Formation of Allyl and Cyclopropylcarbinyl Sulphides in the Regiospecific Reactions of Arenesulphenyl Chlorides with Allyl- and But-3-enylcobaloximes

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Allyl- and substituted-allyl-bis(dimethylglyoximato)pyridinecobalt(III) complexes react regiospecifically with 2,4-dinitrobenzenesulphenyl chloride to give moderate (30—45%) yields of the corresponding rearranged allyl 2,4-dinitrophenyl sulphides. The corresponding rearranged allyl derivative of dimethylglyoxime is a major by-product. But-3-enylbis(dimethylglyoximato)pyridinecobalt(III) complexes also react regiospecifically to give cyclopropylmethyl 2,4-dinitrophenyl sulphides. The reactions are interpreted in terms of an electrophilic attack of the sulphur on the γ- and δ-carbon of the allyl- or butenyl-ligand, respectively, with concurrent or subsequent loss of cobaloxime(III), and with concurrent or subsequent cyclisation of the organic ligand in the case of the butenyl complexes. Benzenesulphenyl bromide and chloride react much more slowly and their reaction with allylbis-(dimethylglyoximato)pyridinecobalt(III) has been briefly explored.

WE have previously described a number of homolytic reactions of organocobaloximes with free radical reagents in which a key step involved the attack of a C- [1,2] or S-centred [3,4] radical (X·) on the organic ligand of the complex $[RCo^{III}(dmgH)_2L]$ with the synchronous or subsequent displacement of the metal as a cobaloxime(II) complex [equation (1)]. Each of these reactions was a part of a chain process, in some cases of very short chain length, in which the cobaloxime(II)

$$X\cdot + RCo^{III}(dmgH)_2L \longrightarrow RX + Co^{II}(dmgH)_2L \quad (1)$$

$$L(dmgH)_2Co^{II} + YX \longrightarrow L(dmgH)_2Co^{III}Y + X\cdot \quad (2)$$

complex was also effective in the generation of the radical X· from the reagent (YX) [equation (2)].

Reaction (1) may take various forms [equations (3) and (4)] depending upon the nature of the organic ligand R, but in each case so far studied it has been an electrophilic radical which has been involved in the attack on the carbon centre. However, several electrophilic radicals, *e.g.* Br·, ArS·, $R_2N\cdot$, and NCS·, may be derived from substrates which are themselves electrophilic reagents, *e.g.* Br_2, ArSCl, R_2NCl, and $(SCN)_2$, respectively, especially towards alkenes.[5] Since organocobaloximes also show some susceptibility towards electrophilic displacement reactions,[6] and indeed to oxidation by some of the same electrophiles,[7] a direct heterolytic cleavage of the carbon–metal bond may take the place of, or compete with, the homolytic pathway. The problem of mixed mechanism is particularly aggravated by the fact that many organocobaloximes are prone to decomposition to cobaloxime(II) (allyl > benzyl > alkyl) [8] and frequently contain traces of cobaloxime(II) which can initiate chain processes *via* reaction (2), even when the heterolytic reaction might otherwise be dominant.

$$Cl_3C\cdot + MeCH{:}CH\cdot CH_2Co(dmgH)_2py \longrightarrow Cl_3C\cdot CHMe\cdot CH{:}CH_2 + Co^{II}(dmgH)_2py \quad (3)$$

$$RSO_2\cdot + CH_2{:}CMe\cdot CH_2CH_2Co(dmgH)_2py \longrightarrow RSO_2\cdot CH_2\cdot \overline{CMe\cdot CH_2\cdot CH_2} + Co^{II}(dmgH)_2py \quad (4)$$

One such electrophilic substrate capable of generating electrophilic radicals is 2,4-dinitrobenzenesulphenyl chloride.[9] Here we describe studies of the products and mechanism of reaction of this reagent with a series of organocobaloximes which have shown to be prone to undergo homolytic displacement reactions.[1,3,4]

