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HOMOLYTIC DISPLACEMENT AT CARBON

X *. TOLUENESULPHONYL IODIDE AS A SOURCE OF TOLUENESULPHONYL RADICALS FOR THE FORMATION OF ALLYL-, BENZYL-, CYCLOPROPYLCARBINYL-, SPIROCYCLOPROPYLCYCLOALKYL-, BICYCLO[1.0.3]ALKYL-, AND BICYCLO[1.0.4]ALKYL-4-TOLYLSULPHONES FROM ORGANOCOBALOXIMES

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Summary

4-Toluenesulphonyl iodide reacts thermally at $\leqslant 40°C$ with a wide range of alkenyl- and benzyl-cobaloximes to give good yields of the organo-4-tolylsulphone. Allylcobaloximes yield predominantly, and in some cases exclusively, the rearranged allylsulphone; alicyclic but-3-enylcobaloximes yield the corresponding cyclopropylcarbinylsulphone; cycloalkenylethylcobaloximes yield the spiro-1,1-cyclopropylcycloalkylsulphone; and cycloalk-2-enylmethylcobaloximes yield the bicyclo-[1.0.*N*]alkylsulphone. Spiro- and bicyclo-alkyl compounds are also formed with other free radical precursors. The reactions are believed to take place through a chain mechanism in which cobaloxime(II), present adventitiously or formed by partial homolysis of the substrate, abstracts iodine from the toluenesulphonyl iodide to give the toluenesulphonyl radical, which attacks the organic ligand of the cobaloxime, preferably at the terminal olefinic carbon, thereby displacing cobaloxime(II) and giving the observed organic product.

In earlier papers we described [1–5] regiospecific substitution reactions between several electrophilic free radical precursors, such as 4-toluene sulphonyl chloride, bromotrichloromethane, trichloromethanesulphonyl chloride and diethyl bromomalonate with some alicyclic allyl-, but-3-enyl-, propa-1,2-dienyl and benzylcobaloximes, to give substituted allyl, cyclopropylcarbinyl, propynyl or benzyl

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products, respectively, in high yield. It was proposed that the mechanism of reaction in each case was a free radical chain process in which one of the chain-propagating species, namely cobaloxime(II) present initially adventitiously or formed through trace homolysis of the organocobaloxime substrate, reacted with the precursor (eq. 1) to give the other chain-propagating radical $\dot{X}$ which then attacked the α-, γ-, or δ-carbon of the organic ligand of the organocobaloxime to give the observed organic product and to regenerate the cobaloxime(II) species (eq. 2). Attack at the α-carbon produces no rearrangement of the organic moiety, attack at γ- or δ-carbon leads to regiospecific rearrangement.

$$\dot{Co}^{II}(dmgH)_2py + XY \rightarrow YCo^{III}(dmgH)_2py + X^{\cdot} \quad (1)$$

$$X^{\cdot} + RCo^{III}(dmgH)_2py \rightarrow R'X + \dot{Co}^{II}(dmgH)_2py \quad (2)$$

(R = MeCH : $CH.CH_2$, R′ = CH_2 : CH.CH(Me);
R = CH_2 : $CH.CH_2CH_2$, R′ = CyclopropylCH_2;
R = benzyl, R′ = benzyl)

In this paper we describe the extension of these studies (a) by investigation of the use of 4-toluenesulphonyl iodide as a more efficient free radical precursor, combined with (b) an investigation of the formation of substituted spirocyclopropancycloalkanes and of fused [1.0.*N*]bicyclic systems using cyclic alkenylcobaloximes as substrates.

Results and discussion

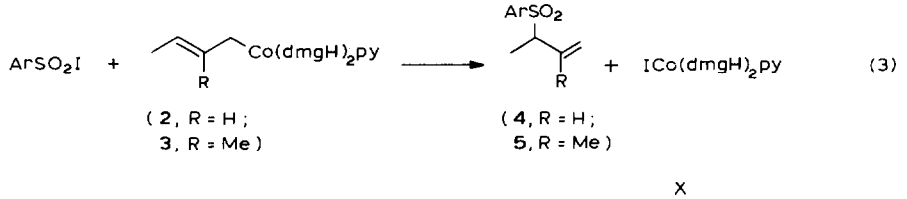
Reactions of 4-toluenesulphonyl iodide

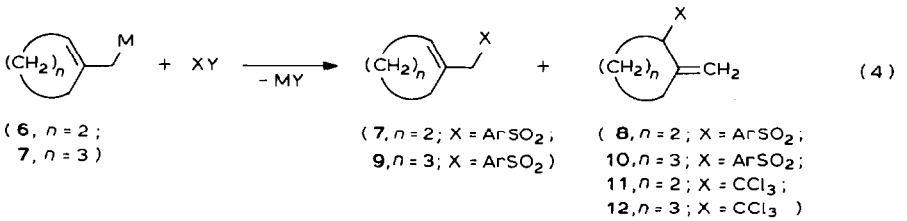
4-Toluenesulphonyl iodide was found to react very readily with all the organocobaloximes described here. It was usually sufficient merely to mix the reagents (each 1.1 mmol) in methylene chloride solution (4–10 ml) and to leave at ambient temperature for from 10 to 60 min. In some cases there was an induction period and the reaction time could be reduced by simply warming the solution until the methylene chloride began to reflux; after 20–40 s the reaction rate and exothermicity were sufficient for refluxing to continue unaided and reaction was then usually complete within 10 min. The iodocobaloxime(III) product was rather unstable and precipitated as a dirty dark solid which was filtered off. The filtrate was washed with aqueous sodium thiosulphate to remove iodine and the organic and inorganic products were separated by column chromatography. Separation of individual organic products was achieved by HPLC as described in the experimental.

Reaction of allylcobaloximes with 4-toluenesulphonyl iodide

The alicyclic but-2-enyl and 2-methylbut-2-enylcobaloximes **1** and **2** reacted regiospecifically with 4-toluenesulphonyl iodide, as above, to give the rearranged allyl-4-tolylsulphone in a manner comparable with, but more rapidly than, the reaction with 4-toluenesulphonyl chloride. However, the cyclohexenylmethyl- and cyclopentenylmethyl-cobaloximes (**5** and **6**) reacted non-regiospecifically with the 4-toluenesulphonyl iodide, though in each case the rearranged *exo*-methylene product (**8** or **10**) predominated.

