# Synthesis of Alkanesulphonyl Chlorides from Alkylcobaloximes and Trichloromethanesulphonyl Chloride
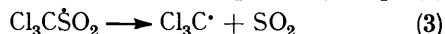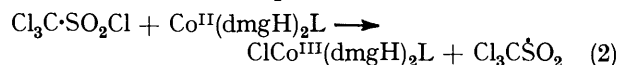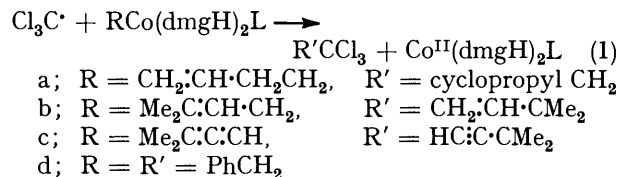
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Alkyl- and substituted alkylcobaloximes react photochemically with trichloromethanesulphonyl chloride to give high yields of alkanesulphonyl chlorides. *erythro*-2-Phenyl[1-$^2$H$_1$,2-$^2$H$_1$]ethylcobaloxime gives an equimolar mixture of *erythro*- and *threo*-2-phenyl[1-$^2$H$_1$,2-$^2$H$_1$]ethanesulphonyl chloride and diastereoisomerically pure 1-phenyl[1-$^2$H$_1$]propan-2-ylcobaloxime gives a 1:1 mixture of diastereoisomers of 1-phenyl[1-$^2$H$_1$]propane-2-sulphonyl chloride. The reaction is believed to proceed through a non-chain process initiated by photolysis of the carbon–cobalt bond. The product alkanesulphonyl chloride is then formed, either by a direct attack of the alkyl radical on the sulphur of trichloromethanesulphonyl chloride, or through capture of the alkyl radical by sulphur dioxide and halogen abstraction by the so-formed alkanesulphonyl radical from trichloromethanesulphonyl chloride. The latter process seems the more likely. No evidence could be obtained for an intermolecular homolytic attack of trichloromethyl radicals on the saturated alkyl ligand.

In previous papers we have described a series of novel homolytic reactions between free radical precursors and diamagnetic $\eta'$-organometallic complexes in which key steps are homolytic displacements of paramagnetic metal complexes by attacks of C- or S-centred radicals on the organic ligands of the organometallic complex.[1-9] One of the free radical precursors used with some success as a source of trichloromethyl radicals was trichloromethanesulphonyl chloride. We have described several examples of reactions in which the trichloromethyl radicals attack the δ-carbon of butenyl ligands, the γ-carbon of allyl or propadienyl ligands, and the α-carbon of benzyl ligands in the corresponding organocobaloximes [equation (1)]. These result in the formation, in good yield, of trichloroethylcyclopropanes [equation (1a)], trichlorobutenes [equation (1b)], trichlorobutynes [equation (1c)], and trichloroethylbenzenes [equation (1d)], respectively. In all cases, the trichloromethyl radicals were believed to arise by the reaction of the displaced paramagnetic complex, *i.e.* cobaloxime(II), with the organic radical precursor, with subsequent loss of sulphur dioxide from the trichloromethanesulphonyl radical so formed [equation (2)]. The combination of equations (1)—(3) thus provide the propagation steps of a chain reaction which, in several of the systems studied, was relatively efficient.

Here we describe studies of the reactions of trichloromethanesulphonyl chloride with a series of alkyl- and substituted alkylcobaloximes which were undertaken in order to establish whether trichloromethyl radicals are capable of displacing cobaloxime(II) from saturated carbon ligands.

$$Cl_3C^{\boldsymbol\cdot} + RCo(dmgH)_2L \longrightarrow$$
$$R'CCl_3 + Co^{II}(dmgH)_2L \quad (1)$$
a; $R = CH_2{:}CH{\cdot}CH_2CH_2,$ $\quad R' = $ cyclopropyl $CH_2$
b; $R = Me_2C{:}CH{\cdot}CH_2,$ $\quad R' = CH_2{:}CH{\cdot}CMe_2$
c; $R = Me_2C{:}C{:}CH,$ $\quad R' = HC{:}C{\cdot}CMe_2$
d; $R = R' = PhCH_2$

$$Cl_3C{\cdot}SO_2Cl + Co^{II}(dmgH)_2L \longrightarrow$$
$$ClCo^{III}(dmgH)_2L + Cl_3C\dot{S}O_2 \quad (2)$$
$$Cl_3C\dot{S}O_2 \longrightarrow Cl_3C^{\boldsymbol\cdot} + SO_2 \quad (3)$$