RESULTS

Allylbis(dimethylglyoximato)pyridinecobalt(III) (1) (0.25 mol dm^{-3}) reacted with 2,4-dinitrobenzenesulphenyl chloride (2) (0.25 mol dm^{-3}) in methylene chloride within a few minutes at ambient temperature to give, after chromatography on silica gel, allyl 2,4-dinitrophenyl sulphide (3) and the *O*-allyl derivative of dimethylglyoxime (4a).

$$ArSCl + R^1R^2C{:}CR^3\cdot CH_2Co(dmgH)_2py \longrightarrow ArSCR^1R^2\cdot CR^3{:}CH_2 + HON{:}CMeCMe{:}NOCR^1R^2\cdot CR^3{:}CH_2 \quad (5)$$

(2)		(3)	(4a)
(1)	$R^1 = R^2 = R^3 = H$		
(5)	$R^3 = R^2 = H$, $R^1 = Me$	(10)	(4b)
(6)	$R^1 = R^2 = H$, $R^3 = Ph$	(11)	(4c)
(7)	$R^1 = R^2 = H$, $R^3 = Me$	(12)	(4d)
(8)	$R^3 = H$, $R^1 = R^2 = Me$	(13)	(4e)
(9)	$R^2 = R^3 = H$, $R^1 = Ph$	(14)	(4f)

Monitoring the corresponding reaction of but-2-enylbis-(dimethylglyoximato)pyridinecobalt(III) (5) in $CDCl_3$ by ^1H n.m.r. spectroscopy showed that but-1-en-3-yl 2,4-dinitrophenyl sulphide (10) was formed in the early stages of the reaction but that the but-3-enyl derivative of dimethylglyoxime (4b) was not formed directly at this stage, but was the result of later decomposition of some precursor during the work-up. Similar reaction of 2-phenyl-, 2-methyl-, 3,3-dimethyl-, and 3-phenylallyl-bis(dimethylglyoximato)pyridinecobalt(III) [compounds (6)—(9), respectively] each gave only a single isomer of the corresponding

rearranged substituted allyl 2,4-dinitrophenyl sulphide (11)—(14), together with a single isomer of the *rearranged*

$$\begin{array}{l}\mathrm{ArSCl} + \mathrm{CH_2{:}CR{\cdot}CH_2CH_2Co(dmgH)_2py} \longrightarrow \\ \quad (15)\ \mathrm{R = H} \\ \quad (17)\ \mathrm{R = Me}\end{array} \qquad \begin{array}{l}\mathrm{ArS{\cdot}CH_2{\cdot}CR{\cdot}CH_2{\cdot}CH_2} \\ (16)\ \mathrm{R = H,\ Ar = C_6H_3(NO_2)_2} \\ (18)\ \mathrm{R = Me,\ Ar = C_6H_3(NO_2)_2}\end{array} \qquad (6)$$

substituted allyl derivative of dimethylglyoxime (4c—f). No allyl chlorides could be detected, but some dicinnamyls were formed in the reaction of compound (9).

reaction of 3-methylbut-3-enylbis(dimethylglyoximato)-pyridinecobalt(III) (17) gave the single sulphide (18), but that of 2-methylbut-3-enylbis(dimethylglyoximato)pyridinecobalt(III) (19) gave a mixture of the isomeric cyclopropylmethyl sulphides (20) and (21), but again no open-chain isomeric sulphides were obtained. During the corresponding reaction of 1-methylbut-3-enylbis(dimethylglyoximato)pyridinecobalt(III) (22), it largely rearranged to compound (19) prior to the formation of the same pair of isomeric cyclopropylmethyl sulphides (20) and (21).