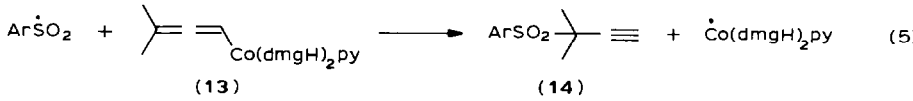
In view of the observation, described in a later section, that the same sulphonyl radical can attack the α-carbon of the benzyl ligand in benzylcobaloximes, and of the fact that other sulphonyl radicals can attack the α-carbon of a substituted saturated alkyl cobaloxime when that attack is intramolecular and capable of forming a five-membered cyclic sulphone [6], it is not surprising that attack at the α-carbon of an allylcobaloxime is also possible, though not normally preferred over attack at the γ-carbon, except when the latter is sterically hindered. The regiospecificity observed in the earlier cases is thus substantially fortuitous. The extent of the regiospecificity is dependent not only on the nature of the allylcobaloxime, but also on the nature of the attacking radical, for the trichloromethyl radical (derived from trichloromethanesulphonyl chloride in a thermal reaction) does react substantially regiospecifically with the cobaloximes **5** and **6** to give the *exo*-methylene products **11** and **12**, whereas α-cyanomethyl radicals seem not to react regiospecifically even with unhindered allyl cobaloximes [7]. Preliminary work on geranylcobaloxime suggested that many of its free radical displacement reactions were not regiospecific.





Reaction of allenylcobaloximes with 4-toluenesulphonyl iodide

The reaction of 3-methylbuta-1,3-dienylcobaloxime (**13**) with 4-toluenesulphonyl iodide gave substantial quantities of organic iodides as by-products, but only one sulphone (**14**), that expected by regiospecific attack at the γ-carbon, was obtained (eq. 5).



Reaction of benzylcobaloximes with 4-toluenesulphonyl iodide

The benzylcobaloximes **15–19** reacted readily with 4-toluenesulphonyl iodide to give in each case a mixture of the benzyl-4-tolylsulphone and the benzyl iodide. As in the (higher temperature) reactions of the same benzylcobaloximes with polyhalogenomethanes and with trichloromethanesulphonyl chloride [5], higher yields of the desired substitution product, in this case the sulphone, were obtained when there were electron-donating groups, relative to H, present in the aromatic ring. The yield of 4-nitrobenzyl-4-tolylsulphone was, like the yield of 4-nitro-trichloroethylbenzene

in the reaction with bromotrichloromethane, rather poor. The proportions of the products formed are shown in Table 1.

$$ArSO_2I + Ar'CH_2Co(dmgH)_2py \rightarrow Ar'CH_2SO_2Ar + Ar'CH_2I \quad (6)$$

(**15**, Ar' = 2,3,6-trimethylC_6H_2;
16, Ar' = 2-methylC_6H_4;
17, Ar' = Ph;
18, Ar' = 4-ClC_6H_4;
19, Ar' = 4-$NO_2C_6H_4$;
20, Ar' = 3-thienyl)

In the reactions of these benzylcobaloximes, in which substantial quantities of benzyl halides were also formed, it was suggested that, because of the ready unimolecular homolysis of the benzylcobaloximes at the higher temperatures used (eq. 7), the chain length was probably rather short. However, in these reactions carried out under very much milder conditions, unimolecular homolysis of the benzylcobaloxime may be neglected except in so far as it provides a means of initiation of the chain. The formation of substantial quantities of the benzyl iodides must therefore be a result of the induced homolysis of the carbon–cobalt bond caused by attack of the sulphonyl radical at a site other than the α-carbon of the benzyl ligand: (eq. 9); i.e. at a peripheral hydrogen, at a C=N bond of the equatorial ligand, at the metal (eq. 9), or possible by an outer-sphere electron transfer. In these circumstances the chain length may still be significant, but competition between the reaction of eq. 10, and the combined reactions of eqs. 8 and 9, each of which is part of a chain, leads to the observed product mixture.

$$Ar'CH_2Co(dmgH)_2py \rightleftharpoons Ar'CH_2^{\cdot} + \dot{C}o(dmgH)_2py \quad (7)$$

$$Ar'CH_2^{\cdot} + ArSO_2I \rightarrow Ar'CH_2I + ArSO_2^{\cdot} \quad (8)$$

$$ArSO_2^{\cdot} + Ar'CH_2Co(dmgH)_2py \rightarrow ArSO_2Co(dmgH)_2py + Ar'CH_2^{\cdot} \quad (9)$$

$$ArSO_2^{\cdot} + Ar'CH_2Co(dmgH)_2py \rightarrow ArSO_2CH_2Ar' + \dot{C}o(dmgH)_2py \quad (10)$$

We selected the 9-anthracylmethylcobaloxime (**21**) for study because of the possibil-

TABLE 1

PRODUCTS OF REACTION OF SUBSTITUTED BENZYLCOBALOXIMES ($Ar'CH_2Co(dmgH)_2py$) WITH 4-TOLUENESULPHONYL IODIDE ($ArSO_2I$)

Ar'	Isolated yield $Ar'CH_2SO_2Ar$ (%)	Product proportions by ^1H NMR	
		$Ar'CH_2SO_2Ar$	$Ar'CH_2I$
2,3,6-TrimethylC_6H_2	50	74	26
2-MethylC_6H_4	31	75	25
Phenyl	42	52	48
4-ChloroC_6H_4	10	40	60
4-Nitrophenyl	–	11	89
3-Thienyl	44	–	–
9-Anthracyl	58	–	–

ity that the attack of the sulphonyl radical might take place at position-10, encouraged by the low aromaticity of the central aromatic ring of the anthracene moiety. In the event, no attack at carbon-10 could be detected, the main product being that from attack of the sulphonyl radical at the α-carbon as in all the other benzylcobaloximes.

Reaction of alicyclic but-3-enylcobaloximes with toluenesulphonyl iodide

The but-3-enylcobaloximes **22–25** reacted very rapidly with 4-toluenesulphonyl iodide at 40°C to give high yields of the single cyclopropylcarbinyl sulphones **26** and **29**, or of mixtures of the two possible isomers of each of **27** and **28**. We had previously shown [1], in the reactions with 4-toluenesulphonyl chloride under tungsten irradiation that substitution at carbon-1 or at carbon-2 did not noticeably hinder cyclisation and indeed that substitution at position-3 clearly encouraged cyclisation to the three-membered ring. The successful cyclisation of the organic ligand in complex **25** demonstrates that substitution at position-4 of the butenyl ligand does not markedly retard the cyclisation process.