## RESULTS

n-Butylbis(dimethylglyoximato)pyridinecobalt(III) (0.24 mol dm$^{-3}$) and trichloromethanesulphonyl chloride (0.37 mol dm$^{-3}$) reacted slowly in methylene chloride in the dark at ambient temperature. When irradiated with tungsten spotlights through all-Pyrex apparatus at *ca.* 18 °C a much faster reaction took place giving butanesulphonyl chloride, isolated in 95% yield, together with chlorobis(dimethylglyoximato)pyridinecobalt(III) and

TABLE 1

Preparation of alkanesulphonyl chlorides (RSO$_2$Cl) from alkylcobaloximes [RCo(dmgH)$_2$py] and trichloromethanesulphonyl chloride in dichloromethane

| R | Reaction [a] time/min | Yield (%) [b] |
|---|---|---|
| $CH_3(CH_2)_2CH_2$ | 210 | 95 |
| $CH_3CH_2CH{\cdot}CH_3$ | 90 | 90 |
| $CH_3(CH_2)_5CH{\cdot}CH_3$ | 120 | 90 |
| Cyclohexyl | 90 | 68 |
| $PhCH_2CH_2$ | 120 | 75 |
| $PhCH_2CH_2CH_2$ | 225 | 77 |
| $CH_3OCO{\cdot}CH_2CH_2$ | 270 | 54 |
| $CH_3O{\cdot}CO{\cdot}CH_2CH_2CH_2$ | 180 | 27 |
| $NC{\cdot}CH_2CH_2CH_2$ | 315 | 26 |
| $ICH_2CH_2CH_2$ | 225 | 24 |
| $ICH_2CH_2CH_2CH_2$ | 180 | 20 |
| $PhCHD{\cdot}CH{\cdot}CH_3$ | 90 | 80 [d] |
| $PhCH{\cdot}CHD{\cdot}CH_3$ | 20 [c] | 85 |

[a] [RCo(dmgH)$_2$py] 0.24 mol dm$^{-3}$, [Cl$_3$C·SO$_2$Cl] 0.36 mol dm$^{-3}$, irradiated by six 150-W spotlights *ca.* 5 cm from all-Pyrex, water-cooled apparatus at *ca.* 18 °C. [b] Isolated material. [c] Reagents mixed at ambient temperatures; no photolysis. [d] Characterised in mixed total product by ${}^1$H n.m.r. spectroscopy as a mixture of two diastereoisomers.

traces of butyl chloride. No 1,1,1-trichloropentane was detected in the reaction product. The corresponding photochemical reaction of s-butyl-, s-octyl-,† cyclohexyl-, 2-phenylethyl-, 3-phenylpropyl-, 2-methoxycarbonyl-ethyl-, 3-methoxycarbonylpropyl-, 3-cyanopropyl-, 3-iodopropyl-, and 4-iodobutylbis(dimethylglyoximato)-pyridinecobalt(III) complexes with trichloromethane-sulphonyl chloride gave the corresponding unrearranged organosulphonyl chlorides in 20—90% yield (Tables 1 and 2), without detectable 1,1,1-trichloroalkyl deriva-

† Throughout s-octyl = 6-methylheptyl.

TABLE 2

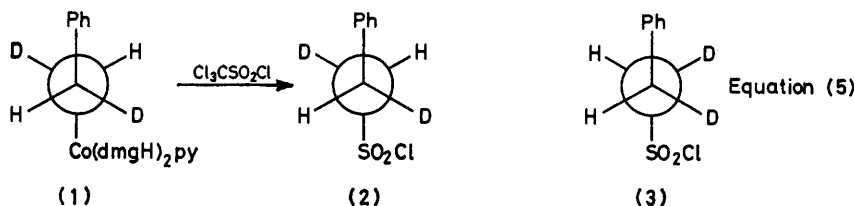¹H and ¹³C N.m.r. spectra and infrared spectra of alkanesulphonyl chlorides $RSO_2Cl$

