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Dehalogenation *via* Pyridinium Salts

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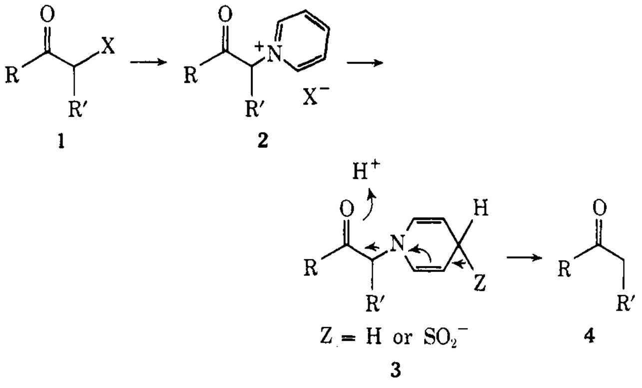
Recently we described a facile dehalogenation using titanous chloride.[1] Our continued effort in the general area of synthetic methodology has led us to explore other means to achieve the removal of halogen atoms adjacent to the carbonyl group.

A new procedure has been developed and is reported here. This method is hinged on the following two separate observations: (a) halogens of α-halo ketones (1) are easily displaced by pyridine,[2] and (b) pyridinium salts undergo facile reduction by dithionite to give 1,4-dihydropyridine derivatives[3] exclusively. Thus reaction of 1 with pyridine followed by addition of aqueous sodium dithionite should afford 3. We conceived that this intermediate would fragment spontaneously to release pyridine and generate the ketone 4. The driving force of the decomposition is aromatization, for which the ketone moiety serves as an excellent leaving group.



The process, although involving sequential addition of two reagents, may be conveniently carried out in a single flask. The novelty of this method lies in the fact that the site of reduction is far removed from the α carbon; thus it is conceptually different from other dehalogenation techniques.[1]

A ketone synthesis[4] which involves alkylation of ketopyridinium betaines has been devised. The pyridine ring was eventually dislodged by zinc dust in acetic acid. (See Table I.)

Table I
Dehalogenation of α-Halo Ketones by Sequential Reaction with Pyridine and Sodium Dithionite

α-Halo ketone	Registry no.	Ketone yield, %	Registry no.
α-Bromocycloheptanone	766-65-4	72	502-42-1
α-Bromocyclododecanone	31236-94-9	56	830-13-7
α-Bromoacetophenone	70-11-1	55	98-86-2
α,*p*-Dibromoacetophenone	99-73-0	65	99-90-1
Desyl chloride	447-31-4	48	451-40-1

Experimental Section

General Procedure for Dehalogenation. The α-halo ketone (5 mmol) was dissolved in acetone (10 ml) and treated with pyridine (10 mmol) either at room temperature (for ArCOCHXR) or at reflux (for alicyclic bromo ketones). Upon complete formation of the salt (monitored by tlc), glacial acetic acid (2 ml) was added, followed by aqueous sodium dithionite (25 mmol in 25 ml). The solution turned orange-brown, then became yellow and finally turbid white. The reaction was exothermic. After 10 min, the product was extracted into benzene and purified by distillation or thick layer chromatography on silica.

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Registry No. Pyridine, 110-86-1; sodium dithionite, 7775-14-6.

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The Facile Oxidation of Thiols to Disulfides with Dithiobis(thioformates)

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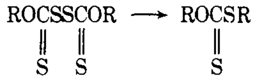
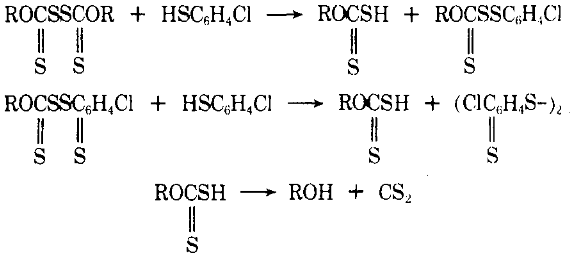
A simple method for replacing hydroxyl groups in starch with thiol groups[2] involves preparing xanthate [ROC(=S)SK], converting it to the dithiobis(thioformate) [ROC(=S)SSC(=S)OR], pyrolyzing to the dithiocarbonate [ROC(=S)SR], and hydrolyzing to the thiol (RSH). The conversion



