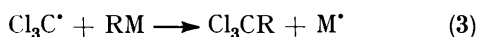# Homolytic Displacements at Carbon. Part 3.[1] Regiospecific Syntheses of Allyl Sulphones in the Reaction of Allycobaloximes with Organosulphonyl Chlorides

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Toluene-p-, toluene-α-, methane-, and chloro-methanesulphonyl chlorides react thermally and photochemically with allyl-, 3-methylallyl-, 3,3-dimethylallyl-, and cinnamyl-cobaloximes to give the corresponding rearranged allyl tolyl, methyl, or chloromethyl sulphone and chlorocobaloxime(III). It is proposed that the mechanism involves a chain reaction in which the organosulphonyl radical and cobaloxime(II) species are the chain-propagating intermediates. Because of competing heterolytic reactions, the yields are higher in the photochemical than in the thermal reactions. Trichloromethanesulphonyl chloride reacts more rapidly, forming the trichloromethylsulphonyl radical which loses sulphur dioxide, so that it is the trichloromethyl radical which reacts with the allylcobaloxime to give the corresponding rearranged trichlorobutene. Dichloromethanesulphonyl chloride reacts similarly, but the dichloromethyl radical, formed by loss of sulphur dioxide, is rather unselective and gives a variety of products in its reaction with the allylcobaloxime.

IN previous papers [1-3] we described a series of reactions between polyhalogenomethanes and organometallic complexes which involved, as a key step, the homolytic displacement of a paramagnetic transition-metal complex from a diamagnetic σ-bonded allyl-,[1,2] allenyl-,[2] or benzyl-[3] transition-metal complex by attack of a poly-halogenomethyl radical on the organic ligand. It was proposed that the mechanism involved chain reactions composed of an initiation step [equation (1)], two propagation steps [equations (2) and (3)] of which reaction (3) is the novel process, and termination steps such as that shown in equation (4).
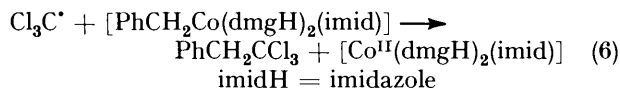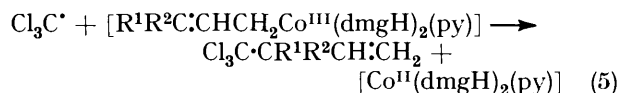
$$RM \rightleftharpoons R^{\bullet} + M^{\bullet} \qquad (1)$$

$$M^{\bullet} + XCCl_3 \longrightarrow MX + {}^{\bullet}CCl_3 \qquad (2)$$

$$Cl_3C^{\bullet} + RM \longrightarrow Cl_3CR + M^{\bullet} \qquad (3)$$

$$M^{\bullet} + {}^{\bullet}CCl_3 \longrightarrow MCCl_3 \qquad (4)$$

R = allyl, benzyl, allenyl; M = Co(dmgH)$_2$(py); X = Cl, Br; dmgH = dimethylglyoximate(1−); py = pyridine.

Besides being of preparative value in organic chemistry, reaction (3) provided the first examples of two novel processes in organic and inorganic chemistry; namely, the first example of a bimolecular homolytic displacement of a transition metal from a carbon-bonded ligand of an organometallic complex with regiospecific rearrangement of that ligand [an S_H2' process, equation (5)],† and the first example of a bimolecular homolytic displacement of any kind at saturated carbon in solution ‡ [an S_H2 process; equation (6)].

The generality of these processes, in particular of the displacement step, merits exploration for series of organometallic substrates RML_n and radicals X$^{\bullet}$, with respect to the nature of the organic ligand R, the metal M in various oxidation states, the ligands L, and the character of the attacking radical X [equation (7)]. Our initial studies have involved some variation of the metal in the sub-group 8B,[1] and of the ligand R.[2,3] In this paper are

$$Cl_3C^{\bullet} + [R^1R^2C\vdots CHCH_2Co^{III}(dmgH)_2(py)] \longrightarrow$$
$$Cl_3C{\cdot}CR^1R^2CH\vdots CH_2 +$$
$$[Co^{II}(dmgH)_2(py)] \quad (5)$$

$$Cl_3C^{\bullet} + [PhCH_2Co(dmgH)_2(imid)] \longrightarrow$$
$$PhCH_2CCl_3 + [Co^{II}(dmgH)_2(imid)] \quad (6)$$
$$imidH = imidazole$$

described further investigations into the ability of sulphonyl radicals to participate as the species X in such reactions.

