BIS(TRIPHENYLSTANNYL)TELLURIDE. A MILD AND EFFICIENT REDUCTIVE DEHALOGENATION REAGENT FOR &-HALOKETONES.

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Abstract: a-Haloketones are efficiently reductively dehalogenated by the combination of telluride 1 and potassium fluoride dihydrate in acetonitrile under very mild conditions.

The dehalogenation of α -halocarbonyl compounds is a common and important procedure which is often used in organic synthesis. Various methods¹ for this purpose have been developed; sodium hydrogen telluride (NaTeH) has been shown to be a powerful reagent for the reduction of various functions². However, all of the reactions with sodium telluride, prepared *in situ* from metal tellurium and sodium borohydride³, involves carrying out the chemistry in a basic medium usually in ethanol solution.

Recently we reported that the combination of bistriphenylstannyltelluride (1) with cesium fluoride is a mild and selective telluration and devicihalogenation system⁴. Now we have discovered that when this telluride combined with potassium flouride hydrate, various α -halogenated ketones can be reductively debrominated in high yield under very mild conditions (Table 1)⁵.

(Ph₃Sn)₂Te

1



Entry	α-Halo ketone	Solvent	Time(h)	Product	Yield ^a
1	PhCOCH ₂ Br	CH₃CN	5	PhCOCH ₃	79(quant)
2	PhCOCH ₂ Br	CD ₃ CN ^b	5	PhCOCH ₃	(35)
3	PhCOCH ₂ Br	CD ₃ CN ^c	5	PhCOCH ₃	(15)
4	PhCOCH ₂ Br	CH3CNd	0.2	PhCOCH ₃	(quant)
5	PhCOCH(CH ₃)Br	CH ₃ CN	5	PhCOCH ₂ CH ₃	87(quant)
6	PhCOCH(CH ₃)Br	CH3CNd	0.2	PhCOCH ₂ CH ₃	(97)
7	PhCOC(CH ₃) ₂ Br	CH ₃ CN	10	PhCOCH(CH ₃) ₂	69(78)
8	PhCOCH ₂ Cl	CH ₃ CN	10	PhCOCH ₃	77(quant)
9	Ğ	CD₃CN	5	Ů	(63)
10	CH₃COCH₂CI	CD3CN	4	CH3COCH3	(92)
11	CH ₃ CH ₂ COCH ₂ Br	CD ₃ CN	5	CH ₃ CH ₂ COCH ₃	(quant)

Table I. Dehalogenation of α -Halo Ketones by bis(Triphenylstannyl)telluride.

All the reactions were carried out at room temperature with the haloketone : telluride : $KF.2H_2O = 1 : 1 : 3$ (mole ratio); ^a isolated yields; ¹Hnmr yields in parentheses; ^bwith CsF as catalyst; ^cwithout KF.2H₂O; ^d refluxing.

The process suggests that during the reaction with $KF.2H_2O$ a tellurol intermediate 2 was formed *in situ*; this would readily reduce the halogen to hydrogen.

 $(Ph_{3}Sn)_{2}Te \xrightarrow{KF.2H_{2}O + 3} [RCOCR^{1}R^{2}TeH] \xrightarrow{-Te^{0}} RCOCHR^{1}R^{2} (Eq. 2)$ $1 \qquad 5 \qquad 4$

An alternative possibility to this process could be via tellurol 5, *i.e.* during the reaction, the semitelluration first takes place; a subsequent detelluration process then would give the reduced product (Eq. 2). A similar detelluration rearrangement has been suggested in the reaction of allyl halides with sodium telluride⁶

A typical procedure is as follows. A mixture of bromoacetophenone (0.4 mmol), telluride 1 (0.4 mmol) and KF.2H₂O (1.2mmol) in 10mL of acetonitrile was stirred at room temperature under N₂; very soon, a black solid deposited. After being stirred for 5h, the reaction mixture was filtered through celite. Evaporation of the solvent gave a crude mixture, and the product acetophenone (79%) was isolated by flash chromatography (hexane/ ethyl acetate = 20:1). The preferred fluoride source appears to be KF.2H₂O and most reactions proceed to completion as demonstrated by GC analysis; isolated yields average about 80%.

Thus, this method appears especially mild for the facile reduction of a variety of α -halo ketones in excellent overall yield; reaction times can be lowered to a few minutes by refluxing the solution. (Table 1).

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