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HOMOLYTIC DISPLACEMENT AT CARBON

V *. FORMATION OF CYCLOPROPYLCARBINYLSULPHONES AND TRICHLOROETHYLCYCLOPROPANES FROM BUT-3-ENYL COBALOXIMES BY A NOVEL PROCESS INVOLVING HOMOLYTIC ATTACK AT THE δ-CARBON OF THE BUTENYL LIGAND

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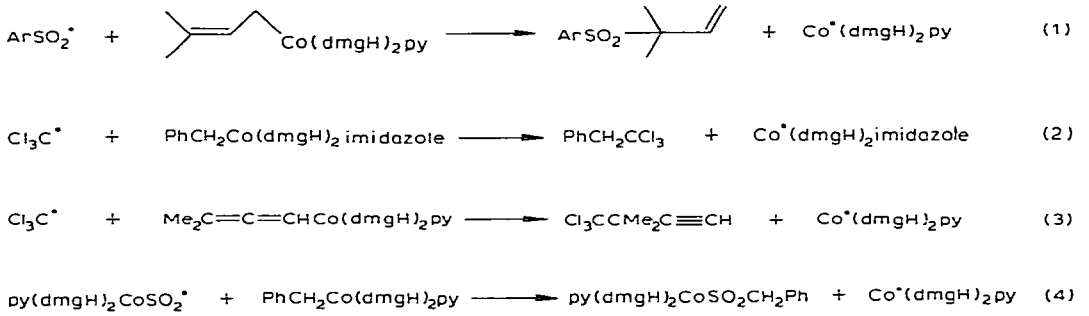
Summary

But-3-enyl- and substituted but-3-enylcobaloximes react with bromotrichloromethane (or trichloromethanesulphonyl chloride) and with 4-toluenesulphonyl chloride thermally or photochemically to give good yields of β,β,β-trichloroethylcyclopropanes and cyclopropylcarbinyl(tolyl)sulphones, respectively. The reactions proceed by a chain mechanism in which a key step is a novel process in which homolytic attack of a trichloromethyl or 4-toluenesulphonyl radical at the δ-carbon of the butenyl ligand leads to synchronous or subsequent attack of the incipient γ-carbon radical on the α-carbon, causing cyclisation and displacement of cobaloxime(II). The other propagation step involves the reaction of the cobaloxime(II) with the bromotrichloromethane, trichloromethanesulphonyl chloride or 4-toluenesulphonyl chloride to give the reactive organic radical.

In a series of papers we have described [1—5] a number of homolytic reactions of σ-bonded organometallic complexes, especially of σ-bonded organocobalt(III) complexes, in which an electrophilic free radical, such as a polyhalogenomethyl radical [2—4], an arenesulphonyl radical [5], or a metallosulphonyl radical [1], attacks the γ-carbon of an allyl or propadienyl ligand, or the α-carbon of a benzyl ligand, with concerted or subsequent loss of a paramagnetic lower-valent metal complex (equations 1—4).

* For Part IV see ref. 1.



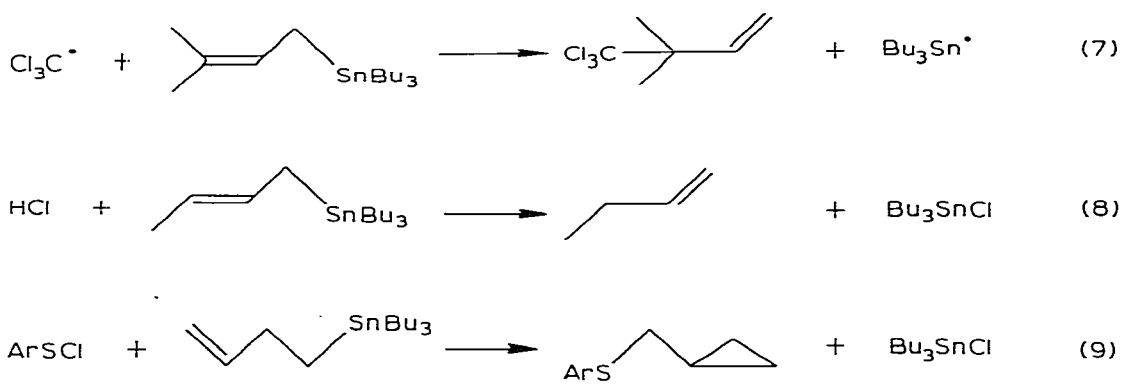
Each of the above reactions forms part of a chain process (equations 5 and 6), sometimes of rather short length, in which the displaced inorganic complex ($M^{\cdot}$ = $Co^{II}(dmgH)_2L$) is instrumental in the production of the electrophilic organic radical ($Y^{\cdot}$ e.g., $Cl_3C^{\cdot}$) from the diamagnetic precursor (XY e.g., $BrCCl_3$).

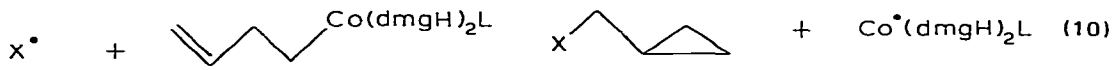
$$M^{\cdot} + XY \rightarrow MX + Y^{\cdot} \quad (5)$$

$$Y^{\cdot} + RM \rightarrow YR' + M^{\cdot} \quad (6)$$

(where R′ represents either a rearranged or an unrearranged organic ligand).

Clearly, there are a variety of substrates (RM) and radical precursors (XY) which might participate in such chain reactions and which might lead to useful regio- and stereo-specific syntheses as a consequence of the concerted character of the organic product-forming step (equation 6). In our search for interesting and synthetically useful examples, two parallels in organocobalt and organotin chemistry suggested to us that such homolytic displacement reactions might be useful in the synthesis of cyclopropane derivatives. First, there is a strong parallel between the regiospecific homolytic displacement of equation 1 and the corresponding regiospecific homolytic displacement of tributyltin(III) radicals from allyltributyltin(IV) compounds (equation 7) [6]. Secondly, there is a strong parallel within organotin chemistry between reaction 7 and the corresponding heterolytic electrophilic displacements (equation 8) from allyltributyltin compounds [7]. Therefore, since but-3-enyltributyltin(IV) reacts with a number of diamagnetic electrophiles to give interesting cyclopropylcarbinyl compounds (equation 9) [8], it seemed possible that the corresponding but-3-enylcobaloximes might undergo similar electrophilic and homolytic displacement reactions, leading to further examples of analogous and novel cyclopropylcarbinyl compounds (e.g. equation 10).