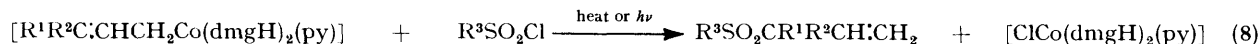$$X^{\bullet} + RML_n \longrightarrow RX + {}^{\bullet}ML_n \qquad (7)$$

RESULTS

Allylbis(dimethylglyoximato)pyridinecobalt(III) (1) and toluene-p-sulphonyl chloride (5) (each *ca.* 0.5M) reacted together in chloroform at ambient temperature within a few hours to give a solution containing allyl p-tolyl sulphone (9) and chlorobis(dimethylglyoximato)pyridinecobalt(III) (21), together with traces of the O-allyldimethylglyoxime derivative (22). Good (50—80%) yields of the sulphones (10)—(15) were also obtained in the corresponding reactions of 3-methylallyl-, 3,3-dimethylallyl-, and cinnamyl-bis-(dimethylglyoximato)pyridinecobalt(III) (2), (3), and (4), respectively, with (5) and with toluene-α-sulphonyl chloride (6) under similar conditions. The characteristics of the sulphones are in Table 1. The corresponding photochemical reaction of (3) with (5) using tungsten light through all-glass apparatus gave a higher yield (87%) of the sulphone (12) at a lower temperature (5 °C) in a shorter time, without the formation of any of the corresponding O-allyldimethyl-glyoxime derivative (24). In all the thermal reactions, except that with the cinnamylcobaloxime (4), from which

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† Hegedus and Miller write a reaction: R$^{\bullet}$ + allyl-NiBr → R-allyl + NiBr, which might be a homolytic displacement at carbon, but they also consider and cannot rule out an alternative process involving attack of R$^{\bullet}$ on the nickel followed by a reductive elimination of the organic product (L. S. Hegedus and L. L. Miller. *J. Amer. Chem. Soc.*, 1975, **97**, 439).

‡ Jackson has observed a homolytic displacement at saturated carbon by trifluoromethyl radicals in the gas phase (J. A. Jackson and M. Townson, *Tetrahedron Letters*, 1973, 193). It seems likely that the ring opening of some strained cyclopropane rings by halogens involves attack of halogen atoms at a ring carbon atom (J. H. Incremona and C. J. Upton, *J. Amer. Chem. Soc.*, 1972, **94**, 301).

some bicinnamyl was isolated, the expected sulphones were accompanied by traces of the appropriate O-allyldimethyl-glyoxime derivatives (23)—(25). In all cases *only a single isomer* of the tolyl allyl sulphone could be detected in the product, irrespective of the yield obtained.

The thermal reactions of the allylcobaloximes (1)—(4)

each case were exclusively the trichlorobutenes (27)—(30), respectively [Table 2; reaction (9)].

In further contrast, dichloromethanesulphonyl chloride (31) gave several products with 3,3-dimethylallylcobaloxime (3) and with cinnamylcobaloxime (4). The main organic product from (4) was the dichlorobutene derivative (32),

$$[R^1R^2C{:}CHCH_2Co(dmgH)_2(py)] \quad + \quad R^3SO_2Cl \xrightarrow{\text{heat or } h\nu} R^3SO_2CR^1R^2CH{:}CH_2 \quad + \quad [ClCo(dmgH)_2(py)] \quad (8)$$

(1) $R^1 = R^2 = H$	(5) $R^3 = p\text{-MeC}_6H_4$
(2) $R^1 = Me, R^2 = H$	(6) $R^3 = PhCH_2$
(3) $R^1 = R^2 = Me$	(7) $R^3 = Me$
(4) $R^1 = Ph, R^2 = H$	(8) $R^3 = ClCH_2$

(9) $R^1 = R^2 = H, R^3 = p\text{-MeC}_6H_4$ (21)
(10) $R^1 = Me, R^2 = H, R^3 = p\text{-MeC}_6H_4$
(11) $R^1 = Me, R^2 = H, R^3 = PhCH_2$
(12) $R^1 = R^2 = Me, R^3 = p\text{-MeC}_6H_4$
(13) $R^1 = R^2 = Me, R^3 = PhCH_2$
(14) $R^1 = Ph, R^2 = H, R^3 = p\text{-MeC}_6H_4$
(15) $R^1 = Ph, R^2 = H, R^3 = PhCH_2$
(16) $R^1 = Ph, R^2 = H, R^3 = Me$
(17) $R^1 = Ph, R^2 = H, R^3 = ClCH_2$
(18) $R^1 = R^2 = R^3 = Me$
(19) $R^1 = R^2 = Me, R^3 = ClCH_2$
(20) $R^1 = R^2 = H, R^3 = ClCH_2$

$$\text{Me} \diagdown \quad \diagup \text{Me}$$
$$\text{N—N}$$
$$\text{HON} \diagup \quad \diagdown \text{NOCR}^1R^2CH{:}CH_2$$
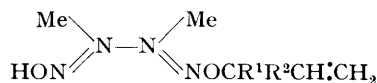
(22) $R^1 = R^2 = H$
(23) $R^1 = Me, R^2 = H$
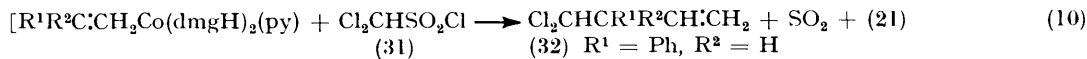(24) $R^1 = R^2 = MX$
(25) $R^1 = Ph, R^2 = H$

with methanesulphonyl chloride (7), and with chloro-methanesulphonyl chloride (8), in methylene chloride were similar in character to those just described, but gave lower yields of the appropriate allyl methyl sulphone (16)—(20), characterised by proton n.m.r. spectroscopy following separation from the inorganic product by column chromato-graphy. Despite the lower yields, only the single rearranged isomer of each sulphone could be detected, in all cases accompanied by the by-products (23)—(25). The photo-chemical reactions of (7) and (8) with (3) and with (4) were much faster, even at 10 °C, and gave very high yields of the