2,3-Dimethylbut-3-enylbis(dimethylglyoximato)-

$$\mathrm{ArSCl} + \mathrm{CH_2{:}CR^3{\cdot}CHR^2{\cdot}CHR^1Co(dmgH)_2py} \longrightarrow \begin{cases} \mathrm{ArSCH_2{\cdot}CH(R){\cdot}CH(Me){\cdot}CH_2} & (20)\ \mathrm{R = H} \\ & (25)\ \mathrm{R = Me} \\ \mathrm{ArSCH_2{\cdot}CH(R){\cdot}CH(Me){\cdot}CH_2} & (21)\ \mathrm{R = M} \\ & (26)\ \mathrm{R = Me} \end{cases} \qquad (7)$$

(2)

(19) $R^1 = R^3 = H,\ R^2 = Me$
(22) $R^1 = Me,\ R^2 = R^3 = H$
(23) $R^1 = H,\ R^3 = R^3 = Me$
(27) $R^1 = R^3 = Me,\ R^2 = H$

Reaction of but-3-enylbis(dimethylglyoximato)pyridinecobalt(III) (15) with compound (2) in methylene chloride proceeded more slowly than the above reactions, but after

pyridinecobalt(III) (23) also reacted with compound (2) in acetic acid at 100 °C to give a mixture of isomers (25) and (26) in near equal proportions. The same pair of

$$\mathrm{PhSBr} + \mathrm{Me_2C{:}CH{\cdot}CH_2Co(dmgH)_2py} \longrightarrow \begin{cases} \mathrm{PhS{\cdot}CMe_2CH{:}CH_2} \\ (29) \\ \mathrm{PhSCH_2CH{:}CMe_2} \\ (28) \end{cases} \qquad (8)$$

2 h at 100 °C in acetic acid gave cyclopropylmethyl 2,4-dinitrophenyl sulphide (16) in comparable yield. No other sulphides could be detected in the product. Similar

isomers in essentially the same proportions were isolated and characterised (as a pair) from the corresponding reaction of 4-methylpent-4-enylbis(dimethylglyoximato)-

TABLE 1

Products $RSC_6H_3(NO_2)_2$ of reaction of 2,4-dinitrobenzenesulphenyl chloride with organocobaloximes $R'Co(dmgH)_2py$

R	R′	Solvent	Time (h)	Temp. (°C)	Yield (%) [a]	Analysis calc. (found) C	H	N	S
$CH_2{:}CH{\cdot}CH_2$	$CH_2{:}CH{\cdot}CH_2$	CH_2Cl_2	1.5	Ambient	37				
$CH_2{:}CMe{\cdot}CH_2$	$CH_2{:}CMe{\cdot}CH_2$	CH_2Cl_2	4.5	Ambient	38	47.2 (46.5)	4.0 (4.1)	11.0 (10.85)	12.6 (12.7)
$CH_2{:}CH{\cdot}CHMe$	$MeCH{:}CH{\cdot}CH_2$	CH_2Cl_2	1.5	Ambient	39	47.2 (47.0)	4.0 (4.2)	11.0 (10.8)	12.6 (12.4)
$CH_2{:}CH{\cdot}CHPh$	$PhCH{:}CH{\cdot}CH_2$	CH_2Cl_2	4	Ambient	32	55.2 (55.6)	4.0 (3.8)	9.2 (9.05)	10.1 (10.1)
$CH_2{:}CHPh{\cdot}CH_2$	$CH_2{:}CPh{\cdot}CH_2$	CH_2Cl_2	2	Reflux	75 [b]	55.2 (55.6)	4.0 (3.9)	9.2 (8.8)	10.1 (10.0)
$CH_2{:}CH{\cdot}CMe_2$	$Me_2C{:}CH{\cdot}CH_2$	CH_2Cl_2	3	Ambient	29	49.2 (49.1)	4.5 (4.8)	10.4 (10.4)	11.95 (12.2)
Cyclopropyl–CH_2	$CH_2{:}CH{\cdot}CH_2CH_2$	AcOH	2	100	38	45.0 (45.0)	3.35 (3.5)	11.7 (11.7)	13.35 (13.3)
1-methylcyclopropyl–CH_2	$CH_2{:}CMe{\cdot}CH_2CH_2$	AcOH	2	100	44	49.2 (49.0)	4.5 (4.7)	10.4 (10.2)	11.95 (12.0)
2-methylcyclopropyl–CH_2 [c]	$CH_2{:}CH{\cdot}CHMe{\cdot}CH_2$	CH_2Cl_2	6	Ambient	30	49.2 (49.3)	4.5 (4.7)	10.4 (10.4)	11.95 (11.9)
2-methylcyclopropyl–CH_2 [c]	$CH_2{:}CH{\cdot}CHMe{\cdot}CH_2$	AcOH	2	100	35				
2-methylcyclopropyl–CH_2 [c]	$CH_2{:}CH{\cdot}CH_2CHMe$	AcOH	2	100	37				
1,2-dimethylcyclopropyl–CH_2 [d]	$CH_2{:}CMe{\cdot}CH_2CHMe$	AcOH	4	100	30	51.0 (51.1)	5.0 (4.9)	9.9 (9.5)	
1,2-dimethylcyclopropyl–CH_2 [d]	$CH_2{\cdot}CMe{\cdot}CHMe{\cdot}CH_2$	AcOH	4	100	~30 [e]				
2-phenylcyclopropyl–CH_2	$CH_2{:}CH{\cdot}CHPh{\cdot}CH_2$	AcOH	2	100	10	56.9 (56.5)	3.8 (3.9)	8.9 (8.75)	10.1 (10.0)

