in the same molar concentration but having 82 mg (0.4 mmol) of iodobenzene were irradiated on a merry-go-round apparatus. The irradiation was stopped at the end of 1 h and an aliquot (0.1 mL) was analyzed after quenching by gas chromatography. Tube 1 showed 20% of the amount of product produced in tube 2 containing iodobenzene. Irradiation was carried for a total of 6 h and the reaction mixtures were quenched with equal amounts of water (1 mL). Triphenylethylene in 2 mL of tetrahydrofuran was added to each tube and the products were quantitated. Tube 2 showed 49% of 1,1,3-triphenylindene and 8.5% of 1,2,3-triphenylindene compared to 11% and 1.7% of the respective products produced in tube 1.

Emission Studies. Purification of Solvent. Dimethyl sulfoxide was purified by the procedure of Bordwell and coworkers.[31] Benzene was purified by repeated washings with cold, concentrated sulfuric acid until the washings were colorless, then with water, and 5% sodium hydroxide, drying over anhydrous potassium carbonate, and distillation.

Fluorescence Quenching Studies. An Aminco-Bowman spectrofluorimeter equipped with a xenon lamp was used to obtain relative quantum yields for 1,3-diphenylindenyl anion in dimethyl sulfoxide. Absorption spectra were recorded on a Beckman-Model 26 spectrometer. 1,3-Diphenylindenyl anion has absorption maxima at 444 nm (ϵ 27 000) and 396 nm (ϵ 19 500) and an emission maximum at 476 nm. For the quenching experiments, solutions of 1,3-diphenylindenyl anion in 10 mL of Me_2SO were prepared by using a measured amount of the hydrocarbon to obtain an absorbance of 1.0 (concentration of the anion was approximately 4.0×10^{-5} M) in a 50-mL cylindrical Pyrex tube equipped with a three-way stopcock and a 1-cm cuvette at the bottom. Concentrated solutions of quencher in dimethyl sulfoxide were prepared so that the addition of 0.1 mL of quencher solution was sufficient to produce measurable quenching. The fluorescence spectrum was obtained after each of five serial additions of quencher, each being traced at least three times, the areas determined by planimetry, and the best slope of the relative quantum yield vs. quencher concentration determined by the least-squares technique. The relative quenching rates ($k_q\tau$) obtained are listed in Table I.

Fluorescence Quantum Yield (ϕ_f) of 1,3-Diphenylindenyl Anion. The quantum yield of fluorescence of 1,3-diphenylindenyl anion was measured relative to the known quantum yield of 0.96 for 1,3-diphenylisobenzofuran chosen as the standard. 1,3-Diphenylisobenzofuran was selected as the standard because of the close similarity between its absorption and emission (λ_{max} 424 nm, λ_{em} 480 nm) and those of 1,3-diphenylindenyl anion (λ_{max} 444 nm, λ_{em} 476 nm). 1,3-Diphenylindenyl anion in dimethyl sulfoxide and 1,3-diphenylisobenzofuran in deoxygenated benzene were made in two separate 50-mL cylindrical Pyrex tubes equipped with a three-way stopcock and a 1-cm cuvette at the bottom. Concentrations were adjusted so as to have almost equal absorbances for the solutions. The solutions were then maintained under an atmosphere of argon. The method of optical dilution was employed, using the following equation:[32]

$$\phi_x = \phi_r(D_x/D_r)\ (n_x^2/n_r^2)$$

where ϕ_x is the fluorescence quantum yield, D is the integrated area under the emission spectrum, n is the refractive index of the solution and, x and r refer to the unknown and reference solutions, respectively. The emission spectra were recorded on an Aminco-Bowman spectrofluorimeter and absorption spectra on a Beckman-Model 26 UV-vis spectrophotometer. The ϕ_f of 1,3-diphenylindenyl anion thus obtained was 0.69 ± 0.03 (an average of 4 separate runs). This value remained reproducible over the excitation range of 400-430 nm.

Lifetime Measurements. The fluorescence lifetime of 1,3-diphenylindenyl anion was determined by single photon counting using a Photochemical Research Associates nanosecond fluorimeter. A lamp flash of 1.6 ns width at half height allowed direct determination of excited-state decay rates by least-squares analysis of the last 350 of 512 channels, ignoring the initial channels involving the excitation region. The lifetime was determined to be 11.0 ns.

Acknowledgment. Support by the office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, is gratefully acknowledged. L.M.T. is a Fellow of the Alfred P. Sloan Foundation.

(32) (a) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991. (b) Parker, C. A. "Photoluminescence of Solutions"; Elsevier: Amsterdam, 1968; p 269.

Homolytic Displacement at Saturated Carbon. 9. The Reactions of Trichloromethanesulfonyl Chloride with Pent-4-enylcobaloximes and with Olefins. A Novel Route to (Trichloroethyl)sulfolanes via an S_Hi Mechanism

Martyn R. Ashcroft, Peter Bougeard, Adrian Bury, Christopher J. Cooksey, and Michael D. Johnson*

Department of Chemistry, University College, London WC1H OAJ, England

James M. Hungerford and Gary M. Lampman

Department of Chemistry, Western Washington University, Bellingham, Washington 98225

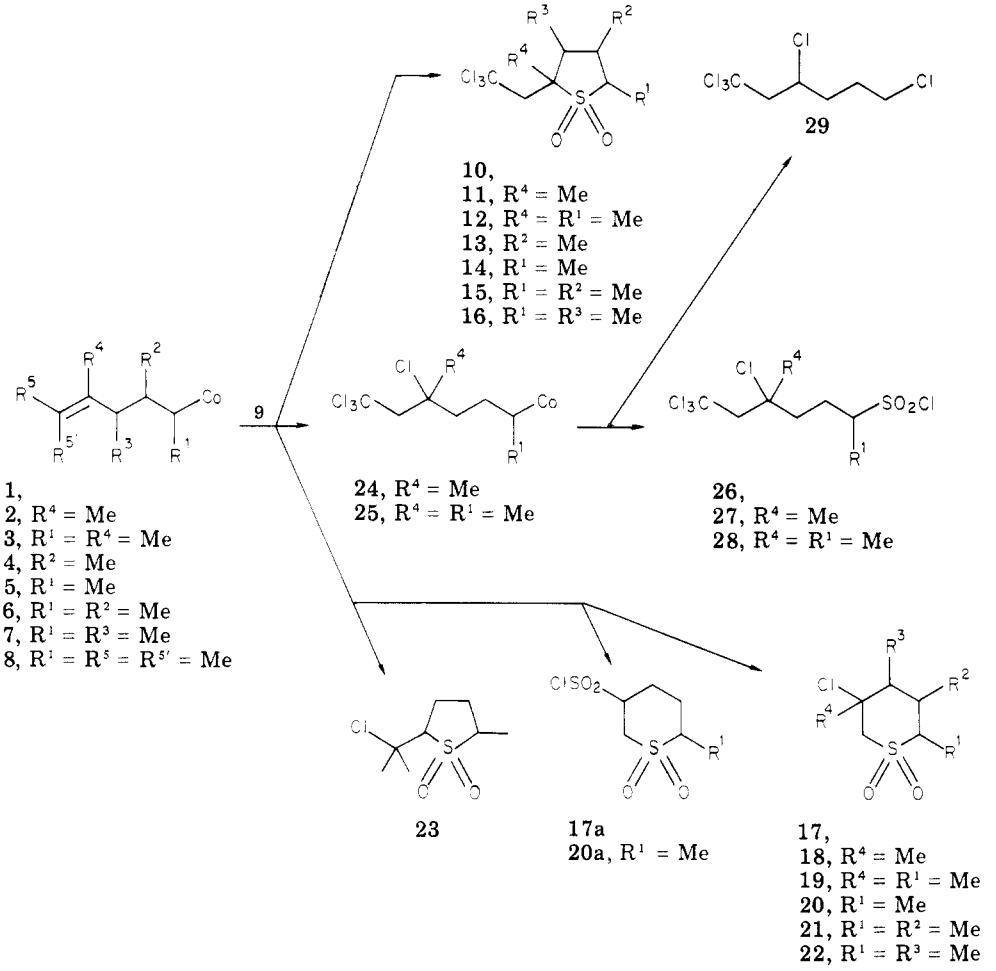
Received September 14, 1983

Pent-4-enylcobaloximes react with trichloromethanesulfonyl chloride in inert solvents under irradiation with tungsten lamps to give good yields of 2-(β,β,β-trichloroethyl)sulfolanes. The same products are formed in the thermal reactions in the presence of an excess of sulfur dioxide. Studies of the reactions of related olefins with trichloromethanesulfonyl chloride catalyzed by the photolysis of secondary organocobaloximes under mild conditions show that substituted 3,3,3-trichloropropyl radicals are capable of capturing sulfur dioxide. This allows us to account for the formation of the sulfolanes by a mechanism which includes a homolytic displacement of cobaloxime(II) from saturated carbon. The latter is confirmed by the observation that the isomers of 2-methyl-5-(β,β,β-trichloroethyl)sulfolane formed from (*R*)-hex-5-en-2-ylcobaloxime are in substantial enantiomeric excess. 3-Chloro-1,1-dioxothiacyclohexanes formed as minor products indicate that pent-4-ene-1-sulfonyl radicals cyclize to 1,1-dioxothiacyclohex-3-yl radicals rather than to the corresponding five-membered sulfolanylmethyl radicals.

We recently described[1] some non-chain free radical reactions of alkylcobaloximes with trichloromethanesulfonyl chloride in which alkyl radicals, formed by photolysis of the carbon-cobalt bond, reacted with sulfur dioxide to give

0022-3263/84/1949-1751$01.50/0

Scheme I[a]



[a] Co = Co(dmgH)$_2$py; R^n = H except where stated.

an alkanesulfonyl radical and hence, by chlorine atom abstraction, an alkanesulfonyl chloride in surprisingly high yield (eq 2–5). Since alkylcobaloximes may be prepared

$$RX + [Co(dmgH)_2py]^- \rightarrow RCo(dmgH)_2py + X^- \quad (1)$$

$$RCo(dmgH)_2py \rightarrow R\cdot + Co(dmgH)_2py \quad (2)$$

$$R\cdot + SO_2 \rightarrow \dot{R}SO_2 \quad (3)$$

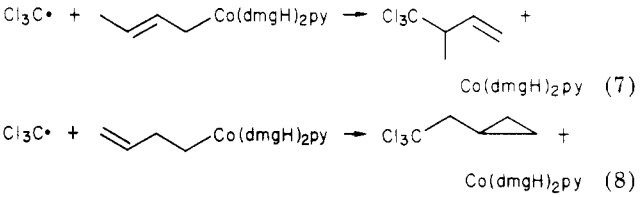
$$\dot{R}SO_2 + Cl_3CSO_2Cl \rightarrow RSO_2Cl + Cl_3C\dot{S}O_2 \quad (4)$$

$$Cl_3C\dot{S}O_2 \rightarrow Cl_3C\cdot + SO_2 \quad (5)$$

$$Co(dmgH)_2py + Cl_3CSO_2Cl \rightarrow Cl_3C\dot{S}O_2 + ClCo(dmgH)_2py \quad (6)$$

readily from alkyl halides and tosylates (eq 1), this provides a useful synthesis of alkanesulfonyl chlorides from these organic precursors.

The corresponding reactions of trichloromethanesulfonyl chloride with allyl- and but-3-enylcobaloximes are however free radical chain reactions, leading in equally high yield to quite different products, namely the trichlorobut-3-enes and (trichloroethyl)cyclopropanes, respectively; no sulfur dioxide being incorporated.[2-4] These reactions are initiated by eq 2, and the propagation steps are (i) attack of cobaloxime(II) on trichloromethanesulfonyl chloride (eq 6), (ii) loss of sulfur dioxide from the trichloromethanesulfonyl radical (eq 5), and (iii) attack of the trichloromethanesulfonyl radical on the terminal unsaturated carbon of the alkenyl ligand with displacement of the cobaloxime(II) radical (eq 7 and 8).



However, preliminary studies of the reactions of the next higher homologue, the pent-4-enylcobaloxime, showed that neither of the above mechanisms were dominant and that novel products were formed in excellent yield. In this paper these products are described, the stereochemistry of their formation is investigated, and the mechanism of their formation is rationalized together with the mechanisms of formation of products in the corresponding reactions of mono- and diolefins with the same reagent under similar conditions.