but little of the corresponding dichlorobutene (33) could be obtained from (3); instead the O-allyldimethylglyoxime derivative (24) was formed in good yield, together with small amounts of dimethylallyl chloride [reaction (10)].
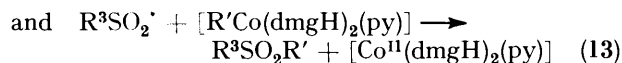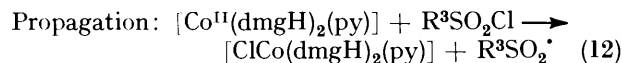
DISCUSSION

The reactions of the four allylcobaloximes (1)—(4) with the toluenesulphonyl chlorides (5) and (6) show characteristics similar to those of the same substrates with bromotrichloromethane; [1-3] they are markedly

$$[R^1R^2C{:}CH_2Co(dmgH)_2(py)] + Cl_3CSO_2Cl \longrightarrow Cl_3CCR^1R^2CH{:}CH_2 + SO_2 + (21) \quad (9)$$
$$\text{(1)—(4)} \qquad\qquad (26)$$

(27) $R^1 = R^2 = H$
(28) $R^1 = Me, R^2 = H$
(29) $R^1 = R^2 = Me$
(30) $R^1 = Ph, R^2 = H$

$$[R^1R^2C{:}CH_2Co(dmgH)_2(py) + Cl_2CHSO_2Cl \longrightarrow Cl_2CHCR^1R^2CH{:}CH_2 + SO_2 + (21) \quad (10)$$
$$\text{(31)}$$

(32) $R^1 = Ph, R^2 = H$
(33) $R^1 = R^2 = Me$

same sulphones without any formation of the by-products (24) and (25). In the reaction of (3) with (7), the sulphone was the sole organic product detected and the reaction was almost quantitative. Whilst not all these exploratory reactions were carried out under tungsten illumination, it is probable that higher yields could have been obtained in all cases using the sulphonyl chlorides (5)—(8) at lower temperatures with the aid of appropriate irradiation.

The same allylcobaloximes react quite differently with trichloromethanesulphonyl chloride (26). Not only was each reaction complete within one hour without irradiation at ambient temperature, but no sulphone could be detected in any of the products. The inorganic product was again the chlorocobaloxime (21), but the organic products in

accelerated by irradiation with tungsten light through glass apparatus, and are subject to concentration-dependent induction periods, especially where the materials are fresh and pure.

We therefore postulate, for the reactions of (5)—(8), a chain reaction similar to that proposed earlier, *i.e.*, equations (11)—(13).

The initiation step may be somewhat more complicated than a simple homolysis of the carbon–cobalt bond as presented in equation (11). The thermolysis and photolysis of allylcobaloximes gives the cobaloxime(II) required in reaction (12), but the decomposition may involve the concerted or stepwise formation of an olefin

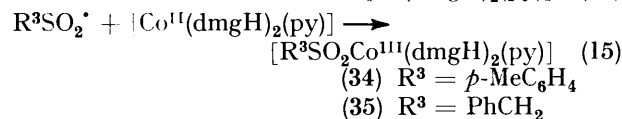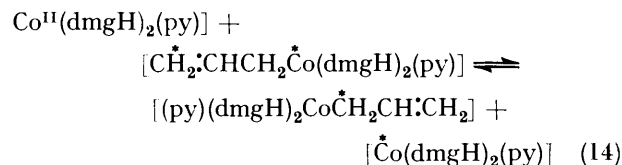and a hydridocobaloxime(III) species by a δ-elimination process, the cobaloxime(II) being derived from further reaction of the hydrido-species with the allylcobaloxime.* Such an initiation step has the particular advantage that organic radicals, which may lead to

Initiation: $[R'Co(dmgH)_2(py)] \longrightarrow$
$$R^{\bullet} + [Co^{II}(dmgH)_2(py)] \quad (11)$$

Propagation: $[Co^{II}(dmgH)_2(py)] + R^3SO_2Cl \longrightarrow$
$$[ClCo(dmgH)_2(py)] + R^3SO_2^{\bullet} \quad (12)$$

and $\quad R^3SO_2^{\bullet} + [R'Co(dmgH)_2(py)] \longrightarrow$
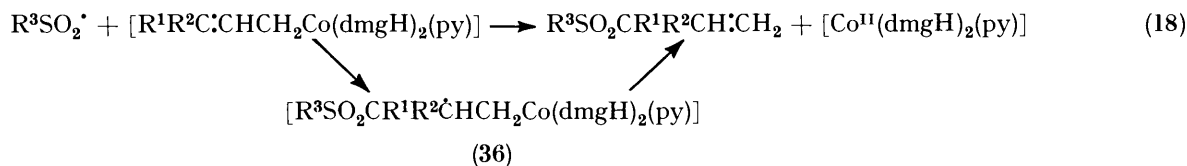$$R^3SO_2R' + [Co^{II}(dmgH)_2(py)] \quad (13)$$
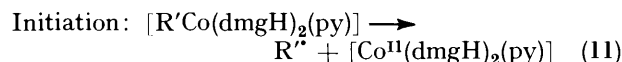
unwanted side products, may not be formed directly in this stage of the reaction.

