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DESULFURIZATION OF MERCAPTANS TO HYDROCARBONS BY CARBON MONOXIDE AND WATER IN THE PRESENCE OF COBALT CARBONYL

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Summary: Benzylic mercaptans and thiophenols undergo desulfurization when exposed to carbon monoxide and water, with cobalt carbonyl as the catalyst; carbonyl sulfide is evolved in these reactions.

Cobalt carbonyl is a valuable catalyst for effecting a number of important chemical processes. Of particular note are the carbonylation of dienes,[1], the hydrosilation and carbonylation of tetrahydrofurans[2], and the hydroformylation of olefins[3]. The cobalt carbonyl catalyzed carbonylation of mercaptans to esters has recently been described.[4] We now wish to report that cobalt carbonyl is a good catalyst for effecting the desulfurization of benzylic and aromatic thiols to hydrocarbons.

When p-methylbenzyl mercaptan [$\underline{1}$,R=p-$CH_3C_6H_4CH_2$] was treated with carbon monoxide, a catalytic amount of cobalt carbonyl [20:1 ratio of RSH/$Co_2(CO)_8$] in benzene-water (30 ml/2 ml), at 185-190°C and 900 psi, p-xylene was isolated in 84% yield. This reacion occurs

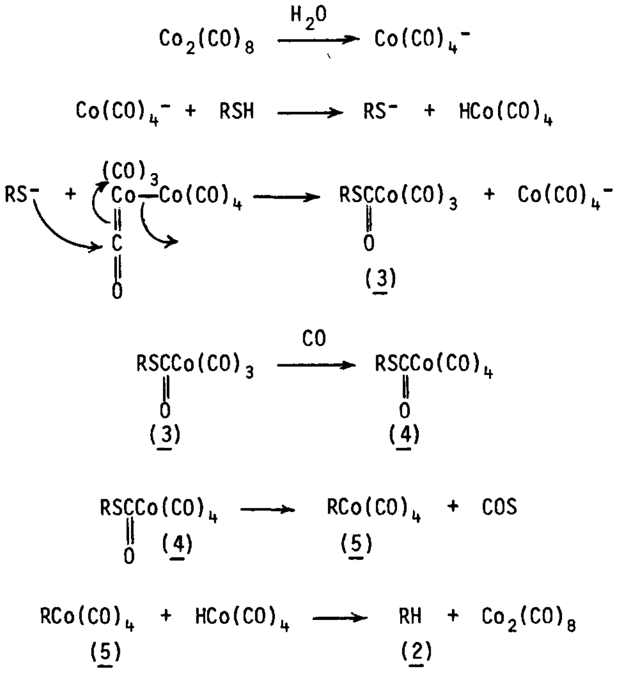
$$\underset{(\underline{1})}{RSH} + CO \xrightarrow[\substack{H_2O,C_6H_6 \\ 185\text{-}190°C \\ 900\ psi}]{Co_2(CO)_8} \underset{(\underline{2})}{RH} + COS$$

using a variety of other benzylic thiols and, as well, thiophenols. Alkane thiols do not react under the described conditions.

This simple, convenient desulfurization process affords hydrocarbons in reasonable yields [see Table 1 for products and yields of the various reactions]. No attempt was made to optimize yields. No reaction occurs in the absence of the metal catalyst. Similarly, starting material was recovered when the reaction was run in the absence of carbon monoxide. In addition, only traces of p-xylene were obtained from p-methylbenzyl mercaptan when the reaction was effected in the absence of water (i.e., water is essential for the desulfurization reaction). Less desulfurization occurred when synthesis gas [i.e., 1:1 CO/H_2] was used instead of carbon monoxide in these reactions, as exemplified by the formation of o-xylene, from o-methylbenzyl mercaptan, in 22% yield with synthesis gas compared with 48% using carbon monoxide. Note that cobalt carbonyl is an ineffective catalyst for the water gas shift reaction[5].

A possible mechanism for the desulfurization reaction is outlined in Scheme 1. The role of water may be to induce disproportionation of cobalt carbonyl to the

Scheme 1



cobalt tetracarbonyl anion[6]. The latter can then deprotonate a thiophenol or benzylic mercaptan affording RS^- and hydridocobalt tetracarbonyl. Attack by $RS^{\ominus}$ on residual cobalt carbonyl would give the thioester cobalt tricarbonyl, 3, and $Co(CO)_4^-$. Carbonylation of 3 would give 4, from which elimination of carbonyl sulfide generates the benzyl or arylcobalt complex 5 (it is of course conceivable that loss of COS occurs from 3). The hydrocarbon (2) is then obtained by reaction of 5 with the previously generated hydridocobalt tetracarbonyl, with $Co_2(CO)_8$ being regenerated. Some evidence for this pathway is that carbonyl sulfide is formed, as determined by mass spectrometric analysis of the evolved gases [intense signal at m/e 60][7].

The following general procedure was used: to the mercaptan (10 mmol.) in benzene (30 ml.) was added cobalt carbonyl (0.5 mmol) and water (2 ml.). The mixture was heated overnight in an autoclave (titanium) at 185-190°C and 900 psi. The solution was cooled to room temperature, analyzed by gas chromatography, and then worked up by distillation or column chromatography.

Table 1

Cobalt Carbonyl Catalyzed Desulfurization of Mercaptans

1,R=	Product[a]	Yield,%[b]
p-$CH_3C_6H_4CH_2$-	p-xylene	84
p-$CH_3OC_6H_4CH_2$-	p-methylanisole	58
p-$ClC_6H_4CH_2$-	p-chlorotoluene	44
2,4-$Cl_2C_6H_3CH_2$-	2,4-dichlorotoluene	63
o-$CH_3C_6H_4CH_2$-	o-xylene	48
m-$CH_3C_6H_4$-	toluene	55
p-BrC_6H_4-	bromobenzene	77
2-$C_{10}H_7$	naphthalene	91

[a] Products were identified by comparison of data [b.p., nmr (^1H,^{13}C),ms] with that for authentic materials. [b] Yields are of purified substances.

In conclusion, cobalt carbonyl is an effective catalyst for the desulfurization of mercaptans. It is clearly superior to the use of cobalt carbonyl (or triiron dodecacarbonyl) under phase transfer conditions. The latter process is stoichiometric as far as the metal carbonyl is concerned, and is applicable only to benzylic mercaptans[8].

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