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HOMOLYTIC DISPLACEMENT AT CARBON: FIRST EXAMPLE OF α-ATTACK IN THE ALLENYL AND PROPARGYL COBALOXIMES

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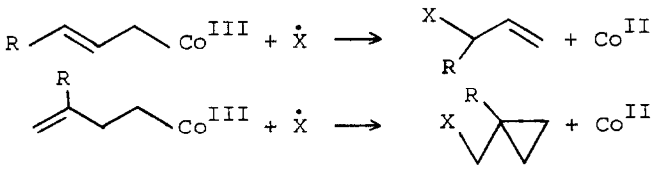
Summary. The reactions of allenyl and propargyl cobaloximes with organosulphonyl chlorides under anaerobic and photochemical conditions form sulphones by a novel homolytic attack at the α carbon to the metal.

A number of papers have described a series of novel displacement reactions between a free radical precursor and diamagnetic σ bonded organometallic complex in which the key step is the homolytic displacement of a paramagnetic metal complex by attack of C, S or N centred radical on the organic ligands of the organometallic complex.[1] The study is of importance in view of very few examples of S_H2 reactions at carbon centre and their use in synthetic organic chemistry.

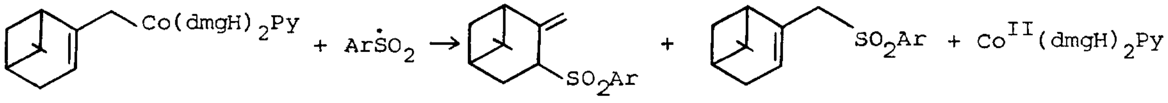


$$R_2\text{-C=C=CH-Co}^{III} + \dot{C}Cl_3 \longrightarrow CCl_3C(R_2)\text{-C}\equiv\text{CH} + Co^{II}$$

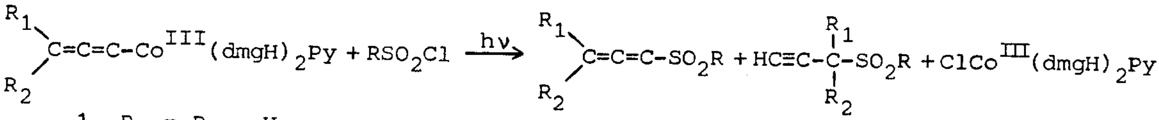
$$\text{Ph-C}\equiv\text{C-CH}_2\text{-Co}^{III} + \dot{C}H(COOEt)_2 \longrightarrow (COOEt)_2CH\text{-C(Ph)=C=CH}_2 + Co^{II}$$

Co = $Co(dmgH)_2Py$; X = CCl_3, CBr_3, CCl_2CN, SPh, RSO_2, $ArSO_2NMe$ etc.

In all these reactions, the organic products are formed by the regiospecific attack of $\dot{X}$ on the terminal carbon of the axial organic group of the organometallic complex. Exception to the terminal attack is rare but has been observed only once when an allylcobaloxime is sterically hindered.[2]



In this paper we report that the allenyl and propargyl cobaloximes undergo an α-attack by the sulphonyl radicals.



1, $R_1 = R_2 = H$

2, $R_1 = R_2 = Me$

3, $R_1 = R_2 = H$

4, $R_1 = R_2 = H$

5, $R_1 = R_2 = Me$

$$\underset{6}{HC{\equiv}C{-}CH_2{-}Co^{III}(dmgH)_2Py} + RSO_2Cl \xrightarrow{h\nu} \underset{4}{HC{\equiv}C{-}CH_2{-}SO_2R} + ClCo^{III}(dmgH)_2Py$$

Products of reactions of allenyl, 3,3-dimethyl allenyl and propargyl cobaloximes (1,2 and 6, respectively) with RSO_2Cl under photolytic and anaerobic conditions.‡

Cobaloxime	RSO_2Cl (R)	Percentage ratio of organic products isolated		
		3	4	5
1, Allenyl $R_1=R_2=H$	CH_3	Nil	100	
	Ph	50	50	
	$4\text{-}FC_6H_4$	100	Nil	
	$4\text{-}ClC_6H_4$	100	"	
	$4\text{-}BrC_6H_4$	100	"	
	$4\text{-}CH_3C_6H_4$	100	"	
	$2,4,5\text{-}Cl_3C_6H_2$	100	"	
	$2\text{-}NO_2C_6H_4$	100	"	
2, 3,3-Dimethyl allenyl $R_1=R_2=Me$	$4\text{-}ClC_6H_4$			100
	$4\text{-}BrC_6H_4$			100
	$4\text{-}CH_3C_6H_4$			100
	$2,4,5\text{-}Cl_3C_6H_2$			100
6, Propargyl	$4\text{-}FC_6H_4$	Nil	100	
	$4\text{-}ClC_6H_4$	"	100	
	$4\text{-}BrC_6H_4$	"	100	
	$4\text{-}CH_3C_6H_4$	"	100	
	$2,4,5\text{-}Cl_3C_6H_2$	"	100	

‡Irradiation with 2 x 200 Watt lamps through all glass apparatus.