| R | ¹³C[a] | | | | | ¹H[a] | | | | | | $\nu(SO_2)$/cm⁻¹ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C-1 | C-2 | C-3 | C-4 | MeO | H-1 | H-2 | H-2' | H-3 | H-4 | Other | |
| $CH_3CH_2CH_2CH_2$ | 65.3 | 26.2 | 20.9 | 13.4 | | 3.7[t] | 2.1[m] | | 1.6[m] | 1.0[t] | | 1 170, 1 380 |
| $CH_3CH_2CH{\cdot}CH_3$ | 73.2 | (10.9 | 14.5 | 24.4)[b] | | 3.6[m] | 2.2[m] | 1.6[d] | 1.1[t] | 1.1[t] | | 1 180, 1 370 |
| $CH_3(CH_2)_5CH{\cdot}CH_3$ | 72.0 | (14.0, 26.4, 31.5)[b] | 15.0, 28.9, 30.9 | 22.5, 30.9 | | 3.6[m] | 2.2[m] | 1.6[d] | (0.9 to 2)[c] | | | 1 170, 1 370 |
| Cyclohexyl | 75.0 | 27.3 | 25.1 | 24.8 | | 3.5[m] | 2.3[m] | | (1.2 to 2.2)[c] | | | 1 170, 1 370 |
| $PhCH_2CH_2$ | 66.2 | 30.4[e] | | | | 3.8[m] | 3.3[m] | | | | 7.3[f] | 1 180, 1 380 |
| $PhCH_2CH_2CH_2$ | 64.5 | 25.8 | 33.3[g] | | | 3.6[t] | 2.3[m] | | 2.8[m] | | 7.3[f] | 1 180, 1 380 |
| $MeO{\cdot}COCH_2CH_2$ | 60.2 | 29.0 | 169.4 | | 52.7 | 4.0[t] | 3.0[t] | | | | 3.8[s] | 1 180, 1 380[h] |
| $MeO{\cdot}CO{\cdot}CH_2CH_2CH_2$ | 64.2 | 19.9 | 31.1 | 172.1 | 52.0 | 3.8[t] | 2.5[m] | | 2.5[m] | | 3.7[s] | 1 180, 1 380[i] |
| $NC{\cdot}CH_2CH_2CH_2$ | 63.0 | 15.7 | 20.8 | 117.4 | | 3.8[t] | 2.6[m] | | 2.6[m] | | | 1 180, 1 380[j] |
| $ICH_2CH_2CH_2$ | 65.7 | 27.9 | 0.6 | | | 3.9[t] | 2.6[m] | | 3.4[t] | | | 1 180, 1 380 |
| $ICH_2CH_2CH_2CH_2$ | 64.1 | (25.4 | 30.8)[b] | 3.7 | | 3.8[t] | 2.1[m] | | 2.1[m] | 3.2[t] | | 1 170, 1 380 |
| $PhCHD{\cdot}CH{\cdot}CH_3$ | | | | | | 3.79[m] | 3.66[k] 2.81[l] | 1.51[d] | | | 7.2—7.5[f,m] | 1 175, 1 390 |
| $PhCH{\cdot}CHD{\cdot}CH_3$ | | | | | | 4.77[d] | 2.09[m] | | 0.99[d] | | 7.2—7.5[f,m] | 1 185, 1 395 |

[a] In p.p.m. from TMS, numbering from sulphur substituent. [b] Assignment uncertain. [c] Complex resonances in range shown. [d] Doublet. [e] Phenyl resonances 127.6, 128.9, 128.5, 129.1. [f] Phenyl resonance. [g] Phenyl resonances 126.9, 128.9, 139.0. [h] $\nu(C{=}O)$ 1 750 cm⁻¹. [i] $\nu(C{=}O)$ 1 740 cm⁻¹. [j] $\nu(C{\equiv}N)$ 2 260 cm⁻¹. [k] One diastereoisomer $J_{1,2}$ 1.5 Hz. [l] Other diastereoisomer $J_{1,2}$ 7 Hz. [m] Multiplet. [s] Singlet. [t] Triplet or doublet of doublets.

tives. In several cases the corresponding alkyl chloride was obtained as a minor product.

$$RCo(dmgH)_2py + Cl_3C{\cdot}SO_2Cl \longrightarrow RSO_2Cl + ClCo(dmgH)_2py \quad (4)$$
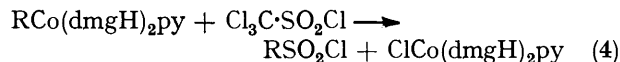
In the corresponding reaction of (R)-s-octylbis(dimethylglyoximato)pyridinecobalt(III) only racemic octane-2-sulphonyl chloride was obtained, while erythro-2-phenyl[1-$^2H_1$,2-$^2H_1$]ethylbis(dimethylglyoximato)pyridinecobalt(III) (1) gave an equimolar mixture of erythro- and threo-2-phenyl[1-$^2H_1$,2-$^2H_1$]ethanesulphonyl chloride [(2) and (3) respectively] [equation (5)].

(7), whether one or both diastereoisomers (8) and/or (9) were present.

3-Phenylpropanesulphonyl chloride was also obtained in 12% yield in the photochemical reaction of 3-phenylpropylcobaloxime with sulphuryl chloride at −4 °C.

