A Novel *O*-Alkyl Cleavage of Carboxylic Esters Effected by Tellurium Reagents

Jian Chen,[1] Xun Jun Zhou*

Department of Chemistry, Hangzhou University, Hangzhou, Zhejiang, People's Republic of China

A new method for producing sodium telluride, sodium hydrogen telluride, and sodium ditelluride from tellurium and sodium borohydride in dimethylformamide is devised. These sodium telluride reagents dealkylate methyl, benzyl, and ethyl carboxylates selectively.

The cleavage of carboxylic esters to afford the acids is a common organic transformation that is usually carried out by acidic or basic hydrolysis. However, certain carboxylic esters are sensitive to hydrolytic conditions. For such sensitive materials, a number of mild methods of ester cleavage, including S_N2 dealkylation, has been devised.[2-10] However, each of the reagents suggested has its own drawback and one cannot expect a single reagent to fulfill all requirements for the cleavage of esters of different kinds. Therefore, the search for new reagents for ester cleavage is still of interest.

Since sodium hydrogen telluride, sodium telluride, and sodium ditelluride are rather weak nucleophiles, they should attack the ester at carbino carbon rather than at the carboxy carbon and therefore accomplish dealkylation via an S_N2 mechanism. However, sodium hydrogen telluride is generally prepared from sodium borohydride and tellurium in boiling ethanol;[11] under these conditions it is little appropriate for S_N2 reactions. In fact, we found that benzyl benzoate is not appreciably debenzylated by sodium hydrogen tellride in refluxing ethanol within 10 hours. Sodium telluride is generated by several methods: tellurium and Rongalite in water;[12] tellurium and sodium borohydride in water;[13] tellurium and sodium in liquid ammonia;[14] tellurium and sodium in dipolar aprotic solvents such as dimethylformamide and HMPT.[15] Only sodium telluride obtained by the last method is suitable for S_N2 reactions. However, sodium often causes problems when handled in very small amounts. In order to overcome this disadvantage we devised a new, convenient method for generating sodium hydrogen telluride, sodium telluride, and sodium ditelluride from tellurium and sodium borohydride in dimethylformamide. The tellurium reagents (NaTeH, Na_2Te, Na_2Te_2) thus produced can effect smooth ester cleavage.

The ester cleavage by the above named tellurium reagents is a typical S_N2 reaction (Scheme). Benzyl, methyl, and some ethyl esters are dealkylated smoothly at a suitable temperature (80–90°C, we have not investigated the temperature effect on the reaction rate). Other alkyl esters remain unaffected under the same conditions although some may be dealkylated using prolonged reaction times at higher temperatures (see Table). The experimental results also show that the three tellurium reagents do not exhibit any significant differences in the ester cleavage reaction.

Method A:

$R^1CO_2R^2$ (**1a-f**) $\xrightarrow{NaHTe/DMF,\ 80\text{-}90°C}$ $R^1CO_2Na + R^2TeH$

$R^1CO_2R^2$ (**1a-f**) $\xrightarrow{R^1CO_2R^2}$ $R^1CO_2H + R^2TeR^2$ (**2a-f**)

Method B:

$R^1CO_2R^2$ (**1a,**) $\xrightarrow{Na_2Te/DMF,\ 80\text{-}90°C}$ $R^1CO_2Na + R^2TeNa$

$R^1CO_2R^2$ (**1a,**) $\xrightarrow[90\%]{R^1CO_2R^2}$ $R^1CO_2Na + R^2TeR^2$ (**3**)

3 $\xrightarrow{H_2O/H^+}$ **2a**

Method C:

$R^1CO_2R^2$ (**1a,**) $\xrightarrow{Na_2Te_2/DMF,\ 80\text{-}90°C}$ $R^1CO_2Na + R^2Te_2Na$

$R^1CO_2R^2$ (**1a,**) $\xrightarrow{R^1CO_2R^2}$ $R^1CO_2Na + R^2Te_2R^2$ (**3**)

3 $\xrightarrow{H_2O/H^+}$ **2a**

The present method for ester dealkylation offers several advantages. The reagents are easily prepared, the conditions are mild, and the work-up is easy. Thus, the method provides a complementary approach to ester demasking.

All dealkylations were carried out under pure nitrogen. Esters used were either commercially available or prepared according to classical esterification methods. They were identified by physical contants and IR spectra. All products gave correct melting points, mixture melting points, and IR spectra. Dimethylformamide was purified prior to use.

