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THERMAL AND PHOTOCHEMICAL REACTIONS OF ALLYLCOBALOXIMES WITH *para*-SUBSTITUTED BENZENESULPHONYL CHLORIDE UNDER AEROBIC AND ANAEROBIC CONDITIONS

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Summary

The compounds p-$XC_6H_4SO_2Cl$ (X = Cl, Br, I, OMe) react regiospecifically with allyl-, 2-methylallyl-, 3-methylallyl- and 3,3-dimethylallyl-cobaloximes under thermal and photochemical conditions. A rearranged organic product is obtained in each case. The yields are much better in photochemical reactions. A chain mechanism is involved in which the organosulphonyl radical and cobaloxime(II) are the chain propagating species. Yields of the sulphones are drastically reduced when the reactions are carried out in the presence of oxygen.

Recently a number of papers have appeared describing the reaction between organometallic complexes of cobalt, rhodium and iridium with polyhalogenomethyl radicals [1,2]. A chain mechanism has been proposed, and the key step involved is the homolytic displacement of a paramagnetic low-valent metal complex by attack of the polyhalogenomethyl radical on the carbon centre of the organometallic complex. The following sequence of reaction is proposed, in which one of the two propagation steps (eq. 3) is a novel process:

$$RM \rightleftharpoons \dot{R} + \dot{M} \qquad (1)$$

$$\dot{M} + XCCl_3 \rightarrow MX + \dot{C}Cl_3 \qquad (2)$$

$$\dot{C}Cl_3 + RM \rightarrow RCCl_3 + \dot{M} \qquad (3)$$

$$\dot{M} + \dot{C}Cl_3 \rightarrow MCCl_3 \qquad (4)$$

R = allyl, butenyl, allenyl, benzyl etc.

Such chain relactions are not confined to polyhalogenomethyl radicals, but have also been observed with other carbon radicals [3] and with sulphur-centred radicals such as sulphonyl radicals [4] derived from arene, alkane, and substituted alkane sulphonyl

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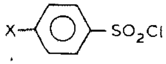
(Continued on p. 204)

TABLE 1

PRODUCTS FROM THE REACTION OF ALLYLCOBALOXIMES, RCo(dmgH)$_2$Py, WITH BENZENESULPHONYL CHLORIDES,



No.	R	X	Product [a]	Yield (%) [b]	M p. (°C) [c]	Analysis (Found (calcd.) (%))		
						C	H	S
1	$CH_2{=}CHCH_2$	Cl	$CH_2{=}CHCH_2SO_2C_6H_4Cl$-*p*	63	32	50.1 (49.9)	4.2 (4.2)	14.7 (14.8)
2		Br	$CH_2{=}CHCH_2SO_2C_6H_4Br$-*p*	80	94	41.2 (41.4)	3.4 (3.5)	12.1 (12.3)
3		I	$CH_2{=}CHCH_2SO_2C_6H_4I$-*p*	57	65	35.2 (35.1)	3.1 (3.0)	10.2 (10.4)
4		OMe	$CH_2{=}CHCH_2SO_2C_6H_4OCH_3$-*p*	65	oil	56.2 (56.6)	5.5 (5.7)	14.9 (15.1)
5	$CH_2{=}C(Me)CH_2$	Cl	$CH_2{=}C(Me)CH_2SO_2C_6H_4Cl$-*p*	81	75	52.1 (52.0)	4.8 (4.8)	13.9 (13.9)
6		Br	$CH_2{=}C(Me)CH_2SO_2C_6H_4Br$-*p*	73	100	43.6 (43.6)	4.1 (4.0)	11.5 (11.6)
7		I	$CH_2{=}C(Me)CH_2SO_2C_6H_4I$-*p*	63	57	37.0 (37.3)	3.3 (3.4)	9.8 (9.9)
8		OMe	$CH_2{=}C(Me)CH_2SO_2C_6H_4OCH_3$-*p*	80	127	58.2 (58.4)	6.2 (6.2)	14.0 (14.2)

9	MeCH=CHCH$_2$	Cl	$CH_2{=}CHCH(Me)SO_2C_6H_4Cl$-*p*	69	67	52.1	4.8	13.8
10		Br	$CH_2{=}CHCH(Me)SO_2C_6H_4Br$-*p*	60	120	43.5 (43.6)	4.0 (4.0)	11.6 (11.6)
11		I	$CH_2{=}CHCH(Me)SO_2C_6H_4I$-*p*	42	oil	37.0 (37.3)	3.3 (3.4)	9.7 (9.9)
12		OMe	$CH_2{=}CHCH(Me)SO_2C_6H_4OCH_3$-*p*	75	oil	58.0 (58.4)	6.1 (6.2)	14.4 (14.2)
13	Me$_2$C=CHCH$_2$	Cl	$CH_2{=}CHC(Me_2)SO_2C_6H_4Cl$-*p*	52	oil	53.9 (54.0)	5.2 (5.4)	13.0 (13.1)
14		Br	$CH_2{=}CHC(Me_2)SO_2C_6H_4Br$-*p*	48	95	45.7 (45.7)	4.5 (4.5)	11.0 (11.1)
15		I	$CH_2{=}CHC(Me_2)SO_2C_6H_4I$-*p*	25	oil	39.0 (39.3)	3.8 (3.9)	9.2 (9.5)
16		OMe	$CH_2{=}CHC(Me_2)SO_2C_6H_4OCH_3$-*p*	54	58	60.0 (60.0)	6.7 (6.7)	13.2 (13.3)