Besides the above general characteristics indicating a free-radical process, two other observations support the proposed mechanism. First, after several minutes in solution, pure allylcobaloxime (1) shows characteristic dynamic behaviour which can be detected in the ^{13}C or ^{1}H n.m.r. spectra of $CDCl_3$ solutions, and which is a result

$[Co^{II}(dmgH)_2(py)] +$

$$[C\overset{\bullet}{H}_2{:}CHCH_2\overset{\bullet}{C}o(dmgH)_2(py)] \rightleftharpoons$$

$$[(py)(dmgH)_2Co\overset{\bullet}{C}H_2CH{:}CH_2] +$$

$$[\overset{\bullet}{C}o(dmgH)_2(py)] \quad (14)$$

$R^3SO_2^{\bullet} + [Co^{II}(dmgH)_2(py)] \longrightarrow$
$$[R^3SO_2Co^{III}(dmgH)_2(py)] \quad (15)$$
$$(34) \ R^3 = p\text{-}MeC_6H_4$$
$$(35) \ R^3 = PhCH_2$$

of the cobalt-for-cobalt displacement reaction of equation (14), which increases in frequency as cobaloxime(II) begins to form in solution through reaction (11) or related decomposition processes.[4] The addition of traces of either (5) or (6) to such a solution causes a marked decrease in the extent of the dynamic character, but the latter again becomes evident in the n.m.r. spectra when the added sulphonyl chloride has been consumed.

Secondly, the reaction of cobaloxime(II) with (5) or with (6) in the absence of allylcobaloxime gives good
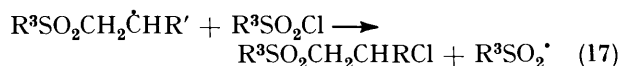
Reaction (15) is thus an important termination step in the chain reaction involving reactions (11)—(13).

Tolylsulphonyl radicals have previously been identified as chain propagating species in other reactions, such as the addition of arenesulphonyl halides to olefins [6] [equations (16) and (17)]. Reaction (16) involves the attack of the arylsulphonyl radical on the unsaturated carbon atom of the olefin; it is therefore not surprising that the attack of the arylsulphonyl radical on the allylcobaloxime also takes place at the unsaturated γ-carbon atom of the allyl ligand, resulting in the formation solely of the rearranged, kinetically controlled, allyl sulphone, perhaps via an intermediate short-lived radical such as (36). There is one distinct difference between reactions (16) and (18); it is common for the incoming radical to attack the least hindered carbon

$$R^3SO_2^{\bullet} + CH_2{:}CHR' \longrightarrow R^3SO_2CH_2\overset{\bullet}{C}HR' \quad (16)$$

$R^3SO_2CH_2\overset{\bullet}{C}HR' + R^3SO_2Cl \longrightarrow$
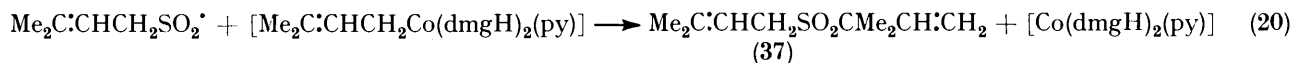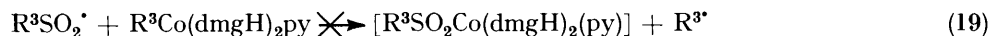$$R^3SO_2CH_2CHRCl + R^3SO_2^{\bullet} \quad (17)$$

atom of the olefin, whereas in order to achieve the subsequent loss of the cobaloxime(II) species, the attack on the allyl ligand in (3) and (4) must take place at the more hindered γ-carbon atom.

These γ-reactions also have some bearing on some proposals for the mechanism of some sulphur dioxide insertion reactions;[7] it has been proposed that a key step might be the attack of the sulphonyl radical $R^3SO_2^{\bullet}$, formed on capture of an organic radical by SO_2, on the metal of the organometallic substrate, thereby regenerating the organic radical R^3 [equation (19)]. Clearly, such a process does not take place, other than as a minor path, in the reactions of the allylcobaloximes, because the arylsulphonyl cobaloximes (34) and (35) are only very minor by-products of these reactions, formed as a result of the chain-terminating step, reaction (15). It is interesting however, that small ($\leqslant 15\%$) yields of the single specific diallyl sulphone (37) are formed in the reaction of (3) with sulphur dioxide at ambient temperature,[8] probably via attack of dimethylallylsulphonyl radicals, formed from dimethylallyl

$$R^3SO_2^{\bullet} + [R^1R^2C{:}CHCH_2Co(dmgH)_2(py)] \longrightarrow R^3SO_2CR^1R^2CH{:}CH_2 + [Co^{II}(dmgH)_2(py)] \quad (18)$$

$$\searrow \qquad\qquad \nearrow$$

$$[R^3SO_2CR^1R^2\overset{\bullet}{C}HCH_2Co(dmgH)_2(py)]$$

$$(36)$$

yields of (21) and the corresponding organosulphonyl-cobaloxime (34) or (35).[5] Thus the decrease in the dynamic character of the allylcobaloxime can be directly ascribed to the removal of substantial quantities of cobaloxime(II) by the same reactions [(12) and (15)] that are responsible for the formation of (34) and (35).

radicals and SO_2, on the γ-carbon atom of the allyl ligand of (3), in a manner directly analogous to that shown in reaction (18) [reaction (20)].