(**22**, $R^1 = R^2 = R^3 = R^4 = H$; **23**, $R^1 = Me$, $R^2 = R^3 = R^4 = H$; **24**, $R^1 = R^3 = R^4 = H$, $R^2 = Ph$; **25**, $R^1 = R^2 = R^3 = R^4 = Et$)

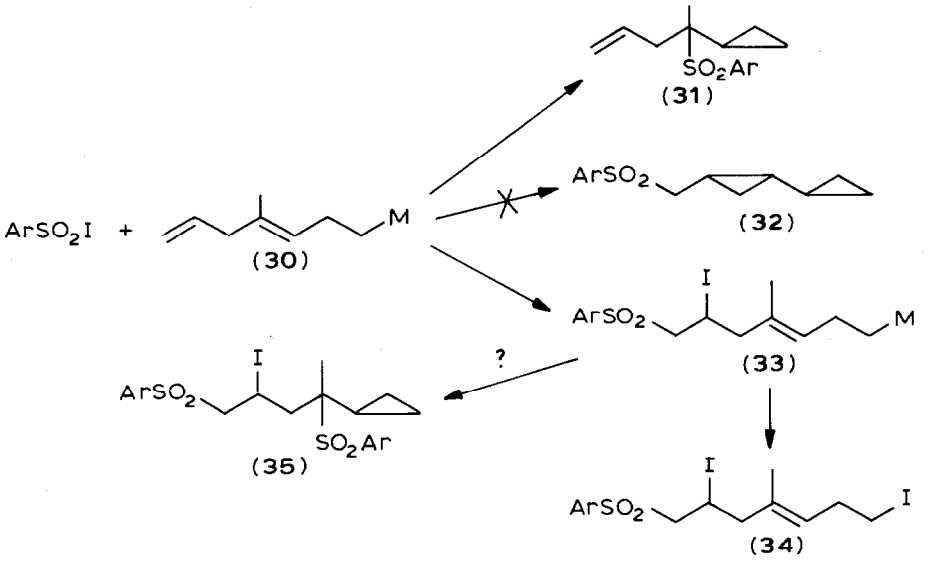
(**26**, $R^1 = R^2 = R^3 = R^4 = H$; **27**, $R^1 = Me$, $R^2 = R^3 = R^4 = H$; **28**, $R^1 = R^3 = R^4 = H$, $R^2 = Ph$; **29**, $R^1 = R^2 = R^3 = R^4 = Et$)

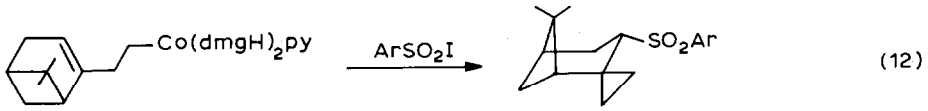
We also investigated the reaction of hepta-3,5-dienylcobaloxime (**30**) because of the possibility that attack of the sulphonyl radical might take place either at carbon-4 to give a butenylcyclopropylcarbinylsulphone (**31**), or at carbon-7 which might lead to the biscyclopropyl derivative **32**. In the event, reaction did occur both at carbon-4 and at carbon-7, but the latter did not lead to the biscyclopropyl product by a double ring closure; instead, further reaction of the intermediate radical with the toluenesulphonyl iodide led to the addition of the elements of toluenesulphonyl iodide across the carbon–carbon double bond to give **33**, which subsequently cleaved to give the diiodo species **34**, and possibly also the disulphone **35**, though the latter was not isolated.

Formation of spirocyclopropylcycloalkylsulphones and related compounds

The reactions of cyclopentenyl- and of cyclohexenyl-ethylcobaloximes (**36** and **37**) with toluenesulphonyl iodide gave high yields of the spirocyclopropylcyclopentyl- and spirocyclopropylcyclohexyl-4-tolylsulphones (**38** and **39**). Even the substantially hindered nopylcobaloxime (**44**) reacted as rapidly to give a very good yield of a single isomer of the polycyclic product **45** (eq. 12). Spiro compounds were also obtained in good yield in the reactions of the cobaloximes **36** and **37** with *N*,*N*′-dimethylsulphamoyl chloride under tungsten irradiation at 0–10°C [8], and in the thermal reaction of cobaloximes **36** and **37** with trichloromethanesulphonyl chloride at 50–70°C (Scheme 2).

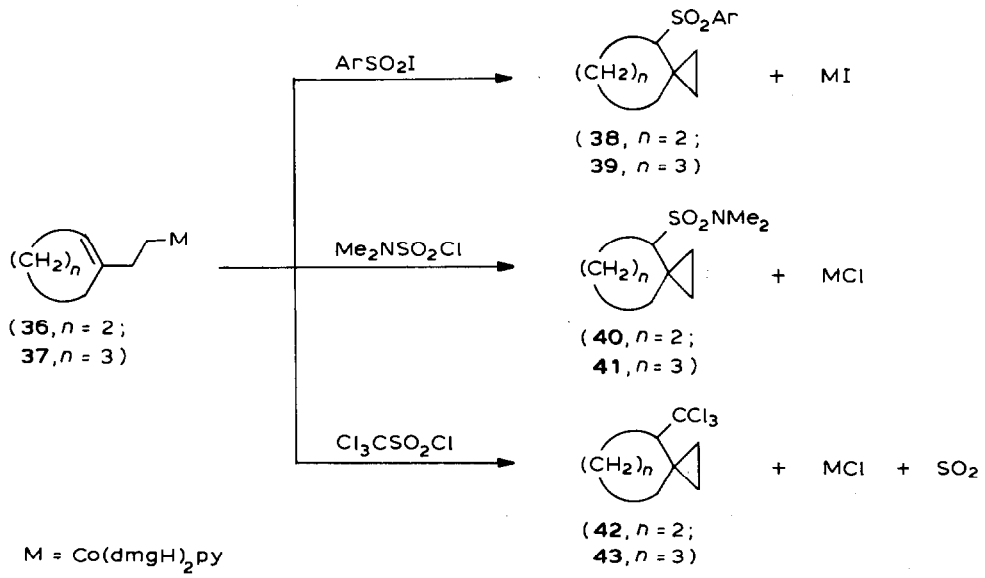
SCHEME 1



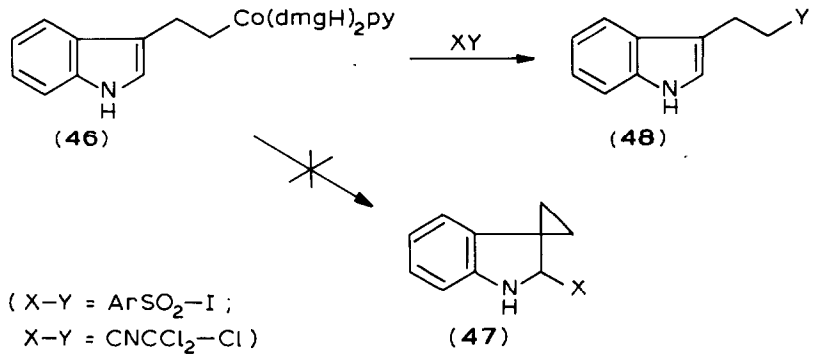


No spiro compounds (**47**) could be obtained from the reaction of the indolylethylcobaloxime (**46**) with either 4-toluenesulphonyl iodide or trichloroacetonitrile; only the corresponding indolylethyl halide **48** could be detected.

