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Radical Substitution on the Sulfur of Thioester Group.
A Substituent Effect on the Reactivity of Thioesters to Methyl Radical

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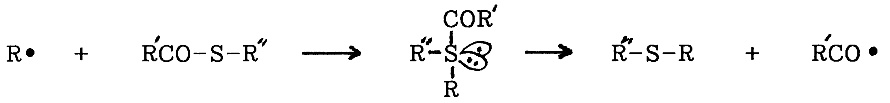
Methyl radical reacts with thioesters (-S-CO-) to give methyl sulfide (CH_3-S-), substitution products on sulfur. The mechanism is proposed in which the methyl radical attacks the sulfur in an nucleophilic manner in the rate determining step to give a sulfuranyl radical intermediate.

We have reported intramolecular or intermolecular radical substitutions on the sulfur of thioesters.[1-3] Thus an alkyl radical attacks the sulfur of a thioester to give a sulfide (Eq. 1), and we proposed the nucleophilic attack of alkyl radical to the sulfur and the rupture of polar acyl group from an axial orientation in an intermediate sulfuranyl radical.[3] Here we like to report the substitution effect on the reactivity of thioesters to the methyl radical generated from methyl-bis(dimethylglyoximato) pyridine-cobalt(III), methyl cobaloxime.

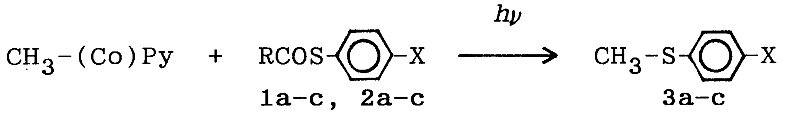


$$R\bullet \;+\; R'CO\text{-}S\text{-}R'' \longrightarrow R''\text{-}\overset{COR'}{\underset{R}{S}}\cdot \longrightarrow R''\text{-}S\text{-}R \;+\; R'CO\bullet \qquad (1)$$

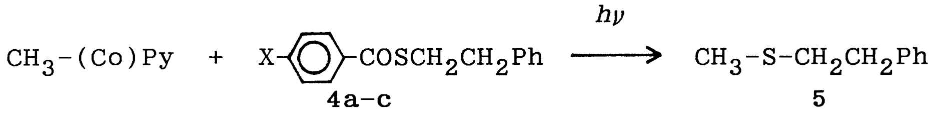
The photoreactions[4] of (arenethio)benzoate (**1**) and methylcobaloxime or (arenethio)pivaloate (**2**) and methylcobaloxime gave sulfides (**3**) as products though most of the starting materials still remained intact (Eq. 2) and the results are listed in Table 1. The mixture of thioester (**4**) and methylcobaloxime was irradiated in the same manner as in the reactions of **1** and **2** (Eq. 3), and the results are also listed in Table 1.

The photolysis of alkylcobaloxime is known to generate a pair of alkyl radical and cobaloxime(II) radical.[5] In the case of methylcobaloxime the photolysis rate is slow since the recombination of the radical pair in the solvent cage is fast.[6] The thioesters are rather stable under the present reaction conditions and the yields are good measure of the relative reactivities of the thioesters to methyl radical. The results show that the para-substituent on the arenethio groups affect the reactivity of the thioesters (1 and 2) to methyl radical. Similar trend is found in the reaction of 4 though the data are less reliable due to the poor reactivity and a little different conditions. Both formation and dissociation of the intermediate sulfuranyl radical are envisaged to be affected by the substituents. Substituent effects in the same direction are expected in the former process whereas it is hardly conceivable that the axial leaving group and the equatorial remaining group have the similar electronic dependence on substituents.

Thus we conclude that the formation of sulfuranyl radical is the rate determining step of the radical substitution and that the sulfuranyl radical intermediate is formed by the attack of methyl radical in a nucleophilic manner since the thioesters having the more electron withdrawing substituent show the higher reactivity (Eq. 1).



(2)



(3)

Table 1. Photoreaction of Methylcobaloxime with Thioesters (1, 2, and 4)

Thioester	R	X	Product	Yield/% in methanol	Yield/% in benzene
1a	Ph	OMe	3a	15	12
1b	Ph	H	3b	24	16
1c	Ph	Cl	3c	32	21
2a	^{t}Bu	OMe	3a	18	17
2b	^{t}Bu	H	3b	22	21
2c	^{t}Bu	Cl	3c	39	33
4a		^{t}Bu	5	6	3[a)]
4b		H	5	13	4[a)]
4c		CN	5	15	13[a)]

a) The photoreactions of 4a-c were carried out by the addition of a 1/7 volume of methanol to benzene to increase the solubility of methylcobaloxime.

References

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3) M. Tada, T. Uetake, and M. Matsumoto, J. Chem. Soc., Chem. Commun., **1990**, 1408.
4) The solutions of thioester (1, 2, and 4) (8.5 mmol/l) were irradiated under the same conditions for 100 h in the presence of 4 equivalents of methylcobaloxime by 350 nm lamps mounted on a Rayonett Photoreactor.
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