The radical-chain mechanism for the reactions of the arenesulphonyl chlorides is further supported by the variation in products in the reaction of the several chloromethanesulphonyl chlorides with allylcobaloximes. In particular, the rapid reactions of trichloromethanesulphonyl chloride, which lead not to the sulphones but to the trichlorobutene derivatives, are indicative of

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* Cobaloxime(II) is formed quantitatively in the thermolysis and photolysis of dimethylallylcobaloxime(III) in inert media (E. Białkowska, K. N. V. Duong, and A. Gaudemer, unpublished work).

the formation of unstable trichloromethylsulphonyl radicals which lose sulphur dioxide to give the trichloromethyl radical [equation (21)]. It is therefore the trichloromethyl radical * which attacks the γ-carbon atom of the allylcobaloxime as described in earlier work [1-3] [equation (5)]. These chain reactions of trichloromethanesulphonyl chloride therefore involve three propagation steps, namely equations (12), (21), and (5).

the change in character of the substrate and the removal of the sulphonyl chloride from the system.

The preparative value of these reactions is that the allylcobaloximes, which can readily be synthesised in 80—90% yield from the corresponding halides, react regiospecifically to give good yields *directly* of 1,1-disubstituted allyl sulphones. Alternative methods usually require the initial formation of the unsubstituted

$$R^3SO_2^{\bullet} + R^3Co(dmgH)_2py \not\longleftrightarrow [R^3SO_2Co(dmgH)_2(py)] + R^{3\bullet} \qquad (19)$$

$$Me_2C\dot{:}CHCH_2SO_2^{\bullet} + [Me_2C\dot{:}CHCH_2Co(dmgH)_2(py)] \longrightarrow Me_2C\dot{:}CHCH_2SO_2CMe_2CH\dot{:}CH_2 + [Co(dmgH)_2(py)] \qquad (20)$$
$$(37)$$

The products of reaction of dichloromethanesulphonyl chloride are more complicated probably because, though the dichloromethylsulphonyl radical is formed as in equation (12), the loss of sulphur dioxide is slower and competes less effectively with the direct displacement of equation (13). Moreover, the dichloromethyl radical so

$$Cl_3CSO_2^{\bullet} \longrightarrow Cl_3C^{\bullet} + SO_2 \qquad (21)$$
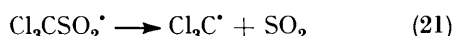
formed is less selective than either the organosulphonyl radicals or the trichloromethyl radical, and therefore does not necessarily and exclusively attack the γ-carbon atom of the allyl ligand. The yield of the dichlorobutene from (31) is therefore much less than that of the trichlorobutene from (26), and other products are formed through attack of the dichloromethyl radical at other sites on the organocobaloxime. Loss of sulphur dioxide from the chloromethylsulphonyl and methylsulphonyl radicals [9] is too slow to compete with the displacement process of equation (13).

The formation of the *O*-organo-dimethylglyoxime derivatives is common in a number of electrophilic and radical reactions of organocobaloximes.[10] and we do not propose to discuss in detail their formation at this stage. However, since they are observed in the thermal but not in the photochemical reactions with the sulphonyl chlorides, it is clear that they are *not* formed as a result of the attack of the organosulphonyl *radical* on any atom of the organocobaloxime substrate. Under the conditions of the thermal reactions, competing heterolytic reactions involving modification of the organocobaloxime, either by removal of the axial pyridine ligand or by direct reaction with equatorial dimethylglyoximato ligands, probably diminish the dominance of the simple bimolecular radical process of equation (13) both through

allyl sulphone followed by stepwise introduction of the α-substituents utilising the nucleophilic character of the conjugate base of the sulphone.[11] The main disadvantage of the present method is that we have so far been unable to obtain 1-substituted allylcobaloximes, either from 1-substituted allyl halides, which give 3-substituted allylcobaloximes, or from 1,3-disubstituted allyl halides, which yield allylcobaloximes that are too unstable for isolation. The method is not therefore applicable to the synthesis of either 1,3-di- or 1,1,3-tri-substituted allyl sulphones.

The application of the method to the synthesis of more
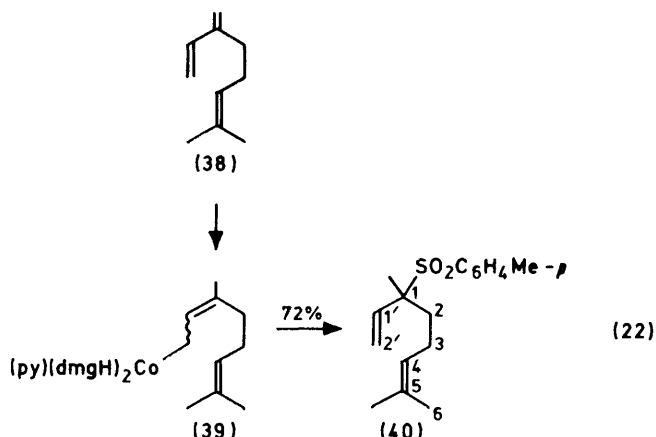
complicated primary allyl sulphones is illustrated by the conversion of myrcene (38) into the sulphone (40) *via* the photochemical reaction of the cobaloxime (39) with toluene-*p*-sulphonyl chloride [reaction (22)].