Results and Discussion

Reaction of Pent-4-enylcobaloximes with Trichloromethanesulfonyl Chloride. The reaction of pent-4-enylbis(dimethylglyoximato)(pyridine)cobalt(III) (1) with an equimolar amount of trichloromethanesulfonyl

(1) Bougeard, P.; Johnson, M. D.; Lampman, G. M. *J. Chem. Soc., Perkin Trans. 2* **1982**, 849.
(2) Bury, A.; Cooksey, C. J.; Funabiki, T.; Gupta, B. D.; Johnson, M. D. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1050.
(3) Ashcroft, M. R.; Bury, A.; Cooksey, C. J.; Davies, A. G.; Gupta, B. D.; Johnson, M. D.; Morris, H. *J. Organomet. Chem.* **1980**, *195*, 89.
(4) Bury, A.; Corker, S. T.; Johnson, M. D. *J. Chem. Soc., Perkin Trans. 1*, **1982**, 645.

chloride (9) in methylene chloride at 5–15 °C under irradiation by tungsten lamps gave one major organic product, 2-(β,β,β-trichloroethyl)sulfolane (10), and at least two minor products including 3-chloro-1,1-dioxothiacyclohexane (17) and 1,4,6,6,6-pentachlorohexane (29), together with substantial quantities of chlorobis(dimethylglyoximato)(pyridine)cobalt(III) (Scheme I). The trichloromethanesulfolane (10) was also isolated (i) in 72% yield from the thermal reaction of 1 with 9 at 100 °C in methylene chloride saturated with sulfur dioxide (under these conditions the main byproduct was not the chlorodioxothiacyclohexane 17, but the corresponding sulfonyl chloride 17a); (ii) in ca. 20% yield from the reaction of 1 with 9 or with bromotrichloromethane in liquid sulfur dioxide in the dark at ambient temperature (the major product in the latter reaction was the sulfur dioxide insertion product, pent-4-enesulfonylbis(dimethylglyoximato)(pyridine)cobalt(III)).

(4-Methylpent-4-enyl)bis(dimethylglyoximato)(pyridine)cobalt(III) (2) (Scheme I) reacted with an equimolar amount of 9 at 5–15 °C under irradiation by tungsten lamps to give mainly (4-methyl-4,6,6,6-tetrachlorohexyl)bis(dimethylglyoximato)(pyridine)cobalt(III) (24) and the (trichloroethyl)sulfolane (11), together with traces of the sulfonyl chloride (27), but the chlorodioxothiacyclohexane (18) could not be detected. When the same reaction was carried out in the presence of a 3-fold molar excess of 9, the sulfonyl chloride 27 was the major organic product. The reaction of 2 with 9 was also carried out at ambient temperature after short initiation by irradiation as above to give 24 in 65% yield, which was subsequently reacted with an excess of 9 to give the sulfonyl chloride 27.

In the corresponding photochemical reaction of 9 with (5-methylhex-5-en-2-yl)bis(dimethylglyoximato)(pyridine)cobalt(III) (3), the main product was a mixture of isomers (substantially one isomer) of the (trichloroethyl)sulfolane (12) together with two isomers of the chlorodioxothiacyclohexane (19) and the sulfonyl chloride (28) as minor products.

(2-Methylpent-4-enyl)bis(dimethylglyoximato)(pyridine)cobalt(III) (4) also reacted with an equimolar amount of 9 under photochemical conditions to give substantially a single isomer of the (trichloroethyl)sulfolane (13), but the reactions of the (1-methyl, (1,2-dimethyl-, and (1,3-dimethylpent-4-enyl)cobaloximes (5–7) with 9 all gave, as major products, mixtures of isomers of the appropriate (trichloroethyl)sulfolane (14–16, respectively) which were not separated. These secondary 1-methyl-substituted pent-4-enylcobaloximes also gave moderate yields of the corresponding chlorodioxothiacyclohexanes (20–22).

In the corresponding photolysis of the more heavily substituted (6-methylhept-5-en-2-yl)bis(dimethylglyoximato)(pyridine)cobalt(III) (8) with 9, the main product is believed to be the (chloromethyl)sulfolane (23); the corresponding (trichloroethyl)sulfolane could not be detected. The thermal reaction of complex 5, in methylene chloride saturated with sulfur dioxide, with 9 at 80 °C over 24 h gave a 41:59 mixture of the two isomers of the (trichloroethyl)sulfolane 14, together with a single isomer of the dioxothiacyclohexanesulfonyl chloride (20a), contaminated with the chloride 20.

The corresponding thermal reaction of optically active (*R*)-5 having essentially identical circular dichroism to that reported earlier for (*R*)-pent-4-en-2-ylbis(dimethylglyoximato)(pyridine)cobalt(III)[5] and prepared from the corresponding (*S*)-pent-4-enyl tosylate, gave a 41:59 mixture of *cis*- and *trans*-14 (or *trans*- and *cis*-14) each in about 65% enantiomeric excess, together with the racemic dioxothiacyclohexane 20a.

Reaction of Monoolefins and Nonconjugated Diolefins with Trichloromethanesulfonyl Chloride. (a) Oct-1-ene. The reaction of oct-1-ene with an equimolar amount of 9 in methylene chloride, catalyzed by the irradiation of cyclohexyl- or *sec*-butylbis(dimethylglyoximato(pyridine)cobalt(III) with tungsten spotlights at 0–10 °C gave 1,1,1-trichloro-3-nonanesulfonyl chloride (30), Scheme V) in addition to the expected tetrachlorononane and uncharacterized oligomeric and polymeric material. When the methylene chloride was saturated with sulfur dioxide the yield of 30 increased to 40%.

(b) *cis*-Cyclooctene. The reaction of *cis*-cyclooctene with an equimolar amount of 9 catalyzed as in a above gave, besides the expected chloroalkanes, *cis*- or *trans*-4-(trichloromethyl)cyclooctanesulfonyl chloride (31, Scheme VI).

(c) Hexa-1,5-diene. The reaction of hexa-1,5-diene with a 2-fold excess of 9 in methylene chloride under the conditions in a above gave, besides the expected polychloroalkanes and polychloroalkenes, *trans*-1,1-dioxo-3-chloro-6-(trichloroethyl)thiacyclohexane (32, Scheme VII, ca. 14% yield) together with uncharacterized dimeric and polymeric material.

(d) Hepta-1,6-diene. The reaction of hepta-1,6-diene with 9 under the same conditions as in c above gave many monomeric, dimeric, and polymeric products, the proportions of which were dependent on the ratio of the concentrations of the reagents but not on the concentration of the cobaloxime catalyst. Besides the expected polychloroalkanes and alkenes, the monomeric species 33 and the dimeric sulfones (34 and 35, Scheme VIII) were isolated.

(e) *cis,cis*-Cycloocta-1,5-diene. The reaction of *cis,cis*-cycloocta-1,5-diene with 1 equiv of 9 under the conditions used in b above gave one major product, which is a bicyclic sulfone (either 36 or 37, Scheme IX). Little polymerization was evident.

Discussion

The majority of the reactions described here are believed to be free radical processes. Much of the evidence is indirect and is included in the discussion below, but it is certain that free radicals abound under the conditions of all the reactions. First, it is well established that organocobalt(III) complexes, including all the alkylcobaloximes, undergo thermolysis and photolysis, even at wavelengths greater than 360 nm,[6] of the carbon–cobalt bond. For primary cobaloximes it is necessary to heat to ca. 100 °C in order to achieve a reasonable rate of thermolysis, but secondary and tertiary alkyl- and benzylcobaloximes require lower temperatures. For secondary benzylcobaloximes homolysis is apparent at 0 °C in solution.[7] Secondly, both the organic radical[8] and the cobaloxime(II) fragment[9] are capable of reacting rapidly with halogen

(5) Atkins, M. P.; Golding, B. T.; Bury, A.; Johnson, M. D.; Sellars, M. P. *J. Am. Chem. Soc.* **1980**, *102*, 3630.

(6) Endicott, J. F.; Netzel, T. L. *J. Am. Chem. Soc.* **1979**, *101*, 4000. Endicott, J. F.; Mok, C. Y. *Ibid.* **1978**, *100*, 123. Endicott, J. F.; Ferraudi, G. J. *Ibid.* **1977**, *99*, 243. Joblin, K. N.; Johnson, A. W.; Lappert, M. F.; Nicholson, B. K. *J. Chem. Soc., Chem. Commun.* **1975**, 441. Roewer, D.; Rehorek, D. *J. Prakt. Chem.* **1978**, *320*, 566. Golding, B. T.; Kemp, T. J.; Sellars, M. P.; Nocchi, E. *J. Chem. Soc., Dalton Trans.* **1977**, 1266. Bougeard, P.; Johnson, M. D.; Lewin, M.; Rajah, F. *J. Chem. Soc., Perkin Trans. 2*, submitted for publication.

(7) Gjerde, H. B.; Espenson, J. H. *Organometallics* **1982**, *1*, 435. Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238.

(8) Kharasch, M. S.; Jensen, E. V.; Urry, W. H. *J. Am. Chem. Soc.* **1947**, *69*, 1100.

atom donors such as carbon tetrachloride and trichloromethanesulfonyl chloride. We have demonstrated that preformed cobaloxime(II) reacts effectively immediately on a preparative scale in non-aqueous solvents with both carbon tetrachloride and trichloromethanesulfonyl chloride, in the absence of an olefin, to give a 1:1 mixture of the unstable and hard to isolate complex (trichloromethyl)bis(dimethylglyoximato)(pyridine)cobalt(III). Related kinetic studies on other reactive halogen atom donors[9,10] suggest that this reaction takes place by a halogen abstraction reaction (eq 6 or 9), loss of sulfur dioxide

$$Co^{II}(dmgH)_2py + Cl_4C \rightarrow ClCo(dmgH)_2py + Cl_3C\cdot \quad (9)$$

$$Co^{II}(dmgH)_2py + Cl_3C\cdot \rightarrow Cl_3CCo(dmgH)_2py \quad (10)$$

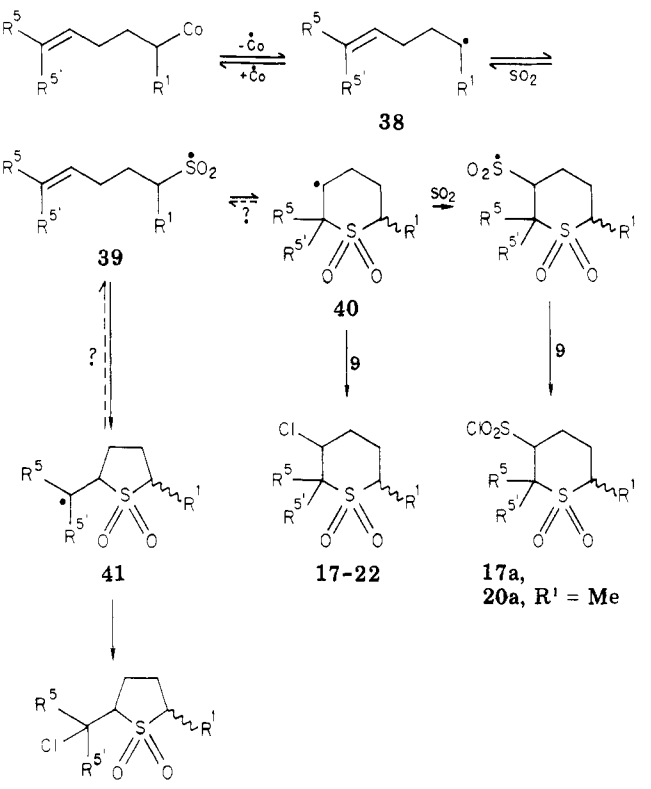
from the trichloromethanesulfonyl radical (eq 5) and, in the absence of any other substrate, capture of the trichloromethyl radical by the cobaloxime(II) as shown in eq 10. In the present work, reaction 10 is a termination process for the several chain reactions, because reaction of the trichloromethyl radical with each of the several substrates becomes the dominant process.

Reaction of Pent-4-enylcobaloximes. From the results of the reactions of trichloromethanesulfonyl chloride discussed below, and the known reactions of **9** with alkyl-,[1] allyl-,[2] and but-3-enylcobaloximes,[3,4] the pent-4-enylcobaloximes would be expected to react with **9** in any of three ways: (i) by a reaction at the double bond, such as the free radical addition of carbon tetrachloride, followed by cleavage of the carbon-cobalt bond; (ii) by cleavage of the carbon–cobalt bond and subsequent reaction of the pent-4-enyl radical to give, for example the pent-4-enesulfonyl chlorides; or (iii) by a reaction in which attack at the olefin by a trichloromethyl radical is directly influenced by the carbon–cobalt bond, or vice versa.