SCHEME 2



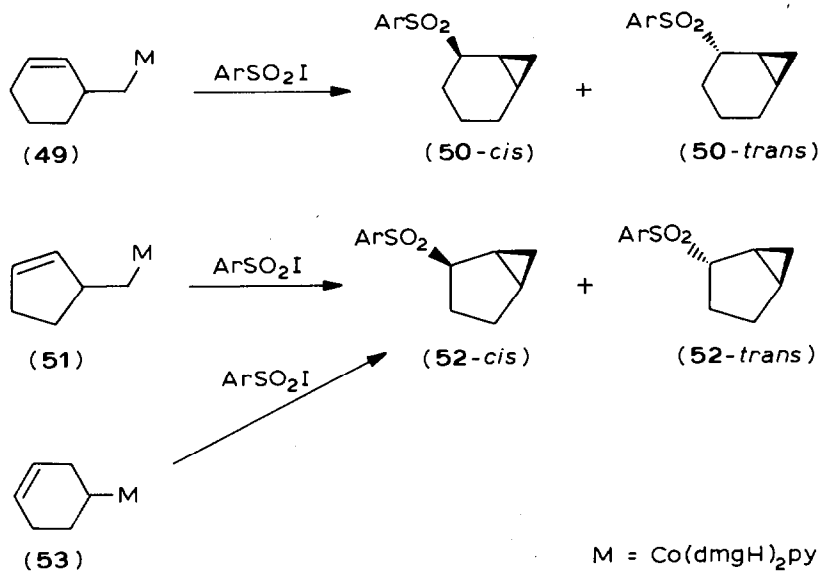
SCHEME 3



Formation of fused [1.0.3]- and [1.0.4]-bicycloalkyl-4-tolylsulphones

The cyclohex-2-enylcarbinylcobaloximes **49** reacted readily with 4-toluenesulphonyl iodide to give an excellent yield of a mixture of the two isomers of bicyclo[1.0.4]heptyl-4-tolylsulphone (**50**). The cyclopent-2-enylcarbinylcobaloxime **51** similarly gave an equimolar mixture of the two isomers of bicyclo[1.0.3]hexyl-4-tolylsulphone (**52**). The same two isomers, but in the ratio 84/16 (or vice-versa) were obtained in the reaction of cyclohex-3-enylcobaloxime (**53**) with toluenesulphonyl iodide under the same conditions. However, iodoalkenes and alkanes were also formed in the latter reaction. The lack of stereospecificity in the reactions of **49** and

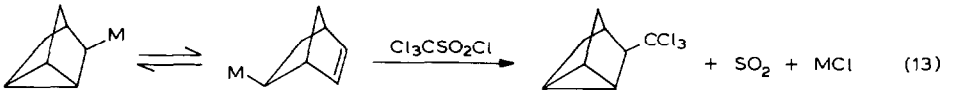
SCHEME 4



51 is surprising, and indicates that there is little steric interaction between the incoming sulphonyl radical and the departing cobaloxime moiety, whether in a transition state for a concerted reaction or in that for the formation of an intermediate radical.

The reaction of the norbornenylcobaloxime (**56**) presents slightly different problems. Many but-3-enylcobaloximes (e.g. 1-methyl [9] and 2-carboxyethyl [10]) equi-

librate slowly in solution by interchange of carbon-1 with carbon-2 (e.g. to 2-methyl and 1-carboxyethyl, respectively). The norbornenylcobaloxime clearly equilibrates much more rapidly, because it has not been prepared free from ca. 15% of the nortricyclylcobaloxime **55**. Thus, though the mixture reacts readily with trichloromethanesulphonyl chloride to give the trichloromethylnortricyclane **57**, it is not evident whether reaction takes place through **55** or **56** or both, though in view of the affinity of the trichloromethyl radical for unsaturated carbon, reaction with **56** is the more likely.



(55) (56) (57)

Experimental

4-Toluenesulphonyl iodide was prepared from 4-toluenesulphonyl chloride [11] via sodium 4-toluenesulphinate [12]. M.p. 90°C (decomp.). ^{1}H NMR 2.45 (s, Me); 7.45 (q, C_6H_4); ^{13}C NMR 21.8 (CH_3); 125.4, 129.7, 146.3, 147.5.

Preparation of alcohols

cis-Hex-3-enol and 4-methylhepta-3,6-dienol were purchased. Nopyl alcohol was prepared by reduction of nopyl acetate (a gift from Bushe Boake Allen) with $LiAlH_4$ (Yield 86%). Cyclohexanone was converted with zinc and ethyl bromoacetate into ethyl (1-hydroxycyclohexyl)acetate (58%; b.p. 80–85°C/0.3 mm Hg) [13]. The latter was dehydrated with P_2O_5 in benzene [14] and the product was reduced with $LiAlH_4$ to give 2-(cyclohexenyl)ethanol (57%; b.p. 82–85°C/4 mm Hg). Cyclopentanone was similarly converted into 2-(cyclopentenyl)ethanol (b.p. 93°C/9 mm Hg). Cyclohexanone cyanohydrin was dehydrated with $POCl_3$ and pyridine to 1-cyanocyclohexene (79%; b.p. 72–84°C/10 mmHg; Found: C, 77.9; H, 8.0; N, 12.8. C_7H_9N calcd.: C, 78.5; H, 8.5; N, 13.1%; ^{13}C NMR δ 20.8, 21.5, 25.8, 26.7, 112.5, 119.7, 145.3) which was hydrolysed to a mixture containing cyclohexenecarboxylic acid contaminated with 5% cyclohex-2-enecarboxylic acid (69%; b.p. 104°C/11 mmHg; ^{13}C NMR δ 21.5, 22.1, 23.9, 26.1, 130.0, 142,5, 173.5). The mixture was reduced with $LiAlH_4$ to give cyclohexenylmethanol (59%). Cyclopentanone cyanohydrin was similarly converted via 1-cyanocyclopentane (^{13}C NMR δ 20.9, 31.8, 32.3, 112.5, 114.5, 147.2) into cyclopentenylmethanol (b.p. 78°C/13 mmHg). Cyclohex-3-enol was prepared (38%; b.p. 164–165°C; Found: C, 73.2; H, 10.1. C_6H_{10} calcd.: C, 73.4; H, 10.3%) by dehydration of *trans*-cyclohexan-1,4-diol with sulphuric acid [15]. Cyclopentene was converted, by reaction with formaldehyde and HCl, into the formal of 1(hydroxymethyl)-2-chlorocyclopentane (b.p. 132°C/2.5 mmHg) which was dehydrochlorinated with KOH in diethylene glycol at 150°C to give a mixture containing mainly cyclopent-2-enylmethanol contaminated with cyclopentenylmethanol (b.p. 99–104°C/0.1 mm Hg [16]. The combined product (22 g was refluxed with methanol (150 ml) containing 4-toluenesulphonic acid (0.5 g) to give, after distillation, cyclopent-2-enylmethanol (b.p. 60–64°C/10 mmHg; ^{1}H NMR δ 1.1–2.7 (m, 4H); 3.10 (m, 1H); 3.43 (d, 2H, J 6 Hz on addition of D_2O);