EXPERIMENTAL

Materials.—Allylcobaloximes were prepared as described earlier.[4] Toluene-*p*-sulphonyl chloride, toluene-α-sulphonyl chloride, and methanesulphonyl chloride (Hopkin and Williams), mono-, di-, and tri-chloromethanesulphonyl chloride (Lancaster Synthesis), and methylene chloride (Koch–Light) were commercial materials used without further purification. Chloroform was washed with water and redistilled immediately prior to use, but contained traces of ethanol which appeared to be beneficial for the reactions.

Preparation of Sulphones.—*Thermal reactions.* In a typical experiment, but-2-enylbis(dimethylglyoximato)-

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* It has been concluded (E. S. Huyser and B. Giddings, *J. Org. Chem.*, 1962, **27**, 3391; E. S. Huyser, H. Schmimke, and R. L. Burnham, *ibid.*, 1963, **28**, 2141) from selectivity measurements in the abstraction of hydrogen by radicals derived from trichloromethylsulphonyl chloride, that it is the trichloromethylsulphonyl radical which is effective, not the trichloromethyl radical, in hydrogen abstraction. However, it seems unlikely under our very mild conditions that any allyl trichloromethyl sulphone would rapidly lose sulphur dioxide. The formation of βββ-trichloroethylcyclopropanes in the reactions of butenylcobaloximes with trichloromethanesulphonyl chloride (A. Bury and M. D. Johnson, unpublished work) similarly excludes direct reaction of the trichloromethylsulphonyl radicals followed by extrusion of sulphur dioxide from the cyclopropylmethylsulphone.

TABLE 1

Products of reaction of allylcobaloximes (0.5M) with toluenesulphonyl chlorides (0.5M) in CH_2Cl_2 and $CHCl_3$

Reagents	Product	Analysis % calc.(found) C	H	N	Yield %	3-H (cis)	3-H (trans)	2-H	1-H	1'-H	Me or CH₃ b	Je c	Jt c	J1,2 c	M.p. (t/°C)	Mass spec. (m/e)
(1) and (5)	CH₂:CHCH₂SO₂C₆H₄Me-p (9)				67				3.84		2.50					
(2) and (5)	CH₂:CHCHMeSO₂C₆H₄Me-p (10)	62.9 (62.8)	6.8 (6.7)	15.1 (15.25)	72	5.26	5.11	5.76	4.31	1.42	2.75 d	10.5	17.3	7.0	60—61	210, 146
(3) and (5)	CH₂:CHCMe₂SO₂C₆H₄Me-p (12)	64.1 (64.25)	7.2 (7.2)	14.25 (14.3)	62;e 87 f	5.24	5.07	5.98		1.39	2.40 g	10.3	17.3		Oil	224, 160
(4) and (5)	CH₂:CHCHPhSO₂C₆H₄Me-p (14)	70.3 (70.6)	6.1 (5.9)	12.0 (11.8)	68	5.42	5.29	6.27	4.67		2.36 h	10.0	16.8	8.8	132—133	
(2) and (6)	CH₂:CHCHMeSO₂CH₂Ph (11)	63.0 (62.8)	6.8 (6.7)	15.1 (15.25)	65	5.37	5.44	5.92	4.56	1.45	4.12	10.5	16.5	7.0	39—40	210, 146
(3) and (6)	CH₂:CHCMe₂SO₂CH₂Ph (13)	64.1 (64.25)	7.3 (7.2)	14.0 (14.3)	60	5.40	5.38	6.13		1.47	4.12	10.2	18.0		87—88	224, 160
(4) and (6)	CH₂:CHCHPhSO₂CH₂Ph (15)	70.5 (70.6)	5.95 (5.9)	11.7 (11.8)	72	5.51	5.39	6.30	4.62		4.11	10.3	16.5	8.8	78—79	272, 208

a Atomic numbering as follows: $\overset{3}{C}H_2:\overset{2}{C}H\cdot\overset{1}{C}HMeSO_2R^3$. b Chemical shift of CH_3 or Me of tolyl groups. c In Hz. d Tolyl aromatic resonances δ 7.40 and 7.88. e Thermal reaction. f Photochemical reaction; irradiation with 500-W tungsten lamps. g Tolyl aromatic resonances δ 7.71 and 7.24. h Tolyl aromatic resonances δ 7.19 and 7.49.

pyridinecobalt(III) (2) (4.22 g, 10 mmol) and toluene-α-sulphonyl chloride (6) (1.90 g, 10 mmol) were dissolved in chloroform (8 cm³). After 6 h at ambient temperature under nitrogen, reaction was complete and ¹H n.m.r. spectroscopy showed an 80% yield of benzyl 1-methylallyl sulphone (11) in the mixture. The entire mixture was chromatographed on silica gel, eluting successively with pentane, methylene chloride, and methylene chloride–acetone mixtures. The first fraction was substantially the dimethylglyoxime derivative (23), followed by the sulphone (11) (1.45 g, 6.5 mmol, 65% yield), and finally the chlorocobaloxime (21). The latter was characterised by comparison with authentic material. The sulphones were characterised by elemental analysis, and ¹H n.m.r. and mass spectrometry (Tables 1 and 2).

