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A NOVEL ROUTE TO α,β-UNSATURATED ESTERS VIA A REFORMATSKY-TYPE REACTION USING SODIUM TELLURIDE

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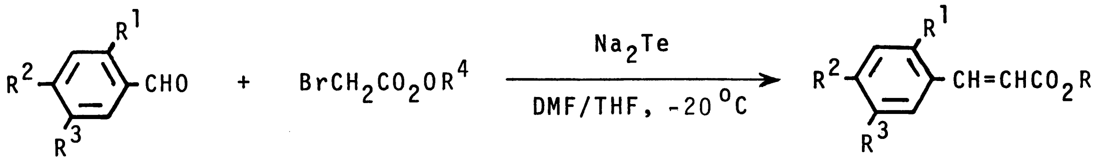
Sodium telluride, prepared by heating tellurium and sodium hydride in a 1:2 molar ratio in dry N,N-dimethylformamide, readily debrominates a bromoacetic ester at low temperatures to generate an enolate anion, which undergoes a Reformatsky-type reaction with various non-enolizable aldehydes to give the corresponding α,β-unsaturated esters in good to moderate yields. Ketones remain almost unaffected under the same conditions.

When metallic tellurium and sodium hydride are heated in a 1:2 molar ratio in dry N,N-dimethylformamide (DMF) at 140 °C under nitrogen, tellurium dissolves into DMF to give a deep purple solution, which gradually loses color on further heating to separate sodium telluride as a pale yellow precipitate.[1)]

$$\mathrm{Te} \xrightarrow[\mathrm{DMF},\ \Delta]{\mathrm{NaH}} [\mathrm{Na_2Te_n}] \xrightarrow[\mathrm{DMF},\ \Delta]{\mathrm{NaH}} \mathrm{Na_2Te}$$

On adding a solution of bromoacetic ester (2) in tetrahydrofuran (THF) to the stirred suspension of sodium telluride thus obtained under cooling at -40— -20 °C, 2 readily loses bromine atom to form an ester enolate anion (4) with liberation of elemental tellurium. Subsequent treatment of enolate anion 4 with aromatic alde-



1 2 3

hydes (1) affords after usual work-up the corresponding cinnamic esters (3) in good to moderate yields (Table 1). Chloroacetic esters react similarly, giving somewhat diminished yields of 3. This novel Reformatsky-type reaction proceeds with exclusive (E)-selectivity and any significant side reactions are not observed. The reaction is apparently subject to polar effect; aromatic aldehydes bearing electron-withdrawing group on the ring give less satisfactory yields and formation of by-products is observed to a small extent. Interestingly, β-hydroxyhydrocinnamic esters are barely detected in the products.

Table 1. α,β-Unsaturated esters 3 obtained from aromatic aldehydes 1

Aromatic aldehyde 1			Bromoacetic ester 2	α,β-Unsaturated ester 3[a)]
R^1	R^2	R^3	R^4	Yield/%[b)]
H	H	H	CH_3	73
H	H	H	C_2H_5	60
CH_3	H	H	C_2H_5	56
H	$-OCH_2O-$		C_2H_5	70
H	$(CH_3)_2N$	H	C_2H_5	66
H	Cl	H	C_2H_5	46
H	F	H	C_2H_5	37

a) All products are known. They are identified by IR, ^1H NMR, and mass spectra as well as by direct comparison with authentic specimens.
b) Yields based on isolated products are not optimized.

The present reaction is also found to work well with non-enolizable aliphatic aldehydes; tertiary aldehyde (6) and α,β-unsaturated aldehydes (7 and 8) are converted to the corresponding unsaturated esters in acceptable yields (Table 2). In the reactions with α,β-unsaturated carbonyl systems, only 1,2-addition products are formed.

