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Preliminary communication

COMPLEXATION OF ORGANIC XANTHATES BY CARBONYLIRON IDENTIFICATION OF NEW DINUCLEAR DERIVATIVES

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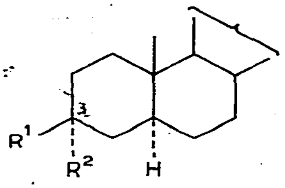
Summary

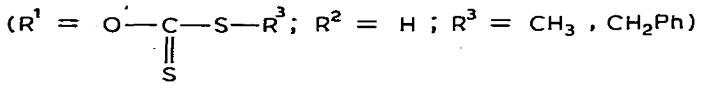
S-Alkyl xanthates of various organic substrates behave as six electron ligands and produce stable dinuclear carbonyliron complexes. The structure proposed for these derivatives is supported by mass spectroscopy, ^{13}C and ^{1}H NMR data, and their chemical properties.

Although *O*-alkyl *S*-alkyl dithiocarbonates (generally referred to as *S*-alkyl xanthates) have been widely used in organic chemistry as protecting groups or during studies of Chugaev elimination, their behaviour towards transition metals does not seem to have been investigated. Transition metal complexes have proved to be useful tools in organic chemistry [1] and for some years we have been interested in organometallic complexes of steroids [2,3] where the metal group can be considered as a protecting group or as a functional centre for syntheses; more recently it has been shown that steroid complexes can be used for immunotherapy studies [4]. In connection with our present studies of activation of C—H bonds of the steroid nucleus we suspected that an electron-rich functional ligand such as an *S*-alkyl xanthate would provide a good site for complexation of transition metal cations. It was also of interest to prepare molecular complexes of xanthates with various carbonylmetals, because the metal would then be in a low oxidation state and bound to the desired site of complexation and so available to be used directly for an activation process. In principle organic xanthates can act as a four or a six electron ligand, and furthermore there can be competition between the *n* orbitals of oxygen and those of sulfur, leading in principle to two different types of complex. We present here preliminary results on the reactions of organic xanthates with nonacarbonyldiiron.

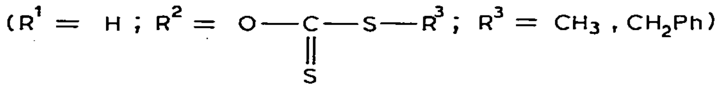
S-Alkyl xanthates of secondary alcohols $R_2CHOC(=S)SR$ were synthetized in one step by known procedures [5]. When various xanthates were allowed to react with $Fe_2(CO)_9$ in toluene at 60°C for fifteen minutes, or in toluene or acetone at room temperature for one day, a complex of type I was obtained in 60—75% yield after TLC on silica.



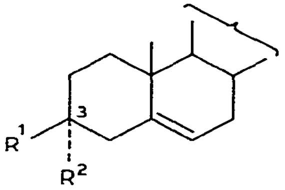
Cholestanol



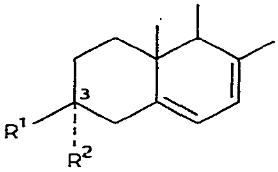
$(R^1 = \mathrm{O{-}\underset{\underset{S}{\|}}{C}{-}S{-}R^3};\ R^2 = \mathrm{H};\ R^3 = \mathrm{CH_3},\ \mathrm{CH_2Ph})$



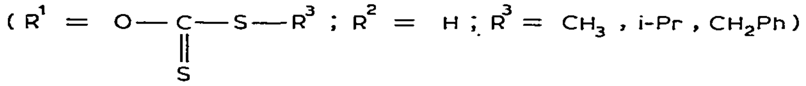
$(R^1 = \mathrm{H};\ R^2 = \mathrm{O{-}\underset{\underset{S}{\|}}{C}{-}S{-}R^3};\ R^3 = \mathrm{CH_3},\ \mathrm{CH_2Ph})$



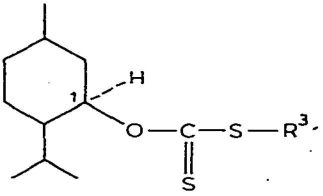
Cholesterol



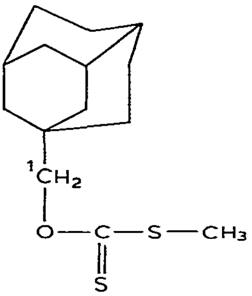
Ergosterol

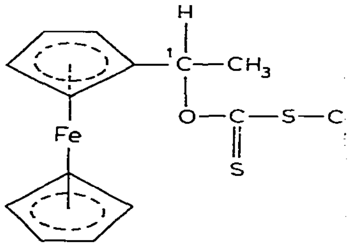


$(R^1 = \mathrm{O{-}\underset{\underset{S}{\|}}{C}{-}S{-}R^3};\ R^2 = \mathrm{H};\ R^3 = \mathrm{CH_3},\ i\text{-}\mathrm{Pr},\ \mathrm{CH_2Ph})$