Reactions of type i form only a very minor path, except in the case of the rather hindered (4-methylpent-4-enyl)- and (5-methylhex-5-en-2-yl)cobaloximes (**2** and **3**) for which the addition of the elements of carbon tetrachloride to the double bond to give **24** and **25**, respectively, is followed by a separate cleavage of the carbon–cobalt bond with the formation of **27** and **28**. Addition of the trichloromethyl radical to **2** and to **3** gives a tertiary radical which is presumably more reluctant to capture sulfur dioxide than the secondary radicals discussed below. It is also possible that a small proportion of each of the products **27** and **28** arises through prior formation of the methyl substituted pent-4-enesulfonyl chloride via path ii, with subsequent addition of the elements of carbon tetrachloride to the double bond.

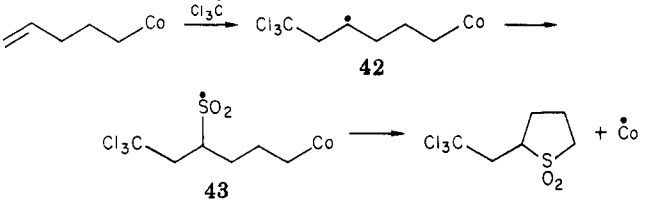
Path ii does, however, account for the formation of the substituted dioxothiacyclohexanes that are minor products in the reactions of the pent-4-enylcobaloximes with **9**, i.e., the cleavage of the carbon-cobalt bond leads to the pent-4-enyl radical (**38**, Scheme II) which captures sulfur dioxide readily and subsequently cyclizes to the six-membered dioxothiacyclohexyl radical (**40**) before it can abstract a chlorine atom from **9**. The radical **40** either reacts further with sulfur dioxide and then abstracts a chlorine atom from **9**, or it abstracts a chlorine atom directly from **9**, to give the six-membered cyclic sulfonyl chloride (**17a** or **20a**) or chloride (**17–22**). The more highly substituted secondary alkenyl radical **39** ($R^1 = R^5 = R^{5'} = Me$) also captures sulfur dioxide, but then apparently cyclizes to the

Scheme II[a]



[a] Co = Co(dmgH)$_2$py

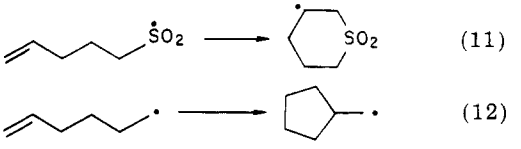
Scheme III[a]



[a] Co = Co(dmgH)$_2$py.

five-membered tertiary cyclic radical **41** (Scheme II).

One feature of this reaction is of special interest. The sulfonyl radical **39** generally prefers cyclization to the six-membered ring (eq 11), whereas the corresponding all



(11)

(12)

carbon hex-5-enyl radical cyclizes predominantly (≥99%) to the five-membered cyclopentylmethyl radical (eq 12).[11] Path ii is, not surprisingly, more in evidence in the reactions of the secondary alkenylcobaloximes, for which the cleavage of the secondary carbon to cobalt bond is more facile.

Mechanism of Formation of Trichloroethylsulfolanes. The formation of the (trichloroethyl)sulfolanes (**10–16**) from the pent-4-enylcobaloximes in high yield is clearly a result of attack of the trichloromethyl radical at the terminal olefinic carbon of the pent-4-enyl

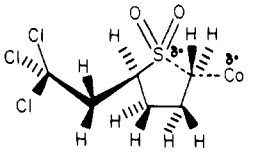
(9) Espenson, J. H.; McDowell, M. S. *Organometallics*, in press.
(10) Schneider, P. W.; Phelan, P. F.; Halpern, J. *J. Am. Chem. Soc.* **1969**, *91*, 77. Halpern, J.; Phelan, P. F. *Ibid.* **1972**, *94*, 188. Marzilli, L. G.; Marzilli, P. A.; Halpern, J. *Ibid.* **1971**, *93*, 1374.

(11) Beckwith, A. L. J.; Ingold, K. U. In "Molecular Rearrangements" de Mayo, P., Ed.; Academic Press: New York, 1978; Vol. 2.

ligand (Scheme III). Capture of the organometallic radical **42** by sulfur dioxide gives the radical **43** which can undergo a novel reaction, not hitherto observed in solution chemistry, namely an intramolecular S_Hi homolytic attack at the α-carbon of the organic ligand, thereby displacing cobaloxime(II), which can take further part in the regeneration of the trichloromethyl radical from **9**. The formation of the (trichloromethyl)sulfolane is thus a chain reaction in which the propagation steps are as in scheme III, reaction 6, and reaction 5. Such a chain reaction need not be very rapid because the cobaloxime(II) radical, which is one of the propagating species, neither dimerizes nor disproportionates under the conditions of the reaction and may remain in solution until reaction with the trichloromethanesulfonyl chloride can take place. Inhibition by galvinoxyl and by α-phenyl-*N*-*tert*-butylnitrone is evident but is not as effective as for many organic chain reactions because the initiator is the pent-4-enylcobaloxime itself, through reaction 2, and because homolysis gives two free radical species, one of which (the organic radical) will be readily trapped by the inhibitor but the other (cobaloxime(II)) is unlikely to be so readily trapped.

The conversion of the radical **43** into the (trichloroethyl)sulfolane represents the first case of a homolytic attack at the α-carbon of an alkyl ligand in solution by a highly reactive conventional radical center.[12] The efficiency with which this reaction occurs, even in the case of the secondary pentenylcobaloximes, in competition with chlorine atom abstraction from **9** by the sulfonyl radical center, and in competition also with the reaction of the sulfonyl radical center with the olefinic group of another molecule of substrate, is remarkable. It seems likely therefore that many other homolytic displacements, particularly intramolecular homolytic displacements leading to five-membered ring products, may be possible.[13]

In view of the inversion of configuration observed in the case of the attack of cobaloxime(II) at the α-carbon of alkylcobaloxime(III) complexes,[14] it seemed likely that the transition state for the intramolecular homolytic displacement of Scheme III would be as shown in **44**, and that



44

the steric effect of the trichloroethyl group will determine the stereochemistry of the product where methyl substituents are present in the pentenyl chain.

The concerted nature of the S_Hi reaction is confirmed by the observation that (*R*)-**5** reacts thermally with **9** in methylene chloride saturated with sulfur dioxide to give the cis and trans isomers of 5-methyl-2-(β,β,β-trichloroethyl)sulfolane **14**, each with substantial enantiomeric purity. The exact enantiomeric purity of the (*R*)-**5** is uncertain, but it was prepared from the enantiomerically pure (*S*)-tosylate[15] and its CD curve is virtually identical with

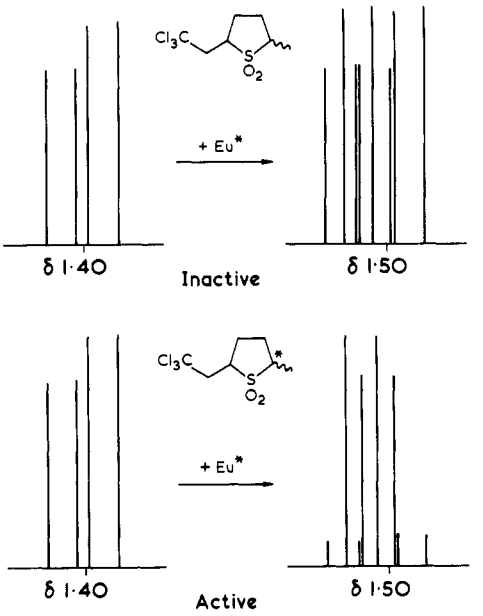
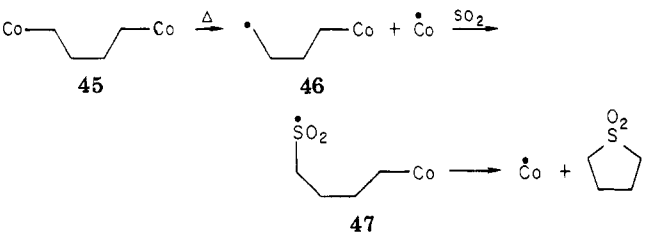


Figure 1. Influence of tris(D-heptafluorobutyrylcamphorate)-europium(III) on the methyl proton resonances of (upper spectra) racemic *cis*- and racemic *trans*-2-methyl-5-(β,β,β-trichloroethyl)sulfolane (**14**) and of (lower spectra) the same product from (*R*)-**5**.

Scheme IV[a]



45 **46** **47**

[a] Co = Co(dmgH)$_2$py.

that obtained for the corresponding enantiomerically pure pent-4-en-2-ylcobaloxime.[5] The enantiomeric purity of the cis and trans isomers of the organic product **14** were determined from the influence of a chiral shift reagent on the methyl proton doublet resonances. For the racemic product derived from the racemic cobaloxime **5**, the two methyl doublet resonances at ca. δ 1.40 were split into four methyl doublet resonances at ca. δ 1.50 (see Figure 1); for the product from (*R*)-**5** in the presence of the shift reagent, two of the latter doublet resonances, one each from the cis and trans isomers, were very weak intensity, corresponding in each case to ≤17% of the second enantiomer. Clearly, it is reasonable to expect that the predominant enantiomer in each case is that formed by inversion, though this experiment alone does not rule out a retentive process. That the partial loss of enantiomeric purity is the same in each case suggests that some racemization occurs in the substrate during reaction and this is confirmed by the observation that (*R*)-**5** racemizes on heating in methylene chloride in a sealed tube at the reaction temperature in the absence of **9**.

In contrast, though no differential shift was observed for the methyl proton resonances of the enantiomers of racemic **20a**, separate resonances were observed for H-6 and H-6′ of each enantiomer in the presence of the same shift reagent. However, no differences in intensity could be detected between this spectrum and that of **20a** derived from (*R*)-**5**, indicating that only racemic **20a** is formed in the latter reaction, in accord with the mechanism outlined in Scheme II.

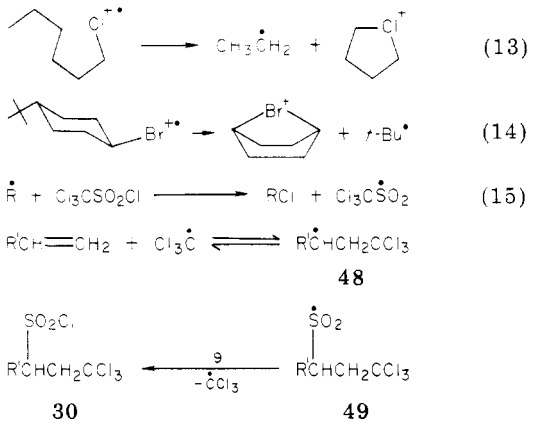
(12) This reaction, and the S_Hi reaction of the radical derived from the addition of a trichloromethyl radical to hex-5-enylcobaloxime, was reported in a preliminary communication: Bougeard, P.; Bury, A.; Cooksey, C. J.; Johnson, M. D.; Lampman, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 5230.

(13) Johnson, M. D. *Acc. Chem. Res.* **1983**, *16*, 343.

(14) Dodd, D.; Johnson, M. D.; Lockman, B. L. *J. Am. Chem. Soc.* **1977**, *99*, 3664.

(15) Nucleophilic displacement by cobaloxime(I) ions takes place with inversion of configuration at the α-carbon. Fritz, H. L.; Espenson, J. H.; Williams, D. A.; Molander, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 2378.

Scheme V[a]



[a] R = *sec*-butyl or cyclohexyl, R′ = C_6H_{13}.