DISCUSSION

In none of the products from the above reactions could any of the appropriate substituted 1,1,1-trichloroalkanes, which would have been formed if trichloromethyl radicals had attacked the α-carbon of the alkylcobaloxime, be detected. It is certain that trichloromethyl radicals were present during the reactions
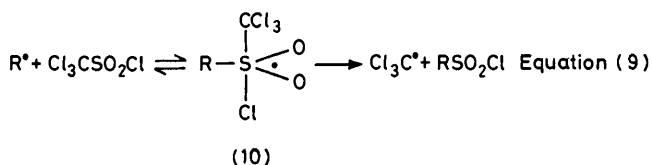
Ph / D / H / H / D / Co(dmgH)₂py  —Cl₃CSO₂Cl→  Ph / D / H / H / D / SO₂Cl      Ph / H / H / D / D / SO₂Cl      Equation (5)

(1)                                (2)                                (3)

The reaction of diastereoisomerically pure 1-phenyl[1-$^2H_1$]propan-2-ylcobaloxime (4) with trichloromethanesulphonyl chloride under the above conditions gave an equimolar mixture of the two diastereoisomeric sulphonyl chlorides (5) and (6) as shown by both ¹H and ²H n.m.r. spectroscopy. We were unable to determine, from the ¹H n.m.r. spectra of the sulphonyl chloride obtained from the corresponding reaction of diastereoisomerically enriched 1-phenyl[2-$^2H_1$]propylcobaloxime

because significant quantities (20—40% yields) of their dimerisation product, hexachloroethane, were detected by g.l.c. in the volatile reaction products. This shows that the intermolecular displacement reaction of equation (1) is unfavourable for saturated carbon ligands except in the special case of benzylcobaloximes described earlier.

The formation of the alkanesulphonyl chloride in such high yield was unexpected, but may be rationalised in terms of two possible non-chain free-radical processes,

Equation (6)

(4)    (5)    (6)
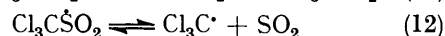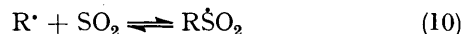
Equation (7)

(7)    (8)    (9)
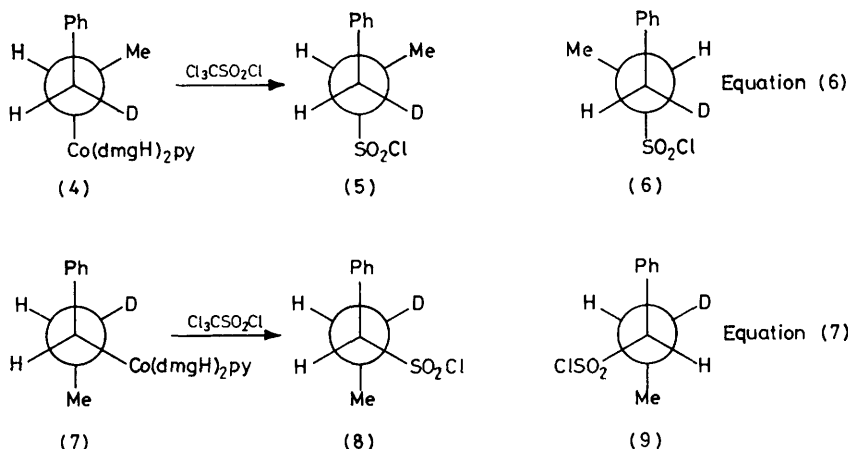
each starting from the photolysis of the carbon-cobalt bond of the alkylcobaloxime [equation (8)]. Such homolysis has been studied for a number of alkylcobalt(III) complexes [10] and there is ample evidence for the formation of both organic radicals and $d^7$ cobaloxime(II) species.

In the first of the possible non-chain mechanisms, the organic radical attacks the sulphur atom of the trichloromethanesulphonyl chloride with synchronous or subsequent displacement of a trichloromethyl radical [equation (9)]. However, there is no precedent for homolytic attack at a sulphonyl sulphur atom [11] except, perhaps, in the reaction between benzyl radicals and compounds of the type $ArSSSO_2Ar$; [12] the attack of radicals on sulphur is clearly established in disulphides, [13] sulphenyl halides, [14] and sulphoxides. [15] It is possible that the presence of the electronegative trichloromethyl group and the chlorine atom on the sulphur in trichloromethanesulphonyl chloride may increase the electrophilic character of the sulphonyl sulphur sufficiently to stabilise the intermediate radical (10).

$$RCo(dmgH)_2py \rightleftharpoons R^{\cdot} + Co^{II}(dmgH)_2py \quad \text{Equation (8)}$$

$$R^{\cdot} + Cl_3CSO_2Cl \rightleftharpoons R-\underset{\underset{Cl}{|}}{\overset{\overset{CCl_3}{|}}{S}}\!\!\begin{smallmatrix}O\\O\end{smallmatrix} \longrightarrow Cl_3C^{\cdot} + RSO_2Cl \quad \text{Equation (9)}$$