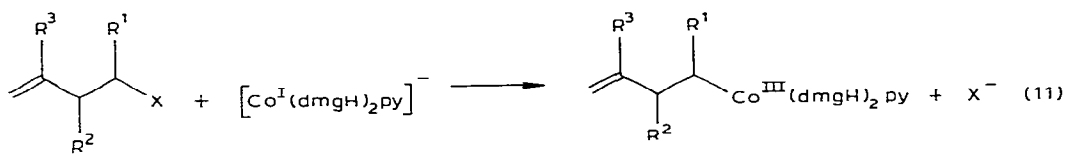
(10)

In this paper are described the syntheses of a number of but-3-enylcobaloximes and details of their reactions, under a variety of conditions, with polyhalogenomethyl and arenesulphonyl radical precursors, which are not themselves electrophilic reagents.

Results

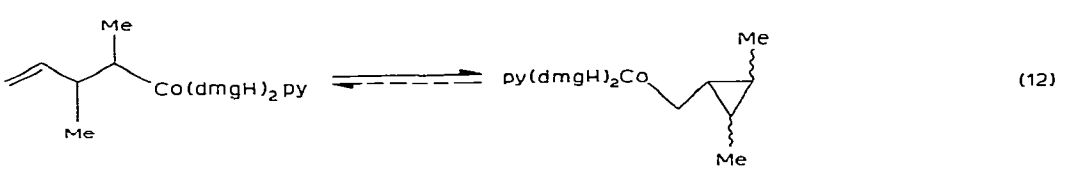
Formation and character of but-3-enylcobaloximes

But-3-enylbis(dimethylglyoximato)pyridinecobalt(III) (**1**) and several mono- and di-methyl, and mono-phenyl-but-3-enylbis(dimethylglyoximato)pyridinecobalt(III) derivatives (**2**—**7**) were prepared by the reaction of the corresponding but-3-enyl bromides or tosylates with the bis(dimethylglyoximato)cobaltate(I) ion in aqueous methanol [9]. No cobaloximes could be recovered from the corresponding reaction of 1-phenylbut-3-enyl bromide, 3-phenylpent-3-en-2-yl bromide, 2-methylpent-4-en-2-yl bromide, or 2,2-dimethylhex-5-en-3-yl tosylate. The crude product of reaction of a mixture of *erythro* and *threo*-3-methylpent-4-en-2-yl tosylate showed the presence of isomers of 3-methylpent-4-en-2-ylcobaloxime (**8**), but on recrystallisation there took place a spontaneous rearrangement into at least two isomers of the cyclic product 2,3-dimethylcyclopropylcarbinylcobaloxime (**9**). The structure of the latter was evident from the absence of olefinic proton resonance and the presence of complex high-field resonances in the region δ0—1 ppm of the proton NMR spectrum, and the number of high field resonances in the carbon-13 NMR spectrum of the product. As reported elsewhere [10,11] pent-4-en-2-ylcobaloxime (**2**) and 2-methylbut-3-enylcobaloxime (**3**) also rearrange on heating into an equilibrium mixture containing **2** and **3** in the ratio ca 1 : 10.



(11)

(1, $R^1 = R^2 = R^3 = H$;
2, $R^1 = Me, R^2 = R^3 = H$;
3, $R^1 = R^3 = H, R^2 = Me$;
4, $R^1 = R^2 = H, R^3 = Me$
5, $R^1 = R^3 = Me, R^2 = H$
6, $R^2 = R^3 = Me, R^1 = H$
7, $R^1 = R^3 = H, R^2 = Ph$

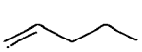
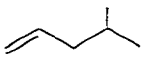
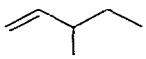
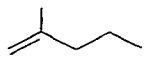
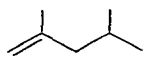
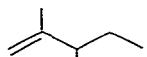
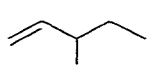
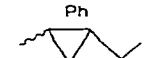


(12)

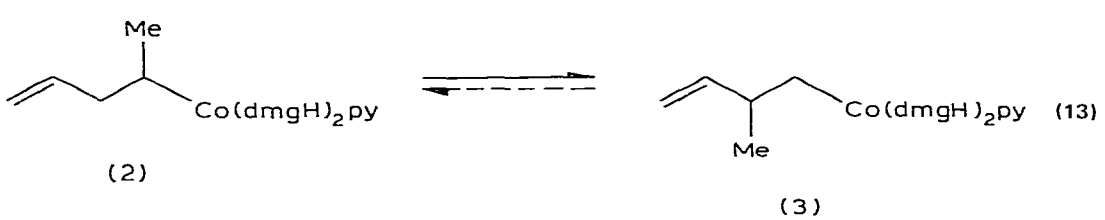
(8) (9)

TABLE 1

CHARACTERISTISTICS OF BUT-3-ENYLBIS(DIMETHYLGLYOXIMATO)PYRIDINECOBALT(III) AND RELATED COMPLEXES ($RCo(dmgH)_2py$)

R	Analysis Found (Calc. %)			^{13}C NMR [a]					
	C	H	N	C(1)	C(2)	C(3)	C(4)	Me	Me
	47.9 (48.2)	6.2 (6.2)	16.7 (16.5)	27.7	34.0	138.9	112.4	—	—
	49.5 (49.4)	6.6 (6.4)	15.4 (16.0)	41.3	43.2	138.4	113.7	21.8	—
	49.1 (49.4)	6.4 (6.4)	16.1 (16.0)	37.0	38.6	146.5	109.6	23.2	—
	49.0 (49.4)	6.5 (6.4)	16.0 (16.0)	28.8	38.4	147.1	108.7	22.6	—
	50.3 (50.6)	6.7 (6.7)	15.1 (15.5)	39.8	47.4	144.9	110.0	21.8	21.8
	49.9 (50.6)	6.7 (6.7)	15.7 (15.5)	35.6	41.7	152.0	106.5	20.0	22.2
 Ph	55.0 (55.3)	6.1 (6.1)	14.2 (14.0)	32.1	50.6	145.9	110.7	—	—
	47.2 (50.6)	6.1 (6.7)	15.0 (15.5)	39.6 [e] 42.0 [e]	[f]				

[a] δ In ppm from TMS. [b] H(2) partially obscured in most cases. [c] Phenyl resonance not shown. [d] Doublet. [e] Main two isomers. [f] Some 13 unassigned resonances in region δ 10—25 ppm due to 3 isomers. [s] singlet. [m] Multiplet.