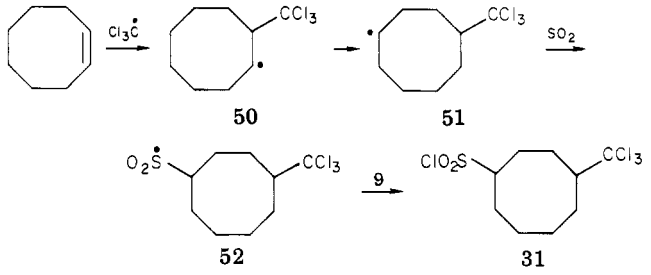
The above S_Hi mechanism is supported by the observation that the tetramethylenebis[cobaloxime(III)] complex **45** reacts thermally in sulfur dioxide to give a moderate yield of sulfolane (Scheme IV). Since it has been postulated that sulfur dioxide insertion reactions of organocobaloximes may take place by free radical mechanisms,[16] it is probable that homolysis of one of the two carbon-cobalt bonds gives **46** which, after capture of sulfur dioxide, undergoes a comparable intramolecular homolytic displacement to sulfolane and cobaloxime(II). The main product of this reaction is, however, a mixture of the anticipated normal mono- and bis(sulfur dioxide) insertion products.[17]

There is clear precedent for the S_Hi reaction at saturated carbon from studies of organic reactions in the gas phase.[18] Thus, mass spectrometric studies of the fragmentation of the parent molecular ions derived from alkyl halides suggest that an alkyl radical, such as *tert*-butyl or ethyl, is readily displaced by an intramolecular homolytic attack of the halogenium cation–radical at carbon-4 of the organic substrate, especially where a 5-membered cyclic product is formed (eq 13 and 14, Scheme V).

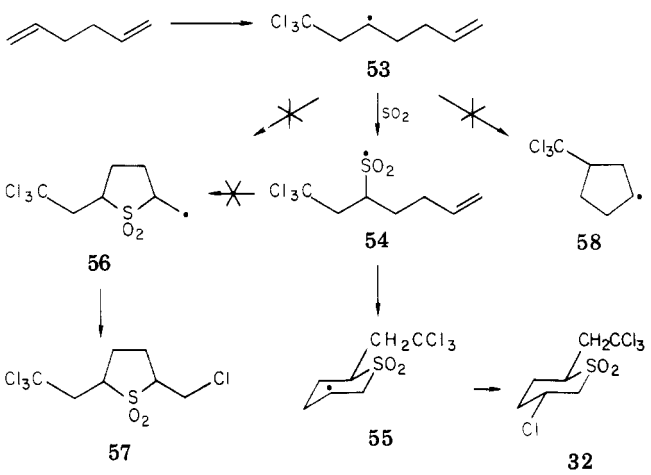
Reaction of Olefins with Trichloromethanesulfonyl Chloride. The reactions of carbon tetrachloride and, to a lesser extent, of trichloromethanesulfonyl chloride with olefins have been studied in considerable depth. The present work on the reaction of **9** with olefins was carried out under much milder conditions, made directly comparable to those above by the use of organocobaloxime initiators, in order specifically to examine the capture of intermediate substituted trichloropropyl radicals with sulfur dioxide and the further reactions of the sulfonyl radicals so formed in order to relate them to the work described above. The discussion is therefore substantially limited to the formation of new products and the exact steps leading to known addition products are mentioned only obliquely.[19]

Initiation is in each case caused by homolysis of the carbon–cobalt bond and reaction of either or both of the radical fragments with **9**. The trichloromethyl radical, generated as in eq 5, then adds to an olefinic carbon of the substrate.[20] A number of new processes, as well as several

Scheme VI



Scheme VII



established processes, can thereafter be identified in the subsequent reactions of the substituted trichloropropyl radicals (**48**, **50**, **53**, **59**, or **63**) so formed, as follows.

The trichloropropyl radicals **48** (Scheme V), **53** (Scheme VII), and **63** (Scheme VIII) all react with sulfur dioxide to give novel substituted trichloropropanesulfonyl radicals **49**, **54**, and **64**, respectively. Of these, only **49** then reacts directly with **9**, by chlorine abstraction, to give the observed sulfonyl chloride **30**. The sulfonyl radical **54**, formed in preference to **58**, predominantly cyclizes to the 5-chloro-1,1-dioxo-2-(trichloroethyl)thiacyclohexyl radical **55** and subsequently abstracts a chlorine atom from **9** to give the observed product **32**. No cyclization of **54** to the corresponding five-membered sulfolanylmethyl radical **56** and hence to **57** could be detected. The sulfonyl radical **64** undergoes a comparable intramolecular cyclization to the 3-(1,1-dioxothiacyclohexyl) radical **65** and subsequently abstracts a chlorine atom from **9** to give the bicyclic sulfone **36** in excellent yield. Alternatively, the bicyclic sulfone may have the structure **37**, in the less likely event that the initial cyclization of **64** gives a five-membered sulfolanyl radical. In the absence of sulfur dioxide, the radical **63** is known rapidly to cyclize to the bicyclic radical **66**,[21] and hence the absence of products having the bicyclo[3.3.0] structure implies that the reaction of **64** with sulfur dioxide must be a rapid and efficient process.

The trichloropropyl radical **50** (Scheme VI) undergoes the expected[22] transannular hydrogen atom shift to **51**

(16) Crease, A. E.; Johnson, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 8013. See also: Crease, A. E.; Gupta, B. D.; Johnson, M. D.; Bialkowska, E.; Duong, K. N. V.; Gaudemer, A. *J. Chem. Soc., Perkin Trans. 1* **1979** 261.

(17) Cooksey, C. J.; Dodd, D.; Gatford, C.; Johnson, M. D.; Lewis, G. J.; Titchmarsh, D. M. *J. Chem. Soc., Perkin Trans. 1* **1972**, 655.

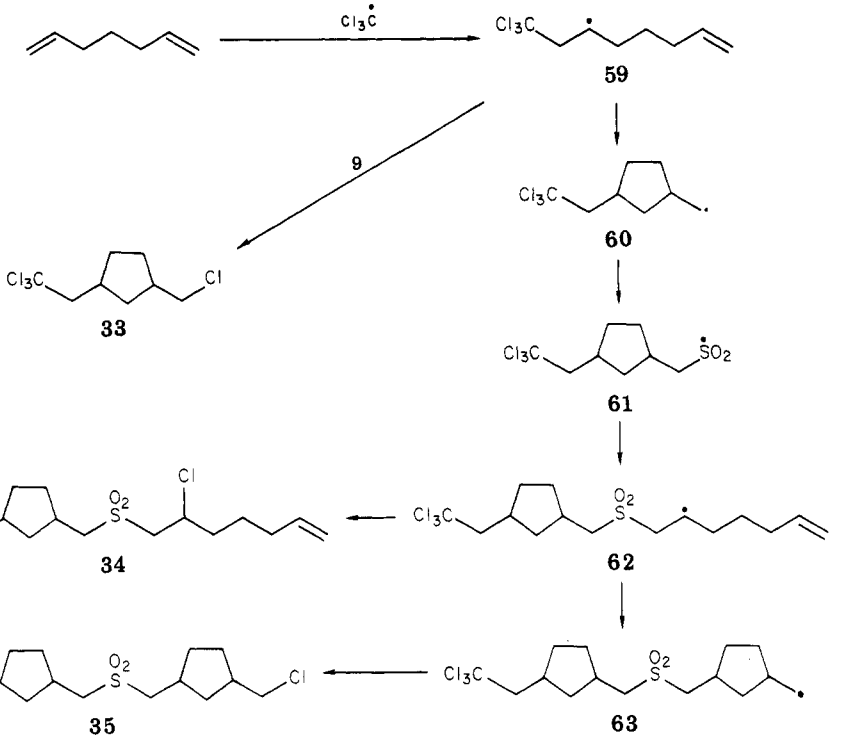
(18) Green, M. M.; Giguere, R. J.; Nicholson, J. R. P. *J. Am. Chem. Soc.* **1978**, *100*, 8020.

(19) Details of the previously known polychlorohydrocarbons have been omitted.

(20) Ladd, E. C.; Kiley, L. Y. U.S. Patent 2606213, 1952. Huyser, E. S.; Kim, L. *J. Org. Chem.* **1967**, *32*, 618. See also: Huyser, E. S.; Giddings, B. *J. Org. Chem.* **1962**, *27*, 3391. Huyser, E. S. *J. Am. Chem. Soc.* **1960**, *82*, 5246.

(21) Walling, C.; Pearson, M. S. *J. Am. Chem. Soc.* **1964**, *86*, 2262. Walling, C.; Cooley, J. H.; Panoras, A. H.; Racah, E. J. *Ibid.* **1966**, *88*, 5361. Garwood, R.; Scott, C. J.; Weedon, B. C. L. *J. Chem. Soc., Chem. Commun.* **1965**, 14. Lamb, R. C.; McNew, W. E.; Sanderson, J. R.; Lunney, D. C. *J. Org. Chem.* **1971**, *36*, 174. Watkins, K. W.; Olsen, D. K. *J. Phys. Chem.* **1972**, *76*, 1089. Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1083. Castaing, M.; Pereyre, M.; Ratier, M.; Blum, P. M.; Davies, A. G. *Ibid.* **1979**, *287*.

Scheme VIII



before capturing sulfur dioxide to give **52** which on abstraction of a chlorine atom from **9**, gives the observed sulfonyl chloride, *cis*- or *trans*-**32**. The trichloropropyl radical **59**, on the other hand, cyclizes to the five-membered radical **60**,[23] prior to capture of sulfur dioxide, and though a little of the monomeric chloride **35** is formed, the predominant reaction under our conditions was the further addition of the sulfonyl radical **61** to another molecule of the olefin to give **62**, and subsequently **63**, and the observed dimeric products **34** and **35**. Further polymerization through reaction of sulfonyl radicals with the olefin substrate is not unexpected.[25]

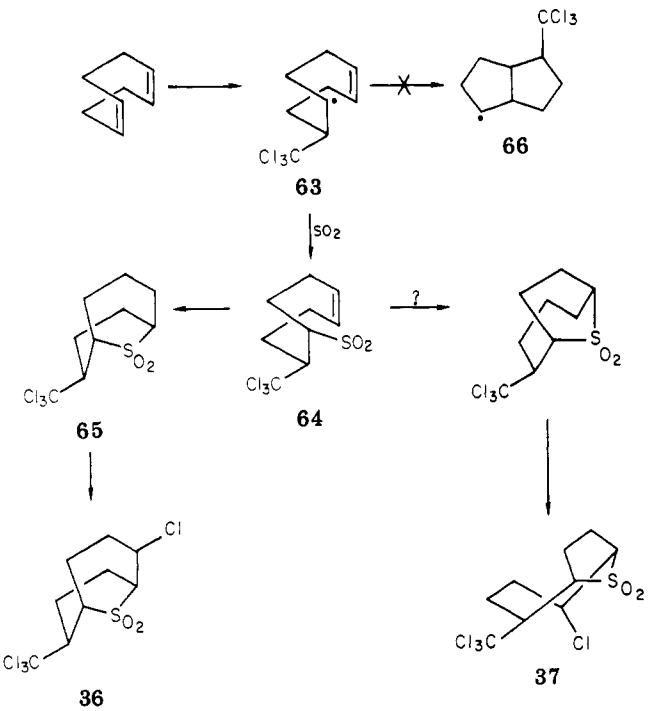
These reactions therefore confirm that the trichloropropyl radicals do react readily with sulfur dioxide[24] and that the balance of the subsequent reactions, cyclization, capture of sulfur dioxide, transannular hydrogen transfer, etc., is delicate. They also provide further confirmation that alkenesulfonyl radicals (in this case **54**, Scheme VII) cyclize predominantly to six in preference to five-membered radicals, though it is not known whether this preference is a result of a kinetic or a thermodynamic control.

Origin of the Sulfur Dioxide. The formation of the sulfur dioxide during the course of the above reactions is a result of the decomposition of the trichloromethanesulfonyl radical as in eq 5. The latter radical may be formed in at least three ways from **9**, namely reaction 4, reaction 6, and a reaction with carbon-centered radicals, including possibly the direct reaction of trichloromethyl radicals with **9** (eq 15a). It is, however, reaction 6 which

$$Cl_3C\cdot + Cl_3CSO_2Cl \rightarrow Cl_4C + Cl_3C\dot{S}O_2 \qquad (15a)$$

plays a dominant part in the chain reactions of the pent-4-enylcobaloximes. What is surprising is that, at the start of the reactions, the concentration of sulfur dioxide is zero and at no time in the reaction does it exceed that of the trichlorometyl moiety, except in the few cases where additional sulfur dioxide was present from the start. Despite this limitation, the high yield of the (trichloroethyl)sulfolane products is also testament to the efficiency with which the organometallic radicals (**42**, Scheme III) capture sulfur dioxide even where the trichloromethyl group probably is a hinderance. The optimum conditions for the formation of the (trichloroethyl)sulfolanes seem to be with a small excess of sulfur dioxide present at the start of the reaction, and about a 10% excess of **9** over the organocobaloxime substrate, when using 0.1 mol dm^{-3} solutions.