(10)

In the second of the possible non-chain mechanisms, the organic radical reacts with sulphur dioxide (present in solution) to give an alkanesulphonyl radical which abstracts the unique chlorine atom from trichloromethanesulphonyl chloride [16] [equations (10) and (11)]. Sulphur dioxide, though not present initially, is formed during the reaction by decomposition of the trichloromethanesulphonyl radical [equation (12)] and is an extremely efficient trap for alkyl radicals. [17] However, some 3-cyanopropyl chloride was formed in the reaction of 3-cyanopropylcobaloxime even when additional sulphur

dioxide was present in solution at the beginning of the reaction, and there was no marked decrease in the yield of 3-cyanopropanesulphonyl chloride when the same reaction was carried out with nitrogen bubbling through the solution.
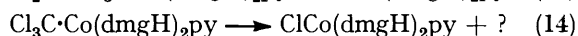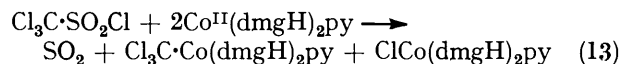
$$R^{\cdot} + SO_2 \rightleftharpoons R\dot{S}O_2 \quad (10)$$

$$R\dot{S}O_2 + Cl_3CSO_2Cl \rightleftharpoons RSO_2Cl + Cl_3C\dot{S}O_2 \quad (11)$$

$$Cl_3C\dot{S}O_2 \rightleftharpoons Cl_3C^{\cdot} + SO_2 \quad (12)$$

The non-chain character of the process is shown by the fact that small quantities of galvinoxyl, di-t-butyl-cresol, and t-butyl-α-phenylnitrone have a negligible influence on the rate and character of the reaction. In the presence of larger amounts of the last inhibitor, some decrease in yield of the alkanesulphonyl chloride was observed, caused by the diversion of alkyl radicals to other products; but even in these cases only minor changes in the rates of reaction were observed. We cannot at present choose definitively between the above non-chain mechanisms, nor can we rule out the possibility that some homolysis of the carbon-cobalt bond is induced by the reaction of trichloromethyl radicals with the alkyl-cobaloxime at a site other than the organic ligand.

These two mechanisms are in accord with the stereochemical studies which show the loss of stereochemical integrity of the 2-phenylethyl and 1-phenyl[1-$^2H_1$]-propan-2-yl radicals in the course of the reaction. We were unable to apply the test for radical intermediates, by cyclisation of hexenyl radicals, because of the competing reaction of trichloromethyl radicals with the olefinic group of hex-5-enylcobaloxime prior to cleavage of the carbon–cobalt bond. [18]
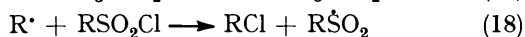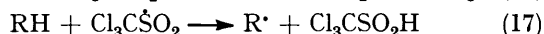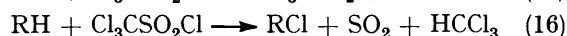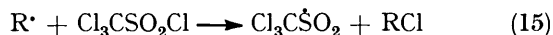
The formation of chlorobis(dimethylglyoximato)-pyridinecobalt(III) is probably the result of more than one process, including: (i) the direct reaction of bis(dimethylglyoximato)pyridinecobalt(II) with trichloromethanesulphonyl chloride, a reaction which also produces sulphur dioxide, and (ii) the further decomposition of the trichloromethylbis(dimethylglyoximato)pyridinecobalt-(III) formed in that reaction. Thus, we have demonstrated that trichloromethanesulphonyl chloride reacts

rapidly with preformed bis(dimethylglyoximato)pyridine-cobalt(II) to give an equimolar mixture of chloro- and trichloro-methylbis(dimethylglyoximato)pyridinecobalt-(III) [equation (13)], and also that the attempted purific-ation of the latter product leads to the formation of further quantities of chlorobis(dimethylglyoximato)-pyridinecobalt(III) [equation (14)], either through a photolytic decomposition with carbene formation, or through hydrolysis on the silica gel adsorbant.[19] The

$$Cl_3C \cdot SO_2Cl + 2Co^{II}(dmgH)_2py \longrightarrow$$
$$SO_2 + Cl_3C \cdot Co(dmgH)_2py + ClCo(dmgH)_2py \quad (13)$$