(2) (3) (13)

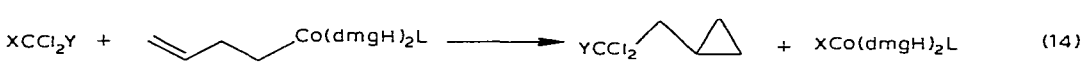
The characteristics and yields of the isolated organocobaloximes are shown in Table 1.

Reaction of but-3-enylcobaloximes with free radical precursors

(a) With polyhalogenomethanes. Butenylcobaloxime (**1**) reacted with bromotrichloromethane in methylene chloride at 50—90°C in sealed tubes to give β,β,β-trichloroethylcyclopropane (**10**) and bromobis(dimethylglyoximato)pyridinecobalt(III) (**11**) in good yield. The yield of **10** was higher when the imidazole complex **1a** was used, when the reaction was carried out photochemically at lower temperature, and when trichlcromethanesulphonyl chloride was used

^{13}C NMR [a]					^{1}H NMR [a]			
Pyridine			dmgH		H(1) [b]	H(4)	Me	dmgH
149.5	137.4	125.0	11.7	149.0	1.62	4.8	—	2.15
149.8	137.4	125.1	12.0	149.5		4.8	0.41	2.14
149.8	137.4	125.1	12.0	149.5		4.7	0.88	2.12
149.9	137.5	125.2	12.0	149.2	1.63 [m]	4.58	1.63 [s]	2.15
149.9	137.3	125.1	12.1	149.4		4.60	1.62 [s] 0.44 [d]	2.23
149.8	137.5	125.2	11.9	149.5	1.2	4.49	1.58 [s] 0.90 [d]	2.12
149.8	137.5	125.1	11.8	149.7 [c]	3.17	4.64 4.68		1.87 [c] 1.89
					~1.7 [d]		~0.98	

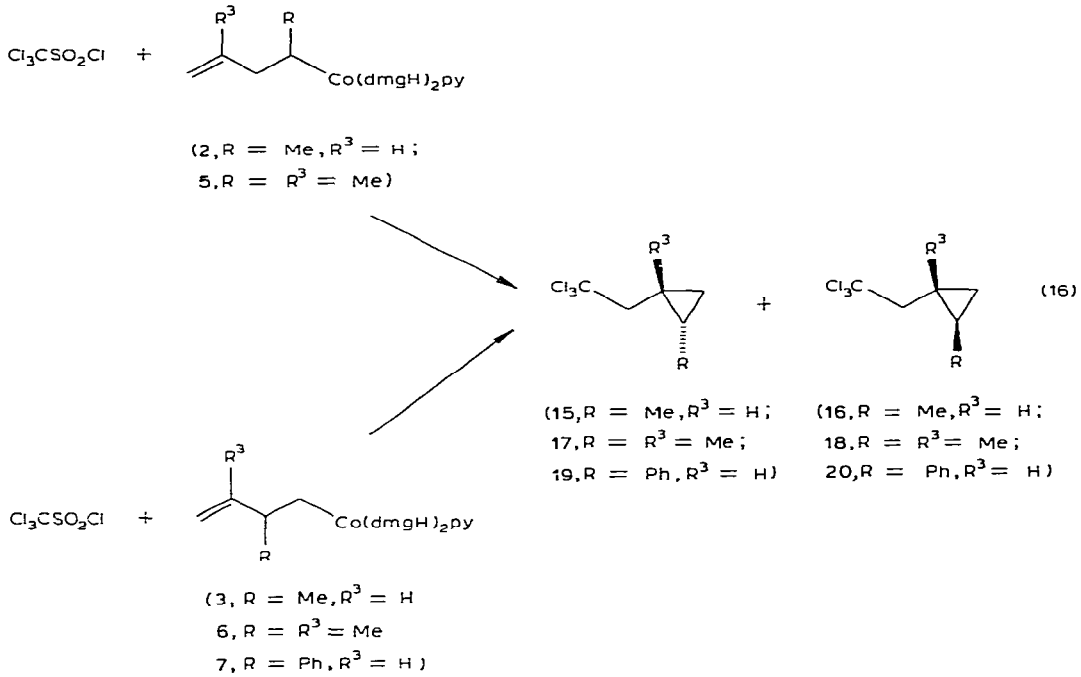
in place of bromotrichloromethane in the thermal reactions (equation 15). Some **10** was formed using carbon tetrachloride as reagent, but the reaction was much slower and the yields were slightly smaller. A similar reaction took place between trichloroacetonitrile and **1** to give β-cyano-β,β-dichloroethylcyclopropane (**12**) (equation 14), but this reaction has not been investigated in detail.



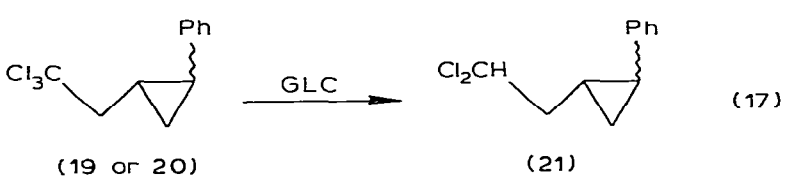
X = Br, Y = Cl (1, L = py; 10, Y = Cl; 11 X = Br;
X = Cl, Y = CN 1a, L = imidazole) 12, Y = CN) 13 X = Cl)

(1, R = H; (10, R = H;
4, R = Me) 14, R = Me)

The reaction of 3-methylbut-3-enylcobaloxime (4) with bromotrichloromethane gave a high yield of the single isomer **14** (equation 14), but reaction of the 1- and 2-methyl derivatives **2** and **3** each gave a similar mixture of the two geometrical isomers **15** and **16**, containing a preponderance of one isomer, the structure of which is discussed below. Two isomeric cyclopropyl derivatives **17** and **18** were formed, but in almost equal proportions, in the corresponding reaction of the dimethylbut-3-enyl derivatives **5** and **6** (equation 16).