$$\mathrm{RO}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SS}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{OR} \longrightarrow \mathrm{RO}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SR}$$

was conveniently followed spectrophotometrically by stopping the reaction, destroying unreacted dithiobis(thioformate), and recording the absorption for dithiocarbonate at 8.4 mμ. Unreacted dithiobis(thioformate) in the mixture was rapidly and quantitatively converted to the parent alcohol and carbon disulfide on treatment with *p*-chlorobenzenethiol. Dithiocarbonate was not affected. The mechanism proposed[3] for this conversion by thiol is



$$\mathrm{RO}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SS}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{OR} + \mathrm{HSC_6H_4Cl} \longrightarrow \mathrm{RO}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SH} + \mathrm{RO}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SSC_6H_4Cl}$$

$$\mathrm{RO}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SS}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{_6H_4Cl} + \mathrm{HSC_6H_4Cl} \longrightarrow \mathrm{RO}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SH} + (\mathrm{Cl}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{_6H_4S}\text{-})_2$$

$$\mathrm{RO}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SH} \longrightarrow \mathrm{ROH} + \mathrm{CS_2}$$

A similar mechanism has been reported by Kobayashi, *et al.*,[4] for the oxidative coupling of dithiols by bis(oxycarbonyl) disulfides.

Since the reaction between dithiobis(thioformates) and thiol appeared to be a novel and facile route for converting thiols to disulfides, we wished to determine the generality of this conversion. We selected dimethyl dithiobis(thioformate) because the methanol generated could be readily removed by evaporation, along with the carbon disulfide produced in the reaction. Table I gives the yields

Table I
Disulfides Prepared from the Thiols and Dimethyl Dithiobis(thioformate)

Thiol	Registry no.	Disulfide Registry no.	Obsd mp, °C	Lit. mp, °C	Yield, %
C_6H_5SH	108-98-5	882-33-7	57–58	61–62[5]	100
p-ClC_6H_4SH	106-54-7	1142-19-4	67–69	71–73[5]	100
$HSCH_2CH(NH_2)COOH$	52-89-1	56-89-3	260 dec	260 dec[6]	89
$HSCH_2CH_2SH$	540-63-6	287-39-8	130–150	132–145[4]	71
p-HOC_6H_4SH	637-89-8	15015-57-3	146–148	150[7]	92
$HSCH_2CH_2CO_2H$	107-96-0	1119-62-6	154–156	156–157[5]	100

after treatment of five thiols and one dithiol with dimethyl dithiobis(thioformate).

The product from the oxidation of 1,2-ethanedithiol is apparently poly(ethylene disulfide), which as described by Kobayashi, *et al.*,[4] is insoluble in all common organic solvents. Where applicable, the structures of the disulfides were established by comparison with authentic samples.

The conversions, complete in a few minutes, are conveniently carried out at room temperature. The by-products, methanol and carbon disulfide, and the pyridine (catalyst) were removed by evaporation under a stream of air to leave the solid (usually crystalline) disulfide in essentially pure form. Another advantage of this procedure is its specificity. Oxidants such as iodine, hydrogen peroxide, potassium ferricyanide, and nitric acid are commonly used for converting thiols to disulfides. However, these reagents are also capable of reacting with oxidizable sites in the molecule. Thiols may also be oxidized by air, but considerable time is required and conditions vary for each thiol.

Experimental Section

Preparation of Dimethyl Dithiobis(thioformate). A solution of KOH (10 g) in 10 ml of H_2O was cooled in an ice bath and methanol (20 ml) was added. Then carbon disulfide (20 ml) was added and the mixture was stirred for 1 hr. To the resulting yellow solution was added $NaNO_2$ (3.0 g) and the solution was acidified to pH 4.0 with acetic acid. The mixture was extracted with ether (twice, 75-ml portions). The ether extracts were washed with water, dried with Na_2SO_4, treated with charcoal, and filtered. Solvent was removed at 40° under reduced pressure to give the dimethyl dithiobis(thioformate) (15.7 g) as a yellow oil.

