_4$ calcd.: C, 57.1; H, 6.1; N, 13.3%. ^{1}H NMR δ 7.05 (m, 3 aromatic H); 6.76 (m, 2 aromatic H); 1.92 (s, dmg); 2.10, 1.82, 1.57, 1.26 (all m, 4 × CH_2); pyridine resonances at δ 8.48, 7.67 and 7.29. Similar treatment of complex **3** for 12 h gave 57% α-(benzylidenecyclohexane)bis(dimethylglyoximato)pyridinecobalt(III) (**7**) contaminated with **3**. Found: C, 57.4; H, 6.2; N, 13.1. $C_{25}H_{34}CoN_5O_4$ calcd.: C, 57.9; H, 6.3; N, 13.0%. ^{1}H NMR δ 7.13 (m, 3 aromatic H); 6.70 (m, 2 aromatic H); 2.03 (s, dmg); 2.0–2.5 (m, 2 × CH_2); 1.1–1.9 (m, 3 × CH_2). Similar photolysis and chromatography of hept-6-en-2-ylbis(dimethylglyoximato)pyridinecobalt(III) gave a mixture of isomers of 2-methylcyclopentylmethylbis(dimethylglyoximato)pyridinecobalt(III) (**11**). Yield 40%. (Found: C, 51.0; H, 6.9; N, 14.8. $C_{20}H_{32}CoN_5O_4$ calcd.: C, 51.6; H, 6.9; N, 15.05%). The ratio of isomers was determined from the areas of the two methyl doublet resonances at δ 0.73 and 0.59 in the ^{1}H NMR spectrum of the mixture; other resonances at δ 2.10 (d, dmg) and 1.1–2.2 (m, 4 × CH_2, 2 × CH).

Irradiation of complex **1** under similar conditions showed no signs of rearrangement. After irradiation for 24 h the only organocobaloxime which could be recovered was unchanged complex **1**.

Photolysis of organocobaloximes in the presence of carbon tetrachloride and chloroform

In a typical reaction complex **1** was photolysed in the presence of carbon tetrachloride (1.4 g, 9 mmol) in pyridine (total volume 1 ml) under the conditions described above until all the complex had decomposed. The product was chromatographed on silica gel to remove the inorganic material and the organic mixture was separated by HPLC using 3 × 25 cm Partisil on a Waters ALC instrument with an M60 pump and RI detection. The principle products were 6-chloro-1-phenylhex-1-yne (*m/e* 192, 194 in ratio 3/1, base peak 115; ^{1}H NMR: δ 7.33 (m, Ph); 3.25 (t, CH_2Cl); 2.45 (t, CH_2C); 1.68 (m, CH_2); 2.02 (m, CH_2)) and α-(cyclopentylidine)benzyl chloride (*m/e* 192, 194 ratio 3/1; 157, 151, base peak 129; ^{1}H NMR: δ 7.4 (m, Ph); 2.45 (t, CH_2C:) 2.57 (t, CH_2C:); 1.75 (m, 2 × CH_2); ^{13}C NMR: δ 25.9, 28.0 (2 × CH_2); 33.7, 34.2 (2 × CH_2); 127.6, 128.0, 128.4, 131.5 (Ph); 143.1 (C:); 167.4 (:CCl)), together with minor amounts of 1-phenylhex-1-yn-5-ene. Similar irradiation and separation of products from complex **2** gave 7-chloro-1-phenylhept-1-yne (*m/e* 206, 208 ratio 3/1; 171, 157, 143, 129, base peak 115; ^{1}H NMR δ 7.05 and 7.38 (m, Ph); 3.57 (t, CH_2Cl); 2.43 (t, CH_2C); 1.63 (m, 2 × CH_2); 1.84 (m, CH_2)) and α-cyclohexylidene)benzyl chloride (*m/e* 206, 208 in ratio 3/1, 171, base peak 138; ^{1}H NMR spectrum δ 7.32 (m, Ph); 2.55 (t, CH_2); 2.15 (t, CH_2); 1.61 (m, 3 × CH_2)) together with some 1-phenylhept-1-yn-6-ene (^{1}H NMR δ 7.3 (m, Ph); 5.8 (m, :CH); 5.05 (m, CH_2); 2.43 (t, CH_2C); 2.25 (m, CH_2); 1.71 (m, CH_2)). Similar irradiation of complex **3** (0.1 mmol) with carbon tetrachloride in pyridine gave 5-chloro-1-phenylpent-1-yne (*m/e* 178, 180 in ratio 3/1; ^{1}H NMR δ 7.1–7.7 (m, Ph); 3.72 (t, CH_2Cl); 2.61 (t, CH_2C); 2.06 (m, CH_2); ^{13}C NMR δ 16.9 (CH_2); 31.4 (CH_2C); 43.7 (CH_2Cl); 123.5, 127.9, 128.4, 128.1 (Ph); 81.5 and 88.0 (C≡C)), and

with trichloromethansulphonyl chloride (0.11 mmol) in methylene chloride (1 ml) gave 1-phenylpent-1-yn-5-sulphonyl chloride [19](^{1}H NMR δ 7.63, 7.44 (m, Ph); 3.15 (t, CH_2); 3.00 (t, CH_2); 2.25 (m, CH_2)).

Irradiation of cobaloxime **4** in carbon tetrachloride, followed by separation of products in the manner described above gave two isomers of the chloride **15** (X = O, $n = 2$) in equal proportions (Mass spectrum m/e 194.0506 $C_{11}H_{11}ClO$ calcd.: 194.0513. ^{1}H NMR (in $CDCl_3$) δ 7.2–7.5 (m, Ph); 4.53, 4.35 (s, CH_2); 4.00, 3.95 (t, CH_2, J 6.5 Hz); 2.85, 2.74 (t, CH_2O)). Similar irradiation and separation of products from complex **18** gave two isomers of the chloride **19** in equal proportions (^{1}H NMR (in $CDCl_3$) δ 5.95 (broad s, CH:); 4.39, 4.29 (broad s, CH_2); 3.98, 3.95 (t, CH_2O); ca. 2.6 (2 × t, CH_2)). Irradiation of complex **18** in $CDCl_3$ gave two isomers of the cyclic ether **20** (^{1}H NMR δ 5.00, 4.92 (broad s, CH:); 4.24 (2 × broad s, CH_2); 3.90 (t, CH_2O); 2.53 (t, CH_2)).

Photolysis of cobaloxime **4** in C_5D_5N gave 2-isomers of the cobaloxime **8** in near equal proportions (^{1}H NMR (in C_5D_5N) δ 7.00, 6.90, 6.66 (3 × m Ph); 4.32 and 3.70 (s, CH_2); 3.50, 3.12 (t, CH_2O); 2.47, 1.90 (t, CH_2C); (in $CDCl_3$) δ 7.38, 7.13 and 6.58 (3 × m, Ph); 4.22, 3.80 (s, CH_2); 3.54, 3.88 (t, CH_2O) 2.00, 1.97 (s, dmg); with one pair of methylenes masked. Similar photolysis of cobaloxime **5** in C_5D_5N gave isomers of the complex **9** in equal proportions (^{1}H NMR (in $CDCl_3$) δ 7.29, 7.02, 6.55 (3 × m, Ph); 3.40 and 4.22 (s, CH_2); 3.56 (2 × t, CH_2O); 2.54? (t, CH_2C:); 2.03 and 2.00 (s, dmg).

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