No other monomeric trichloromethyl-containing products were identified in the reaction products, though the more volatile but-3-enyl chlorides and bromides were by-products, together with some but-3-enylsulphonyl chlorides from those reactions of trichloromethanesulphonyl chloride [12]. The products **15**—**18** were successfully purified as pairs by HPLC, but attempted purification of **19** and **20** by GLC did not yield either of the products evident in the crude mixture, but a single dichloromethyl derivative **21**. The nature of the reduction process has not been elucidated.

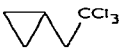
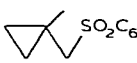
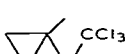
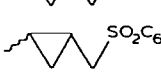
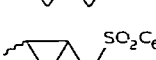
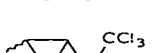
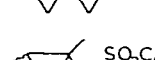
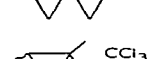
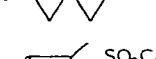
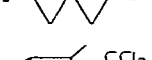
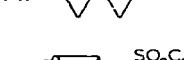


Yields of representative reactions are shown in Table 2, and the characteristics of the cyclopropylcarbinyl products are shown in Table 3.

(b) 4-Toluenesulphonyl chloride. The thermal reactions of 1—7 with 4-toluenesulphonyl chloride gave a variety of products, including low (5—10%) yields

TABLE 2

FORMATION OF CYCLOPROPYLCARBINYLCOMPOUNDS FROM THE REACTION OF BUT-3-ENYLCOBALOXIMES ($RCo(dmgH)_2py$) WITH TRICHLOROMETHYL AND 4-TOLUENESULPHONYL RADICAL PRECURSORS IN METHYLENE CHLORIDE

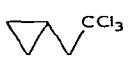
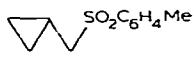
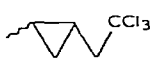
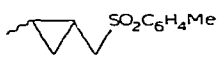
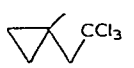
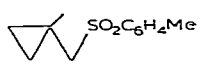
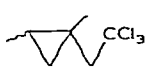
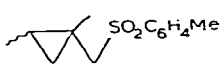
R	Precursor	Conditions [a]	Product(s)	Yield
CH_2=$CHCH_2CH_2$	4-$CH_3C_6H_4SO_2Cl$	15°C 900 watt 1 h 15°C 300 watt 2 h		65 35
	$BrCCl_3$ Cl_3CSO_2Cl	90°C 2.5 h 25°C 1 h		46 75
CH_2=$CMeCH_2CH_2$	4-$CH_3C_6H_4SO_2Cl$	18°C 300 watt 2 h 15°C 900 watt 1 h		18 75
	$BrCCl_3$ Cl_3CSO_2Cl	55°C 2 h 25°C 1 h		85 85
CH_2=$CHCHMeCH_2$	4-$CH_3C_6H_4SO_2Cl$	18°C 450 watt 2 h		65 [b]
	Cl_3CSO_2Cl	60°C 14 h		25 [b]
CH_2=$CHCH_2CHMe$	4-$CH_3C_6H_4SO_2Cl$	18°C 450 watt 2 h		45 [b]
	$BrCCl_3$ $BrCCl_3$ Cl_3SCO_2Cl	90°C 2 h 25°C 0.5 h 300 watt 25°C 20 m		44 [b] 82 [b] 75
CH_2=$CMeCHMeCH_2$	4-$CH_3C_6H_4SO_2Cl$	20°C 300 watt		66 [c]
	Cl_3CSO_2Cl	60°C 14 h		25 [c]
CH_2=$CMeCH_2CHMe$	4-$CH_3C_6H_4SO_2Cl$	18°C 300 watt		34 [c]
	Cl_3CSO_2Cl	60°C 14 h		(55) [c,d]
CH_2=$CHCHPhCH_2$	Cl_3CSO_2Cl	60°C 4 h		(45) [b,e]
	4-$CH_3C_6H_4SO_2Cl$	15°C 900 watt 2 h		35

[a] Irradiation is tungsten spotlights 10 cm from all-glass apparatus. [b] Two isomers in ratio ≥5 : 1. [c] Two isomers in ratio 60 : 40. [d] Not isolated from this experiment, (see above). [e] Identified by NMR. Decomposed in GLC see text.

of cyclopropylcarbinyl(4-tolyl)sulphones. In contrast, the corresponding photochemical reactions, using tungsten illumination through water-cooled Pyrex apparatus and a 1.5—3 fold excess of 4-toluenesulphonyl chloride, gave appreciably higher yields (30—80%) of the expected sulphones **22** and **23** (equation 18), and of mixtures of pairs of sulphones (**24**—**29**; equation 19). The yields (Table 2) of cyclopropylcarbinylsulphones were markedly dependent upon the conditions, being a function of the concentrations and quantities used as well as upon the intensity of the tungsten irradiation. Under our conditions, the best yields

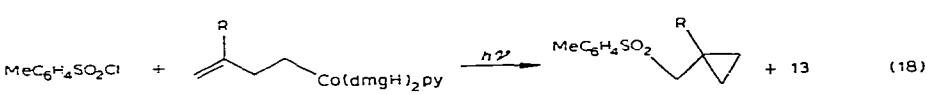
TABLE 3

CHARACTERISTICS OF CYCLOPROPYLCARBINYLSULPHONES AND OF TRICHLOROETHYL-CYCLOPROPANES

Compound	Analysis Found (Calc.) (%)				^{13}C NMR [a]			
	C	H	Cl	S	C(1)	C(2)	C(3)	C(4)
	34.1 (34.6)	4.1 (4.1)	61.8 (61.3)		59.4 [f]	8.5 [g]	4.4 [g]	4.4 [g]
	61.8 (62.8)	6.7 (6.7)			61.4	4.9	4.3	4.3
	38.8 (38.4)	5.0 (4.8)	56.8 (56.7)		59.1 [j]	(12.3, 13.2, 16.9, 18.1) [k]		
					61.9 [j]	(12.4, 12.6, 12.7, 18.1) [k]		
	38.0 (38.4)	4.9 (4.8)	58.1 (56.7)		63.2	obs [n]	14.0	14.0
	63.6 (64.2)	7.2 (7.2)		14.2 (14.3)	65.6	11.0	12.9	12.9
	41.9 (41.7)	5.7 (5.5)	52.5 (52.8)					
	65.1 (65.5)	7.6 (7.6)		13.4 (13.5)	67.9	(13.2, 13.4, 14.4, 14.8, 15.4, 16.8, 16.9, 17.2, 17.8, 19.4, 20.3, 25.0) [k]		
	61.6 (61.4)	5.7 (5.6)	32.3 (32.0)					
	71.2 (71.3)	6.5 (6.3)		11.2 (11.2)	60.7	(22.6, 16.2, 14.5) [k]		

