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OXIDATION OF ALLYL-AND ALLENYLCOBALOXIMES BY MANGANESE (III) ACETATE. A NEW ROUTE TO DIMETHYLGLYOXIME MONOETHERS.

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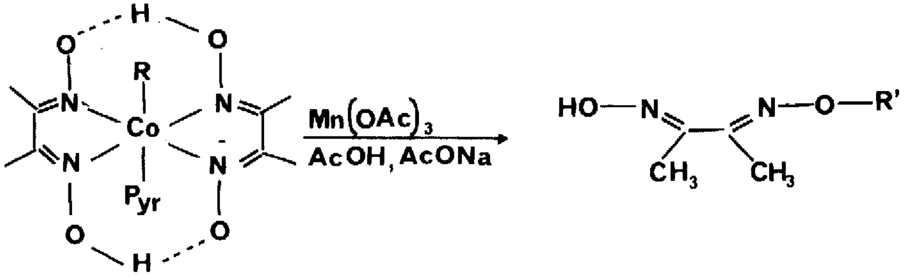
Summary : Oxidation of allyl-and allenylcobaloximes by manganese (III) acetate yields allyl and propargyl ethers of dimethylglyoxime

Great interest has recently been focused on the reaction of allyl(pyridine)cobaloximes RCo(dmgH)$_2$Py 1 (dmgH = dimethylglyoximate monoanion, Py = pyridine) with organic radical precursors (1-4). Manganic acetate Mn(OAc)$_3$ has been shown to be a good source of CH$_2$COOH radical when heated at 150°C (5) and it was tempting to try and prepare substituted acetic acid R-CH$_2$COOH by an SH$_2$ type reaction between this radical and the organocobalt complexes. In fact, heating a solution of Mn(OAc)$_3$ and RCo(dmgH)$_2$Py did not lead to the expected products but instead, when R = benzyl, allyl or allenyl, an intramolecular transfer of the R ligand to one of the dimethylglyoximato ligands was observed giving rise to monoether of dimethylglyoxime of general formula 2. Compound 2a was previously obtained by Halpern *et al.* (6) by oxidation of benzyl(aquo)cobaloxime $C_6H_5CH_2Co(dmgH)_2\ H_2O$ with $IrCl_6^{2-}$ and its structure was elucidated by Johnson *et al.* (7). Moreover the formation of dimethylglyoxime monoethers has been mentioned to occur as a side-reaction in a number of reactions involving organocobaloximes and various electrophilic or oxidising reagents (4,7). However these compounds, except for 2a, have never been fully characterised previously.

In a typical experiment, a solution containing 1 mMole of cobaloxime 1, 2 mMoles of Mn(OAc)$_3$ and 6 Moles of CH$_3$COONa in 20 ml of glacial acetic acid was warmed to 70°C for 30 minutes. After addition of water and extraction of the reaction product by ether, monoether 2 was obtained in relatively pure state and purified by recristallisation. The yields (Table 1) varied markedly with the R group. In the case of allylcobaloximes 1c, d total rearrangement of the allyl group occured as shown by the NMR spectra of the corresponding allyl ethers 2c, d. A similar rearrangement was observed with allenylcobaloximes 1e, f leading to the propargylic ethers 2e, f.

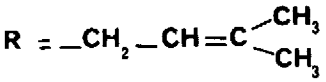
These reactions probably involve the intermediate formation by a one-electron oxydation, of the Co(IV) radical-cation (RCo(dmgH)$_2$Py)$^{\dot{+}}$. Halpern *et al.* (8) have conclusively shown that such species are formed by chemical (Br_2,PbO_2, Ce^{IV}, I^{IV}) or electrochemical oxidation of alkylcobaloximes 1. This radical-cation, which is stable at low temperature, undergoes decomposition at room temperature: in particular nucleophilic attack at the α-carbon is observed when a good nucleophile (e.g.Cl^-) is present. To confirm that the ethers 2 resulted from the rearrangement of an intermediate cobalt(IV) complex, oxydation of the complex 1d with Cerium(IV) ammonium nitrate was performed: the monoether 2d was obtained in 60% yield. The intramolecular transfer of the benzyl, allyl or allenyl group to the equatorial ligand can be viewed either as a nucleophilic displacement of cobalt(IV) by the dmgH anion (S_N2' reaction) or as a homolytic displacement of cobalt(III) by the dimethylglyoximate radical (S_H2' reaction). Although there is no experimental way to distinguish between the two mechanisms, it should be mentioned in support to the latter mechanism, that the reactions between allylcobaloximes and $BrCCl_3$ (1,2), $BrCH(CO_2C_2H_5)_2$ (3) and $ArSO_2Cl$ (4), which have been postulated to be S_H2' reactions, exhibit the same regiospecificity as the present reaction (9).

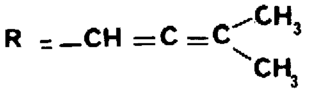


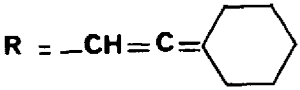
1a R = $C_6H_5-CH_2-$

1b R = $-CH_2-CH=CH_2$

1c R = $-CH_2-CH=CH-CH_3$

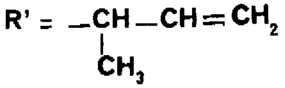
1d 
R = $-CH_2-CH=C(CH_3)_2$

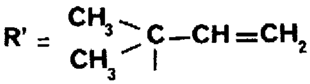
1e 
R = $-CH=C=C(CH_3)_2$

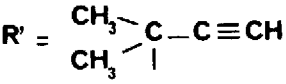
1f 

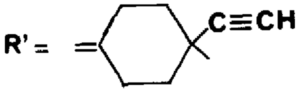
2a R' = $C_6H_5-CH_2-$

2b R' = $-CH_2-CH=CH_2$

2c 
R' = $-CH(CH_3)-CH=CH_2$

2d 
R' = $(CH_3)_2C(-)-CH=CH_2$

2e 
R' = $(CH_3)_2C(-)-C\equiv CH$

2f 

TABLE

REACTION PRODUCTS	YIELD %	MP °C	CHEMICAL SHIFTS (ppm)						
					-O-R'				
			CH_3-C=N	OH	CH_3	=CH	=CH_2	≡CH	O-CH
2a	38	90-92	1.98-2.05	8.37					5.19
2b	41	60-62	2.00-2.06	8.78		6.02	5.27		4.64
2c	47	34-36	2.00-2.07	8.86	1.36	5.90	5.17		4.71
2d	78	oil	2.02-2.11	9.51	1.44	6.05	5.14		
2e	70	90-92	2.06-2.16	8.9	1.67			2.42	
2f	93	102-105	2.00-2.11	9.35				2.45	

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(9) All new compounds prepared in this study were fully characterised by spectroscopic (IR, NMR and mass spectroscopy) methods.

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