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PHASE TRANSFER CATALYZED DESULFURIZATION REACTIONS

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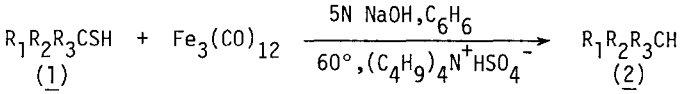
Summary: Mercaptans react with triiron dodecacarbonyl or dicobalt octacarbonyl, under phase transfer catalysis conditions, to give hydrocarbons in good yields.

Phase transfer catalysis [1,2] is a valuable method for effecting a variety of reactions involving organometallic compounds as stoichiometric reagents or catalysts[3]. Examples include the dicobalt octacarbonyl induced carbonylation of Schiff bases to allyl amides,[4] the palladium(o) catalyzed conversion of vinylic dibromides to monoacids or diacids,[5], and the ruthenium(II) catalyzed reduction of nitrocompounds by synthesis gas[6]. We now wish to report the first examples of desulfurization reactions effected by phase transfer catalysis.

Treatment of o-methylbenzyl mercaptan [1,R_1=o-$CH_3C_6H_4$,R_2=R_3=H] with triiron dodecacarbonyl in benzene, sodium hydroxide as the aqueous phase, and tetra-n-butylammonium hydrogen sulfate as



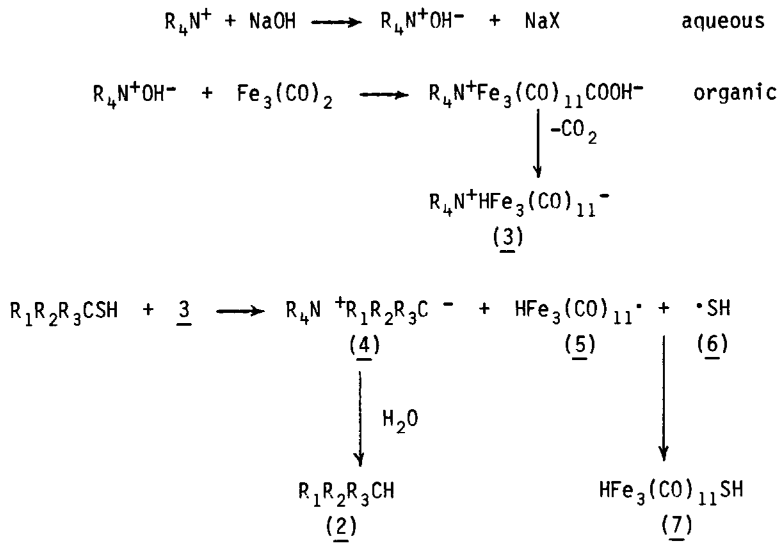
$$\underset{(1)}{R_1R_2R_3CSH} + Fe_3(CO)_{12} \xrightarrow[60°,(C_4H_9)_4N^+HSO_4^-]{5N\ NaOH,C_6H_6} \underset{(2)}{R_1R_2R_3CH}$$

the phase transfer catalyst, for 16 hours at 60°, afforded o-xylene [2,R_1=o-$CH_3C_6H_4$,R_2=R_3=H] in 87% yield. By-products of the reaction were the sulfide and disulfide. No desulfurization occurred when the reaction was repeated in the absence of either the metal carbonyl or the quaternary ammonium salt.

Fine yields of hydrocarbons were obtained from a variety of benzylic, diarylmethyl or triphenylmethyl mercaptans. The products of these reactions, and the yields, are listed in Table 1. The reaction fails when applied to 1-octanethiol or 2-napthalenethiol. Equimolar quantities of mercaptan and triiron dodecacarbonyl were used in these reactions. Using less metal carbonyl (e.g., 3/1:1/$Fe_3(CO)_{12}$) afforded complex mixtures of products. Tetrahexylammonium hydrogen sulfate, benzyltriethylammonium chloride, and dodecyltrimethylammonium chloride are effective phase transfer catalysts, in addition to tetrabutylammonium hydrogen sulfate.