[a] In ppm from TMS, numbering from SO_2Ar or Cl_3C, aromatic resonances excluded. [b] Cyclopropane substituent. [c] Tosyl CH_3. [d] Doublet. [e] Complex resonances in range shown. [f] J(CH) 130 Hz. [g] J(CH) 161 Hz. [h] J 7.7 Hz. [j] Predominant isomer. [k] Assignment uncertain. [l] Diastereotopic CH_2, J = 14.5 Hz. [m] Multiplet. [n] Obscured. [p] Diastereotopic CH_2, major isomer J 15.5 Hz. [q] Diastereotopic CH_2, minor isomer J 16.0 Hz. [r] Diastereotopic CH_2, major isomer J 14.6 Hz. [s] Diastereotopic CH_2, minor isomer J 14.3 Hz. [t] Triplet.

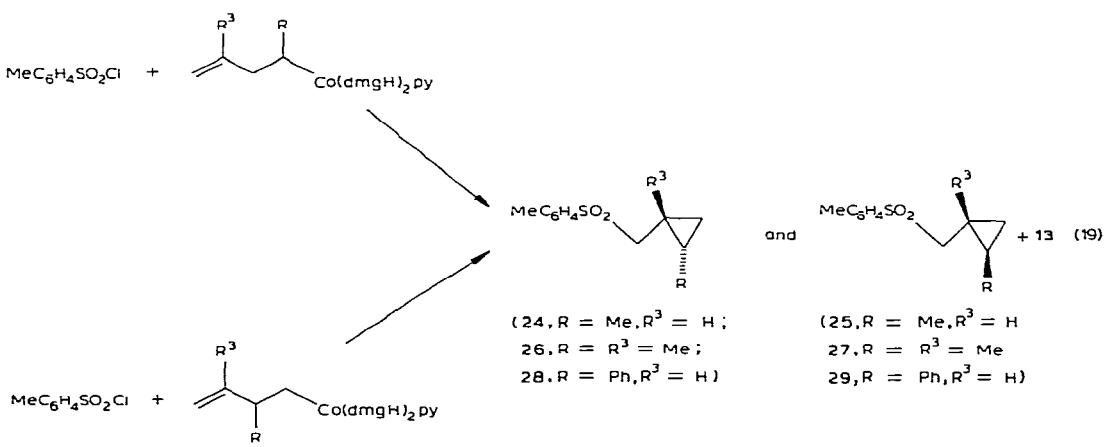
were obtained with 2.5 mmol scale in 10—20 cm^3 with 6 × 150 watt spotlamps at ca. 10 cm from the solution at ⩽18°C.



(18)

(22, R = H;
23, R = Me)

^{13}C NMR			^{1}H NMR [a]				
Me [b]	Cl_3C	CH_3 [c]	H(1)	cyclopropane	Me [b]	CH_3	Other
—	100.3	—	2.63 [d]	0.3—2.0 [e]			
—	—	21.6	2.99 [dh]	0.2—1.5 [e]			
	100.5	—	2.50 [l] 2.70 [l]	0.2—1.0 [e]		2.44	
	—	21.4	3.06 [dh]	0.3—0.7 [e]	0.98	2.54	
23.3	99.9	—	2.73 [s]	0.38 [m] and 0.63 [m]	1.30 [s]		
22.6	—	21.3	3.03 [s]	0.34 [s]	1.20 [s]	2.36	
			2.46 [p] 2.70 [p] 2.77 [q] 3.00 [q]	ca. 0.6 [e]	1.13		
	—	21.6	2.91 [r] 3.16 [r] 3.01 [s] 3.26 [s]	0.05—0.53 [e]	0.93 [d] 1.18 [s]	2.52	
			2.27 [dd]	1.6 —2.0 [e]			5.79 ClC<u>H</u> [t]
	—	21.5	3.18 [d]	0.45—2.3 [e]			



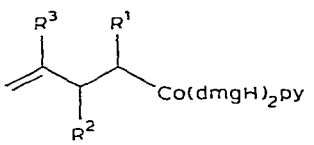
The characteristics of the cyclopropylcarbinylsulphones are shown in Table 3.

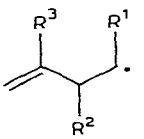
Discussion

Mechanism of the reactions

The cyclic products of the reactions of the several butenylcobaloximes with bromotrichloromethane and the two sulphonyl chlorides are consistent with a process involving attack of a reactive species at the δ-carbon of the butenyl ligand with synchronous or subsequent cyclisation and displacement of the metal complex. The products are inconsistent with the formation and subsequent capture of any but-3-enyl fragment, whether radical [13], carbocation [14], or carbanion [15], each of which would react further to give predominantly open-chain products. The marked photocatalysis and the very weakly electrophilic character of the reagents themselves thus indicate that the reactions are of a radical chain character (equations 20—27), though of relatively short chain length and that the key step involves the anticipated homolytic attack of the trichloromethyl or arylsulphonyl radical at the δ-carbon of the but-3-enyl ligand. In the absence of the bromotrichloromethane, trichloromethanesulphonyl chloride, or 4-toluenesulphonyl chloride, the rate of decomposition of the substrates under the same photochemical conditions is appreciably less.

