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HOMOLYTIC DISPLACEMENT AT SATURATED CARBON CENTRE: SYNTHESIS OF BENZYLSULPHONES

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Summary: The reactions of benzyl cobaloximes with p-substituted benzene sulphonyl chlorides under photochemical conditions form benzyl sulphones by novel S_H2 process.

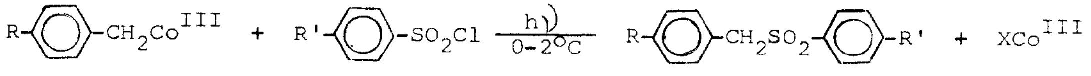
Homolytic displacement of a radical $\dot{Y}$ from a carbon centre by another radical $\dot{X}$, the S_H2 reaction (Eqn. 1) is of immense importance in synthetic organic chemistry:

$$\dot{X} + RCH_2Y \rightarrow RCH_2X + \dot{Y} \qquad .. (1)$$

We have recently described regiospecific substitution reaction of many C or S centred electrophilic free radical precursors with allyl, allenyl, propargyl & butenylcobaloximes to give the substituted allyl, allenyl, propargyl and cyclopropyl methyl products, respectively in high yields.[1,2] In all these reactions a chain reaction has been proposed in which the key steps involved are the homolytic displacement of a paramagnetic cobaloxime(II) by attack of the free radical on the α, γ or δ carbon of the axial organic ligand of the cobaloxime. The similar homolytic displacement reactions at a saturated carbon centre, which until recently were thought to be highly improbable, are only few and are studied only with the polyhalogenomethyl radicals.[3] These reactions are accompanied by many side reactions.

In this paper we report that the reactions of benzylcobaloximes with para-substituted benzenesulphonyl chlorides under thermal and photochemical conditions form organic suphones by the above process. 4-Chlorobenzene sulphonyl chloride 2a reacts with p-methylbenzyl cobaloxime 1b in 1:1 molar ratio in dichloromethane at 0-2°C under anerobic and photolytic conditions. A smooth reaction takes place and is complete within 2 hours to give the sulphone 3e in 37% yield. The reaction is, however, subject to induction period, the length of which depends upon the purity of the substrate cobaloxime. The rate of reaction is lowered by added galvinoxyl and is accelerated by benzoyl peroxide. Similar reactions of benzylcobaloximes 1a-e with 4-chloro-, 4-bromo-, 4-methyl- and 4-methoxy-benzenesulphonyl chlorides 2a-d under identical conditions form benzyl sulphones 3a-t in 8-46% yield. All the reactions are accompanied by bibenzyls 4a-e (p-R-C_6H_4-CH_2-CH_2-C_6H_4-R-p) (R = H, Me, Br, CN, NO_2). Benzyl dimethylglyoxime monoether (p-R-C_6H_4-CH_2-ON=CMe-C(Me)=NOH) (R = H, Me, Br, CN, NO_2) are formed as side products in certain cases (see Table). $ClCo^{III}(dmgH)_2Py$ and p-R'-C_6H_4-$SO_2Co^{III}(dmgH)_2Py$ (R' = Cl, Br, Me, OMe) 5a & 5b are the inorganic cobaloximes isolated in all cases. When the reactions are carried out with one mole excess of pyridine, the yields of the sulphones are improved by approx. 20% and the amount of bibenzyls decreased with no trace of the formation of monoethers. The reaction takes longer time under thermal conditions and the yields are much lower as compared to those under photolytic conditions.

The nature of the products and the influence of initiators and inhibitors on the rates of reaction point to the free radical nature of these reactions. We believe that a chain reaction is involved in which cobaloxime(II) and sulphonyl radicals are the chain carriers and the organic sulphone is formed



1 2 3 4

a, R = H
b, R = Me
c, R = Br
d, R = CN
e, R = NO_2

Co^{III} = $Co(dmgH)_2Py$

dmgH = Dimethylglyoxime monoanion

a, R' = Cl
b, R' = Br
c, R' = Me
d, R' = OMe

a, R = H; R' = Cl
b, R = H; R' = Br
c, R = H; R' = Me
d, R = H; R' = OMe

e, R = Me; R' = Cl
f, R = Me; R' = Br
g, R = Me; R' = Me
h, R = Me; R' = OMe

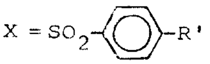
i, R = Br; R' = Cl
j, R = Br; R' = Br
k, R = Br; R' = Me
l, R = Br; R' = OMe

m, R = CN; R' = Cl
n, R = CN; R' = Br
o, R = CN; R' = Me
p, R = CN; R' = OMe

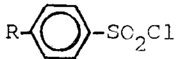
q, R = NO_2; R' = Cl
r, R = NO_2; R' = Br
s, R = NO_2; R' = Me
t, R = NO_2; R' = OMe