[a] Isolated product from 1 : 1 reagents. [b] Using five-fold excess of organocobaloxime, yield based on sulphenyl chloride. [c] Mixture of two isomers *ca.* 70 : 30. [d] Mixture of two isomers *ca.* 50 : 50. [e] Not isolated, yield estimated from formation of identical products in previous experiment.

pyridinecobalt(III) (27). No interconversion between (23) and (27) was observed during the reactions.

In marked contrast, benzenesulphenyl chloride reacted only partially with compound (17) over several days at 50 °C in CH_2Cl_2 to give a low yield of a cyclic product analogous to (18), evident from the ^1H n.m.r. spectrum of the crude product. Benzenesulphenyl bromide also reacted much more slowly than compound (2) with 3-methylbut-2-enylcobaloxime (8); after heating the reagents in benzene–methylene chloride (1 : 1) at 55 °C for 24 h, the main organic product was a mixture of 3-methylbut-2-enyl phenyl sulphide (28) [4] and 1,1-dimethylallyl phenyl sulphide (29) in the ratio 46 : 54, the former being the more stable isomer. Benzenesulphenyl bromide also reacted slowly with *p*-bromobenzylbis(dimethylglyoximato)pyridinecobalt(III) during 16 h at 55 °C to give *p*-bromobenzyl phenyl sulphide,[4] but no *p*-bromobenzyl bromide was evident in the product.