A possible mechanism for this reaction is outlined in Scheme 1. The quaternary ammonium hydroxide, once generated in the aqueous phase and then transferred to the organic phase, will convert triiron dodecacarbonyl to the trinuclear iron hydride 3[3]. Single electron transfer reaction of the hydride with the mercaptan would give the carbanion 4, and radicals 5 and 6.

Scheme 1



(perhaps as a geminate radical pair)[7]. Protonation of the carbanion would then afford the organic product, while 7 may be obtained from coupling of 5 and 6. Therefore, any mercaptan capable of generating a reasonably stable carbanion will undergo desulfurization.

Dicobalt octacarbonyl is one of the most useful metal complexes for phase transfer catalyzed reactions, with cobalt tetracarbonyl anion being generated in a facile manner[3,4,8]. When cobalt carbonyl is used in place of triiron dodecacarbonyl in the desulfurization reactions, hydrocarbons are formed. In fact, the product yields are superior to those realized using $Fe_3(CO)_{12}$ as the reagent (Table 1). It is conceivable that the cobalt carbonyl mediated reaction proceeds by an electron transfer pathway, as proposed for $Fe_3(CO)_{12}$.

The following general procedure was used: a mixture of 5N NaOH, C_6H_6 (25 ml.), and tetrabutylammonium hydrogen sulfate (1.0 mmol) was degassed for 30 minutes. Triiron dodecacarbonyl or dicobalt octacarbonyl (2.0 mmol) was added, the solution was stirred for four hours, followed by addition of the mercaptan (2.0 mmol). The reaction mixture was stirred overnight at 60° (nitrogen atmosphere). The phases were separated, the organic phase was dried ($MgSO_4$), and fractionally distilled.

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TABLE 1

Products Obtained from the Phase Transfer Catalyzed Desulfurization of 1

		Yield(%)^b	
1,$R_1=R_2=R_3=$	Products^a	$Fe_3(CO)_{12}$	$Co_2(CO)_8$
$o\text{-}CH_3C_6H_4$,H,H	2	87	
	$(o\text{-}CH_3C_6H_4CH_2)S$	10	
	$(o\text{-}CH_3C_6H_4CH_2S)_2$	3	
$p\text{-}CH_3C_6H_4$,H,H	2	58	79
	$(p\text{-}CH_3C_6H_4CH_2)_2S$	4	3
	$(p\text{-}CH_3C_6H_4CH_2S)_2$	5	3
$p\text{-}CH_3OC_6H_4$,H,H	2	73	82
	$(p\text{-}CH_3OC_6H_4CH_2S)_2$	12	11
$2,4\text{-}Cl_2C_6H_3$,H,H	2	95	
	$(2,4\text{-}Cl_2C_6H_3CH_2S)_2$	2	
	$(2,4\text{-}Cl_2C_6H_3CH_2)_2S$	3	
Ph,Ph,H	2	82	84
	Ph_3CH	11	10
	$(Ph_2CH)_2S$	5	2
	$(Ph_2CHS)_2$	1	4
Ph,$p\text{-}CH_3OC_6H_4$,H	2	85	100
$p\text{-}CH_3C_6H_4$,$p\text{-}CH_3C_6H_4$,H	2	80	98
Ph,Ph,Ph	2	65	82

[a] Products were identified by comparison of spectral properties (i.r., n.m.r., [^1H, ^{13}C],m.s.) and g.c. retention times with those for authentic samples. [b] Yields by gas chromatography.

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7. It is of course conceivable that the electron transfer reaction could proceed so as to generate $R_1R_2R_3C\cdot$, $HFe_3(CO)_{11}\cdot$, and SH^-. However, in such a process one would expect to isolate at least small amounts of coupled product [e.g., $(o\text{-}CH_3C_6H_4CH_2)_2$ from 1, R_1=o-$CH_3C_6H_4$,R_2=R_3=H].

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