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AN EXCEPTIONALLY MILD, PHASE TRANSFER CATALYZED METHOD FOR THE CONVERSION OF THIOCARBONYL COMPOUNDS TO CARBONYLS

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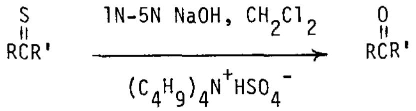
Summary: The thiocarbonyl group of thioketones, dithioesters, thioamides, and thioureas can be converted to the carbonyl function by treatment with sodium hydroxide under phase transfer conditions.

A number of reagents and catalysts have been developed to convert thioketones into ketones, including the recently described use of clay-supported ferric nitrate ["clayfen"].[2] The latter reagent, while superior to many other methods, requires the deposition of ferric nitrate on clay, and works well only for thiobenzophenones. We now wish to report a remarkably simple phase transfer system which enables one to economically desulfurize a wide variety of substrates, at room temperature and one atmosphere.

Treatment of 4,4'-dimethoxythiobenzophenone with 3N sodium hydroxide, methylene chloride as the organic phase, and tetrabutylammonium hydrogen sulfate as the phase transfer agent (N_2 atmosphere), for 40 minutes at room temperature, affords 4,4'-dimethoxybenzophenone in 63% yield.



$$\overset{S}{\underset{}{\|}}\atop{RCR'} \quad \xrightarrow[(C_4H_9)_4N^+HSO_4^-]{1N\text{-}5N\ NaOH,\ CH_2Cl_2} \quad \overset{O}{\underset{}{\|}}\atop{RCR'}$$

R = alkyl, aryl, amino
R' = alkyl, aryl, thioalkyl, amino

This is an authentic phase transfer process since no reaction occurs in the absence of the quaternary ammonium salt. The reaction is applicable to diene thiones such as thioxoandrosta-1,4-dien-3,17-dione and thiocamphor, a simple cyclic thione. This phase transfer process has considerable scope, since the thiocarbonyl group of a dithioester is efficiently converted to the carbonyl group, and amides and ureas are obtained from thioamides and thioureas, respectively (see Table 1 for results).

It is instructive to compare the present process with two other known methods for effecting the noted transformation. One reaction involves treatment of a thiocarbonyl compound with aqueous base [potassium carbonate or triethylamine], chloroform or methylene chloride as the organic phase, bis[4-methoxyphenyl]telluride and an excess of 1,2-dibromotetrachloroethane.[3] The above results demonstrate that an inexpensive, easy to handle quaternary ammonium salt, can be used instead of the toxic organotellurium compound. The second method is the halogen [Cl_2 or Br_2] catalyzed conversion of thiocarbonyl to carbonyl using alkoxides and hydroxide ion.[4] The hydroxide ion phase transfer reaction utilizes very strong base [50% NaOH], benzyltriethylammonium chloride as the phase transfer agent, and requires halogen. While the yield for the phase transfer reaction was only reported in the case of thiobenzamide, it was stated that thiocamphor and benzyl dithiobenzoate afforded many products.[4] Halogen and strong base are not required for the reaction described herein. Note that 4,4'-dimethoxythiobenzophenone was recovered unchanged when exposed to 3N NaOH, CH_2Cl_2, and benzyltriethylammonium chloride for 58 hours at room temperature. The difference in behavior of the latter phase transfer agent and tetrabutylammonium hydrogen sulfate is probably due to the relative extractability, into methylene chloride, of the two quaternary ammonium hydroxides.[5]

Table 1

Desulfurization of Thiocarbonyl Compounds

Reactant	NaOH concentration,N	Reaction time, hours	Product, %[a]
4,4'-dimethoxythiobenzophenone	3	0.67	4,4'-dimethoxybenzophenone, 63
thiobenzophenone	3	1	benzophenone, 90
thiocamphor	5	2	camphor, 79
thioxoandrosta,1,4-dien-3,17-dione	5	8	androsta-1,4-dien-3,17-dione, 72
ethyl dithioacetate	1	7	ethyl thioacetate, 99
γ-dithiobutyrolactone	1	4	γ-thiobutyrolactone, 86
thiobenzanilide	5	3	benzanilide, 51
tetramethylthiourea	5	5	tetramethylurea, 75

[a] Products were identified by comparison with authentic materials.

The following general procedure was used (N_2 atmosphere): a mixture of the $(C_4H_9)_4N^+$ HSO_4^-[0.5-2.0 mmol], NaOH[20 mL], and CH_2Cl_2[25 mL] was stirred for 30 minutes. The substrate [0.15-0.25 g], dissolved in 2-4 mL of CH_2Cl_2, was added and the reaction mixture was stirred at room temperature [see Table 1 for base concentration and reaction times]. The organic phase was separated, washed with dilute HCl and then water, dried ($MgSO_4$) and then concentrated. Further purification, when necessary, was effected by silica gel column chromatography.

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