TABLE 2

^{13}C and ^1H n.m.r. spectra of organic products $RSC_6H_3(NO_2)_2$

	^{13}C [a]				^1H [a]					
R	C-1	C-2	C-3	Me	H-1	H-2	H-3 [b]	H-3′ [c]	Me	M.p. (°C)
$CH_2{:}CH{\cdot}CH_2$	35.6	130.3	120.6		3.85,d	5.9,m	5.45	5.48		71
$CH_2{:}CMe{\cdot}CH_2$					3.77,s		5.17	5.10	1.95	72.5
$CH_2{:}CH{\cdot}CHMe$	44.3	137.8	111.5	20.2	4.08	?	5.30	5.16	1.56,d	73
$CH_2{:}CH{\cdot}CHPh$	54.3	135.1	119.6		5.24	6.15	5.37	5.40		76
$CH_2{:}CPh{\cdot}CH_2$					4.14		5.60	5.51		78—79
$CH_2{:}CH{\cdot}CMe_2$ [10]	53.7	145.2	115.6	28.9		6.17	5.32	5.32	1.60	
cyclopropylCH$_2$ [10]	38.5	8.4	3.9		3.05,d	0.2—1.2 [d]				80
1-MecyclopropylCH$_2$ [10]	44.0	13.7	14.0	22.4	3.07,s		0.62	0.62	1.28,s	121—122
2-MecyclopropylCH$_2$	33.5 [f]	10.9 [f]	12.9 [f]	13.4,[f] 14.2 [f]	3.1,m	0.0—1.4 [d]			1.1	49—50
	38.2 [g]	14.5 [f]	16.6	18.3 [f]						
1,2-Me$_2$cyclopropylCH$_2$					3.13,d [i]				1.23,s [k]	
					3.26,d [i]	0.1—1.6 [j]			1.15,d [l]	
					3.05,s [i]					

[a] δ From $SiMe_4$; numbering of R is from the substituent S. [b] *cis*-H. [c] *trans*-H. [d] Cyclopropyl proton resonances. [e] Isomer A. [f] Cyclopropyl and methyl resonances of isomers A and B. [g] Isomer B. [h] Diastereotopic protons of same methylene group, $J = 11$ Hz, *cis*-isomer. [i] Both protons of methylene group of *trans*-isomer. [j] Cyclopropyl resonances of *cis*- and *trans*-isomers. [k] 1-Methyl resonances of *cis*- and *trans*-isomers. [l] 2-Methyl resonances of *cis*- and *trans*-isomers.

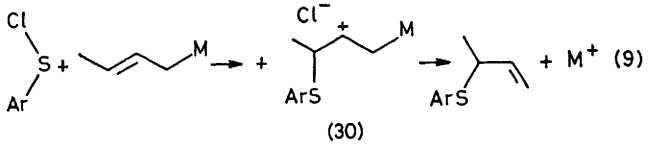
DISCUSSION

The reactions of 2,4-dinitrobenzenesulphenyl chloride show characteristics of a heterolytic electrophilic displacement reaction, being neither influenced by tungsten irradiation nor by the presence of cobaloxime(II). The rapid regiospecific formation of single isomeric, kinetically controlled, organic sulphides from both allyl- and butenyl-cobaloximes is indicative of an attack of the electrophilic sulphur on the γ- and δ-carbon of the allyl and butenyl ligands, respectively, with synchronous or subsequent loss of the cobaloxime(III) complex [equations (9) and (10)]. Intermediates such as (30) and (31), which may be formed, might also be adequately written as the corresponding episulphonium ions. Indeed these reactions parallel the corresponding reactions of allyl- and butenyl-tributyltin compounds,[10] except in so far as the latter are slower, involve fewer side reactions and consequently give higher yields of dinitrophenyl sulphides. They differ markedly from the corresponding radical reactions of diphenyl disulphide, which were strongly accelerated by tungsten light and which gave thermodynamically controlled products from the allylcobaloximes *via* arylthiyl and organic radical intermediates.

The much slower reactions of benzenesulphenyl bromide and chloride are also indicative of heterolytic reactions. The absence of *p*-bromobenzyl bromide in the products of reaction of benzenesulphenyl bromide with *p*-bromobenzylcobaloxime is a good indication that the radical-chain mechanism of equations (1) and (2) is not operative, because all the examples of such radical-chain reactions involving benzylcobaloximes so far investigated [11,12] have had very short chain lengths and appreciable quantities of benzyl radicals have been formed; detectable quantities of *p*-bromobenzyl bromide would therefore have been expected through reaction of *p*-bromobenzyl radicals, formed in the homolysis of *p*-bromobenzylcobaloxime, with benzenesulphenyl bromide [equations (11) and (12)].