5.8–6.0 (m, 2H); ^{13}C NMR δ 26.2, 32.2, 48.5, 66.4, 131.5, 132.9). 1-Bromocyclohex-2-ene was converted, with NaCN in DMF, into 1-cyanocyclohex-2-ene and thence to methyl cyclohex-2-enecarboxylate (b.p. 74–76°C/12 mmHg) by reaction with HCl in methanol. Reduction with $LiAlH_4$ gave cyclohex-2-enemethanol (80%; b.p. 84–86°C/16 mmHg). Commercial tiglic acid (2.0 g, 0.02 mol) was reduced with $LiAlH_4$ (0.52 g, 0.015 mol) in ether (120 ml) to give 2-methylbut-2-enol (1.03 g, 60%) [17]. Indole-3-acetic acid was similarly reduced to indole-3-ethanol (^{1}H NMR δ 2.90 (t, CH_2); 3.80 (t, CH_2)).

Preparation of organic halides

9-Chloromethylanthracene was purchased. 1-Bromo-4-methylhepta-3,6-diene, 1-bromo-2-methylbut-2-ene, α-bromo-1-methylcyclopentene and α-bromo-1-methylcyclohexene, were prepared from the corresponding alcohols by reaction with PBr_3 at $\leqslant$ 7°C overnight. Substituted benzyl bromides were prepared by reaction of the corresponding methylbenzene or methylthiophene with *N*-bromosuccinimide in carbon tetrachloride with benzoyl peroxide as initiator.

Preparation of tosylates

The following tosylates were prepared by the method of Golding [18]: cyclohex-4-enyl tosylate (82%; m.p. 46–74°C; Found: C, 61.7; H, 6.5; S, 12.7. $C_{13}H_{16}O_2S$ calcd.: C, 61.9; H, 6.4; S, 12.7%); cyclohex-2-enylmethyl tosylate; 2(cyclohexenyl)ethyl tosylate; cyclopent-2-enylmethyl tosylate; 2(cyclopentenyl)ethyl tosylate; *cis*-hex-3-enyl tosylate; and 2(3-indolyl)ethyl tosylate. (^{1}H NMR δ 3.11 (t, CH_2); 4.26 (t, CH_2); 2.41 (s, CH_3); 7.0–7.9 (m, aromatics).

Preparation of organocobaloximes

Reaction of bis(dimethylglyoximato)pyridinecobaltate(I), prepared by alkaline disproportionation of bis(dimethylglyoximato)pyridinecobalt(II), with the corresponding tosylate, halide, or in one case the alkene, gave the following organocobaloximes [17].

Nopylbis(dimethylglyoximato)pyridinecobalt(III) ***(44)***. (79% from tosylate. Found: C, 55.1; H, 7.05; N, 14.0. $C_{24}H_{36}CoN_5O_4$ calcd.: C, 55.7; H, 7.0; N, 13.5%. ^{13}C NMR δ 12.0 (dmg methyls); 21.3, 26.4, 28.9 (C-Co); 31.4, 32.0, 37.6, 38.0, 40.8, 46.1, 114.8, 125.2, 137.4, 149.0, 150.0).

2-(Cyclohex-1-enyl)ethylbis(dimethylglyoximato)pyridinecobalt(III) ***(35)***. (74% from tosylate; Found: C, 52.5; H, 6.7, N, 14.2. $C_{21}H_{32}CoN_5O_4$ calcd.: C, 52.8; H, 6.8; N, 14.7%. ^{1}H NMR δ 1.69–1.85 (m, 10H); 2.12 (dmg); 2.19 (m, CH_2); 5.27 (m, :CH); pyridine resonances at δ 8.60, 7.72, and 7.32. ^{13}C NMR δ 12.0 (dmg); 22.6, 23.2, 25.4, 28.6, 29.2 (C-Co); 38.5, 120.0, 125.2, 137.5, 138.9, 149.1, 150.0); *2-(cyclopentenyl)-ethylbis(dimethylglyoximato)pyridinecobalt(III)* ***(34)***. (70% from tosylate; Found: C, 51.2; H, 6.6, N, 15.0. $C_{20}H_{30}CoN_5O_4$ calcd.; C, 51.8; H, 6.5; N, 15.1%. ^{1}H NMR δ 1.4–2.0 (m, 10H); 2.16 (s, dmg); 5.37 (m, :CH); pyridine resonances at δ 8.66, 7.78 and 7.37. ^{13}C NMR δ 12.0 (dmg methyls); 23.1, 31.7, 32.5, 35.3, 122.1, 125.2, 137.5, 150.0); *Cyclohex-2-enylmethylbis(dimethylglyoximato)pyridinecobalt(III)* ***(50)*** (40% from tosylate; Found: C, 52.1; H, 6.8; N, 14.65. $C_{20}H_{32}CoN_5O_4$ calcd.: C, 51.8; H, 6.5; N, 15.1%); *cyclopent-2-enylmethylbis(dimethylglyoximato)pyridinecobalt-(III)* ***(51)***. (41% from tosylate; Found: C, 50.7; H, 6.5; N, 15.5. $C_{19}H_{28}CoN_5O_4$ calcd.: C, 50.8; H, 6.3; N, 15.6%; ^{1}H NMR δ 1.30, 1.56, 1.81, 1.95 (4 $\times$ m, 7H); 2.18