The reaction between allenyl bis(dimethylglyoximato)pyridine cobalt(III) (0.61 g, 1.5 mmol), p-toluene sulphonyl chloride (0.48 g, 2.5 mmol) and pyridine (4 drops) in dichloromethane (25 ml) at $10^{o}C$ under photolytic and anaerobic conditions is subject to induction time, the length of which depends upon the conditions, including the purity of the substrate cobaloxime. The rate of reaction is lowered by the added galvinoxyl and is appreciably increased by the addition of radical initiator like benzoyl peroxide ($\leqslant$5% w/w). In most cases, the reaction starts immediately and is complete within 4 hours. p-Tolylallenyl sulphone is the sole organic product isolated in 53% yield. Careful monitoring of this reaction by checking product distribution after every hour indicates the formation of p-tolylallenyl sulphone from the beginning itself and points out further that the sulphone does not isomerise at any stage even when p-toluene sulphonyl chloride and cobaloxime(II) are present in solution. Similar reactions with p-bromo, p-chloro, p-fluoro, o-nitro and 2,4,5-trichlorobenzene sulphonyl chlorides give the corresponding allenyl sulphones in 45-76% yield. However, benzene sulphonyl chloride forms a mixture of allenyl and propargyl sulphone whereas methane sulphonyl chloride forms exclusively the propargyl sulphone. The reaction of allenyl cobaloxime with p-toluene sulphonyl chloride in anaerobic and thermal conditions (refluxing dichloromethane) gives rise to the regiospecific rearranged propargyl sulphone. The corresponding reactions of 3,3-dimethyl allenyl cobaloxime (2) with p-chloro, p-bromo, p-methyl and 2,4,5-trichlorobenzene sulphonyl chlorides under thermal or photochemical conditions afford the regiospecific rearranged propargylic sulphones (5) in 50-75% yield. Propargyl cobaloxime (6) on the other hand, under similar photochemical conditions with p-fluoro, p-chloro, p-bromo-, p-methyl and 2,4,5-trichlorobenzene sulphonyl chloride yields exclusively the propargyl sulphones[3] (4).

The regiospecific nature of the products and the influence of the galvinoxyl and benzoyl peroxide point to a free radical mechanism and indicate that a chain reaction is involved in which $R\dot{S}O_2$ radical and cobaloxime(II) are the chain propagating species. We believe that the mechanism is similar to the one proposed by us for the reaction of allyl cobaloximes with p-substituted benzene sulphonyl chlorides.[1a,b] Since we have not observed any isomerisation of allenyl cobaloxime and allenyl sulphone to the propargyl derivative and vice versa under similar conditions in independent experiments, it is, therefore, a case of first example of the homolytic attack of sulphonyl radicals on the α carbon to the metal. The initial studies indicate that the electrophilicity of the attacking radical and the substituents on the allenyl group play some role in controlling the α or the γ attack, for example, the relatively less electrophilic $CH_3\dot{S}O_2$ radical attacks the γ-carbon whereas the more electrophilic arylsulphonyl radicals attack the α-carbon of the allenyl cobaloxime.

References

1. (a) S. Roy, B.D. Gupta and S. Chaklanobis, J. Organometal. Chem., 269, 201 (1984).
    (b) S. Roy, B.D. Gupta and S. Sen, Indian J. Chem., 24B, 1032 (1985).
    (c) Maheswar Roy, Manoj Kumar and B.D. Gupta, Inorg. Chim. Acta, 114, 87 (1986).
    (d) P. Bougeard, B.D. Gupta and M.D. Johnson, J. Organometal. Chem., 206, 211 (1981).
    (e) M.R. Ashcroft, A. Bury, C.J. Cooksey, A.G. Davies, B.D. Gupta, M.D. Johnson and H. Morris, J. Organometal. Chem., 195, 89 (1980).
    (f) A. Bury, C.J. Cooksey, B.D. Gupta, T. Funabiki and M.D. Johnson, J. Chem. Soc. Perkin II, 1050 (1979).
    (g) B.D. Gupta, T. Funabiki and M.D. Johnson, J. Am. Chem. Soc., 98, 6697 (1976).
    (h) M.D. Johnson, G. Lampman and B.D. Gupta, J. Chem. Soc. Perkin II, submitted.
2. M.D. Johnson, Unpublished work; Acc. Chem. Res., 16, 343 (1983).
3. All products described have been characterised by ^{1}H NMR, mass spectra and elemental analysis.

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