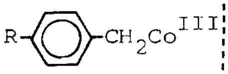
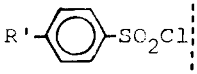
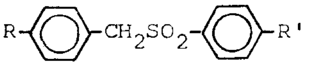
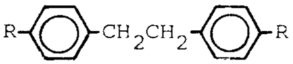
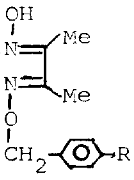
a, X = Cl

b, X =



(R' = Cl, Br,
Me, OMe)

TABLE: Products* of Reaction of Benzylcobaloximes 1a-e with  2a-d Under Photochemical Conditions Using 2 x 200 W Tungsten Lamps

Cobaloxime 				
1a	2a	31	59	-
	2b	30	55	5
	2c	30	58	8
	2d	40	43	-
1b	2a	37	43	8
	2b	33	32	20
	2c	46	21	24
	2d	45	15	-
1c	2a	30	55	5
	2b	32	23	16
	2c	36	57	-
	2d	45	22	-
1d**	2a	15	35	15
	2b	27	31	17
	2c	41	9	9
	2d	40	5	5
1e**	2a	8	38	6
	2b	15	28	9
	2c	20	17	8
	2d	32	22	5

* % isolated yield after chromatographic separation

** Reactions are also carried out in Srinivasan's photoreactor at 25°C using 400 W UV lamp

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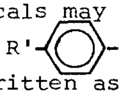
by attack of sulphonyl radical on the α carbon of the benzylcobaloxime (Eqn. 4). The formation of bibenzyls in all cases is indicative of the presence of benzyl-radicals as intermediates which are known to dimerise (Eqn. 6). The formation of the organic sulphones, however, by a combination of benzyl and sulphonyl radicals may also be possible (Eqn. 5). The formation of the termination product $SO_2Co^{III}(dmgH)_2Py$ (Eqn. 7) supports this view. The mechanism can be written as follows:

Initiation: $RCH_2Co^{III}(dmgH)_2Py \rightleftharpoons R\dot{C}H_2 + Co^{II}(dmgH)_2Py$ .. (2)

Propagation: $Co^{II}(dmgH)_2Py + ClSO_2Ar \rightleftharpoons ClCo^{III}(dmgH)_2Py + Ar\dot{S}O_2$ .. (3)

$Ar\dot{S}O_2 + RCH_2Co^{III}(dmgH)_2Py \longrightarrow RCH_2SO_2Ar + Co^{II}(dmgH)_2Py$ .. (4)

Termination: $Ar\dot{S}O_2 + R\dot{C}H_2 \longrightarrow RCH_2SO_2Ar$ .. (5)

$R\dot{C}H_2 + R\dot{C}H_2 \longrightarrow RCH_2CH_2R$ .. (6)

$Co^{II}(dmgH)_2Py + Ar\dot{S}O_2 \longrightarrow ArSO_2Co^{III}(dmgH)_2Py$ .. (7)

The increase in the yield of organic sulphones when the reactions are done in the presence of 1 mole excess of pyridine point that the six coordinate complex is the reactive species which may (i) increase the rate of reaction (4), (ii) prevent the alternative pathway partly or completely in which the free radical $Ar\dot{S}O_2$ attacks the metal and lead to the formation of benzyl radicals.

$$RCH_2Co^{III}(dmgH)_2Py \xrightleftharpoons[+Py]{-Py} RCH_2Co^{III}(dmgH)_2 \xrightleftharpoons[-ArSO_2]{+Ar\dot{S}O_2} RCH_2Co^{IV}(dmgH)_2SO_2Ar$$

$$\longrightarrow R\dot{C}H_2 + ArSO_2Co^{III}(dmgH)_2 \xrightleftharpoons[-Py]{+Py} ArSO_2Co^{III}(dmgH)_2Py$$

The formation of benzyl dimethylglyoxime monoethers supports the intermediate formation of cobalt(IV) species in solution which is known to undergo decomposition with simultaneous abstraction of the organic moiety by S_N2 or S_H2 process[4].

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