Initiation:





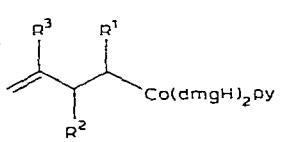
+ $Co^{III}(dmgH)_2py$ (2

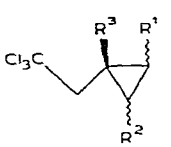
Propagation: $Co^{II}(dmgH)_2py + BrCCl_3 \longrightarrow BrCo^{III}(dmgH)_2py + Cl_3C^{\bullet}$ (2

or $Co^{II}(dmgH)_2py + Cl_3CSO_2Cl \longrightarrow ClCo^{III}(dmgH)_2py + Cl_3C^{\bullet} + SO_2$ (2

or $Co^{II}(dmgH)_2py + MeC_6H_4SO_2Cl \longrightarrow ClCo^{III}(dmgH)_2py + MeC_6H_4SO_2^{\bullet}$ (2

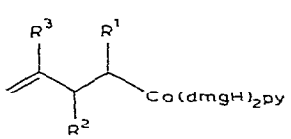
$Cl_3C^{\bullet}$ + and

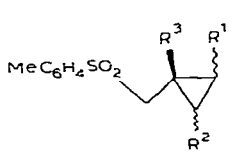




+ $Co^{II}(dmgH)_2py$ (24)

$MeC_6H_4SO_2^{\bullet}$ or





+ $Co^{II}(dmgH)_2py$ (25)

Termination:

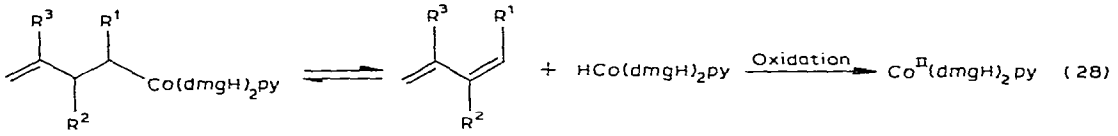
$Cl_3C^{\bullet} + Co^{II}(dmgH)_2py \rightleftharpoons Cl_3CCo^{III}(dmgH)_2py$ (26)

(30)

$MeC_6H_4SO_2^{\bullet} + Co^{II}(dmgH)_2py \longrightarrow MeC_6H_4SO_2Co^{III}(dmgH)_2py$ (27)

(31)

The initiation step (e.g. equation 20) is achieved without added conventional initiators because of the susceptibility of butenylcobaloximes to both thermal and photochemical decomposition into cobaloxime(II) [16,17]. Such initiation is not necessarily only the simple homolysis of the carbon—cobalt bond indicated in equation 20, but may involve the formation and subsequent oxidation of a hydridocobaloxime(III) (equation 28) [17]. Indeed, we have demonstrated the slow formation of the diolefin and hydridocobaloxime(III) in the thermal and photochemical decomposition of several butenylcobaloximes (**2**—**5**) in deuteriochloroform in the presence of phenylacetylene, which is an excellent trap for the hydrido-complex [18], giving the much more stable 1-phenylvinylcobaloxime **32** (equation 29). Such an initiation process would have the particular advantage that organic radicals, which would give rise to unwanted by-products, are not formed and all initiation would involve cobaloxime(II).



(28)

$$PhC{\equiv}CH + HCo^{III}(dmgH)_2py \rightarrow H_2C{=}CPhCo^{III}(dmgH)_2py \quad (29)$$

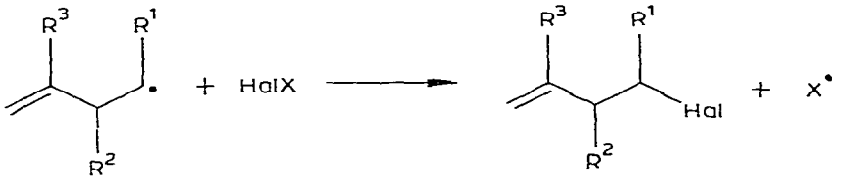
(32)

The evidence for the propagation steps involving bromotrichloromethane, trichloromethanesulphonyl chloride, and toluenesulphonyl chloride, has been discussed in connection with our work on the reactions of allylcobaloximes [2,4,5]. Briefly, both bromotrichloromethane and toluenesulphonyl chloride have been shown to react rapidly with preformed cobaloxime(II) in the absence of organocobaloximes to give good yields of trichloromethylcobaloxime(III) (**30**) and **11**, or toluenesulphonylcobaloxime(III) (**31**) and **13**, respectively, by a radical mechanism involving a combination of equations 21 and 26 or 23 and 27. Under the conditions of our reactions, the concentration of cobaloxime(II) remains sufficiently low so that the termination steps 26 and 27 take place less readily than the propagation steps 24 and 25 involving the high concentration of organometallic substrate. Since cobaloxime(II) neither dimerises nor disproportionates [19] under the reaction conditions, two of the normal termination steps found in conventional chain reactions are excluded, thereby contributing to greater efficiency in the chain propagation.

However, there are undoubtedly a number of other processes which take place to a smaller extent and which lead to unwanted side products. These include intramolecular reactions leading to traces of butenyl derivatives of dimethylglyoxime and, in the reactions of trichloromethanesulphonyl chloride, the formation of sulphonyl chlorides perhaps via chlorosulphonyl radical attack on the substrates [12]. The main side reaction is the formation of but-3-enyl chlorides and bromides by halogen abstraction from the reagent by a but-3-enyl radical (equation 30), which was particularly noticeable in the case of 2-phenylbut-3-enylcobaloxime, probably because of the much lower volatility of the corresponding halides.

We ascribe the poor yields of cyclopropylcarbinyl sulphones in the thermal

reactions of toluenesulphonyl chloride to competition between the radical chain process and heterolytic processes involving the reagent and other ligands on the butenylcobaloxime. For example, with dioximato hydroxyl groups and with the low concentration of free pyridine present in equilibrium with the complex. In order to obtain a reasonable yield of the sulphone, the rate of initiation must be sufficiently high for the rate of the chain reaction to be much greater than those of competing heterolytic processes, as demonstrated by the higher yields using the more intense irradiation. In the case of bromotrichloromethane, heterolytic side reactions play a much less significant role.