[a] Organic product. [b] Isolated yield. [c] Uncorrected.

halides, but there are few examples of this type:

$$RCo^{III}(dmgH)_2Py + \dot{X} \rightarrow RX + Co^{II}(dmgH)_2Py$$

R = allyl, butenyl, allenyl, benzyl etc.,
X = $CH_3\dot{S}O_2$, *p*-$\dot{S}O_2C_6H_4CH_3$, $NMe_2\dot{S}O_2$ etc.
dmgH = dimethylglyoximato

In this paper we describe the thermal and photochemical reactions of allyl and substituted allyl-cobaloximes with *para*-substituted benzenesulphonyl chloride *p*-$XC_6H_4SO_2Cl$ (X = Cl, Br, I, OMe), under aerobic and anerobic conditions.

TABLE 2

SPECTRAL CHARACTERISTICS OF ALLYLSULPHONES, $\overset{3}{C}H_2=\overset{2}{C}H\overset{1}{C}H(\overset{1'}{Me})SO_2C_6H_4X$-*p*

No.[a]	^{1}H NMR chemical shift (ppm)[b]					Mass (*m/e*)[c]	UV λ (in CH_3OH) (nm)
	Aromatic	1H	2H	3H	1H′		
1	7.5, 7.8 (*J* 9 Hz)	3.8	5.9	5.3	–	216, 175, 111	229, 270, 278
2	7.7	3.75	5.7	5.3	–	260, 219, 155 262, 221, 157	230, 272, 280
3	7.5, 7.8 (*J* 9 Hz)	3.75	5.65	5.2	–	308, 267, 203	247, 278, 289
4	7.0, 7.8 (*J* 8 Hz)	3.8	5.7	5.35	–	212, 171, 107	243, 266, 276
5	7.4, 7.7 (*J* 8.5 Hz)	3.75	–	4.6, 5.0	–	230, 175, 111	230, 265, 274
6	7.7	3.8	–	4.7, 5.1	–	274, 219, 155 276, 221, 157	232, 265, 275
7	7 4, 7.85 (*J* 8.Hz)	3.75	–	4.6, 5.0	–	322, 267, 203	247, 272, 280
8	7.0, 7.75 (*J* 7.5 Hz)	3.75	–	4.7, 5.0	–	226, 171, 107	242, 266, 276
9	7.5, 7.8 (*J* 9.5 Hz)	3.75	5.8	5.2, 5.35	1.45	230, 171, 107	230, 264, 276
10	7.65	3.7	5.75	5.2, 5.35	1.45	274, 219, 155 276, 221, 157	231, 264, 274
11	7.4, 7.6 (*J* 9 Hz)	3.7	5.75	5.0, 5.2	1.4	322, 267, 203	253, 275, 283
12	7.0, 7.7 (*J* 8.5 Hz)	3.8	5.8	5.2,	1.4	226, 171, 107	243, 266, 276
13	7.5, 7.75 (*J* 9 Hz)	–	6.1	5.2, 5.35	1.45	244, 175, 111	232, 260, 274
14	7.7	–	6.0	5.2, 5.3	1.45	288, 219, 155 290, 221, 157	238, 262, 275
15	7.65, 7.9 (*J* 9 Hz)	–	5.94	5.18	1.42	336, 267, 203	262, 268, 280
16	6.95, 7.7 (*J* 7.5 Hz)	–	6.0	5.2,	1.45	240, 171, 107	240, 266, 275

[a] For No. 1 to 16 refer to Table 1. [b] For No. 4, 8, 12, 16; δ (OMe) 3.85 ppm; For No 5 to 8; δ (Me) 1.9; For 9 to 12 ^{1}H appears as quintriplet. [c] *m/e* values refer to M^+, $(M-R)^+$, $(M-R-SO_2)^+$, respectively.