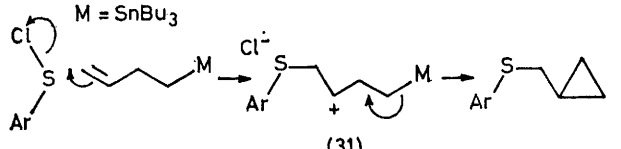
The formation of the less-stable 1,1-dimethylallyl sulphide as the sole product in the reaction of (8) with (2), and as the major product in the reaction of (8) with benzenesulphenyl bromide, is also indicative of a kinetically controlled non-radical process, because rearrangement of the less-stable 1,1-dimethylallyl isomer takes place exclusively to the 3-methylbut-2-enyl isomer in the presence of arylthiyl radicals under milder conditions than obtain in this work.[13] However, the moderate yields of sulphides were clearly a result of competition from other heterolytic side reactions of the sulphenyl chlorides with other ligands of the cobaloxime. Release of pyridine from the axial site would rapidly result in the formation of 2,4-dinitrophenylsulphenylpyridinium chloride and removal of the reagent sulphenyl chloride, but the major side-reaction appears to take place either on the equatorial ligand or on the metal and leads eventually to the *O*-allyl derivative of dimethylglyoxime. Such derivatives are frequently encountered in the reactions of allylcobaloximes with electrophiles,[14] oxidising

agents,[15] and radicals; and whilst it is certain that the attachment of the allyl group to the dimethylglyoxime is an intramolecular process, the nature of the reaction remains obscure. In this case it is possible that the



(30)

M = Co(dmgH)$_2$py
M = SnBu$_3$



(31)

M$^+$ (10)

precursor to the *O*-allyl derivative of dimethylglyoxime contains that molecule bound either to the metal or *via* N or S to the 2,4-dinitrobenzenesulphenyl moiety. One consequence of the substantial loss of dimethyl-

$$PhCH_2Co(dmgH)_2py \rightleftharpoons PhCH_2\cdot + Co^{II}(dmgH)_2py \quad (11)$$

$$PhCH_2\cdot + PhSBr \longrightarrow PhCH_2Br + PhS\cdot \quad (12)$$

glyoxime from the cobaloxime is that the expected chlorobis(dimethylglyoximato)pyridinecobalt(III) is only one of several inorganic products, which were not investigated in detail.

EXPERIMENTAL

Materials.—2,4-Dinitrobenzenesulphenyl chloride (Aldrich), diphenyl disulphide (Fluka), α-methylstyrene, pyridine, bromine, thiophenol, dimethylglyoxime, and cobalt chloride hexahydrate (B.D.H.) were commercial materials used without further purification. Benzenesulphenyl chloride and bromide were prepared from thiophenol and the *N*-halogenosuccinimide [16] and used directly.

2-Phenylallylbis(dimethylglyoximato)pyridinecobalt(III).—α-Methylstyrene was brominated with *N*-bromosuccinimide in carbon tetrachloride to give a mixture of 3-bromo-2-phenylpropene (70%) and 1-bromo-2-phenylpropene (30%).[17] Bis(dimethylglyoximato)pyridinecobalt(II) (0.25 mol) was prepared from cobalt chloride hexahydrate, dimethylglyoxime, pyridine, and sodium hydroxide in aqueous methanol under N_2, and disproportionated with an excess of sodium hydroxide.[18] The crude 3-bromo-2-phenylpropene (very lachrymatory) (0.125 mol) was added and the 2-phenylallylbis(dimethylglyoximato)pyridinecobalt(III) which precipitated was filtered off, washed with water, and dried *in vacuo*. This product was very labile in solution and generally decomposed further during attempted purification by extraction and recrystallisation. It was, therefore, characterised by n.m.r. spectroscopy and by the formation of 2-phenyl-4,4,4-trichlorobutene with bromotrichloromethane.[1] The ^{1}H n.m.r. spectrum showed appreciable dynamic character [19] in $CDCl_3$ [δ 4.20 (4 H, all CH_2 protons) 7.30 (5 H, Ph), 2.05 (12 H, dmgH methyls)] which was greatly reduced in the presence of CCl_4 due to the removal of cobaloxime(II), but could not be entirely eliminated. 2-Phenyl-4,4,4-trichlorobutene had b.p. 107 °C/0.9 mmHg [^{1}H n.m.r. ($CDCl_3$) δ 3.89 (2 H, CH_2), 5.50 and 5.59 (2 H, CH_2=), and 7.53 (5 H, Ph); ^{13}C n.m.r. ($CDCl_3$) δ 58.6 (CH_2), 121.9 (CH_2=), 141.7 or 140.8 (–C=), 126.5 (2C), 128.2 (2C), 127.6 (1C), and 140.8 or 141.7 (1C, Ph), and 98.1 (CCl_3)]. The crude 2-phenylallylbis(dimethylglyoximato)pyridinecobalt(III) was, therefore, used in subsequent experiments.