Scheme IX



(22) Dowbenko, M. *Tetrahedron* **1964**, *20*, 1843.
(23) Traynham, J. G.; Couvillon, T. M. *J. Am. Chem. Soc.* **1967**, *89*, 3205.
(24) Julia, M.; Maumey, M. *Bull. Soc. Chim. Fr.* **1966**, 434.
(25) Kharasch, M. S.; Friedlander, H. N. *J. Org. Chem.* **1948**, *13*, 882.
(26) James, F. C.; Kerr, J. A.; Simons, J. P. *J. Chem. Soc., Faraday Trans.* **1973**, 2124.

Experimental Section

Materials. Trichloromethanesulfonyl chloride was prepared by the oxidation of trichloromethanesulfenyl chloride.[27] Oct-1-ene, hexa-1,5-diene, hepta-1,6-diene, allyl chloride, and crotyl chloride were commercial materials redistilled before use. Ethylene oxide, propylene oxide, hex-5-en-2-one, *cis,cis*-cycloocta-1,5-diene, cyclooctene, allyl alcohol, ethyl cyanoacetate, butanone, 6-methylhept-5-ene-2-one, 5-methylheptyl-5-en-2-one, cobalt chloride hexahydrate, dimethylglyoxime, methanol, galvinoxyl, and α-phenyl-*N*-*tert*-butylnitrone were commercial materials used without further purification. 4-Toluenesulfonyl chloride was recrystallized before use and pyridine was redistilled and dried over molecular sieves (4 Å). Silica gel was Mallinckrodt CC4 or CC7 grade. HPLC columns were 3 × 25 cm Partisil on a Waters ALC 100 instrument, using an M60 pump and RI detection. ^{1}H NMR spectra were measured on Varian T60 and XL200 instruments, and in a few cases on a Bruker WH-400 instrument. Mass spectra were measured on a VG Micromass 7070 instrument. Microanalyses were carried out by A. Stones of the University College London microanalytical service.

Preparation of Alcohols. Pent-4-enol was prepared in 67% yield by the reaction of allyl magnesium chloride with ethylene oxide: bp 66–68 °C (60 mmHg). Hex-5-en-2-ol was prepared in 86% yield by the reduction of hex-5-en-2-one with lithium aluminum hydride: bp 80–84 °C (85 mmHg); ^{1}H NMR δ 1.2 (d, CH_3), 1.5 (m, CH_2), 2.25 (m, CH_2), 3.86 (m, CH), 5.0 (m, :CH_2), 5.9 (m, :CH); ^{13}C NMR δ 23.4 (CH_3), 3.02 (CH_2), 38.4 (CH_2), 67.2 (CHOH), 114.6 (:CH_2), 138.6 (:CH).

2-Methylpent-4-enol was prepared by the method of Felkin et al.[28] Allyl magnesium bromide in diethyl ether was added dropwise to allyl alcohol and the mixture was refluxed for two days. After addition of aqueous ammonium chloride, the organic layer was separated and the alcohol was recovered by distillation: bp 53–58 °C (14 mmHg); yield 45%; ^{1}H NMR, δ 0.90 (d, CH_3), ca. 2.0 (m, CH and CH_2), 3.44 (d, CH_2OH), 5.0 (m, :CH_2), 5.8 (m, :CH); ^{13}C NMR, δ 16.4 (CH_3), 35.7 (CH), 37.9 (CH_2), 67.4 (C-H_2OH), 116.0 (:CH_2), 137.0 (:CH).

4-Methylpent-4-enol was prepared in 35% yield by the reaction of (2-methylallyl)magnesium bromide with ethylene oxide: bp 84 °C (60 mmHg); ^{1}H NMR, δ 1.80 (s, CH_3), ca. 2.0 (m, 2 × CH_2), 3.67 (t, CH_2OH), 4.78 (m, :CH_2).

A mixture of diastereoisomers of 4-methylhex-5-en-2-ol was prepared by the method of Hill and Myers[29] in 32% yield from dicrotylmagnesium and propylene oxide.

Ethyl (3-methylhex-5-en-2-ylidene)cyanoacetate was prepared from allyl chloride, ethyl cyanoacetate, and butan-2-one by the method of Cope.[30] It was converted by treatment with ammonium hydroxide to 3-methylhex-5-en-2-one: bp 78–80 °C (100 mmHg); ^{13}C NMR, δ 15.9 (CH_3), 28.3 (CH_3) 37.1 (CH_2), 46.7 (CH), 116.7 (:CH_2), 135.8 (:CH). 3-Methylhex-5-en-2-one was reduced with lithium aluminum hydride to give an equimolar mixture of diastereoisomers of 3-methylhex-5-en-2-ol: bp 89–90 °C (70 mmHg); ^{13}C NMR δ 14.3 and 14.7 (CH_3), 19.5 and 20.1 (CH_3), 37.4 and 37.6 (CH_2), 39.8 and 40.1 ($CHCH_3$), 70.6 and 71.0 (CHOH), 115.8 (:CH_2), 137.7 (:CH).

6-Methylhept-5-en-2-ol was prepared by the reduction of 6-methyl-hept-5-en-2-one with lithium aluminum hydride: ^{1}H NMR δ 1.60 and 1.63 (s, CH_3), 2.05 (s, CH_3CO), 2–2.6 (m, 2 × CH_2), 4.90 (m, :CH).

5-Methylhex-5-en-2-ol was prepared in 93% yield by the reduction of 5-methylhex-5-en-2-one with sodium borohydride: ^{1}H NMR δ 1.20 (d, CH_3), 1.77 (singlet, CH_3), 1.4–2.6 (m, CH_2), 3.84 (quartet of doublets, CH), 4.74 (m, :CH_2).

Preparation of Tosylates. The tosylates of the above alcohols were prepared by the methods of Golding[31] or Schleyer[32] in 65–95% yield. They were not purified but were used directly in the preparation of the organocobaloximes.

Preparation of the Cobaloximes. Cobalt chloride hexahydrate (23.8 g 0.1 mol) and dimethylglyoxime (23.2 g, 0.2 mol) were stirred in methanol at 0–5 °C under nitrogen for 20 min. Deoxygenated pyridine (7.9 g) and aqueous sodium hydroxide (16 g, 0.4 mol, in 30 cm^3 of water) were added cautiously and the mixture was stirred until dark blue-black. The appropriate alkenyl tosylate (0.05 mol) was added and the stirred solution was allowed to attain ambient temperature for up to 4 h. The orange mixture was then poured into iced water containing 0.5% pyridine and the organocobaloxime which precipitated was filtered off, washed copiously with water, dried, and purified either by recrystallization from methylene chloride light petroleum or by chromatography on silica gel with methylene chloride containing 5% ethyl acetate. The following cobaloximes were thus prepared:

(4-Methylpent-4-enyl)bis(dimethylglyoximato)(pyridine)cobalt(III): 85% yield. Anal. Found: C, 50.3; H, 6.9; N, 15.5. $C_{19}H_{30}CoN_5O_4$ requires: C, 50.55; H, 6.7; N, 15.5. ^{1}H NMR δ 1.57 (CH_3), 1.05 (CH_2Co), 2.14 (dmgH), 1.4–2.0 (CH_2CH_2), 4.52 (:CH_2), 7.38, 7.77, and 8.62 (pyridine).

(2-Methylpent-4-enyl)bis(dimethylglyoximato)(pyridine)cobalt(III): 65% yield. Anal. Found: C, 50.3; H, 6.65; H, 15.5. $C_{19}H_{30}CoN_5O_4$ requires: C, 50.55; H, 6.7; N, 15.5. ^{1}H NMR δ 0.75 (d, CH_3), 1.49 (m, CH), 1.65–2.0 (m, CH_2), 2.12 (s, dmg), 4.87 (J = 12 Hz doublet and J = 15.5 Hz doublet, :CH_2), 5.63 (m, :CH), 7.28, 7.75, and 8.60 (pyridine).

Hex-5-en-2-ylbis(dimethylglyoximato)(pyridine)cobalt(III): 68% yield. Anal. Found: C, 49.8; H, 6.7; N, 15.7. $C_{19}H_{30}CoN_5O_4$ requires: C, 50.55; H, 6.7; N, 15.5. ^{1}H NMR δ 0.43 (d, J = 6.6 Hz, CH_3), 0.95 (m, CH), 1.7–2.1 (m, 2 × CH_2), 2.13 (s, dmg), 4.85 (d, J = 10 Hz, cis :CH_2), 4.91 (d, J = 16.9 Hz, trans :CH_2), 5.70 (m, :CH), 7.28, 7.70, and 8.60 (pyridine).

(5-Methylhex-5-en-2-yl)bis(dimethylglyoximato)(pyridine)cobalt(III): 62% yield. Anal. Found: C, 51.2; H, 6.8; N, 15.1. $C_{20}H_{32}CoN_5O_4$ requires: C, 51.6; H, 6.9; N, 15.05. ^{1}H NMR δ 0.44 (d, J = 6.8 Hz, CH_3), 1.63 (s, CH_3), 0.94 (doublet of quartets, CH), 1.6–2.1 (2 × CH_2), 4.59 (m, :CH_2), 7.32, 7.71, and 8.59 (pyridine).

A mixture of diastereoisomers of (4-methylhex-5-en-2-yl)bis(dimethylglyoximato)(pyridine)cobalt(III): 56% yield. Anal. Found: C, 51.5; H, 6.8; N, 15.1. $C_{20}H_{32}CoN_5O_4$ requires: C, 51.6; H, 6.9; N, 15.05. ^{1}H NMR δ 0.39 and 0.40 (d, 2 × CH_3), 0.78 and 0.89 (d, 2 × CH_3), 1.2–2.1 (m, CH_2 and CH) 4.78 and 4.82 (d, J = 10.1 and 11.5 Hz, 2 × cis :CH_2), 4.80 and 4.87 (d, J = 15.5 and 17.0 Hz, 2 × trans :CH_2), 5.45 and 5.75 (m, :CH), 7.29, 7.70, and 8.61 (pyridine).

A mixture of diastereoisomers of (3-methylhex-5-en-2-yl)bis(dimethylglyoximato)(pyridine)cobalt(III): 77% yield. Anal. Found: C, 51.1; H, 7.05; N, 14.9. $C_{20}H_{32}CoN_5O_4$ requires: C, 51.6; H, 6.9; N, 15.05. ^{1}H NMR (principal isomer) δ 0.28 (d, CH_3), 1.4–2.0 (m, CH_2CH), 2.12 (s, dmg), 4.86 (m, :CH_2), 5.62 (m, :CH), 7.31, 7.71, and 8.60 (pyridine).

(6-Methylhept-5-en-2-yl)bis(dimethylglyoximato)(pyridine)cobalt(III): 68% yield. Anal. Found: C, 52.6; H, 7.1; N, 14.4. $C_{21}H_{34}CoN_5O_4$ requires: C, 52.6; H, 7.15; N, 14.6. ^{1}H NMR δ 0.44 (d, CH_3), 0.91 (m, CH), 1.54 and 1.64 (s, 2 × CH_3), 1.6–2.1 (m, CH_2CH_2), 2.13 (s, dmg), 5.04 (m, :CH), 7.29, 7.70, and 8.60 (pyridine). Similarly prepared were the known complexes pent-4-enyl-,[17] cyclohexyl-,[1] *sec*-butyl-,[1] and tetramethylenebis-(dimethylglyoximato)(pyridine)cobalt(III).[33]

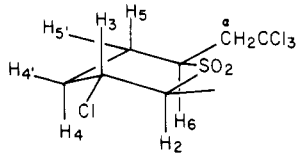
Reactions with Trichloromethanesulfonyl Chloride. Pent-4-enylcobaloxime. (A) Pent-4-enylcobaloxime (1, 0.94 g, 2.2 mmol) and **9** (0.51 g, 2.3 mmol) in methylene chloride (10 cm^3) was irradiated in a test tube open to the air by 4 × 150 W tungsten spotlights at 5–15 °C for 135 min. The mixture was chromatographed on silica gel (CC4), eluting with methylene chloride to remove all the organic products. The latter were separated by HPLC using methylene chloride as eluent to give 2-(β,β,β-trichloroethyl)sulfolane: 0.45 g, 82%. Found: C, 28.45; H, 3.65; Cl, 41.4; S, 12.9. $C_6H_9Cl_3SO_2$ requires: C, 28.65; H, 3.6; Cl, 42.3; S, 12.75. ^{13}C NMR δ 20.4 (C^4), 30.7 (C^3), 53.2 (C^5), 59.0 (C^2), 50.7

(27) Schollkopf, U.; Hilbert, P. *Liebigs Ann. Chim.* **1973**, 1061.
(28) Cherest, M.; Felkin, H.; Frajerman, C.; Lion, C.; Roussi, G.; Swierezewski, G. *Tetrahedron Lett.* **1966**, 875.
(29) Hill, E. A.; Myers, M. M. *J. Organometal. Chem.* **1979**, *173*, 1.
(30) Cope, A. C.; Hancock, E. M. "Organic Syntheses"; Wiley: New York, 1975; Collect. Vol. 3, p 399.
(31) Golding, B. T.; Kemp, T. J.; Sell, C. S.; Sellars, P. J.; Watson, W. P. *J. Chem. Soc., Perkin Trans. 2* **1978**, 839.
(32) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; p 1180.
(33) Schrauzer, G. N.; Windgassen, R. J. *J. Am. Chem. Soc.* **1966**, *88*, 3738; **1967**, *89*, 6391.