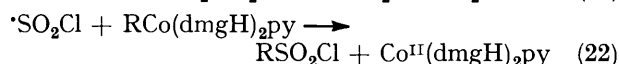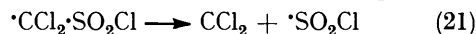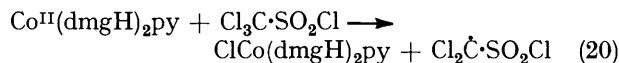$$Cl_3C \cdot Co(dmgH)_2py \longrightarrow ClCo(dmgH)_2py + ? \quad (14)$$

formation of alkyl chlorides as minor products can be accommodated if a proportion of the alkyl radicals abstract the unique chlorine atom from the trichloro-methanesulphonyl chloride [equation (15)], especially in the early stages of the reaction before the sulphur dioxide concentration becomes appreciable. Such chlorine ab-straction is well established in the reaction of alkyl radicals with alkanesulphonyl chlorides [16] and is reported to be dominant in the high-temperature free radical chlorination of some alkanes with trichloromethane-sulphonyl chloride [equation (16)]. Indeed, the ratio of alkanesulphonyl chloride to alkyl chloride decreases as the concentration of trichloromethanesulphonyl chloride increases; this is consistent with the com-petitive reactions of the alkyl radical with sulphur dioxide and with trichloromethanesulphonyl chloride.

It has been suggested [20] that alkyl and trichloro-methanesulphonyl radicals are the chain propagating species in the high-temperature chlorination of hydro-carbons with trichloromethanesulphonyl chloride [equ-ations (15) and (17)]. The role of the latter reagent was based on the rather negative evidence that the selectivity of hydrogen atom abstraction is too high for the trichloro-methyl radical to be the effective species leaving the tri-chloromethanesulphonyl radical as the only other pos-sible reactive species [equation (17)]. It seems possible from the above results that reactions such as those shown in equations (9), (10), (18) or (19) may mediate in these processes.

$$R \cdot + Cl_3CSO_2Cl \longrightarrow Cl_3C\dot{S}O_2 + RCl \quad (15)$$

$$RH + Cl_3CSO_2Cl \longrightarrow RCl + SO_2 + HCCl_3 \quad (16)$$

$$RH + Cl_3C\dot{S}O_2 \longrightarrow R \cdot + Cl_3CSO_2H \quad (17)$$

$$R \cdot + RSO_2Cl \longrightarrow RCl + R\dot{S}O_2 \quad (18)$$

$$R\dot{S}O_2 + RH \longrightarrow RSO_2H + R \cdot \quad (19)$$

We have also considered the possibility that some alkanesulphonyl chlorides may be formed from the corresponding alkylcobaloxime by attack of $\cdot SO_2Cl$ radicals on the $\alpha$-carbon of the alkyl ligand. Not only would such a reaction be expected to proceed with reten-tion or inversion at the $\alpha$-carbon, but it would also require processes such as those shown in equations (20) and (21), which have not been described. We are, however, currently studying the feasibility of the reaction

shown in equation (20) using derivatives such as tri-chloromethyl-$N,N$-dialkylsulphonamides.

$$Co^{II}(dmgH)_2py + Cl_3C \cdot SO_2Cl \longrightarrow$$
$$ClCo(dmgH)_2py + Cl_2\dot{C} \cdot SO_2Cl \quad (20)$$

$$\cdot CCl_2 \cdot SO_2Cl \longrightarrow CCl_2 + \cdot SO_2Cl \quad (21)$$

$$\cdot SO_2Cl + RCo(dmgH)_2py \longrightarrow$$
$$RSO_2Cl + Co^{II}(dmgH)_2py \quad (22)$$

The formation of alkanesulphonyl chlorides from alkylcobaloximes is of some preparative value in those cases where conventional methods are too forcing for functional groups elsewhere in the molecule.[21] The conditions for the reaction of alkylcobaloximes with tri-chloromethanesulphonyl chloride are extremely mild and a very wide range of substituted alkylcobaloximes can be prepared. The limitations appear to be dependent on the rates of competing reactions, e.g. heterocyclic reaction with dioximato-ligands and the reaction of cobaloxime(II) with the alkanesulphonyl chlorides [equ-ation (20)]. Optimum yields were therefore obtained in some cases before complete conversion of the alkyl-cobaloxime had occurred. Solubility plays an important role, the lowest yields being obtained with the least soluble alkylcobaloximes, possibly because of the com-peting reactions described above. Additional limitations with alkenylcobaloximes will be described elsewhere.[18]

$$RSO_2Cl + Co^{II}(dmgH)_2py \longrightarrow$$
$$RSO_2 + ClCo(dmgH)_2py \quad (23)$$
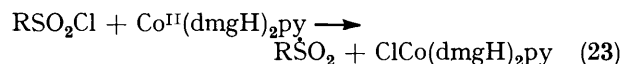
## EXPERIMENTAL