(s, dmg); 5.60 (m, 2 × :CH); pyridine resonances at δ 8.68, 7.78 and 7.38); *cyclohex-3-enylbis(dimethylglyoximato)pyridinecobalt(III)* (**53**). (37% from tosylate; Found: C, 50.3; H, 6.2; N, 15.75. $C_{19}H_{28}CoN_5O_4$ calcd.: C, 50.85; H, 6.3; N, 15.6%. ^{1}H NMR δ 1.6–2.4 (m, 7H); 2.15 (s, dmg); 5.50 (m, 2 × :CH); ^{13}C NMR δ 12.1 (dmg methyls), 28.5, 32.2, 35.0, 44.0, (C-Co), 125.1, 126.6, 128.7, 137.7, 149.6, 149.9); *2-methylbut-2-enylbis(dimethylglyoximato)pyridinecobalt(III)* (**2**). (65% from bromide. Found: C, 48.9; H, 6.5; N, 15.3. $C_{18}H_{23}CoN_5O_4$ calcd.: C, 49.4; H, 6.45; N, 16.0%); *2-(3-indolyl)ethylbis(dimethylglyoximato)pyridinecobalt(III)* (**46**) (80% from tosylate. Found: C, 54.0; H, 5.80; N, 16.1. $C_{23}H_{29}CoN_6O_4$ calcd.: C, 53.95; H, 5.7; N, 16.4%. ^{1}H NMR δ 1.91 (q, CH_2Co); 2.09 (s, dmg); 2.35 (q, CH_2); 6.91 (d, 1H); 7.08 (m, 2H); 7.25 (s, 1H); 7.52 (q, 1H); pyridine resonances at δ 7.32, 7.71 and 8.63); *cis-hex-3-enylbis(dimethylglyoximato)pyridinecobalt(III)* (**25**). (57% from tosylate). Found: C, 49.9; H, 6.7; N, 16.1. $C_{19}H_{25}CoN_5O_4$ calcd.: C, 50.55; H, 6.7; N, 15.5%. ^{1}H NMR δ 0.82 (t, CH_3); 1.47 (m, 4H); 1.84 (quintuplet, 2H); 2.06 (s, dmg); 5.18 (m, 2 × :CH); pyridine resonances at δ7.26, 7.80 and 8.52); *4-methylhepta-3,5-dienylbis(dimethylglyoximato)pyridinecobalt(III)* (**30**), (43% from bromide. Found: C, 52.75; H, 6.8; N, 14.5. $C_{21}H_{32}CoN_5O_4$ calcd.: C, 52.8; H, 6.8; N, 14.7%. ^{1}H NMR δ 1.46 (s, Me); 1.52 (m, 2 × CH_2); 2.12 (s, dmg); 2.60 (d, CH_2); 4.94 (m, :CH_2); 5.12 (m, :CH); pyridine resonances at δ7.33, 7.67 and 8.60); *3-thienyl methylbis(dimethylglyoximato)pyridinecobalt(III)* (**20**). (40% from bromide. Found: C, 44.8; H, 4.8; N, 13.8. $C_{18}H_{24}CoN_5O_4S$ calcd.: C, 46.4; H, 5.2; N, 13.8; S, 6.7%. ^{1}H NMR δ 2.03 (s, dmg); 2.83 (s, CH_2); 6.70 (q, 1H, *J* 1.2, 4.9 Hz); 6.77 (q, 1H, *J* 1.2, 3.0 Hz); 6.95 (q, 1H, *J* 3.0, 4.9 Hz; pyridine resonances at δ7.27, 7.68, 8.53); and *9-anthracylmethylbis(dimethylglyoximato)pyridinecobalt(III)* (**21**), (33% from chloride. Found: C, 58.5; H, 5.2; N, 11.8. $C_{28}H_{30}CoN_5O_4$ calcd.: C, 60.25; H, 5.4; N, 12.5%. ^{1}H NMR δ1.60 and 2.05 (2s, dmg); 2.28 (s, CH_2); 7.2–7.8 (aromatics). Norbornenylbis(dimethylglyoximato)pyridinecobalt(III) (**55**) containing nortricyclobis(dimethylglyoximato)pyridinecobalt(III) (**56**) (82% from norbornene; Found: C, 52.4; H, 6.3; N, 15.0. $C_{20}H_{28}CoN_5O_4$ calcd.: C, 52.4; H, 6.1; N, 15.2%. ^{13}C NMR δ12.0, 17.1, 31.0, 31.8, 34.0, 35.9, 36.1, 41.3, 41.9, 46.7, 47.8, 49.8, 50.4, 125.1, 132.9, 135.2, 135.4, 137.4, 149.3, 149.7, 150.5. ^{1}H NMR δ0.15–2.7 (m); 2.10 (dmg); pyridine resonances at 7.22, 7.64, δ 8.47). 5.80 (m, :CH)). Also prepared but not analysed because of instability, or because already known, cyclohexenylmethylbis(dimethylglyoximato)pyridinecobalt(III) (**6**) (^{1}H NMR δ1.6–1.95 (m, 6H); 2.14 (s, dmg); 2.33 (m, 2H); 2.46 (s, CH_2Co); 5.28 (m, :CH); pyridine resonances at δ8.57, 7.72, 7.30); cyclopentenylmethylbis(dimethylglyoximato)pyridinecobalt(III) (**5**), and geranylbis(dimethylglyoximato)pyridinecobalt(III); benzyl- [19],4-chlorobenzyl- [19], 2-methylbenzyl- [19], 2,3,6-trimethylbenzyl- [19] and 4-nitrobenzyl-bis(dimethylglyoximato)pyridinecobalt(III) [19].

Reactions of 4-toluenesulphonyl iodide

4-Toluenesulphonyl iodide (1.1 mmol) and the organocobaloxime (1.0 mmol) in methylene chloride (ca. 5 ml) were warmed to 40°C for 20–30 s and then allowed to stand for a further 10–30 min. The solution was filtered and the precipitate was washed with a mixture of methylene chloride/petroleum ether (5/1). The filtrate and washings were washed with saturated aqueous sodium thiosulphate and then chromatographed on silica gel (Malinckrodt CC4) to separate organic from inorganic products; the former were further separated by HPLC as described below.

