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Dehalogenation *via* Pyridinium Salts

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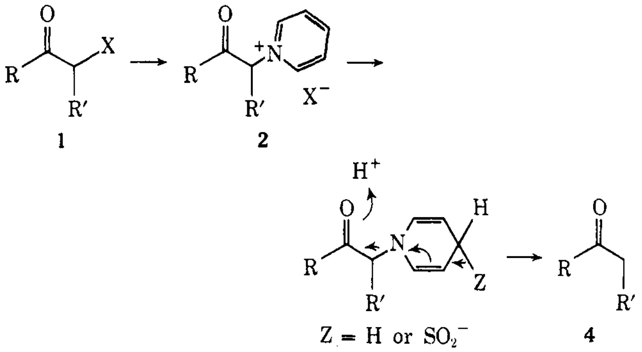
Received September 12, 1973

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.



1 **2**

$Z = H$ or SO_2^-

3 **4**

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.

Acknowledgment. This work was supported by NRC of Canada.

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

References and Notes

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

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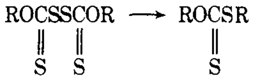
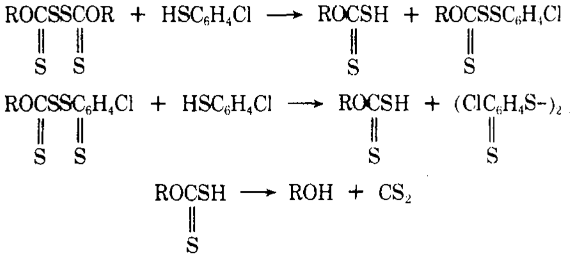
Received September 25, 1973

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



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

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



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

$$\mathrm{RO}\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{S}}\mathrm{SC_6H_4Cl} + \mathrm{HSC_6H_4Cl} \longrightarrow \mathrm{RO}\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}\mathrm{SH} + (\mathrm{ClC_6H_4}\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{S}}\text{-})_2$$

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

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