Photochemical reactions. 3-Methylbut-2-enylbis(dimethylglyoximato)pyridinecobalt(III) (3) (211 mg, 0.5 mmol) and methanesulphonyl chloride (7) (114 mg; 1.0 mmol) were dissolved in methylene chloride (12 cm³). The solution was degassed and then maintained at 5 °C for 1.25 h whilst it was irradiated with two 150-W tungsten lamps 15 cm from the water-cooled Pyrex flask. 1,1-Dimethylallyl methyl sulphone (18) (67 mg, 0.45 mmol, 90%) was isolated

as above. In this case, the first fraction contained only the excess of methanesulphonyl chloride, and no dimethylglyoxime derivative (24) could be detected.

Reactions of Trichloromethanesulphonyl Chloride.—In a typical experiment, cinnamylcobaloxime (4) (0.12 g, 0.24 mmol) and trichloromethanesulphonyl chloride (0.05 g, 0.25 mmol) were dissolved in deuteriochloroform. After 5 min the chlorocobaloxime was precipitated by addition of pentane and filtered off. The pentane solution was dried (Na_2SO_4) and evaporated to dryness. The ¹H n.m.r. spectrum of the residue showed only one product, 3-phenyl-4,4,4-trichlorobut-1-ene, identical with that formed in the reaction of (4) with bromotrichloromethane.[2]

Reaction of Myrcene.—Bis(dimethylglyoximato)pyridinecobalt(II), prepared from cobalt chloride hexahydrate (952 mg, 4 mmol), dimethylglyoxime (932 mg, 8 mmol), pyridine (0.21 cm³, 4 mmol), and aqueous sodium hydroxide (1.5 cm³; 8 mol dm⁻³) in methanol (20 cm³), and myrcene (0.7 cm³, 4 mmol) were hydrogenated at ambient temperature and pressure. After ca. 30 min, when 45 cm³ of hydrogen had been absorbed, the mixture was poured into water and the orange solid cobaloxime was filtered off, washed with water, and dried *in vacuo*. The crude cobaloxime (400 mg,

TABLE 2

Products of reaction of allylcobaloximes (ca. 0.5M) with methane- and chloromethane-sulphonyl chlorides in methylene chloride

¹H N.m.r. δ values a

Reagents	Product	3-H (cis)	3-H (trans)	2-H	1-H	1'-H	R³SO₂	Je b	Jt b	J1,2 b	Other	Yield %
(3) and (7)	MeSO₂CMe₂CH:CH (18)	5.34	5.34	6.02		1.41	2.65	10.0	17.5			90 c
(4) and (7)	MeSO₂CHPhCH:CH₂ (16)	5.56	5.54	6.31	4.75		2.76	11.5	16.5	9.0	Ph, δ 7.42	75 c
(1) and (7)	MeSO₂CH₂CH:CH₂				3.75		2.86			6.7		ca. 25 d
(2) and (7)	MeSO₂CHMeCH:CH₂	5.24	5.22	5.95		1.52	2.75					ca. 30 d
(1) and (8)	ClCH₂SO₂CH₂CH:CH₂ (20)				3.95		4.44			6.6		ca. 40 d
(3) and (8)	ClCH₂SO₂CMe₂CH:CH₂ (19)	5.56	5.55	6.15		1.60	4.56	9.4	18.0			ca. 45;d 65 c
(4) and (8)	ClCH₂SO₂CHPhCH:CH₂ (17)	5.57	5.68	6.29	4.16		e	10.3	16.9		Ph, δ 7.5	ca. 45 d
(4) and (31)	Cl₂CHCHPhCH:CH₂ (32)	5.33	5.29	6.3	3.93		5.89				J1,1' b 5.4	ca. 20 d
(3) and (31)	Cl₂CHCMe₂CH:CH₂ (33)	5.24	5.22	5.93		1.14	5.6	9.5	17.5			ca. 10 d
	(24)	5.08	5.10	6.08		1.42		10.0	17.5		Me, δ 1.99, 2.07	40
(1) and (26)	Cl₃CCH₂CH:CH₂ (27)	5.32	5.37	5.99	3.40			11.0	16.0	7.9		S f
(2) and (26)	Cl₃CCHMeCH:CH₂ (28)	5.27	5.28	5.95	3.21	1.44		9.3	17.3	7.6	J1,1' b 7.6	S f
(3) and (26)	Cl₃CCMe₂CH:CH₂ (29)	5.26	5.27	6.21		1.44		10.5	17.5			S f
(4) and (7)	Cl₃CCHPhCH:CH₂ (30)	5.28	5.38	6.42	4.29			9.8	16.6	8.2		S f

a Atomic numbering as follows: $\overset{3}{C}H_2:\overset{2}{C}H\cdot\overset{1}{C}HMeSO_2R$ for the sulphones and $\overset{3}{C}H_2:CHCHMeC\overset{1}{X}_3$ for the butenes. b In Hz. c Photochemical reactions, yield of isolated product. d Thermal reaction, product isolated but not analysed. e Two methylene resonances, δ 4.44 and 4.17, J 12 Hz. f Sole organic product, identified by comparison with authentic material.