Allyl-, 2-methylallyl-, but-2-enyl-, cinnamyl-, 3-methylbut-2-enyl-, but-3-enyl-, 3-methylbut-3-enyl-, 1-methylbut-3-enyl, 2-methylbut-3-enyl-, 1,3-dimethylbut-3-enyl-, and 3,4-dimethylbut-3-enyl-bis(dimethylglyoximato)pyridinecobalt(III) were prepared as described earlier.[1,2,20]

Reactions of 2,4-Dinitrobenzenesulphenyl Chloride with Allylcobaloximes.—In a typical reaction but-2-enylbis(dimethylglyoximato)pyridinecobalt(III) (0.38 g, 1.0 mmol) and 2,4-dinitrobenzenesulphenyl chloride (0.80 g, 3.2 mmol) were stirred in CH_2Cl_2 (20 cm^3) for 15 min. The product was chromatographed directly on silica gel (Mallinckrodt CC4 Special), the first fraction eluted by methylene chloride being 1-methylallyl 2,4-dinitrophenyl sulphide, m.p. 73 °C (117 mg, 0.45 mmol, 45%), followed by *O*-(1-methylallyl)dimethylglyoxime (33 mg, 0.22 mmol, 22%).

Reactions of 2,4-Dinitrobenzenesulphenyl Chloride with But-3-enylcobaloximes.—In a typical reaction, 2-methylbut-3-enylbis(dimethylglyoximato)pyridinecobalt(III) (1.0 g, 2.5 mmol) and 2,4-dinitrobenzenesulphenyl chloride (0.6 g, 2.5 mmol) were stirred in methylene chloride (10 cm^3) for 6 h. The reaction mixture was poured into water and extracted with methylene chloride. The organic extract was dried (Na_2SO_4) and chromatographed on silica gel (Mallinckrodt CC4). The first fraction eluted with methylene chloride was a mixture of isomers of 2-methylcyclopropylmethyl 2,4-dinitrophenyl sulphide (200 mg, 0.75 mmol, 30%) uncontaminated with 2-methylbut-3-enyl 2,4-dinitrophenyl sulphide.

Reactions with Benzenesulphenyl Halides.—The reactions with benzenesulphenyl halides were carried out as above, but using freshly prepared solutions of reagent. 1-Methylcyclopropylmethyl phenyl sulphide was identified by ^{1}H n.m.r. spectroscopy [δ 1.16 (s, 3 H, methyl), 0.36 (m, 4 H, cyclopropane), and 2.85 (s, 2 H, CH_2S)], as were 1,1-dimethylallyl phenyl sulphide [δ 1.33 (s, 6 H, methyls), 4.90 and 4.72 (each 1 H, m, CH_2=), and 5.96 (q, 1 H, –CH=)] and 3-methylbut-2-enyl phenyl sulphide [δ 1.57br and 1.70br (each 3 H, s, methyls), 3.55 (d, 2 H, CH_2), and 5.34 (m, 1 H, –CH=)].[4]

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