(C^{α}), 96.9 (CCl_3); ^1H NMR δ 1.9–2.8 (m, 1 H), 2.86 (q, J = 7.1 and 14.9 Hz, H^{α}), 3.1–3.3 (m, 2 H), 3.4 (m, H^{2}), 3.52 (q, J = 3.4 and 14.9 Hz, $H^{\alpha'}$); mass spectrum, m/e 250 (with the pattern expected for three chlorine atoms, M, M + 2, M + 4, and M + 6). 3-Chloro-1,1-dioxothiacyclohexane (ca. 40 mg, 8%; mass spectrum, m/e 169, 171 (M + 1), 133.0349 and 135.0261 (base peak), M – Cl requires 133.0342 (^{32}S) and 135.0241 (^{34}S); ^1H NMR δ 1.73 (doublet of quartets, H^4), 2.07 (m H^5), 2.18 (doublet of quintets, $H^{5'}$), 2.41 (m, $H^{4'}$), 2.98 (doublet of triplets, H^6), 3.05 (doublet of quartets, $H^{6'}$), 3.18 (q, H^2), 3.55 (m, $H^{2'}$), 4.31 (triplet of triplets, H^3) (couplings identical with those described for compound **17a** below)) and a minor product believed to be a mixture of 1,4,6,6,6-pentachlorohexane and 4,6,6,6-tetrachlorohexanesulfonyl chloride (^1H NMR δ 4.29 (m, H^4), 3.74 (t) and 3.61 (t) (H^1 of both products), 3.14 (q) and 3.25 (q, 2 × H^5)).

(B) Complex **1** (0.07 g) and **9** (0.05 g) were similarly irradiated as in A above, in $CDCl_3$ (0.5 cm^3) (i) alone, (ii) in the presence of galvinoxyl (0.01 g), or (iii) in the presence of α-phenyl-*N*-*tert*-butylnitrone (0.04 g). Reaction i was substantially complete within 1 h; in reaction ii the color of the galvinoxyl was discharged within 10 min and the reaction was ca. 40% complete within 1 h; in reaction iii the substrate was ca. 50% decomposed within 1 h.

(C) Complex **1** (3.67 g, 8.4 mol), **9** (2.2 g, 10 mmol), and liquid sulfur dioxide (1 cm^3) in methylene chloride (10 cm^3) were sealed in a glass tube and heated to 100 °C for 20 min. The crude product was chromatographed on silica gel (CC4) to give 2-(β,β,β-trichloroethyl)sulfolane (**3**, 1.5 g, 6.0 mmol, 72%), **17**, and 1,1-dioxothiacyclohexane-3-sulfonyl chloride (**17a**): mass spectrum, m/e 133.0321 and 135.0269, $C_5H_9O_2S$ (M – SO_2Cl) requires 133.0343 (^{32}S) and 135.0241 (^{34}S); ^1H NMR δ 1.91 (doublet of quartets, H^4), 2.22 (m, H^5), 2.39 (doublet of quintets, $H^{5'}$), 2.72 (m, $H^{4'}$), 3.03 (doublet of triplets, H^6), 3.22 (doublet of quartets, $H^{6'}$), 3.32 (q, H^2), 3.78 (m, $H^{2'}$), 4.17 (triplet of triplets, H^3); positional assignments as shown in **38** J (in Hz) 5,5′ 14.9, 6,6′ 14.1, 2,2′ 13.6,



38

4,4′ 13.6, 4,5 13.6, 5,6 13.6, 3,2 and 4,3 12.6, 3,2′, 5,6′, 4′,5, 5′,6, 5′,6′, 4′,5′, and 3,4′ all 3.5; 4′,2′ 1.8, 6′4′ 1.1.

(D) **1** (0.5 g, 1.15 mmol) and **9** (0.5 g, 2.3 mmol; 1.0 g, 4.6 mmol; or 1.5 g, 6.9 mmol) or bromotrichloromethane (0.5 g, 2.5 mmol) were sealed with liquid sulfur dioxide (ca. 4 cm^3) in a glass tube and allowed to stand in the dark for 48 h. the crude products were chromatographed as above to give **3** (40–60 mg) in each case together with (pent-4-enylsulfonyl)bis(dimethylglyxoimato)-(pyridine)cobalt(III) which was not purified.

(E) **(4-Methylpent-4-enyl)cobaloxime (2).** **2** (0.97 g, 2.15 mmol) and **9** (0.51 g, 2.35 mmol) in methylene chloride (10 cm^3) were irradiated for 165 min and chromatographed as in A above. The combined organic products were eluted with methylene chloride and the organometallic product was eluted with ethyl acetate/methylene chloride (1:1 v/v) to give **(4-methyl-4,6,6,6-tetrachlorohexyl)bis(dimethylglyoximato)(pyridine)cobalt(III) (24)**: 0.48 g, 0.8 mmol, 37%. Anal. Found: C, 39.1; H, 4.6; Cl, 23.55; N, 11.4. $C_{20}H_{30}Cl_4CoN_5O_4$ requires: C, 39.7; H, 5.0; Cl, 23.4; N, 11.6. ^1H NMR δ 1.22 (m, CH_2Co), 1.4–2.0 (m, CH_2CH_2), 1.75 (s, CH_3), 2.14 (s, dmg), 3.29 (s, CH_2CCl_3), pyridine resonances 7.44, 7.84, and 8.69 (pyridine). The organic product was separated by HPLC using methylene chloride and methylene chloride/methanol (100:0.13) as eluent to give **2-methyl-2-(β,β,β-trichloroethyl)sulfolane** (125 mg, 0.47 mmol, 22%; mass spectrum, 264.9612 (M + 1); $C_7H_{12}Cl_3O_2S$ requires 264.9601 (with appropriate pattern for three chlorine atoms); ^1H NMR δ 1.64 (s, CH_3), 2.13 (m, CH_2), 2.39 (m, CH_2), 3.08 (m, CH_2SO_2), 3.22 (d, J = 15.8 Hz, H^{α}), 3.33 (d, $H^{\alpha'}$); ^{13}C NMR δ 17.2 and 35.0 (C^3 and C^4), 19.1 (CH_3), 47.5 (C^5?), 56.25 ($CCCl_3$), 61.9 (C^2), 96.4 (CCl_3)) and **4-methyl-4,6,6,6-tetrachlorohexanesulfonyl chloride (27**; 25 mg, 0.75 mmol, ca. 4%. Anal. Found: C, 26.5; H, 3.1; Cl, 51.6. $C_7H_{11}Cl_5O_2S$ requires: C, 25.0; H, 3.3; Cl, 52.7; S, 9.5%. Mass spectrum, 264.9634; M – 2Cl + 1 requires 264.9644 (with the appropriate pattern for three chlorine atoms); ^1H NMR δ 1.89 (s, CH_3), 2.1–2.45 (CH_2CH_2), 3.40 (s, CH_2CCl_3), 3.72 (m, CH_2SO_2Cl)).

(F) **2** (1.07 g, 2.36 mmol) and **9** (0.57 g, 2.6 mmol) in $CDCl_3$ (2 cm^3) were irradiated by a 150-W lamp for 90 s and then kept in the dark for 30 min at ambient temperature. The ^1H NMR spectrum showed that the main product was the (tetrachlorohexyl)cobaloxime **25** (ca. 90%). Methylene chloride (8 cm^3) and **9** (0.98 g, 4.5 mmol) were added and the mixture was irradiated for 180 min and chromatographed as in E above to give the sulphonyl chloride **27** (0.58 g, 1.58 mmol, 67%).

(G) **2** (1.07 g, 2.36 mmol) and **9** (1.54 g, 7.1 mmol) in methylene chloride (10 cm^3) were irradiated for 210 min and chromatographed as in E above to give **27** (0.136 g, 0.4 mmol, 17% isolated yield).

(H) **2** (0.21 g, 0.47 mmol), **9** (0.31 g, 1.4 mmol), and galvinoxyl (2 mg) in $CDCl_3$ were irradiated as above by 4 × 150 W lamps. No reaction was detected in 10 min. In the absence of the galvinoxyl the reaction was ca. 95% complete within the same period.

(I) **(5-Methylhex-5-en-2-yl)cobaloxime (3).** Irradiation of a mixture of **3** (1.0 g, 2.15 mmol) and **9** (0.51 g, 2.33 mmol) in methylene chloride (10 cm^3) as in A above for 70 min gave, after column chromatography, 0.32 g of combined organic products. Separation of this product by HPLC gave **2,5-dimethyl-2-(β,β,β-trichloroethyl)sulfolane (12)** (two isomers in the ration 5:1, 0.28 g, 1 mmol, 48%; mass spectrum, 279 (with the appropriate pattern for three chlorine atoms) (M + 1). Anal. Found: C, 34.7; H, 4.4; Cl, 37.2. $C_8H_{13}Cl_3O_2S$ requires: C, 34.4; H, 4.7; Cl, 38.0. ^1H NMR (main isomer δ 1.40 (d, J = 6.9 Hz, CH_3), 1.71 (s, CH_3), 2.15–2.53 (m, CH_2CH_2), 3.27 (m, CH), 3.26 (d J = 16.2 Hz, H^{α}), 3.38 (d, $H^{\alpha'}$); minor isomer δ 1.42 (d, CH_3), 1.63 (s, CH_3), 3.25 (d) and 3.46 (d) (H^{α} and $H^{\alpha'}$); ^{13}C main isomer δ 12.9 (CH_3), 20.4 (CH_3), 25.9 and 33.3 (C^3 and C^4), 51.7 (C^5), 56.3 (C^{α}), 62.0 (C^2), 96.4 (CCl_3)) and **3-chloro-1,1-dioxo-3,6-dimethylthiacyclohexane (19)**: ca. 40 mg, 10%; mass spectrum, 161.0634 and 131.0614; M – Cl and M – SO_2H require, 161.0633 and 131.0601; ^1H NMR δ 1.35 (d, CH_3), 1.87 (s, CH_3), 1.7–2.3 (m, CH_2CH_2), 2.92 (m, H^6), 3.45 (s, H^2 and $H^{2'}$).

(J) **(2-Methylpent-4-enyl)cobaloxime (4).** **4** (1.0 g, 2.2 mmol) and **9** (0.53 g, 2.42 mmol) in methylene chloride (10 cm^3), were irradiated for 200 min and chromatographed as in A above to give a single isomer of **4-methyl-2-(β,β,β-trichloroethyl)sulfolane (13)**: Anal. Found: C, 32.3; H, 4.7; Cl, 39.9, S, 12.8. $C_7H_{11}Cl_3O_2S$ requires: C, 31.6; H, 4.1; Cl, 40.1; S, 12.05. ^1H NMR δ 1.27 (d, CH_3), 2.32 (t, H^3 and $H^{3'}$), 2.57 (quintuplet, H^4), 2.78 (q, $H^{5'}$), 2.83 (q, H^{α}), 3.21 (q, H^5), 3.53 (m, H^2), 3.53 (m, $H^{\alpha'}$, $J_{\alpha,\alpha'}$ = 14.8 Hz). That the resonance at δ 2.32 is a clean triplet indicates that this molecule has the trans configuration with H^3 and $H^{3'}$ having the same coupling constants to the two vicinal protons. ^{13}C NMR δ 19.7 (CH_3), 28.3 (C^4), 38.0 (C^3), 53.3, 57.5 and 58.0 (C^2, C^{α}, and C^5).