*Preparation of Organobis(dimethylglyoximato)pyridine-cobalt(III) Complexes.*—Butyl-, 1-methylpropyl-, cyclohexyl-, 2-phenylethyl-, 3-phenylpropyl-, 3-methoxycarbonyl-propyl-, 3-cyanopropyl-, 3-iodopropyl-, and 4-iodobutyl-bis(dimethylglyoximato)pyridinecobalt(III) were prepared by reaction of the corresponding chloride, bromide, or di-iodide with the bis(dimethylglyoximato)pyridinecobaltate(I) ion in aqueous methanol under nitrogen. The bis(dimethyl-glyoximato)pyridinecobaltate(I) ion (0.5 mol) was prepared by the addition of aqueous sodium hydroxide (1.5—2 mol) to a methanolic solution of bis(dimethylglyoximato)-pyridinecobalt(II) (1 mol). (R)-s-Octylbis(dimethylgly-oximato)pyridinecobalt(III) and erythro-2-phenyl[1-$^2H_1$,2-$^2H_1$]ethylbis(dimethylglyoximato)pyridinecobalt(III) [22] were prepared from (S)-s-octyl bromide and threo-2-phenyl-[1-$^2H_1$,2-$^2H_1$]ethyltosylate, respectively.* 2-Methoxycar-bonylethylbis(dimethylglyoximato)pyridinecobalt(III) was prepared by the reaction of methyl acrylate with the bis-(dimethylglyoximato)pyridinecobaltate(I) ion.[23] In all cases the organocobaloxime product was isolated by pouring the reaction mixture into water and filtering off the solid which was dried under reduced pressure, and either re-crystallised from methanol or methylene chloride–pentane mixtures or chromatographed on silica gel (Mallinckrodt CC4 Special) with elution by methylene chloride–ethyl acetate mixtures.

* (R)- and (S)-s-Octylbis(dimethylglyoximato)pyridine-cobalt(III) have [$\alpha$]$_{546}^{20}$ −53° and +53°, respectively, whether prepared from the (S)- or (R)-s-octyl tosylate, respectively, or the s-octyl bromides.

For 3-iodopropylbis(dimethylglyoximato)pyridinecobalt-(III) (Found: C, 36.1; H, 4.8; I, 22.9; N, 13.3. $C_{16}H_{25}Co-IN_5O_4$ requires C, 35.8; H, 4.7; I, 23.6; N, 13.0%. For 4-iodobutylbis(dimethylglyoximatopyridinecobalt(III) (Found: C, 36.7; H, 4.9; I, 22.5; N, 12.5. $C_{17}H_{27}CoIN_5O_4$ requires C, 37.0; H, 4.9; I, 23.0; N, 12.7%); $\delta_H$ 3.2 (t, 4-H); 1.0—1.8 (1-H—3-H) and 2.17 (dmgH-CH$_3$). For 3-cyanopropylbis(dimethylglyoximato)pyridinecobalt(III) (Found: C, 46.7; H, 5.9; N, 19.4. $C_{17}H_{25}CoN_6O_4$ requires C, 46.8; H, 5.8; N, 19.3%); $\delta_H$ *ca.* 1.4 (m, 1-H and 2-H) 2.2 (3-H, beneath dmgH-CH$_3$) and 2.17. For 3-methoxy-carbonylpropylbis(dimethylglyoximato)pyridinecobalt(III) (Found: C, 45.3; H, 6.0; N, 14.9. $C_{18}H_{28}CoN_5O_6$ requires C, 46.1; H, 5.0; N, 14.9%); $\delta_H$ *ca.* 1.5 (m, 1-H and 2-H), 2.2 (3-H, beneath dmgH-CH$_3$), and 3.7. For 3-phenyl-propylbis(dimethylglyoximato)pyridinecobalt(III) (Found: C, 53.6; H, 6.1; N, 14.6. Calc. for $C_{22}H_{30}CoN_5O_4$: C, 54.2; H, 6.2; N, 14.4%); $\delta_H$ 1.5 (br m, 1-H and 2-H), 2.5 (t, 3-H), 2.08 (dmgH-CH$_3$), and 7.1 (phenyl). Diastereoiso-merically pure 1-phenyl[1-$^2H_1$]propan-2-ylbis(dimethylgly-oximato)pyridinecobalt(III) was a gift from Dr. A. Gaudemer and 1-phenyl[2-$^2H_1$]propylbis(dimethylglyoximato)pyri-dinecobalt(III) was prepared by the method of Gaudemer *et al.*[24] Using 200 MHz $^1H$ and $^2H$ n.m.r. spectroscopy, we were able to show that this cobaloxime had substantial but not complete diastereoisomeric purity and that the di-astereoisomeric protons had different chemical shifts from those previously reported; one diastereoisomer [equation (7)], had $\delta$ 1.60 (H$_\beta$), while the other diastereoisomer had $\delta$ 1.24 (H$_\beta$).

