Title	Facile Cleavage of Aryl Haloacetates and 2-Chloroethyl Carboxylic Esters with Sodium Telluride. A One-pot Conversion of Aryl Esters into Aryl Ethers under Aprotic Conditions
Author(s)	Suzuki, Hitomi; Padmanabhan, Seetharamaiyer; Ogawa, Takuji
Citation	CHEMISTRY LETTERS. 18(6) p.1017-p.1020
Issue Date	1989-06
oaire:version	VoR
URL	https://hdl.handle.net/11094/3387
rights	
Note	

Osaka University Knowledge Archive : OUKA

<https://ir.library.osaka-u.ac.jp/>

Osaka University

Facile Cleavage of Aryl Haloacetates and 2-Chloroethyl Carboxylic Esters
with Sodium Telluride.

A One-pot Conversion of Aryl Esters into Aryl Ethers under Aprotic Conditions

Hitomi SUZUKI,^{*} Seetharamaiyer PADMANABHAN, and Takuji OGAWA^{*}Department of Chemistry, Faculty of Science,
Ehime University, Bunkyo-cho, Matsuyama 790

Sodium telluride, prepared under aprotic conditions, cleaved aryl haloacetates and 2-chloroethyl carboxylates at room temperature to give phenolic compounds and carboxylic acids, respectively. Based on this cleavage a one-pot conversion of aryl esters into aryl ethers was achieved.

In continuation of our work on the use of sodium telluride for organic functional group transformations, we wish to report herein the reaction of aryl haloacetates and 2-chloroethyl carboxylates with sodium telluride under aprotic conditions. Both the title compounds eliminate neutral molecules, ketene and ethylene respectively to give the parent phenolic and carboxylic acid derivatives in good to moderate yields.

Recently we observed a facile elimination of ketene from o-(bromoacetoxy)benzaldehyde during our attempts on the coumarin synthesis through intramolecular Reformatsky-type reaction using sodium telluride.¹⁾ Intrigued by this facile elimination under mild conditions, we considered the application of this reaction for synthetic purposes. Addition of 2-naphthyl chloroacetate (**1**) to a solution of sodium telluride in N,N-dimethylformamide (DMF) at room temperature immediately led to separation of free tellurium to afford 2-naphthol(**2**) in 91% yield. Similarly other aryl haloacetates gave the parent phenolic compounds in fairly good yields (Table 1). The reaction was clean and no side products were detected.

Under the conditions employed, functional groups such as nitro and ordinary ester were found to be stable (entries e and f). Stability of the ester function was checked by intermolecular competition experiment. Reaction of an equimolar mixture of 1-naphthyl chloroacetate and 1-naphthyl acetate with sodium telluride resulted in the recovery of the 1-naphthyl acetate almost intact after 1 h.

Table 1. Phenols and alkyl aryl ethers isolated

ArOCOCH ₂ X	ArOH Yield/% ^{a)}	RX	ArOR Yield/% ^{a)}
a 1-(BrCH ₂ CO ₂)C ₁₀ H ₇	72	—	—
b 1-(ClCH ₂ CO ₂)C ₁₀ H ₇	80	C ₂ H ₅ I	42 ^{b)}
c 2-(ClCH ₂ CO ₂)C ₁₀ H ₇	91	C ₂ H ₅ I	50 ^{b)}
d 4-C ₆ H ₅ -C ₆ H ₄ OCOCH ₂ Cl	87	—	—
e 4-(n-C ₃ H ₇ COO)C ₆ H ₄ OCOCH ₂ Cl	70	CH ₃ I	70
f 4-NO ₂ C ₆ H ₄ OCOCH ₂ Cl	81	—	—
g 2,7-(ClCH ₂ CO ₂) ₂ C ₁₀ H ₆	—	C ₂ H ₅ Br	51 ^{c)}

a) Yields refer to the isolated compounds and are not optimized.

b) Diethyltellurium diiodide was isolated in 34 - 36% yields.

c) 2,7-Diethoxynaphthalene.

However, only 20% of the 1-naphthyl acetate was recovered after 12 h. Attempted reaction of 3-phenylpropyl chloroacetate, to find its applicability to alcohols, led to a complex mixture.

Formation of phenolic compounds would arise from the attack of telluride ion on the halogen atom followed by a rapid elimination of a ketene molecule from the resulting enolate anion.

These results suggest that haloacetate group may be a potential protecting group for the phenolic function. General protection of phenols was done either as ethers or esters. The most common protecting groups of carboxylic acid types are acetyl,²⁾ benzoyl,³⁾ pivaloyl,⁴⁾ vinylloxycarbonyl,⁵⁾ and fluorene-9-carboxyl.⁶⁾ The latest protecting reagent for phenols is 2-formylbenzenesulfonyl chloride, reported by Bhatt.⁷⁾ Ready availability of the protecting reagent (haloacetyl halides), easy access to the deprotecting agent (sodium telluride), mild aprotic conditions and short reaction time make the present procedure a new addition to the existing methodology. Although protection of alcohols and amines as the corresponding haloacetyl derivatives has been employed,⁸⁾ analogous reactions with phenolic derivatives have not yet been reported. Extension of the present reaction to N-(bromoacetyl)-p-toluidine gave no p-toluidine as the product.

It was conceived that addition of alkyl halide into the reaction mixture would trap the phenoxide generated from aryl haloacetate thus leading to the one-pot conversion of aryl esters to aryl ethers. Indeed it was the case where ethyl 2-naphthyl ether (**3**) was isolated from 2-naphthyl chloroacetate (**1**) and ethyl iodide. Similarly several alkyl aryl ethers were prepared by using different

alkylating agents and the results are shown in Table 1. General synthesis of aryl alkyl ethers from aryl esters would involve a two-step process under protic conditions, *i.e.*, hydrolysis followed by alkylation.