Results and discussion

p-Chlorobenzenesulphonyl chloride, (V), reacts with allylbis(dimethylglyoximato)pyridine cobalt(III) (I) in 1/1 molar ratio in refluxing dichloromethane under nitrogen. A smooth reaction takes place [5], and is complete within 1.5 h, to give the product IX in 80% yield. Similarly 2-methylallyl-, 3-methylallyl- and 3,3-dimethylallyl-cobaloximes (II, III and IV, respectively) react with *p*-chloro-, -bromo-, -iodo- and methoxy-benzenesulphonyl chloride (V, VI, VII and VIII, respectively) under similar conditions to give rise to the corresponding sulphones (IX–XXIV) in 25–81% yield. (A trace amount of *o*-allyldimethylglyoxime ($< 5\%$) was detected in each reaction and characterised by its ^{1}H NMR spectrum [8]. The same products are obtained in higher yields when the reactions are done under photolytic conditions at lower temperature. The characteristics of the products, including their ^{1}H NMR spectral data are given in Tables 1 and 2.

The reactions are regiospecific, and rearranged allyl sulphones are obtained in all cases. (The reactions are regiospecific even in cases in which only small yields are obtained.) The inorganic product in all cases is chlorocobaloxime(III).

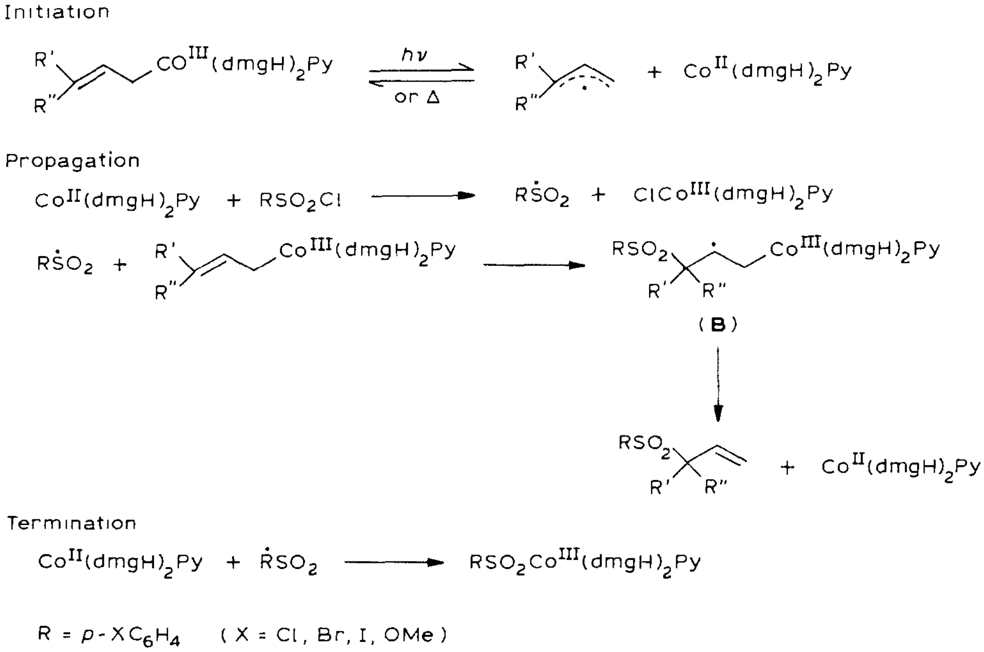
$$\mathrm{R^1R^2C{=}CR^3CH_2Co(dmgH)_2Py + RSO_2Cl \rightarrow}$$
$$\mathrm{RSO_2CR^1R^2CR^3{=}CH_2 + ClCo(dmgH)_2Py}$$

Compound nr.	R	R^1	R^2	R^3
I		H	H	H
II		H	H	Me
III		Me	H	H
IV		Me	Me	H
V	*p*-ClC_6H_4			
VI	*p*-BrC_6H_4			
VII	*p*-IC_6H_4			
VIII	*p*-$OMeC_6H_4$			
IX	*p*-ClC_6H_4	H	H	H
X	*p*-ClC_6H_4	H	H	Me
XI	*p*-ClC_6H_4	Me	H	H
XII	*p*-ClC_6H_4	Me	Me	H
XIII	*p*-BrC_6H_4	H	H	H
XIV	*p*-BrC_6H_4	H	H	Me
XV	*p*-BrC_6H_4	Me	H	H
XVI	*p*-BrC_6H_4	Me	Me	H
XVII	*p*-IC_6H_4	H	H	H
XVIII	*p*-IC_6H_4	H	H	Me
XIV	*p*-IC_6H_4	Me	H	H
XX	*p*-IC_6H_4	Me	Me	H
XXI	*p*-$OMeC_6H_4$	H	H	H
XXII	*p*-$OMeC_6H_4$	H	H	Me
XXIII	*p*-$OMeC_6H_4$	Me	H	H
XXIV	*p*-$OMeC_6H_4$	Me	Me	H

In the thermal reactions, when nitrogen containing oxygen as impurity is bubbled into the reaction mixture, the yield of the required product is drastically lowered, and substantial amounts of cobalt sulphate ($> 25\%$) and a dimethylglyoxime ether product [8] ($> 20\%$) are obtained. However, the reaction remains regiospecific.