The tellurium-mediated condensation of aldehydes with bromoacetic esters has proved to exhibit high chemoselectivity in the reaction of carbonyl moieties. Thus, benzaldehyde can be successfully converted to cinnamic ester in the presence of benzophenone. The latter carbonyl compound is recovered mostly unchanged. The use of a large excess of bromoacetic ester and sodium telluride is necessary

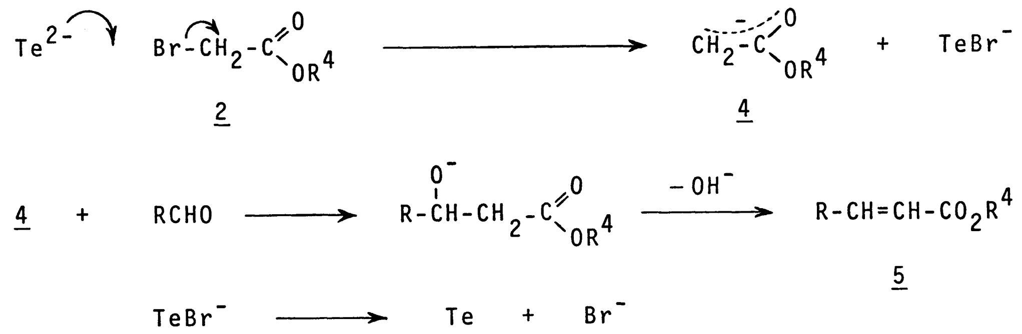
Table 2. α,β-Unsaturated esters obtained from aliphatic aldehydes

Aliphatic aldehyde	Reaction temperature $\theta_m/^{\circ}C$	α,β-Unsaturated ester[a)] Yield/%[b)]
$C_6H_5C(CH_3)_2CHO$ (6)	- 20	70
$C_6H_5CH=CHCHO$ (7)	- 20	55
$(H_3C)_2C=CHCH_2CH_2C(CH_3)=CHCHO$ (8)	- 40	42

a,b) See footnotes in Table 1.

to accomplish satisfactory conversion of aldehydes, although the reaction is apparently complete within 1 h at temperatures as low as -40 °C. No feasible explanation for this can be given at present.

The mechanism of the reaction is thought to involve the nucleophilic attack of telluride anion on bromine atom of bromoacetic ester 2 to generate ester enolate anion 4, which then reacts with aldehyde to afford α,β-unsaturated ester (5).



The reaction of a carbonyl compound with an α-halo ester in the presence of zinc metal is commonly known as the Reformatsky reaction and constitutes a method for preparing β-hydroxy esters and α,β-unsaturated esters.[2)] Our method for the generation of ester enolates by means of sodium telluride provides an interesting complement to the classical Reformatsky procedure, since the reaction is highly specific to aldehydes and can be conducted within short time under much milder conditions. The reaction leads directly to α,β-unsaturated esters without any need to dehydrate the intermediate β-hydroxy esters as is usually the case with the original ones.

The typical experimental procedure is as follows: A mixture of powdered tellurium (4.0 mmol), sodium hydride (8.6 mmol; commercial 60% dispersion was washed thoroughly with hexane prior to use) and DMF (7 ml) was stirred at 140 °C for 0.5 h under nitrogen. A deep purple color soon developed and faded again as the reaction proceeded further. The resulting pale yellow suspension of sodium telluride was cooled to - 20 °C and a solution of benzaldehyde (1.0 mmol) in dry THF (1.5 ml) followed by ethyl bromoacetate (4.0 mmol) in the same solvent (1.5 ml) was added dropwise. The reaction immediately occurred with separation of elementary tellurium. After the complete addition the mixture was kept with stirring at this temperature for another hour and then 0.5 M sulfuric acid (5 ml) saturated with sodium chloride followed by ether (10 ml) were added. The remaining telluride was destroyed by allowing the mixture open to air with stirring for 1 h and then filtered through a thin layer of Celite. The organic phase was separated and aqueous layer was extracted twice with ether. The combined extracts were washed with brine, dried over sodium sulfate, and evaporated to leave a yellow oil, which was purified by bulb-to-bulb distillation under reduced pressure to give pure ethyl cinnamate. Bp 95-100 °C/1.5 mmHg (Lit.3) 271 °C). Yield, 60%.

References

1) Sodium telluride is also prepared by reacting tellurium with sodium metal in liquid ammonia4) or DMF5) and reducing tellurium with Rongalite in aqueous sodium hydroxide6) or with sodium borohydride in ethanol.7)

2) For reviews of the Reformatsky reaction, see R.L. Shriner, Org. React., 1, 1 (1942); M.W. Rathke, ibid., 22, 423 (1975).

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