0.8 mmol) and toluene-*p*-sulphonyl chloride (153 mg, 0.8 mmol) in chloroform (5 cm³) were irradiated at 12 °C using two 350-W tungsten lamps at a distance of 12 cm from the all-glass apparatus. After 2 h the mixture was chromatographed first on silica gel (Mallincrodt CC4) with methylene chloride as eluant; t.l.c. on silica gel using acetone–hexane (1 : 9 v/v) as eluant gave 1,5-*dimethyl-1-vinylhex-4-enyl* p-*tolyl sulphone* (40) (168 mg, 0.58 mmol, 72%) (Found: C, 69.9; H, 8.0; S, 10.6. $C_{17}H_{24}O_2S$ requires C, 69.8; H, 8.3; S, 10.9%); ¹H n.m.r.: δ 1.38 (s, 1-Me), 1.56 and 1.68 (each s, 5-Me and 3 × 6-H), *ca.* 1.92 (m, 2- and 3-H), 2.45 (Ar*Me*) 5.12 (m, 4-H), 5.11 (d, *trans*-2'-H, *J* 17.5 Hz), 5.42 (d, *cis*-2'-H, *J* 10.8 Hz), 5.96 (1'-H), and δ 7.38 and 7.75 (m, ArH).

Preparation of the Sulphone (37).—3-Methylbut-2-enyl-bis(dimethylglyoximato)pyridinecobalt(III) (3) (1.3 g, 3.3 mmol) was dissolved in sulphur dioxide (5 cm³) at *ca.* −20 °C. The vessel was sealed and maintained at 25 °C for 2 h, and then cooled and unsealed and the excess of sulphur dioxide allowed to evaporate. The residue was chromatographed on silica gel (CC4) using methylene chloride as eluant. The sulphone (37) (49 mg, 0.24 mmol, 15%) [¹H n.m.r. (a) 1,1 dimethyllallyl group: δ 1.51 (s, Me) quartet 6.14 (q, =CH−), 5.39br. (d, *trans*-=CH₂), and 5.41br (d, *cis*- =CH₂); (b) 3-methylbut-2-enyl group: δ 1.70 and 1.82 (Me), and 3.67 (*d*, =CH₂)] was eluted first contaminated with the dimethylglyoxime derivative (24) [¹H n.m.r. δ 1.99 and 2.04 (s, dimethylglyoxime Me) and 1.41 (s, allyl Me)].

REFERENCES

¹ E. Crease, B. D. Gupta, M. D. Johnson, and S. Moorhouse, *J.C.S. Dalton*, 1978, 1821, is considered to be Part 2.
² A. Bury, C. J. Cooksey, T. Funabiki, B. D. Gupta, and M. D. Johnson, *J.C.S. Perkin II*, in the press, is considered to be Part 1 of this series; B. D. Gupta, T. Funabiki, and M. D. Johnson, *J. Amer. Chem. Soc.*, 1976, **98**, 6692.
³ B. D. Gupta, T. Funabiki, and M. D. Johnson, *J.C.S. Chem. Comm.*, 1977, 653.
⁴ C. J. Cooksey, D. Dodd, M. D. Johnson, and B. L. Lockman, *J.C.S. Dalton*, 1978, 1814.
⁵ K. N. V. Duong, A. Gaudemer, and M. D. Johnson, unpublished work; see also M. D. Johnson and G. J. Lewis, *J. Chem. Soc. (A)*, 1970, 2153.
⁶ M. S. Kharasch and R. A. Moser, *J. Org. Chem.*, 1952, **17**, 453; P. S. Skell, R. C. Woodworth, and T. H. McNamara, *J. Amer. Chem. Soc.*, 1957, **79**, 1253.
⁷ J. M. Swan and D. St. C. Black, ' Organometallics in Organic Synthesis,' Chapman and Hall, London, 1974, p. 22.
⁸ M. D. Johnson, unpublished work.
⁹ W. K. Busfield, K. J. Ivin, H. Mackle, and P. G. A. O'Hare, *Trans. Faraday Soc.*, 1961, **57**, 1064; W. K. Busfield and K. J. Ivin, *ibid.*, p. 1044; W. K. Busfield, H. Mackle, and P. A. G. O'Hare, *ibid.*, p. 1054.
¹⁰ S. N. Anderson, D. H. Ballard, and M. D. Johnson, *J.C.S. Perkin II*, 1972, 311; J. Halpern, M. S. Chan, J. Hanson, T. S. Roche, and J. A. Topich, *J. Amer. Chem. Soc.*, 1975, **97**, 1606; A. Gaudemer and F. Gaudemer, unpublished work; D. Widdowson, personal communication.
¹¹ D. Savoia, C. Trombini, and A. Umani-Ronchi, *J.C.S. Perkin I*, 1977, 123.