The rates of the reactions are lowered by added galvinoxyl and are markedly increased by radical initiators such as benzoyl peroxide (≈ 5% w/w).

The regiospecific nature of products, and the influence of galvinoxyl and benzoyl peroxide point to a free radical mechanism, and indicate that a chain reaction is involved in which the p-$XC_6H_4SO_2\cdot$ radical and cobaloxime(II) are the chain carrying species. It is believed that the mechanism is that proposed by Johnson and coworkers for the reaction of p-toluenesulphonyl chloride with allylcobaloximes [4]. A trace amount of cobaloxime(II) present in all organocobaloximes is sufficient to initiate the reaction. The initiation can also be achieved by thermolysis or photolysis of allylcobaloximes, which is known to generate cobaloxime(II) [6]. The p-$XC_6H_4SO_2\cdot$ radical generated by abstraction of chloride from the sulphonyl chloride by cobaloxime(II) attacks the γ-carbon atom of the allylcobaloxime, displacing the cobaloxime(II), and forms the product either in one step or through a transient intermediate (**B**). The displaced cobaloxime(II) then participates in the chain process by reacting with p-$XC_6H_4SO_2Cl$. The following sequence represents the mechanism (Scheme 1).



SCHEME 1

The attack of sulphonyl radical is regiospecific, and seems to prefer the γ-carbon of the allyl group, resulting in the rearranged organic product. One might expect the sulphonyl radical to attack the less hindered α-carbon of the allyl group but probably attack on the terminal carbon takes place because this leads to subsequent loss of cobaloxime(II). The absence of any product from α-attack confirms the above view.

The formation of o-organodimethylglyoxime derivatives has been observed in many electrophilic and radical reactions of organocobaloximes [7]. The formation of substantial amounts of these ether products along with cobalt sulphate when the reactions are carried out in the presence of oxygen, suggests that whenever a suitable oxidising agent is present, the reactions probably involve the intermediate formation of the radical cation $RCo(dmgH)_2Py^{+}$ by one electron oxidation; the intramolecular transfer of the allyl group to the equatorial ligand can then be viewed either as a nucleophilic displacement of cobalt(IV) by the dimethylglyoxime anion (S_N2' reaction) or as a homolytic displacement of cobaloxime(III) by the dimethylglyoxime radical (S_H2' reaction) and it is very difficult to distinguish between these two mechanisms. The regiospecificity we observed is similar to that noted in earlier studies for reactions for which the S_H2' mechanism was proposed [1,4,7d].

Experimental

Materials

Allyl chloride, 2-methylallyl chloride, and crotyl bromide were all commercial materials, and were used without purification. *para*-Chloro-, -bromo-, -iodo- and -methoxy-benzenesulphonyl chloride were recrystallised before use. Allyl and substituted allylcobaloximes were prepared by the literature procedures from cobaloxime(I) and organic halides [9]. The cobaloxime(I) was generated in situ by anaerobic alkaline disproportionation of cobalt(II) in methanol, as described by Schrauzer [10].

Dimethyl allyl bromide was prepared from isoprene [11].

Preparation of sulphones

Thermal reaction. In a typical experiment a solution of *p*-bromobenzenesulphonyl chloride in dichloromethane (0.60 g in 5 ml) was added with stirring under nitrogen to a solution of 3-methyl-allylcobaloxime (1 g in 15 ml). The mixture was heated under reflux on the water bath, and the progress of the reaction was monitored by TLC. When reaction was complete, mixture was concentrated and poured into ether. The chlorocobaloxime was filtered off and the solvent evaporated from the filtrate to give the organic sulphone in 60% yield. (The sulphones are crystalline in most cases.) The product was further chromatographed on a silica gel plate, with elution with a mixture of CH_2Cl_2 and petroleum ether (1/4). A trace of dimethylglyoxime was isolated in each reaction. The sulphone was recrystallized from n-hexane.

The products were characterised by ^1H NMR, mass spectrometry and elemental analysis.

Photochemical reaction. A mixture of 3-methyl-allylcobaloxime (1.0 g) and *p*-bromobenzenesulphonyl chloride (0.60 g) in dichloromethane (20 ml) was deoxygenated with a nitrogen stream. The solution was irradiated by two 200 W tungsten lamps placed at a distance of 5 cm apart from a water-cooled Pyrex glass apparatus. The temperature was maintained at 0–5 °C during irradiation. The progress of the reaction was monitored by TLC, and it was complete in approx. 1 h. The sulphone was isolated in 75% yield as described above.

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