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REDUCTION OF α-HALOCARBONYL COMPOUNDS WITH SODIUM HYDROGEN TELLURIDE

Atsuhiro OSUKA and Hitomi SUZUKI
Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790

Sodium hydrogen telluride is an efficient reagent for dehalogenation of α-halocarbonyl compounds.

Reduction of α-halocarbonyl compounds to the corresponding carbonyl compounds has recently received considerable attention. As a result, a number of methods have been developed to bring about such a conversion — triphenyl phosphine,[1a] zinc in acetic acid,[1b] metal carbonyls,[1c] aqueous Ti(III),[1d] LiI-BF_3,[1e] NaI-SO_3-amine,[1f] NaI-chlorotrimethylsilane,[1g] iodide ion,[1h] and pyridine followed by sodium dithionite.[1i] The application of tellurium in organic synthesis has been actively investigated in recent years.[2] Strong affinity of tellurium for activated halogen could be utilized for synthetic work, and this led us to investigate the reduction of α-halocarbonyl compounds with sodium hydrogen telluride (NaTeH) (1).[3]

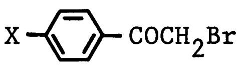
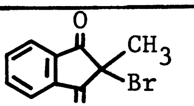
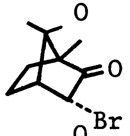
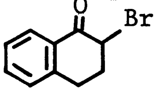
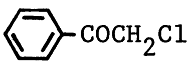
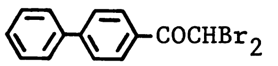
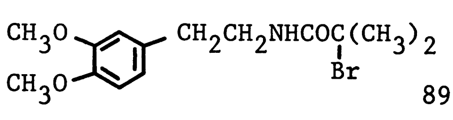
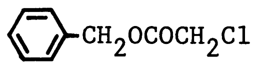
$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}\overset{|}{\underset{|}{C}}{-}X} \xrightarrow{\mathrm{NaTeH}} \mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}\overset{|}{\underset{|}{C}}{-}H} \qquad (1)$$

Thus a convenient procedure for the selective removal of halogen atoms adjacent to the carbonyl group using (1) was developed. A number of representative examples are presented in the Table. All dehalogenation were performed at room temperature, and it gave good to excellent yields. In addition, the dehalogenation effected by this reagent proved to be general and chemo-selective. This was in contrast to the reduction of phenacyl bromide with sodium borohydride in ethanol at room temperature, which resulted only in the formation of styrene oxide.

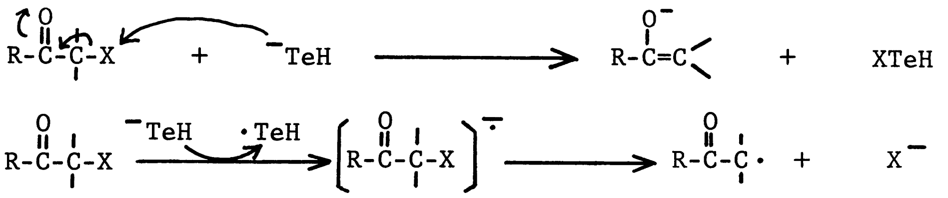
The mechanism of the reaction by (1) has not been studied yet. It may be envisaged that nucleophilic attack of tellurolate ion on halogen could lead to the formation of enolate (eq. 2). Alternatively, it may involve electron transfer from (1) to α-carbonyl compounds, and subsequent detachment of halogen (eq. 3). However, the latter would not be favored due to the absence of 1,4-diketones or enones which would arise from the intermediate radical.

Although there are several methods available to bring about the dehalogenation of α-halocarbonyl compounds, we consider the present method a useful addition to them in view of the mild conditions, simple manipulation, and the absence of side-reactions.

Table. Dehalogenation of α-Halocarbonyl Compounds with NaTeH

α-Halocarbonyl Compound	Yield(%)[a]	α-Halocarbonyl Compound	Yield(%)[a]
			98
X=H	94		78
X=Ph	92		
X=Br	93		96
X=OH	85		
	95		
	98[b]		89
	85		

[a] Yields based on isolated dehalogenated products. [b] Twice amounts of NaTeH (1) were used. Product was *p*-phenylacetophenone.



$$\mathrm{R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}X + {}^{-}TeH \longrightarrow R\text{-}\overset{O^-}{\overset{|}{C}}{=}C\!< + XTeH} \quad (2)$$

$$\mathrm{R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}X \xrightarrow{{}^{-}TeH \quad \cdot TeH} \left[R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}X\right]^{\cdot -} \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{|}{\underset{|}{C}}\cdot + X^{-}} \quad (3)$$

In a typical experiment, a solution of p-bromophenacyl bromide (1.112 g, 4mmol) in ethyl acetate (20 ml) was added to a solution of (1), prepared *in situ* from tellurium (1.3 g, 10mmol) and $NaBH_4$ (0.9 g) in 20 ml of ethanol. An instantaneous reaction occurred and the color of the reaction mixture changed to deep black. The mixture was further stirred at room temperature for 1 h. Then it was filtered through Celite 545, and the filtrate was extracted with ether. The organic layer was washed with water and dried over Na_2SO_4. The solvent was removed to give pure product, which was recrystallized from ethanol to give p-bromoacetophenone (737 mg, 93%; mp 50-51°C, lit. mp 50-52°C).

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Note Added. After the acceptance of this paper for publication, we learned that the similar results were obtained with 2-thiophenetellurolate by Prof. M. P.Cava, recently (L. Engman and M. P.Cava, J. Org. Chem., 47, 3946 (1982)).

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