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COBALT CARBONYL CATALYZED REACTIONS OF DISULFIDES: CARBONYLATION TO THIOESTERS AND DESULFURIZATION TO SULFIDES

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Summary: aromatic and benzylic disulfides react with carbon monoxide and a catalytic amount of cobalt carbonyl to give thioesters and carbonyl sulfide, while the presence of t-butyl peroxide results in the formation of sulfides in high yields.

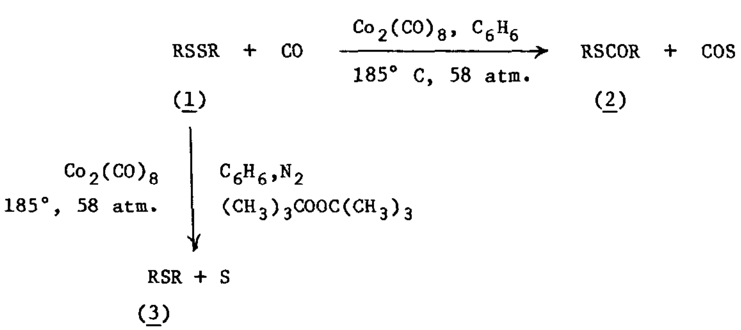
Recently we initiated a study of the desulfurization and/or carbonylation of organic sulfur compounds catalyzed by metal complexes. Cobalt carbonyl is an effective catalyst for the conversion of mercaptans to carboxylic esters using carbon monoxide in aqueous alcohol[1]. Desulfurization to the hydrocarbon occurred when benzene was employed as the reaction

$$\mathrm{RSH} + \mathrm{CO} + \mathrm{R'OH} \xrightarrow[\substack{\mathrm{Co_2(CO)_8} \\ 190^\circ,\ 58\text{-}61\ \mathrm{atm.}}]{\mathrm{H_2O}} \mathrm{RCOOR'} + \mathrm{H_2S}$$

medium[2].

Disulfides are another class of important organic sulfur compounds. It was anticipated that cobalt carbonyl catalyzed carbonylation would result in the formation of thioesters while sulfides or hydrocarbons might be formed on desulfurization. We now describe the interesting results of this investigation.

Reaction of benzyl disulfide (1, R = $PhCH_2$) with carbon monoxide and a catalytic quantity of cobalt carbonyl in aqueous ethanol, at 185°C and 58 atmospheres, afforded the thioester 2, R = $PhCH_2$ in 5% yield, benzyl sulfide (3, R = $PhCH_2$) in 12% yield, and 4% of ethyl benzoate. The use of benzene as the solvent resulted in somewhat higher yields of 2 (22%) and 3 (41%).

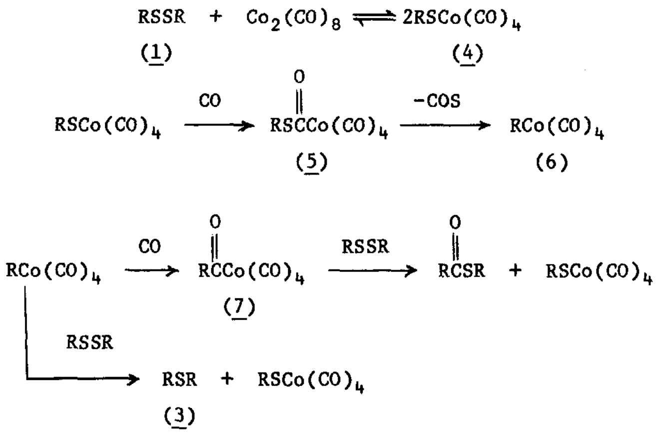


$$\begin{tikzcd}
\underset{(1)}{\mathrm{RSSR}} + \mathrm{CO} \arrow[r, "\mathrm{Co_2(CO)_8},\ \mathrm{C_6H_6}", "185^\circ\ \mathrm{C},\ 58\ \mathrm{atm.}"'] \arrow[d, "\substack{\mathrm{C_6H_6,N_2} \\ \mathrm{(CH_3)_3COOC(CH_3)_3}}", "\substack{\mathrm{Co_2(CO)_8} \\ 185^\circ,\ 58\ \mathrm{atm.}}"'] & \underset{(2)}{\mathrm{RSCOR}} + \mathrm{COS} \\
\underset{(3)}{\mathrm{RSR}} + \mathrm{S} &
\end{tikzcd}$$

When an aromatic disulfide, phenyl disulfide [1, R = Ph], was used as the reactant in aqueous alcohol, phenyl thiobenzoate (2, R = Ph) was formed in low yield (8%). However, in benzene, analytically pure thioester was isolated in 69% yield. This reaction is applicable to a variety of aromatic disulfides, giving thioesters in good yields (See Table 1 for results). No sulfide by-products were detected in these cases. The presence of carbonyl sulfide, which accompanied the thioester, was confirmed by mass spectrometric analysis of the evolved gases. Starting material was recovered when an aliphatic disulfide (e.g., n-butyl disulfide) was used as the reactant.