The following sulphones were obtained (a) from but-2-enylcobaloxime, 1-methylallyl-4-tolylsulphone (**4**) identical with material previously prepared [3]. (b) From 2-methylbut-2-enylcobaloxime, *1,2-dimethylallyl-4-tolylsulphone* (**5**; yield 75%; Found: C, 64.5; H, 7.4; S, 13.7. $C_{12}H_{16}O_2S$ calcd.: C, 64.25; H, 7.2; S, 14.3%). (c) From cyclopentenyl-methylcobaloxime, a mixture of 60% *exo-2-methylenecyclopentyl-4-tolylsulphone* and 40% *cyclopentenylmethyl-4-tolylsulphone* (Found: C, 65.9; H, 6.7; S, 13.6. $C_{13}H_{16}O_2S$ calcd.: C, 66.1; H, 6.8; S, 13.5%). (d) From cyclohexenylmethylcobaloxime, a mixture containing 62% *exo-2-methylenecyclohexyl-4-tolylsulphone* (^{1}H NMR δ 3.98 (m, $CHSO_2$); 5.11, 5.22 (m, 2 :CH)) and 38% *cyclohexenylmethyl-4-tolylsulphone* (^{1}H NMR δ3.89 (m, CH_2SO_2); 5.52 (s, CH_2)). (e) From 3-methyl-buta-1,3-dienylcobaloxime, *2-methylbut-3-yn-2-yl-4-tolylsulphone* (40%; ^{13}C NMR 21.7 (Ar*Me*), 24.2 (2Me), 58.5 (CSO_2), 75.1, 82.2, 129.3, 131.0, 131.7, 145.2; ^{1}H NMR δ1.62 (s, 2Me); 2.47 (s, Me); 2.46 (s, CH); 7.36, 7.86 (Ar)). (f) From benzylcobaloximes, *2,3,6-trimethylbenzyl-4-tolylsulphone* (Found: C, 70.0; H, 6.9; S, 10.9. $C_{17}H_{18}SO_2$ calcd.: C, 70.8; H, 7.0; S, 11.1%); 2-methylbenzyl-4-tolylsulphone (^{1}H NMR δ2.17 (s, CH_3); 2.49 (s, CH_3); 4.43 (s, CH_2)); benzyl-4-tolylsulphone (Found: C, 67.4; H, 6.00; S, 12.4. $C_{14}H_{14}O_2S$ calcd.: C, 68.3; H, 5.7; S, 13.0%. ^{1}H NMR δ 2.45 (s, CH_3); 4.3 (s, CH_2)); 4-chlorobenzyl-4-tolylsulphone (Found: C, 59.4; H, 4.65; S, 11.0; Cl, 12.5. $C_{14}H_{13}ClO_2S$ calcd.: C, 59.7; H, 4.6; Cl, 12.65; S, 11.0%); 4-nitrobenzyl-4-tolylsulphone (^{1}H NMR δ2.45 (s, CH_3); 3.70 (s, CH_2)); *3-thienyl-4-tolylsulphone* (Found: C, 56.8; H, 5.1; S, 24.3. $C_{12}H_{12}O_2S_2$ calcd.: C, 57.2; H, 4.7; S, 25.4%. ^{1}H NMR δ2.50 (s, CH_3); 4.4 (s, CH_2); 6.8–7.6 (m, Ar); ^{13}C NMR δ21.6 (CH_3), 57.5 (CH_2), 126.0, 126.7, 128.2, 128.5, 129.1, 129.5, 135.0, 144.7); and *9-anthracylmethyl-4-tolylsulphone* (Found: C, 75.9; H, 5.7; S, 8.5. $C_{20}H_{18}O_2S$ calcd.: C, 76.3; H, 5.2; S, 9.25%). (g) From but-3-enylcobaloxime, cyclopropylcarbinyl-4-tolylsulphone (60% [1]. (h) From 2-phenylbut-3-enylcobaloxime, 2-phenylcyclopropylcarbinyl-4-tolylsulphone (72% 2-isomers) [1]. (i) From *cis*-hex-3-enylcobaloxime, *1-(cyclopropyl)propyl-4-tolylsulphone* (Found: C, 65.3; H, 7.6; S, 13.6. $C_{13}H_{18}O_2S$ calcd.: C, 65.5; H, 7.6; S, 13.5%. ^{13}C NMR δ4.6, 10.1, 11.7, 21.6, 22.8, 71.4, 129.2, 129.5, 135.8, 144.3. ^{1}H NMR δ0.06 (m, 1H); 0.18 (m, 1H); 0.38 (m, 1H); 0.68 (m, 2H); 1.08 (t, 3H); 1.73 (m, 1H); 2.13 (m, CH_2); 2.43 (s, CH_3); 7.3, 7.75 (2d, C_6H_4)). (j) From 4-methylhepta-3,6-dienylcobaloxime, *1-cyclopropylpent-4-enyl-4-tolylsulphone* (22%; ^{1}H NMR δ0.14–0.50 (m, 4H); 0.92 (m, 1H); 0.87 (s, CH_3); 2.38 (s, CH_3); 2.52 (d, CH_2, *J* 6.8 Hz); 4.87 (m, :CH_2); 5.72 (m, :CH), 7.26, 7.72 (m, C_6H_4)); together with a mixture of isomers of 2,7-diiodo-4-methylhept-4-enyl-4-tolylsulphone (^{1}H NMR δ1.55, 1.63 (s, CH_3); 2.5, 3.3, 3.7 (m, 4CH_2); 5.15, 5.30 (t, :CH); 2.39 (s, CH_3); 7.31, 7.73 (m, C_6H_4)). (k) From cyclohexenylethylcobaloxime, *spiro-1,1-cyclopropylcyclohex-2-yl-4-tolylsulphone* (76%; Found: C, 68.2; H, 7.7; S, 11.7. $C_{15}H_{20}O_2S$ calcd.: C, 68.1; H, 7.6; S, 12.1%. ^{1}H NMR δ0.05–0.4 (m, 3H); 0.62 (m, 1H); 1.45, 1.60, 1.80, 2.05, 2.35 (all m, 8H); 2.45(s, CH_3). ^{13}C NMR δ12.9, 13.2, 17.9, 20.9, 21.6, 24.6, 25.4, 31.2, 68.8 (CSO_2), 128.8, 129.7, 137.5, 144.3). (l) From cyclopentenylethylcobaloxime, *spiro-1,1-cyclopropylcyclopent-2-yl-4-tolylsulphone* (78%; Found: C, 67.1; H, 7.3; S, 12.4. $C_{14}H_{18}O_2S$ calcd.: C, 67.2; H, 7.25; S, 12.8%. ^{1}H NMR δ 0.48 (q, 2H); 0.72 (t, 1H); 1.10 (m, 1H); 1.43 (m, 1H); 1.80 (m, 3H); 2.12 (m, 2H); 2.45 (s, CH_3); 3.08 (q, $CHSO_2$); 7.33, 7.77 (m, C_6H_4). ^{13}C NMR δ 9.2, 13.9, 16.1, 16.3, 21.3, 28.2, 61.3 ($CHSO_2$), 121.0, 122.0, 128.6, 136.6). (m) From nopylcobaloxime, the *sulphone* (**45**) (80%; Found: C, 70.4; H, 7.9; S, 9.9. $C_{18}H_{24}O_2S$ calcd.: C, 71.0; H, 7.9; S, 9.9%. ^{1}H