*Reactions with Trichloromethanesulphonyl Chloride.*—The alkylcobaloxime (2.36 mmol) and trichloromethanesulphonyl chloride (3.66 mmol, Eastman Kodak) in methylene chloride (10 cm$^3$) were irradiated in a stoppered test-tube by six 150-W tungsten spotlights placed *ca.* 10 cm from an all-Pyrex vessel which was cooled to *ca.* 10 °C by circulating methanol. The reaction was monitored by $^1H$ n.m.r. spectroscopy and continued until 80—100% of the substrate had been destroyed, the incomplete reactions being those cases where the substrate was not completely dissolved. The total reaction mixture was chromatographed directly on silica gel (Mallinckrodt CC-4 special) using methylene chloride to elute the organic products, which were then re-chromatographed using pentane–methylene chloride (4 : 1 v/v) as eluant. The excess of trichloromethanesulphonyl chloride and any alkyl chloride were eluted first followed by the desired sulphonyl chloride. For 3-phenylpropanesul-phonyl chloride (Found: C, 49.5; H, 4.9; Cl, 15.7; S, 14.0. Calc. for $C_9H_{11}ClO_2S$: C, 49.4; H, 5.1; Cl, 16.2; S, 14.7%). Cyclohexanesulphonyl chloride (Found: C, 38.5; H, 5.5. Calc. for $C_6H_{11}ClO_2S$: C, 39.4; H, 6.1%). Cyclo-hexanesulphonamide had m.p. 93—94 °C (lit.[25] 94—95 °C). 2-Phenylethanesulphonyl chloride (Found: C, 46.9; H, 4.2; Cl, 17.6. Calc. for $C_8H_9ClO_2S$: C, 47.0; H, 4.4; Cl, 17.3%). Butanesulphonyl chloride (Found: C, 30.7; H, 5.8; Cl, 22.6. Calc. for $C_4H_9ClO_2S$: C, 31.0; H, 5.7; Cl, 22.8%). 3-Cyanopropanesulphonyl chloride (Found: C, 29.4; H, 3.8; N, 8.0. Calc. for $C_4H_6ClNO_2S$: C, 28.7; H, 3.6; N, 8.4%). 3-Iodopropanesulphonamide had m.p. 89—91 °C, and 4-iodobutanesulphonamide had m.p. 87—89 °C.

*Inhibition Experiments.*—Two solutions of n-butyl-cobaloxime (0.1 g) and trichloromethanesulphonyl chloride (0.08 g) in CDCl$_3$ (1 cm$^3$) were placed in separate n.m.r. tubes. Galvinoxyl (10 mg) was placed in one of the tubes

and the two tubes were together irradiated as above. The decrease in the $^1H$ resonances of the substrate were moni-tored at intervals. In the early stages of the reaction, the uninhibited reaction was some three times faster but, as the reactions proceeded, this difference decreased so that by *ca.* 20% reaction the difference was less than two-fold. Similar experiments carried out using 2,6-di-t-butylcresol, *N*-t-butyl-α-phenylnitrone, and phenothiazine, showed negligible inhibition. When *N*-t-butyl-α-phenylnitrone (0.1 g) was added, little inhibition was observed, but there were sub-stantial changes in the t-butyl resonances and less butane-sulphonyl chloride was detected in the product mixture.

*Attempted Decomposition of Alkanesulphonyl Chlorides.*—Cyclohexanesulphonyl chloride (1 mmol) was refluxed in carbon tetrachloride in the presence of benzoyl peroxide (0.05 mmol) for 3 d. The $^1H$ n.m.r. spectrum of the solution showed the presence of the reagent, but no cyclo-hexyl chloride could be detected.

*Reactions with Sulphuryl Chloride.*—Sulphuryl chloride (0.32 g, 2.4 mmol) in methylene chloride (10 cm$^3$) was cooled to −4 °C. 3-Phenylpropylbis(dimethylglyoximato)-pyridinecobalt(III) (1.16 g, 2.36 mmol) was added in portions to the stirred solution. When *ca.* 50% of the solid had been added the tungsten lamps (6 × 150-W) were switched on and the remainder of the solid was added. After 2.5 h the solution was worked-up as above to give 3-phenylpropane-sulphonyl chloride (65 mg, 0.29 mmol, 12%) and a trace of 3-phenylpropyl chloride.

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