(K) **Hex-5-en-2-ylcobaloxime (5).** Complex **5** and **9** were reacted as in K above for 3 h to give a mixture of isomers of 5-methyl-2-(β,β,β-trichloroethyl)sulfolane (**14**) (Anal. Found: C, 32.3; H, 4.7; Cl, 39.9; S, 12.8. C_7H_{11} Cl_3O_2S requires: C, 31.7; H, 4.1; Cl, 40.1; S, 12.8. NMR spectra are described under experiment M below) and ***trans*-5-chloro-2-methyl-1,1-dioxothiacyclohexane (20)**: Anal. Found: C, 39.3; H, 6.1; S, 18.1. $C_6H_{11}ClO_2S$ requires: C, 39.5; H, 6.0; S, 17.5. ^1H NMR spectrum δ 1.3 (d, CH_3), 1.80 (m, H^3), 2.05 (m) and 2.40 (m, H^4 and $H^{4'}$), 2.92 (m, H^2), 3.15 (q, H^6), 3.60 (m, $H^{6'}$), 4.28 (m, H^5); $J_{6,6'}$ 14 Hz, $J_{5,6}$ 12 Hz, $J_{5,6'}$ 4 Hz; mass spectrum, m/e 182 and 184 (ratio 3:1), 147, 117 and 119 (ratio 3:1), 81 (base peak).

(L) Complex **5** (0.45 g; 1 mmol) in methylene chloride (3 cm^3) saturated with sulfur dioxide was reacted with **9** (0.23 g, 1.1 mmol) at 80 °C in a sealed tube for 24 h to give a 41:59 mixture of isomers of **14** (0.15 g, 0.6 mmol, 60%). ^1H NMR spectrum of the major isomer (believed from the coupling constants to be the trans isomer) δ 1.85 (*m*, $H^{4'}$), 2.08 (m, H^4), 2.34 ($H^{3'}$), 2.84 (doublet of doublets, $H^{\alpha'}$), 3.21 (m, H^5), 3.45 (m, H^2), 3.52 (doublet of doublets, H^{α}); coupling constants (in Hz) α,α' 15.3, 3,3′ 14.5, 4,4′ 14, 3,4 8.5, 2,3′ and 2,α' 8.1, 4,5 and 2,3 7.8, 3,4′ 7.3, 3′,4 7.0, 2,α 3.1. ^1H NMR of the minor isomer δ 1.85 (m) 1.71 (m) 2.37 (m) and 2.69 (m, 4-H), 2.87 (doublet of doublets, $H^{\alpha'}$), 3.02 (m, H^5), 3.36 (m, H^2), 3.55 (doublet of quartets, H^{α}); coupling constants (in Hz) α,α' 15.5, 4,5 11.5, 2,α' 2,3 and 2,3′ 6.5, 4′,5′ 6.5. Mass spectrum of mixed

isomers, m/e 265 (with appropriate pattern for three chlorine atoms).

2-Methyl-1,1-dioxothiacyclohexane-5-sulfonyl chloride (20a) (40 mg, 0.17 mmol, 17%): ^{1}H NMR spectrum δ 1.43 (d, CH_3), 1.98 (m) 2.25 (m) 2.67 (m) 3.07 (m, H^1), 3.30 (q, $H^{6'}$), 3.83 (m, H^6), 4.17 (m, H^5) (couplings as for **20** above).

(M) **(3-Methylhex-5-en-2-yl)cobaloxime (6).** Complex **6** and **9** were irradiated and chromatographed as in E above to give predominantly a mixture of two main and one minor isomer of **4,5-dimethyl-2-(β,β,β-trichloroethyl)sulfolane (15)** (Anal. Found: C, 34.1; H, 4.5; Cl, 37.0; S, 11.0. $C_8H_{13}Cl_3O_2S$ requires: C, 34.4; H, 4.6; Cl, 38.2; S, 11.4. Mass spectrum, m/e 278 (with the pattern for three chlorine atoms); ^{13}C NMR δ 14.2, 14.4, 15.2, 15.4 (4 × CH_3), 31.9, 36.4, 53.2 54.1, 56.4, 58.8, 59.7, 60.2 (C^2–C^5), 97.2 (Cl_3C)) and a smaller yield of three isomers of **5-chloro-2,3-dimethyl-1,1-dioxothiacyclohexane (21)**: ^{1}H NMR spectrum of isomer a, δ 1.35 (d, CH_3), 1.70 (m), 1.95 (m), 2.10 (d, CH_3), 3.05 (m, H^2), 3.20 (g, J = 14 and 12.3 Hz, H^6), 3.55 (q, J = 14 and 4 Hz; $H^{6'}$), 3.95 (m, H^5); ^{1}H NMR spectrum of isomers b and c, δ 1.20 (d), 1.35 (d), and 1.50 (d, 3 × CH_3), 1.70 (m), 2.05 (m), 3.10 (m), 3.35 (q, J = 10 and 14 Hz, H^6), 3.60 (m, J = 14 and 4 Hz, $H^{6'}$), 3.95 (m, H^5).

(N) **(4-Methylhex-5-en-2-yl)cobaloxime (7).** Complex **7** and **9** were reacted and separated as in E above to give a mixture of isomers of **3,5-dimethyl-2-(β,β,β-trichloroethyl)sulfolane (16)** (Anal. Found: C, 33.6; H, 4.5; Cl, 35.3; S, 10.3. $C_8H_{13}Cl_3O_2S$ requires: C, 34.4; H, 4.6; Cl, 38.2; S, 11.4. Mass spectrum, m/e 278 (with appropriate pattern for three chlorine atoms); ^{13}C NMR δ 13.5, 14.4, 18.0, 18.9 (4 × CH_3), 31.5, 35.5 (C^3), 36.4, 37.4 (C^4), 53.3, 55.9, 58.0, 97.2 (Cl_3C)) together with two isomers of **5-chloro-2,4-dimethyl-1,1-dioxothiacyclohexane (22)**: ^{1}H NMR spectrum of isomer a, δ 1.10 (d), 1.35 (d, 2 × CH_3), 1.70 (m, H^4), 2.55 (m, H^3), 2.95 (m, H^5), 3.15 (q, H^α), 3.45 (m, $H^{\alpha'}$, $J_{\alpha,\alpha'}$ = 13.9 Hz, $J_{2,\alpha}$ = 12.1 Hz); ^{1}H NMR spectrum of isomer b, δ 1.20 (d) and 1.35 (d, 2 × CH_3), 1.95 (m, H^4), 3.10 (m, H^3 and H^5), 3.15 (q, H^α), 3.55 (m, $H^{\alpha'}$), 3.95 (m, H^2, $J_{\alpha,\alpha'}$ = 14 Hz).

(O) **(6-Methylhept-5-en-2-yl)cobaloxime (8).** Complex **8** and **9** were reacted together and chromatographed as in E above to give one main product, believed to be 2-(α-chloro-α-methylethyl)-5-methylsulfolane (**23**): mass spectrum, m/e 311 (M + 1), 275 (M − Cl), 146 and 148 (M + 1 − SO_2) in ratio 3:1.

(P) **Tetramethylenebis(cobaloxime) (45).** **45** (1.4 g, 2 mmol) in liquid sulfur dioxide in a sealed tube was maintained at ambient temperature in the dark for 24 h. The sulfur dioxide was removed and the residue was chromatographed on silica gel using pentane/methylene chloride as eluent. The sole organic product was identified as sulfolane (33 mg, 20%) by comparison with authentic material. The main product was a mixture having characteristics of the mono- and bis(sulfur dioxide) insertion products.

Preparation and Reaction of Chiral Complexes. Hex-5-en-2-ol was resolved by recrystallization of the brucine salt of the hydrogen phthalate of the (*S*)-alcohol. It was converted into (*S*)-hex-5-en-2-yl tosylate and thence, by reaction with the bis(dimethylglyoximato)(pyridine)cobaltate(I) ion, as above, into (*R*)-hex-5-en-2-ylbis(dimethylglyoximato)(pyridine)cobalt(III)[15] **5a**. Reaction of **5a** with **9** as in M above gave a 41:59 mixture of isomers of **14a**, each in 65% enantiomeric excess, as shown by the changes in chemical shift and intensity of the methyl resonances in the presence of tris(D-3-heptafluorobutyrylcamphorate)europium(III) (see Figure 1). Racemic 2-methyl-1,1-dioxothiacyclohexane-5-sulfonyl chloride (**20a**) was also formed.

Reactions of Olefins with Trichloromethanesulfonyl Chloride. Oct-1-ene. Oct-1-ene (0.88 g, 7.8 mmol), **9** (2.2 g, 8.0 mmol), and *sec*-butylbis(dimethylglyoximato)(pyridine)cobalt(III) (0.2 g, 0.5 mmol) in methylene chloride (5 cm^3) was irradiated in all Pyrex, water cooled apparatus by tungsten lamps (4 × 150 W at 10 cm distance) for 90 min. The crude reaction mixture was chromatographed on silica gel using pentane and then methylene chloride to elute the expected organic products[34] (80%) and 1,1,1-trichlorononane-3-sulfonyl chloride (**30**; 15%). The same experiment carried out at 0–5 °C in methylene chloride saturated with sulfur dioxide gave **30** in 40% yield (isolated 0.3 g, 12%). Anal. Found: C, 33.4; H, 4.4; Cl, 43.2; S, 9.7. $C_9H_{16}Cl_4O_2S$ requires: C, 32.8; H, 4.9; C, 42.9; S, 9.8. ^{13}C NMR δ 14.0 (C-9), 22.5, 26.0, 28.5 (C-6 to C-8), 31.6, 39.1, (C-4 and C-5), 57.7 (CHCl), 62.3 (CH_2CCl_3); ^{1}H NMR δ 3.87 (m, $CHSO_2Cl$), 3.62 (q, $CHCCl_3$, J = 15.6 and 1.8 Hz), 3.06 (q, $CHCCl_3$, J = 7.6 and 15.6 Hz).

Cyclooctene. Cyclooctene (1 cm^3, 7.6 mmol), **9** (3.3 g, 15 mmol), and cyclohexylbis(dimethylglyoximato)(pyridine)cobalt(III) (0.45 g, 1 mmol) in methylene chloride (10 cm^3) were irradiated at 0–10 °C for 3 h as above. The reaction mixture was chromatographed on silica gel with elution by methylene chloride to remove the inorganic products, and the organic fraction was further purified by HPLC using ethyl acetate/light petroleum (bp 40–60 °C; 3.5:96.5 v/v) as eluent, to give 4-(trichloromethyl)cyclooctanesulfonyl chloride (**31**). Anal. Found: C, 33.6; H, 4.3; Cl, 42.8; S, 9.8. $C_9H_{14}Cl_4O_2S$ requires: C, 32.9; H, 4.3; Cl, 43.3; S, 9.8. ^{1}H NMR δ 1.8 (m, n × CH_2), 2.1–2.8 (m, CH_2 and $CHCCl_3$), 3.75 (tq, $CHSO_2Cl$); yield (by NMR) 14%. When the reaction was repeated wtih 7.6 mmol each of the two reagents, or thermally in a sealed tube in methylene chloride saturated with sulfur dioxide, the yield of **31** was 21%.

Hexa-1,5-diene. Hexa-1,5-diene (0.82 g, 10 mmol), **9** (4.32, 20 mmol), and *sec*-butylcobaloxime (0.69 g, 0.1 mmol) in methylene chloride (10 cm^3) were photolyzed as above. The organic product was separated by column chromatography and HPLC as above to give, among the expected products,[34] *trans*-3-chloro-1,1-dioxo-6-(trichloroethyl)thiacyclohexane (**32**) (28 mg, white crystals mp 164 °C). Anal. Found: C, 28.4; H, 3.3; Cl, 47.0; S, 10.5. $C_7H_{10}Cl_4O_2S$ requires: C, 28.0; H, 3.4; Cl, 47.3; S, 10.7. ^{13}C NMR 29.25, 35.3, 49.4, 51.6, 58.6, 59.5, 96.8 (CCl_3); ^{1}H NMR (see diagram below) δ 4.32 (tt, H-3), 3.53 (q, H-α), 3.67 (octet, H-2′), 3.30 (q, H-2) 3.27 (m, H-6), 2.79 (q, H-α'), 2.75 (m, H-5′), 2.50 (m, H-4′), 2.0 (m, H-5), 1.90 (m, H-4); coupling constants (Hz) α,α' 15.5, α,6 2.0, α',6 7.4, 5′,4′ 2.2, 4′,4 15.0, 4′,3 1.9, 4′,2′ 1.9, 4,3 12.0, 3,2′ 4.0, 3,2 12.1, 2,2′ 13.9.