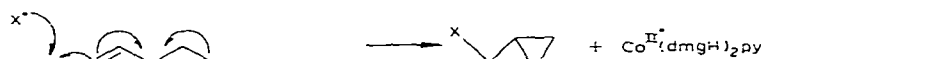


(30)

HalX = $Cl—SO_2C_6H_4Me$, $Cl—SO_2CCl_3$, or $BrCCl_3$

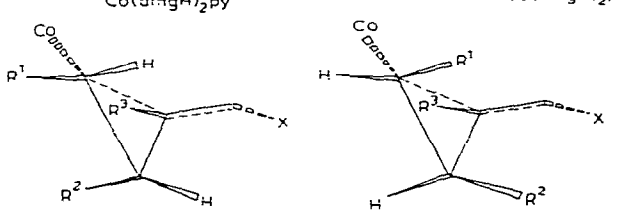
Character of the homolytic displacement step

The exact character of the ring closure step is uncertain, for both truly concerted processes (equation 31) and stepwise processes (equation 32) are possible. However, from the isomer distribution in the products of reaction of the butenylcobaloximes **2, 3, 6** and **7**, the conformation of the transition state for the ring closure can be ascertained. Thus the mono-substituted but-3-enylcobaloximes **2, 3** and **7** each give predominantly one (presumably *trans*) isomer of the cyclic product **16, 20, 25** or **29**, whereas the disubstituted but-3-enyl-cobaloximes give products containing nearly equal proportions of the *cis*- and *trans*-isomers **17** and **18**, or **26** and **27**. Clearly, the 3-methyl substituent and the (initially) olefinic methylene group of the but-3-enyl ligand must lie in equivalent positions with respect to the plane of the forming cyclopropane ring thereby exerting almost equal steric interaction with 1- and 2-methyl groups irrespective of the side of the ring on which they lie (see **32a** and **b**). In the absence of the 3-methyl substituent, the steric interaction is not the same on the two sides of the incipient cyclopropane ring and one product isomer is formed preferentially.



(31)

(32)

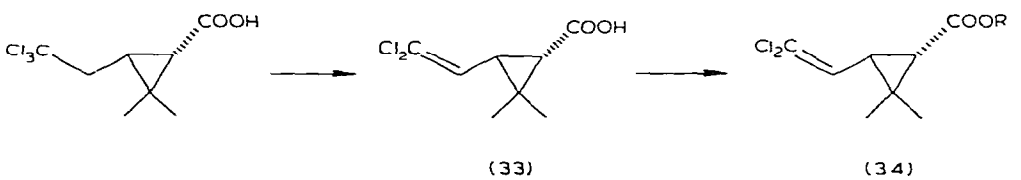


(32a, R^3 = Me or H, R^1 or R^2 = Me or H)

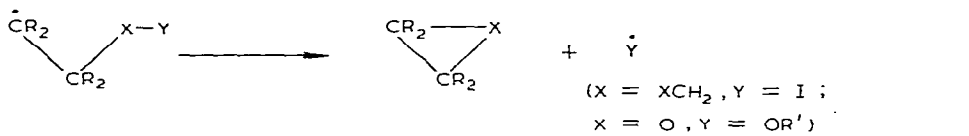
(32b, R^3 = Me or H R^1 or R^2 = Me or H)

Synthetic utility of the homolytic displacement reactions

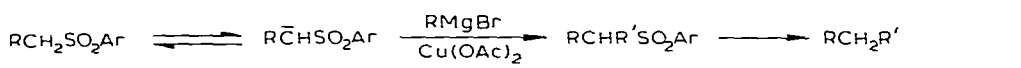
A large number of trichloroethylcyclopropanes have undoubtedly been synthesised, but not necessarily characterized, in the quest for efficient routes to β,β-dichlorovinylcyclopropanes such as NRDC 149 and 143 (34) [20] which are immensely important synthetic pyrethroid insecticides. The homolytic displacement reaction provides a novel route to such compounds, though probably not for **33** because of the problem of synthesising the appropriate substituted butenylmetal precursor. However, the potential of the homolytic displacement reaction may be much wider, not only because of the range of cyclopropylcarbinyl sulphones that might be prepared, but also because of the large number of other electrophilic radicals which might be effective, provided heterolytic side reactions can be eliminated. Moreover, three-membered ring formation may not be confined to cyclopropane ring systems but may be extended to isoelectronic systems, for there are strong analogies between the displacement of cobaloxime(II) shown in equation 32 and the displacement of iodine atoms [21] and alkoxy radicals [22] shown in equation 34. The cyclopropylcarbinylsulphones are also potentially important intermediates in organic synthesis because of the high acidity of protons α to the sulphonyl group, the ease of their copper-catalysed coupling with Grignard reagents [23], and the ease of removal of the sulphonyl group from reaction products (equation 35). [23,23]



(33) (34) (33)



(34)



(35)

Experimental

Materials

Acetaldehyde, acetone (A.R.), 1-chlorobut-2-ene, cinnamyl chloride, ethyl 2-bromopropionate, and 2-methylallyl chloride were commercial materials dried over 4A molecular sieve and distilled just prior to use. Tetrahydrofuran was stored over and distilled from sodium benzophenone ketal under dry nitrogen. Paraformaldehyde was dried over phosphorus pentoxide and used directly or, preferably, depolymerised by heating to 180°C in a stream of dry nitrogen before passing into the reaction mixture. But-3-enyl bromide, trimethylborate, 2,2-dimethylhex-5-en-3-ol were commercial materials used without further puri-

fication, and zinc (A. R. 20 mesh) was dried in the apparatus at 150°C and treated with a crystal of iodine during cooling.