General procedure for cleavage of aryl haloacetates: To a suspension of sodium telluride⁹⁾ (2.0 mmol; prepared from tellurium and sodium hydride) in dry DMF (5 ml) under nitrogen a solution of an aryl haloacetate (2.0 mmol) in DMF (3 ml) was added. Immediate separation of tellurium was observed and the dark reaction mixture was stirred at room temperature for 1 h. The reaction was quenched by the addition of saturated aqueous ammonium chloride solution (5 ml) and the organic phase was extracted into benzene (10 ml). After stirring the mixture open to atmosphere for sometime, the inorganic insolubles were removed by filtering through a thin bed of Celite. The organic layer was separated, washed with brine, and dried. The solvent was removed in vacuo to give a crude product, which was purified by chromatography on silica gel by using a mixture of dichloromethane and hexane as the eluent.

General procedure for the preparation of aryl ethers: After the addition of aryl haloacetate (1.0 mmol) to sodium telluride (1.0 mmol) in DMF (3 ml) at room temperature as described above, the dark reaction mixture was stirred for 10 min, followed by the addition of an alkylating agent (10.0 mmol). The reaction mixture was stirred at room temperature for 30 min in the case of ethyl iodide (2 h for ethyl bromide or methyl iodide as the alkylating agent) followed by heating at 50°C for 2 h. With iodides, the tellurium separated initially went into solution to give a clear yellow reaction mixture during this period. With ethyl bromide the reaction mixture remained dark in color throughout. The mixture was cooled to room temperature and worked up as usual to give a crude product, which was purified by column chromatography. When alkyl iodide was used as the alkylating agent, dialkyltellurium diiodide was also obtained as the side product, formed by the reaction between the tellurium separated and the alkylating agent present in excess.

Reaction of ethyl bromoacetate with aromatic aldehydes⁹⁾ by using sodium telluride proceeds forming enolates. It was anticipated that a possible attack of telluride ion on the chlorine atom in 2-chloroethyl esters would lead to an E₂-type fragmentation of the alkyl moiety to give the starting carboxylic acid and ethylene.

This was found to be the case; the addition of a solution of 2-chloroethyl benzoate to sodium telluride in DMF at room temperature resulted in the formation of copious precipitate within a few minutes, a similar observation reported by Zhou.¹⁰⁾ Additional examples are given in Table 2. Similar deblocking reactions were previously observed by using other nucleophiles such as sodium hydrogenselenide,¹¹⁾ trimethylstannyl lithium,¹²⁾ sodium ethanedithiolate,¹³⁾ and sodium trithiocarbonate.¹⁴⁾

Table 2. Cleavage of 2-chloroethyl carboxylates

R-CO ₂ CH ₂ CH ₂ Cl	RCOOH Yield/%
C ₆ H ₅ -CO ₂ CH ₂ CH ₂ Cl	92
C ₆ H ₅ -CO ₂ CH ₂ CH ₂ Cl	53 ^{a)}
4-CH ₃ C ₆ H ₄ -CO ₂ CH ₂ CH ₂ Cl	93
C ₆ H ₅ CH ₂ -CO ₂ CH ₂ CH ₂ Cl	92

a) Refers to the yield when the reaction was carried out for 2 h.

General procedure for the cleavage of 2-chloroethyl esters: To sodium telluride (2.0 mmol) in DMF (3 ml) was added a solution of 2-chloroethyl ester (2.0 mmol) in DMF (2 ml) at room temperature and the resulting thick mixture was stirred for 12 h at room temperature. The reaction was quenched by the addition of 0.5 M sulfuric acid (5 ml) and the organic phase was extracted into ether (10 ml). The mixture was filtered through Celite to remove the inorganic materials and the ether layer was separated, washed twice with 0.5 M sulfuric acid (5 ml each) followed by saturated sodium chloride solution, and dried over sodium sulfate. The solvent was removed in vacuo to leave pure carboxylic acid, which was further purified by crystallization from water containing a little ethanol.

References

- 1) S. Padmanabhan, T. Ogawa, and H. Suzuki, Bull. Chem. Soc. Jpn., 62, in press.
- 2) V. O. Illi, Tetrahedron Lett., 1979, 2431.
- 3) M. Gates, J. Am. Chem. Soc., 72, 228 (1950).
- 4) L. K. T. Lam and K. Farhat, Org. Prep. Proced. Int., 10, 79 (1978).
- 5) R. A. Olofson and R.C. Schnur, Tetrahedron Lett., 1977, 1571.
- 6) D. H. R. Barton, Y. L. Chow, A. Cox, and G. W. Kirby, J. Chem. Soc., Chem. Commun., 1965, 3571.
- 7) M. S. Shashidhar and M. V. Bhatt, J. Chem. Soc., Chem. Commun., 1987, 654.
- 8) T. W. Greene, "Protective Groups in Organic Synthesis," John Wiley and Sons, New York (1981).
- 9) H. Suzuki and M. Inouye, Chem. Lett., 1986, 403.
- 10) J. Chen and X. J. Zhou, Synthesis, 1987, 586.
- 11) T. -L. Ho, Synth. Commun., 8, 301 (1978).
- 12) T. -L. Ho, Synth. Commun., 8, 359 (1978).
- 13) T. -L. Ho, Synthesis, 1978, 510.
- 14) T. -L. Ho, Synthesis, 1974, 715.

(Received March 24, 1989)