The formation of thioesters can be rationalized by the pathway outlined in Scheme 1. Reaction of disulfide with cobalt carbonyl may give the thioaryl (or benzyl) cobalt complex 4[3]. This reaction is akin to the known reaction of cobalt carbonyl and hydrogen which affords hydridocobalt tetracarbonyl[4]. Insertion (via ligand migration) would give 5, analogous to the conversion of alkoxy to carboalkoxycobalt tetracarbonyl.[5] Elimination of carbonyl sulfide (see preceding paragraph) would afford 6 and subsequently 7 by carbonyl insertion. The thioester can then result by reaction of disulfide with 7, the by-product being the regenerated catalytic species 4. Sulfide may arise by reaction of $RCo(CO)_4$ (6) with disulfide. Sulfide is not a precursor to thioester, since starting material was recovered on attempted $Co_2(CO)_8$ catalyzed carbonylation of phenyl sulfide.

Scheme 1



In 1964, it was reported that ethyl disulfide reacts with cobalt carbonyl in hexane to form the clusters $Co_4(CO)_5(C_2H_5S)_7$ and $Co_4(CO)_7(C_2H_5S)_3$[6]. The latter types of complexes are not involved in the carbonylaton of disulfides to thioesters since aliphatic disulfides such as n-butyl disulfide do not react under the described conditions, and since $C_4H_9\overset{O}{\overset{\|}{C}}SC_4H_9$ was not formed on attempted carbonylation of $Co_4(CO)_5(C_4H_9S)_7$. However, it is not known whether such polynuclear complexes participate in the carbonylation of n-butyl disulfide under very stringent conditions [250°,990 atm.] - the only previously reported example of

Table 1

Products Obtained from $Co_2(CO)_8$ Catalyzed Reactions of Disulfides in Benzene

1, R=	Reaction Atmosphere	Di-t-butyl Peroxide	Products[a]	Yield,%[b]
$PhCH_2$	CO	No	2,R=$PhCH_2$	22
			3,R=$PhCH_2$	41
	CO	Yes	2,R=$PhCH_2$	19
			3,R=$PhCH_2$	53
	N_2	Yes	3,R=$PhCH_2$	85
p-$CH_3C_6H_4CH_2$	CO	No	2,R=p-$CH_3C_6H_4CH_2$	43
			3,R=p-$CH_3C_6H_4CH_2$	28
	N_2	Yes	3,R=p-$CH_3C_6H_4CH_2$	91
o-$CH_3C_6H_4CH_2$	N_2	Yes	3,R=o-$CH_3C_6H_4CH_2$	90
Ph	CO	No	2,R=Ph	69
p-$CH_3C_6H_4$	CO	No	2,R=p-$CH_3C_6H_4$	41
p-$CH_3OC_6H_4$	CO	No	2,R=p-$CH_3OC_6H_4$	75
m-$CH_3C_6H_4$	CO	No	2,R=m-$CH_3C_6H_4$	82
2-$C_{10}H_7$	CO	No	2,R=2-$C_{10}H_7$	75

[a] Products were identified by comparison of spectral data with those for authentic materials.

[b] Yields are of pure materials, and are based on the disulfide (not on the R group of 1).

the $Co_2(CO)_8$ catalyzed carbonylaton of a disulfide to a thioester.[7]

One can also explain the formation of thioesters and sulfides by a free radical mechanism. The carbonylation reaction of benzyl disulfide in benzene was repeated in the presence of di-t-butyl peroxide, which can function as a radical initiator. The yield of thioester changed only slightly (from 22% to 19%) indicating that peroxide had no influence on its formation. However the yield of sulfide increased appreciably (from 41% to 53%) suggesting that sulfide may arise via the pathway outlined in Scheme 1 and/or by a radical process. In fact, cobalt carbonyl is a fine catalyst for the desulfurization of benzyl disulfide to benzyl sulfide (85% yield - 4% without $Co_2(CO)_8$) when the reaction is conducted with di-t-butyl peroxide in a nitrogen atmosphere - i.e., carbon monoxide retards the desulfurization reaction. Other benzylic disulfides can also experience desulfurization under these conditions (Table 1), but n-butyl disulfide and, as expected, aromatic disulfides are inert.

The following general procedure was used: a mixture of disulfide [6 mmol] and $Co_2(CO)_8$[0.3 mmol] in benzene [30 ml] was heated overnight with stirring at 185°C, under a carbon monoxide atmosphere (58 atm.). After cooling to room temperature, the solution was filtered, and concentration of the filtrate gave the crude thioester. Purification was achieved by preparative thin-layer chromatography using hexane-benzene as the developing solvent mixture. The same procedure was used to obtain sulfides, except that 3-4 drops of di-t-butyl peroxide was added at the beginning of the reaction.

In conclusion, thioesters and sulfides can be obtained from disulfides by simple and convenient cobalt carbonyl catalyzed reactions in the absence or presence of di-t-butyl peroxide.

Acknowledgements

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