$(R^3 = \mathrm{CH_3},\ \mathrm{CH_2Ph})$





The analytical data and the mass spectra (except for steroid complexes*) are in agreement with the association of a $Fe_2(CO)_6$ group with the xanthate, thus suggesting that the ligand is probably behaving as a six electron donor. The IR spectra of the complexes show a complex pattern in the 2100—1950 cm^{-1} region for terminal carbonyl ligands, and no bridging carbonyl; in addition a bathochromic shift of $>C{=}S$ is always observed (1050—1080 cm^{-1} in the xanthate and 960—980 cm^{-1} in the complex) as well as bonds associated with Fe—CO bonds (580—600 cm^{-1}). ^{13}C NMR data are also consistent with complexation by the —C(=S)S— grouping: there is a marked downfield shift (80 ppm) for the $>C{=}S$ sp^2 carbon atom, suggesting a significant increase of its

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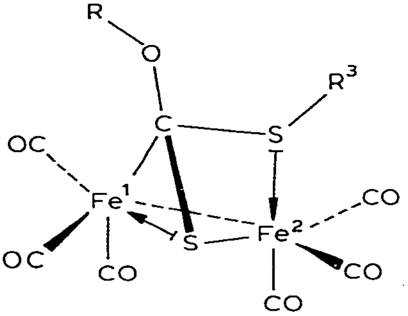
***Molecular peaks of steroid complexes could not be measured owing to the enhanced facility of the Chugaev elimination for these compounds.**

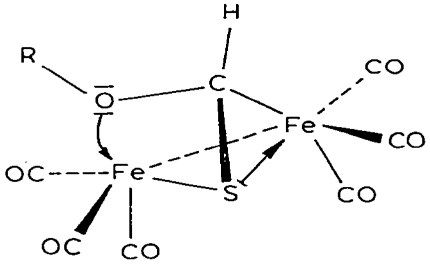
cationic character; the R^3 carbon atoms next to the sulfur are more deshielded in the complexes than C(3) in steroid complexes or C(1) in menthol, adamantane or ferrocene complexes. Proton NMR data favour the same conclusions; there is an upfield shift for the R^3 protons of 0.1 to 0.5 ppm, which is larger than that generally observed for C(3) or C(1) hydrogens.

For comparison cholestanyl and cholesteryl thioformates $R_2CHOC(=S)H$ were prepared [5]. They readily give the $Fe_2(CO)_6$ complexes II, but these are much less stable than xanthate complexes I. The proton NMR of the $Fe_2(CO)_6$ coordinated thioformates show, in addition to the expected high field resonance of the formate hydrogen a considerable upfield shift for C(3) proton (2 ppm), which is consistent with coordination through the *n* orbitals of oxygen.

Structures I (xanthate complexes) and II (thioformate complexes) can be suggested to account for the results.



(I)



(II)

Some complexes of $Fe_2(CO)_6$ containing a metal—metal bond have been produced from azo compounds [6,7] and thio esters [8] which act as six electron ligands; in the latter case the existence of metal—metal bonding is supported by mass spectroscopic data. With our complexes when the molecular peaks can be measured we observe the elimination of carbon monoxide, and in all the mass spectra fragments containing the two iron atoms are present. The $[Fe_2S_2]^+$ (176) and $[Fe_2]^+$ (112) fragments, always present, indicate the presence of a metal—metal bond in complexes I.

A non-classical participation of the π-electrons of the $>C=S$ double bond can account for the chemical properties of complexes I. For instance, attempts at decomplexation by the oxidation—reduction routes usually employed for carbonyl-iron π-complexes do not lead to liberation of the xanthate ligand. Free organic molecules can be recovered as secondary alcohols with retention of configuration after reduction with $LiAlH_4$; this reaction is quantitative and much faster than reduction of xanthates. ^{13}C patterns of the carbonyl ligands in complexes I suggest that the two metal atoms are not equivalent, and only one carbonyl ligand can be replaced by trimethyl phosphite, giving the stable monosubstituted complexes III or IV ($P(OMe)_3$ on iron-1 or iron-2, respectively).

X-ray structure determination now in progress will permit complete understanding of the structure of complexes I, II and III, as well as of their ^{13}C spectra, and should explain the stabilisation of the metal—metal bonds in these derivatives.

Acknowledgement

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