Ester Cleavage of Alkyl Carboxylates 1 with Tellurium Reagents; Typical Procedures, exemplified by the Cleavage of Methyl Benzoate (1a$_2$):

Method A, using Sodium Hydrogen Telluride: Tellurium powder (1.27 g, 10 mmol) and sodium borohydride (0.57 g, 15 mmol) are placed in a 50 ml three-necked flask. The flask is evacuated and purged with nitrogen three times. Dimethylformamide (20 ml) and *t*-butanol (0.2 ml, used as hydrogen donor) are added. The mixture is heated at 80–90°C for ~ 30 min until nearly all the tellurium has disappeared to give a deep violet solution. Methyl benzoate (2.47 g, 18 mmol) is added and the mixture is heated (80–90°C) for 15 min. At the end of the reaction, a copious precipitate often appears. Water (30 ml) is then added and the mixture is extracted with ether (3 × 50 ml). The aqueous phase is acidified with hydrochloric acid, extracted with ether (3 × 20 ml), and dried with magnesium sulfate. The solvent is stripped off to give pure benzoic acid; yield 2.12 g (95%); m.p. 121–122°C. The acid may be further purified by recrystallization from an appropriate solvent.

Table. Dealkylation of Alkyl Carboxylates (**1**) by the Tellurium Reagents NaTeH, Na_2Te, and Na_2Te_2

1	R^1	R^2	Method[a]	Time	Product	Yield[b] (%)	m.p. (°C) found	m.p. (°C) reported[16]
$\mathbf{a}_1$	C_6H_5	$CH_2C_6H_5$	A	5 min	**2a**	98	121–122	122
$\mathbf{a}_2$	C_6H_5	CH_3	A	15 min	**2a**	95		
$\mathbf{a}_2$			B	20 min	**2a**	90		
$\mathbf{a}_2$			C	20 min	**2a**	85		
$\mathbf{a}_3$	C_6H_5	C_2H_5	A	1.5 h	**2a**	91		
$\mathbf{a}_4$	C_6H_5	n-C_3H_7	A	25 h	**2a**	49		
$\mathbf{a}_5$	C_6H_5	i-C_3H_7	A	25 h	**2a**	13		
b	$C_6H_5CH_2$	CH_3	A	1 h	**2b**	89	75–76	76–77
c	3-ClC_6H_4	CH_3	A	5 h	**2c**	91	158	158
d	2-$C_{10}H_7$	CH_3	A	5 h	**2d**	95	185	185.5
e	1-$C_{10}H_7CH_2$	CH_3	A	5 h	**2e**	97	128–129	129
f	n-$C_{11}H_{23}$	CH_3	A[d]	2 h	**2f**	88	44–45	45

[a] A: NaTeH, 80–90 °C; B: Na_2Te, 80–90 °C; C: Na_2Te_2, 80–90 °C.

[b] Yield of isolated product. In general, the dialkyl tellurides formed in the reactions were not isolated because of their instability towards oxygen and light and their unpleasent smell. In one case, dimethyl telluride was identified as the complex $CH_3TeCH_3 \cdot HgCl_2$; m.p. 178–179 °C (Lit.[17] m.p. 179 °C). ^{1}H-NMR (acetone-d_6/TMS): δ = 3.0–3.1 ppm (s).

[c] Uncorrected.

[d] Room temperature.

Method B, using Sodium Telluride: A mixture of tellurium (0.64 g, 5 mmol) and sodium borohydride (0.45 g, 12 mmol) in dimethylformamide (20 ml) is heated at (80–90 °C) under nitrogen for 30 min to give an almost colorless suspension (which has been proven to be a sodium telluride suspension by reaction with 1-bromobutane to yield dibutyl telluride). Methyl benzoate (1.23 g, 9 mmol) is added and the mixture is heated at 80–90 °C for 20 min. Work-up as in Method A affords pure benzoic acid; yield 0.99 g (90%); m.p. 121–122 °C.

Method C, using Sodium Ditelluride: Tellurium (1.00 g, 7.5 mmol) and sodium borohydride (0.19 g, 5.0 mmol) in dimethylformamide (20 ml) is heated at 80–90 °C under nitrogen for 20 min to give a homogeneous, deep purple solution (which has been proven to be a sodium ditelluride solution by treatment with 1-bromobutane to give dibutyl ditelluride). Methyl benzoate (1.23 g, 9 mmol) is added and the mixture is heated at 80–90 °C for 20 min. Work-up as in Method A gives pure benzoic acid; yield: 0.94 g (85%); m.p. 121–122 °C.

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(1) Present address: Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada.
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