Hepta-1,6-diene. Hepta-1,6-diene (0.96 g, 10 mmol), **9** (4.32 g, 20 mmol), and *sec*-butylcobaloxime (0.06 g, 0.1 mmol) in methylene chloride (1 cm^3) were photolyzed as above. The insoluble polymeric material was filtered off and the solvent was removed in vacuo. The excess of **9** was sublimed at 60-70 °C (15 mmHg) and the oil which remained was separated by HPLC using light petroleum with up to 10% ethyl acetate to give, besides known polychlorohydrocarbons,[19] a mixture of diastereoisomers of **34**. First isomer: ^{1}H NMR δ 5.78, 5.02, 4.96, 1.34–3.72 (all m), 4.24 (sextet); mass spectrum, M − HCl 375 (with the typical pattern for three chlorine atoms). Second isomer: ^{1}H NMR δ 5.79, 5.05, 5.00, 4.42, 1.3–1.7 (all m); mass spectrum, M 411 (with a typical pattern for four chlorine atoms). Also a single isomer of **35** was obtained: ^{1}H NMR 3.57 (m, J = 8.1, 4.4, 1.2, and 1.2 Hz), 3.49 (m, J = 10.9, 4.7, 1.8, and 0.8 Hz), 3.26 (m, J = 13.5, 4.2, and 3.1 Hz), 3.13 (m, J = 13.5, 3.1, and 3.1 Hz), 2.4–3.0 (m); mass spectrum, M − HCl 375 (with characteristic pattern for three chlorine atoms). Traces of **33** were obtained: ^{1}H NMR δ 3.62 (q, J = 10.7 and 4.9 Hz), 3.39 (q, J = 10.7 and 8.3 Hz), 2.97 (m, J = 14.8 Hz), 2.94 (m, J = 14.8 Hz), 2.69 (m, J = 14.8 Hz), 2.65 (m, J = 14.8 Hz).

***cis,cis*-Cycloocta-1,5-diene.** *cis,cis*-Cycloocta-1,5-diene (0.54 g, 5 mmol), **9** (0.99 g, 5.5 mmol), and cyclohexylcobaloxime (0.2 g, 0.5 mmol) in methylene chloride (10 cm^3) were irradiated as above for 2 h. The crude organic product was separated by column chromatography on silica gel using methylene chloride as eluent, and recrystallized from pentane/methylene chloride to give white crystals of 3-chloro-5′-(trichloromethyl)-1,1-dioxobicyclo[3.3.1]-thiaoctane (**36**, or the isomer **37**): 850 mg, 53% yield; mass spectrum, m/e 323.9333; $C_9H_{12}Cl_4O_2S$ requires, 325.9354, 325.9226; $C_9H_{12}{}^{37}Cl^{35}Cl_3O_2S$ requires, 325.9182 (M − Cl) (with the typical pattern for three chlorine atoms); ^{1}H NMR δ 4.63 (octet, CHCl, J = 12.4, 4.9, and 3.4 Hz), 3.39 (m, $CHSO_2$), 3.31 (m, $CHSO_2$, J = 3.4, 3.4, 2.6, and 2.6 Hz), 3.01 (octet, $CHCCl_3$, J = 12.6, 5.3, and 2.6 Hz), 1.7–2.6 (m); ^{13}C NMR δ 18.8, 19.5, 25.3, 30.1, 54.0, 56.1, 57.7, 58.6.

Registry No. (*R*)-**5a**, 89616-44-4; *trans*-**12**, 89555-83-9; *cis*-**12**, 89556-01-4; **13**, 89555-85-1; *trans*-**14**, 89555-86-2; *cis*-**14**, 89555-87-3; (±)-*cis*-**14a**, 89555-95-3; (±)-*trans*-**14a**, 89655-87-8; **15**, 89555-90-8; **16**, 89555-92-0; **17a**, 89555-80-6; **19**, 89555-84-0; **20**, 89555-88-4;

(34) Gandolfi, O.; Cais, M. *J. Organometal. Chem.* **1977**, *125*, 141. Elzing, J.; Hogeveen, H. *J. Org. Chem.* **1980**, *45*, 3957.

20a, 89555-89-5; **21**, 89555-91-9; **22**, 89555-93-1; **23**, 89555-94-2; **24**, 89530-52-9; **25**, 89530-53-0; **27**, 89555-82-8; **29**, 82639-77-8; **30**, 89555-96-4; **31**, 89555-97-5; **32**, 89555-98-6; **34**, 89555-99-7; **36**, 89556-00-3; **45**, 10170-53-3; (*R**,*R**)-4-methylhex-5-en-2-ol, 71228-22-3; (*R**,*S**)-4-methylhex-5-en-2-ol, 71228-23-4; (*R**,*R**)-3-methylhex-5-en-2-ol, 1499-66-7; (*R**,*S**)-3-methylhex-5-en-2-ol, 1695-93-8; (4-methylpent-4-enyl)bis(dimethylglyoximato)(pyridine)cobalt(III), 89530-45-0; (2-methyl-4-enyl)-bis(dimethylglyoximato)(pyridine)cobalt(III), 89530-46-1; hex-5-en-2-ylbis(dimethylglyoximato)(pyridine)cobalt(III), 89530-47-2; (5-methylhex-5-en-2-yl)bis(dimethylglyoximato)(pyridine)cobalt(III), 89530-48-3; (*R**,*R**)-(4-methylhex-5-en-2-yl)bis(dimethylglyoximato)(pyridine)cobalt(III), 89530-49-4; (*R**,*S**)-(4-methylhex-5-en-2-yl)bis(dimethylglyoximato)(pyridine)cobalt(III), 89614-94-8; (*R**,*R**)-(3-methylhex-5-en-2-yl)bis(dimethylglyoximato)(pyridine)cobalt(III), 89530-50-7; (*R**,*S**)-(3-methylhex-2-en-2yl)bis(dimethylglyoximato)(pyridine)cobalt(III), 89614-95-9; (6-methylhept-5-en-2-yl)bis(dimethylglyoximato)-(pyridine)cobalt(III), 89530-51-8; pent-4-enylbis(dimethylglyoximato)(pyridine)cobalt(III), 36630-47-4; 2-(β,β,β-trichloroethyl)sulfolane, 82639-78-9; 3-chloro-1,1-dioxothiacyclohexane, 38690-82-3; 4,6,6,6-tetrachlorohexanesulfonyl chloride, 89555-79-3; 2-methyl-2-(β,β,β-trichloroethyl)sulfolane, 89555-81-7; *sec*-butylbis(dimethylglyoximato)(pyridine)cobalt(III), 54712-55-9; cyclohexylbis(dimethylglyoximido)(pyridine)cobalt(III), 28206-03-3; pent-4-enol, 821-09-0; hex-5-en-2-ol, 626-94-8; 2-methylpent-4-enol, 5673-98-3; 4-methylpent-4-enol, 22508-64-1; 6-methylhept-5-en-2-ol, 1569-60-4; 5-methylhex-5-en-2-ol, 50551-88-7; allyl bromide, 106-95-6; allyl alcohol, 107-18-6; 3-methyl-5-en-2-one, 2550-22-3; dimethylglyoxime, 95-45-4; trichloromethanesulfonyl chloride, 2547-61-7; oct-1-ene, 111-66-0; cyclooctene, 931-88-4; hexa-1,5-diene, 592-42-7; hepta-1,6-diene, 3070-53-9; *cis,cis*-1,5-cyclooctadiene, 1552-12-1; 3,3,3-trichloropropyl, 6565-20-4; sulfur dioxide, 7446-09-5; $CoCl_2$, 7646-79-9.

Catalytic Uses of $Fe(CO)_5$: Formation of Carboxylic Acid Derivatives

Gerald C. Tustin* and Robert T. Hembre

Research Laboratories, Eastman Chemicals Division, Eastman Kodak Company, Kingsport, Tennessee 37662

Received January 24, 1983

Carboxylic acid derivatives were prepared by carbonylating an alkyl or aralkyl halide in the presence of a catalytic amount of iron carbonyl, a base, and an alcohol or water.

Although iron pentacarbonyl, $Fe(CO)_5$, is one of the most ubiquitous and least expensive metal carbonyls, few catalytic uses have been found for it. This is largely attributable to the difficulty associated with removal of a CO ligand to generate a site of coordinative unsaturation. Most of the catalytic uses of $Fe(CO)_5$ where CO is used as one of the reactants employ a base to chemically activate the CO ligand by converting it to CO_2, as follows:

$$\underset{\mathbf{1}}{Fe(CO)_5} + OH^- \rightarrow \underset{\mathbf{2}}{HFe(CO)_4^-} + CO_2$$

The anion **2** is the species that initiates the catalysis. The most famous example of this catalysis is the Reppe reaction whereby an olefin is treated with CO and water to form the next higher alcohol.[1] Pettit and others have applied this catalytic system in the hydroformylation of olefins,[2] aldehyde and ketone hydrogenation,[3,4] water gas shift reaction,[2,5] and the reduction of nitro compounds.[6] In these reactions $Fe(CO)_5$ is continuously being regenerated and remains an integral part of the catalytic cycle. Examples are also known where $Fe(CO)_5$ is used as a catalyst precursor in reactions where CO is not a reactant. In these cases $Fe(CO)_5$ usually does not reappear in the catalytic cycle. Thus, extremely active olefin isomerization and hydrosilation catalysts result from the removal of CO from $Fe(CO)_5$ by photolysis.[7] Back-reaction of CO destroys the coordinatively unsaturated species produced in these reactions, and catalysis stops when the light is turned off. Activation of $Fe(CO)_5$ can also be accomplished thermally, but again $Fe(CO)_5$ is removed from the catalytic cycle.[8]

Numerous stoichiometric carbonylation reactions have utilized $Fe(CO)_5$, usually in a reduced form. Probably the most well-known examples are those developed by Collman et al., where an alkyl halide is reacted with $Fe(CO)_4^{2-}$ in a stoichiometric reaction and then in a second step is converted to aldehyde, ketone, acid, ester, or hydrocarbon by the addition of the appropriate reagents.[9] In a related stoichiometric process investigated by Tsutsumi and coworkers, ketones and aldehydes were synthesized by reacting $Fe(CO)_5$ with organolithium reagents. The resulting lithium acyl carbonyl ferrate was then reacted with alkyl halides or protons, respectively.[10,11]

Here we report another catalytic process that uses the combination of $Fe(CO)_5$, base, CO, and hydroxylic solvent. The other reactant in this case is an alkyl or aralkyl halide, and the product is a carboxylic acid derivative:

$$RX + CO + R'OH \xrightarrow[\text{base}]{Fe(CO)_5} RC(O)OR'$$

The reactions typically occur under the mild conditions

(1) Reppe, W.; Vetter, H. *Liebigs Ann. Chem.* **1953**, *582*, 133.
(2) Kang, M. C.; Maulding, C. H.; Cole, T.; Slegeir, W.; Cann, K.; Pettit, R. *J. Am. Chem. Soc.* **1977**, *99*, 8323.
(3) Sternberg, H. W.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1957**, *79*, 6116.
(4) Marko, L.; Radhi, M. A.; Ötvös, I. *J. Organomet. Chem.* **1981**, *218*, 369
(5) Ungarmann, C.; Landis, V., Mayo, S. A.; Cohen, H.; Walker, H.; Pearson, R. G.; Rinker, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 5922.
(6) Cann, K.; Cole, T.; Slegeir, W.; Pettit, R. *J. Am. Chem. Soc.* **1978**, *100*, 3969.
(7) Mitchener, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 975.
(8) Kagayama, T.; Okabayashi, S.; Amaike, Y.; Matsukawa, Y.; Ishii, Y.; Ogawa, M. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2297.
(9) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342.
(10) Sawa, Y.; Ryang, M.; Tsutsumi, S. *J. Org. Chem.* **1970**, *35*, 4183.
(11) Ryang, M.; Rhee, I.; Tsutsumi, S. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 341.

0022-3263/84/1949-1761$01.50/0