Oxidation of Benzenethiol. To benzenethiol (1.0 g) were added dimethyl dithiobis(thioformate) (1.0 g) and pyridine (0.3 g). The resulting solution was stirred for 1 min, allowed to stand for 5 min, and evaporated to leave a crystalline solid (1.0 g). The product was recrystallized from ethanol, mp 57–58°. Further purification gave mp 60–61° which was unchanged when the product was mixed with an authentic sample.

Anal. Calcd for $C_{12}H_{10}S_2$: S, 29.4. Found: S, 29.4.

In a similar manner p-chlorobenzenethiol and p-mercaptophenol were oxidized to the corresponding disulfides in 100 and 92% yields, respectively.

Oxidation of 1,2-Ethanedithiol. To 1,2-ethanedithiol (1.5 g) were added dimethyl dithiobis(thioformate) (3.52 g) and pyridine (3.0 ml). Within 1 min the product precipitated as a white solid, which was washed with acetone, yield 1.1 g, mp 130–150°. The product was insoluble in all common organic solvents.

Anal. Calcd for $C_2H_4S_2$: S, 69.6. Found: S, 71.0.

Oxidation of Cysteine Hydrochloride. To a solution of cysteine hydrochloride (1.75 g) in ethanol (5.0 ml) were added dimethyl dithiobis(thioformate) (1.07 g) and pyridine (0.5 ml). Immediately, a white percipitate formed. The mixture was stirred for 1 min, kept for 5 min, and filtered. The solid was washed with ethanol (10 ml) and acetone (10 ml) and dried, yield 1.09 g (89%), mp 260° dec.

Anal. Calcd for $C_6H_{12}N_2O_4S_2$: S, 26.7. Found: S, 26.5.

Registry No. Dimethyl dithiobis(thioformate), 1468-37-7.

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Sulfinic Esters. III. A New Sulfinic Ester Synthesis[1]

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In previous publications[2,3] from this laboratory we described the preparation of sulfinic esters by the reaction of alcohols with sulfinyl chlorides. This remains a good general method of wide application especially in view of the ease with which sulfinyl chlorides may be prepared by the chlorination of disulfides or thiol esters in acetic anhydride.[4,5]

We have recently observed that sulfinic esters may also be synthesized directly by the low-temperature chlorination of disulfides in alcohols (eq 1). When the disulfide and chlorine are used in stoichiometric amounts with a small excess over the theoretical amount of alcohol, the crude ester is produced in 60–85% yield. The crude product is contaminated with chlorine-containing by-products, chiefly the sulfinyl and sulfonyl chlorides, and the yield is somewhat further reduced by the formation of the corresponding thiolsulfonic ester, RSO_2SR. The symmetrical thiolsulfonic esters boil higher than the sulfinic esters and can be removed by distillation. The sulfinyl and sulfonyl chloride impurities may be removed by treatment with additional alcohol[6] and with a high-boiling primary amine, such as p-toluidine, and subsequent distillation.

$$\mathrm{RSSR} + 4\mathrm{R'OH} + 3\mathrm{Cl_2} \xrightarrow{-20^\circ} 2\mathrm{RS(O)OR'} + 2\mathrm{R'Cl} + 4\mathrm{HCl} \quad (1)$$

The reaction by which sulfinic esters are formed by direct chlorination of disulfides in alcohols undoubtedly involves a series of sequential steps, the first of which is the formation of the sulfenyl chloride, which then reacts as outlined in previous papers from this laboratory.[5,7] When methyl disulfide is chlorinated in methanol, for example, the succession of compounds formed is believed to be CH_3SCl, CH_3SOCH_3, $CH_3S(O)SCH_3$, $CH_3S(O)Cl$, and $CH_3S(O)OCH_3$.

The sulfinyl chloride found in the final product remains from the equilibrium reaction by which the sulfinic ester is formed (eq 2). The sulfonyl chloride results, at least in part, from the action of chlorine on the sulfinic ester (eq 3). At temperatures above 10° this is a quantitative reac-

$$\mathrm{CH_3S(O)Cl} + \mathrm{CH_3OH} \rightleftharpoons \mathrm{CH_3S(O)OCH_3} + \mathrm{HCl} \quad (2)$$