Preparation of alcohols

The alcohols were prepared by either the Grignard reaction [25], or the Barbier reaction [26]. The apparatus, consisting of a three-neck, round bottomed flask equipped with a teflon True-bore stirrer, nitrogen inlet, cond ser and pressure relieving dropping funnel, and the magnesium were heated t 150°C. The magnesium was activated during cooling by addition of a crystal iodine. The flask was cooled to —10°C, the magnesium was covered with anh drous diethyl ether and the reaction was started by dropwise addition of the organic halide in ether containing 0.2% v/v ethylene dibromide. The Grignarc reagent so prepared from 1-chlorobut-2-ene [27] (1 mol), magnesium (2—12 mol) in ether (1 dm^3) was decanted from the excess of magnesium and treate in similarly dried apparatus with acetone (1 mol), or acetaldehyde (1 mol) at —5°C, or with paraformaldehyde (⩾ 1 mol) under reflux. When all the Grign reagent had been consumed [29] the mixture was hydrolysed with saturated aqueous ammonium chloride. The ether was decanted and the remaining sem solid was extracted with ether. The combined ether fractions were dried (Na_2SO_4) and fractionally distilled to give 2,3-dimethylpent-4-en-2-ol (63%), 3-methylpent-4-en-2-ol (78%), and 2-methylbut-3-enol (47%), respectively. S lar treatment of the Grignard reagent from cinnamyl chloride with acetyldeh or gaseous formaldehyde gave 3-phenylpent-4-en-2-ol (83%), and 2-phenylbu enol (54%), respectively. Similar treatment of the Grignard reagent derived fi 2-methylallyl chloride gave 4-methylpent-4-en-2-ol (72%), and 3-methylbut-3 enol (65%).

2,3-Dimethylbut-3-enol

The method of Rathke and Lindert using trimethyl borate and tetrahydro furan with zinc at room temperature was used for the Reformatsky reaction [29]. The reaction was temperamental at the start unless the reagent was drie (4A molecular sieve) and the reaction mixture was initiated before warming; otherwise a violent exothermic reaction ensued. Acetone (73 cm^3, 1 mol), tri methyl borate (250 cm^3) and tetrahydrofuran (250 cm^3) were added to iodine-activated zinc (65.4 g, 1 mol) at 30°C under nitrogen. Ethyl bromoace tate (130 g, 1 mol) was added dropwise while the temperature was carefully monitored. When the reaction started (evident from the formation of a white precipitate and the disappearance of the iodine colour), half of the ester was added. The second half was added after 4 h and the mixture was stirred over night and then kept at 45°C for 4 days until the zinc had all reacted. After treatment with conc. ammonia (250 cm^3) and glycerine (250 cm^3) the organi phase was separated and the aqueous phase was extracted with ether (3 × 25 cm^3). The combined extracts were dried (Na_2SO_4) and fractionally distilled t give ethyl-2,3-dimethyl-3-hydroxybutyrate (91 g.; b.p. 68°C/5 torr) identifie by NMR. The latter was dehydrated with phosphorus pentoxide (98 g) in be zene (400 cm^3) under reflux for 3 h. The benzene phase was washed with wa dried (Na_2SO_4) and distilled to give 2,3-dimethylbut-3-enoate (21 g; b.p. 54–60°C) which was reduced with lithium aluminium hydride (10 g in 500 cm^3

anhydrous ether). Hydrolysis of the mixture with water (10 cm^3), 15% sodium hydroxide (10 cm^3) and water (38 cm^3) followed by ether extraction and work-up gave 2,3-dimethylbut-3-enol (7.9 g; b.p. 76°C/58 torr).

Pent-4-en-2-yl (81%), 2-methylbut-3-enyl- (52%) and 3-methylpent-4-en-2-yl (69%) tosylates were prepared from the alcohols by the method of Golding [30]. 2,2-Dimethylhex-5-en-3-yl and 3-methylbut-3-enyl bromides were each prepared in 30% yield from the corresponding alcohols and PBr_3 in ether.

Preparation of organobis(dimethylglyoximato)pyridinecobalt(III) complexes

But-3-enyl- [31] (76%), pent-4-en-2-yl- (73%), 2-methylbut-3-enyl- (22%), 3-methylbut-3-enyl- (83%), 4-methylpent-4-en-2-yl- (46%), and 2-phenylbut-3-enyl-bis(dimethylglyoximato)pyridinecobalt(III) (20%) were prepared by the reaction of the corresponding bromide or tosylate with a slight excess of the bis(dimethylglyoximato)pyridinecobaltate(I) ion in methanol under nitrogen for 1—48 h at ambient temperature. The mixture was poured into water and the crude organocobaloxime was filtered off, washed copiously with water, dried in vacuo, and either recrystallised before further use from methanol or methylene chloride/pentane mixtures or chromatographed on silica gel (Mallinckrodt CC4) with elution by methylene chloride/ethyl acetate mixtures. The bis(dimethylglyoximato)pyridinecobaltate(I) ion was prepared in situ by the disproportionation of bis(dimethylglyoximato)pyridinecobalt(II) (2 mol) with 8 mol dm^{-3} sodium hydroxide (3.5—4 mol). 2,3-Dimethylcyclopropylcarbinylbis(dimethylglyoximato)pyridinecobalt(III) was similarly prepared in 67% yield by the corresponding reaction of 3-methylpent-4-en-2-yl tosylate with the bis(dimethylglyoximato)pyridinecobaltate(I) ion.

Reactions with 4-toluenesulphonyl chloride

In a typical reaction, the butenylcobaloxime (2.5 mmol) and 4-toluenesulphonyl chloride (5—7.5 mmol) were dissolved in methylene chloride (10 cm^3) and irradiated in a sealed test-tube (1 × 20 cm) with either (a) 2 × 150 watt tungsten spot lamps, or (b) 6 × 150 watt tungsten spot-lamps, at 15—25°C until reaction was complete (usually 1—2 h). The total reaction mixture was chromatographed on silica gel using methylene chloride as eluent giving first the excess of 4-toluenesulphonyl chloride and then the product sulphone (Table 2). Elution with ethyl acetate/acetone mixtures gave chlorobis(dimethylglyoximato)-pyridinecobalt(III) as the major inorganic product.

Reactions with polyhalogenomethanes

In a typical reaction, the butenyl cobaloxime (2.5 mmol) and bromotrichloromethane (20 mmol) in methylene chloride were heated in a sealed tube at from 50—90°C for from 4—1 h, respectively. The excess of methylene chloride was evaporated and the residue was extracted with pentane. After careful evaporation of the pentane, the crude trichloroethylcyclopropane was separated by HPLC or preparative GLC (Table 2).

Reactions with trichloromethanesulphonyl chloride

The butenylcobaloxime (2.5 mmol) and trichloromethanesulphonyl chloride (5 mmol) in methylene chloride (10 cm^3) were allowed to stand in a closed vessel at up to 60°C for 0.5—14 h and worked up as described above.

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