NMR δ 0.35 (m, 1H); 0.58 (m, 1H); 0.73 (m, 1H); 0.94 (s, CH_3); 1.04 (t, 1H); 1.15 (s, Me); 1.45 (d, 1H); 1.6–2.3 (m, 4H); 2.44 (s, CH_3); 3.65 (q, $CHSO_2$); 7.34, 7.76 (m, C_6H_4). ^{13}C NMR δ 14.2, 20.6, 24.8, 25.5, 25.6, 30.1, 32.6, 33.0, 43.6, 43.9, 56.8, 65.7, 79.4, 81.1, 82.3, 132.6, 133.6, 140.1, 148.0). (n) From cyclohex-2-enylmethylcobaloxime, *bicyclo[1.0.4]heptyl-4-tolylsulphone* (**50**) (77%; Mass spectrum $(M+1)^+$ Found: 251.1105. $C_{14}H_{19}O_2S$ Calcd.: 251.11056; M^+ Found: 250.1026. $C_{14}H_{18}O_2S$ calcd.: 250.10274. ^1H NMR Isomer A, δ 0.10 (q, 1H); 0.72 (dt, 1H); 1.04, 1.3–1.8, 3.08 (all m); 2.45 (s, CH_3); 7.39, 7.83 (m, C_6H_4). Isomer B, δ 0.43 (q, 1H); 0.69 (m, 1H); 0.95–1.45, 1.6, 1.9 (all m); 2.47 (s, CH_3); 7.38&7.83 (m, C_6H_4)). (o) From cyclopent-2-enylmethyl-cobaloxime and from cyclohex-3-enylcobaloxime, *bicyclo[1.0.3]hexyl-4-tolylsulphone* (**52**) (Total analysis, Found: C, 65.7; H, 6.9; S, 13.5. $C_{13}H_{16}O_2S$ calcd.: C, 66.1; H, 6.8; S, 13.6%. Isomer A, 40% yield from **51** and 30% yield from **53**, ^1H NMR δ0.48 (m, 1H); 0.70 (m, 1H); 1.2, 1.6–2.0 (all m); 2.48 (s, CH_3); 3.70 (m, CH); 7.42, 7.85 (m, C_6H_4). Isomer B 40% yield from **51** and 5% yield from **53**, separated by HPLC on Partisil S using 20% EtOAc/petrol, ^1H NMR δ 0.16, (q, 1H); 0.60 (t, 1H); 1.35–1.55, 2.15 (all m); 2.45 (s, CH_3); 3.50 (d, CH); 7.38, 7.83 (m, C_6H_4)).

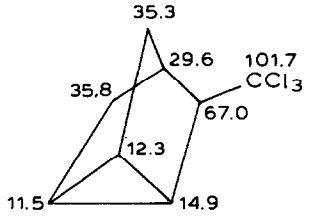
Reactions with dimethylsulphamoyl chloride

The cobaloxime (1 mmol) in methylene chloride (ca. 15 ml) and *N,N*-dimethylsulphamoyl chloride (1.2 mmol) were irradiated as a concentric thin film retained between all-pyrex glass by two 150 watt tungsten lamps. Reaction occurred within 30 min and the products were worked up as for the reactions with toluenesulphonyl iodide except that washing with thiosulphate was omitted. Thus prepared from cyclohexenylethylcobaloxime was, *spiro-,1,1-cyclopropylcyclohexen-2-yl-N,N-dimethylsulphonamide.* (72%; Mass spectrum $(M-SO_2)^+$ 153; ^1H NMR δ 0.2 (m, 2H); 0.70 (m, 1H); 0.85 (m, 1H); 1.6, 1.96, 2.42 (all m); 2.97 (s, NMe_2); 3.10 (m, CH). From cyclopentenylethylcobaloxime, *spiro-1,1-cyclopropyl-N,N-dimethylcyclopenten-2-ylsulphonamide* (68%; Mass spectrum $(M-SO_2)^+$ 139; ^1H 0.52 (m, 2H); 0.76 (m, 1H); 1.24 (m, 2H); 1.46 (m, 1H); 1.9–2.4 (m); 2.90 (s, NMe_2); 3.11 (m, CH)).

Reactions with trichloromethanesulphonyl chloride

The cobaloxime (1 mmol) and trichloromethanesulphonyl chloride (2 mmol) in methylene chloride (10 ml) were heated in a sealed tube at 50–60°C until reaction was complete (usually within 2 h). The product was worked up as described above.

The cobaloxime (1 mmol) and trichloromethanesulphonyl chloride (2 mmol) in methylene chloride (10 ml) were heated in a sealed tube at 50–60°C until reaction was complete (usually within 2 h). The product was worked up as described above.



(57a)

Thus prepared, from norbornenylcobaloxime, trichloromethylnortricyclane (**57**) (^{13}C NMR spectrum as shown in structure **57a**. From cyclohexenyl ethylcobaloxime, 2-trichloromethylspiro-1,1-cyclopropylcyclohexane (^{13}C NMR δ 14.2, 14.4, 21.6, 24.6, 28.6, 32.3, 61.5 ($CHCCl_3$)). From cyclopentenylethylcobaloxime 2-trichloromethyl-spiro-1,1-cyclopropylcyclopentane (^{13}C NMR δ 8.9, 17.2, 24.4, 34.5, 38.8, 53.4, 64.6 ($CHCCl_3$)). From cyclohexenylmethylcobaloxime, *exo*-2-methylenetrichloromethylcyclohexane (^1H NMR δ 1.50, 1.90, 2.15 (all m, 8H); 3.58 (m, $CHCCl_3$); 5.25, 5.46 ($:CH_2$)). Similarly prepared from trichloroacetonitrile and cyclohexenylmethylcobaloxime, 2-methylenecyclohexyl-α,α-dichloro-α-cyanomethane (^1H NMR δ 1.55, 1.85, 2.05, 2.30, 2.42 (all m, 8H); 2.91 (q, $CHCCl_2CN$, J 4.4, 9.3 Hz); 5.08, 5.14 ($:CH_2$)).

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