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SELECTIVE REDUCTION OF α,β-UNSATURATED CARBONYL COMPOUNDS BY SODIUM HYDROTELLURIDE

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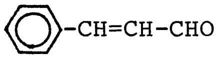
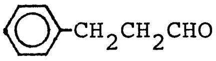
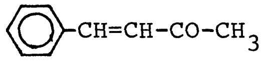
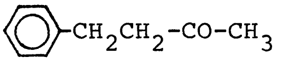
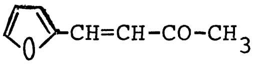
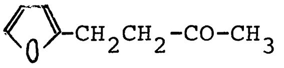
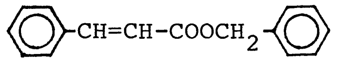
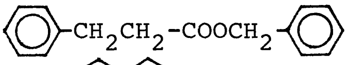
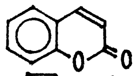
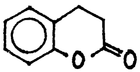
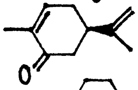
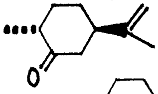
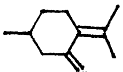
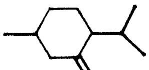
Sodium hydrotelluride was found to serve as a new efficient agent for selective reduction of α,β-unsaturated carbonyl compounds under mild reaction conditions.

Selective reduction of α,β-unsaturated carbonyl compounds (ketones, aldehydes, esters, lactones, etc.) is one of the most important organic reactions.[1,2) In this letter, we wish to report that sodium hydrotelluride (NaHTe) (I), prepared from tellurium powder and sodium borohydride,[3) is found to be a useful and practical reducing agent for these compounds. As exemplified in Table 1, this reaction is applicable to a wide variety of α,β-unsaturated carbonyl compounds including ketones, aldehydes, esters, lactones, etc.

Representative procedure is as follows. To a solution of (I), prepared *in situ* from tellurium powder (0.65 g) and sodium borohydride (0.45 g) in ethanol (20 ml),[3) was added an ethanol solution (2 ml) of 3-phenylpropenal (2 mmol) under argon. The reaction mixture was stirred at room temperature for 4-5 h. Then the mixture was filtered through Celite and the filtrate was evaporated. The residual liquid was almost pure 3-phenylpropanal (examined by GLC). The product was purified by distillation and identified by IR, NMR, MASS, and GLC.

The present procedure posseses the following characteristics: a) over-reduction of the carbonyl groups and ester functions is negligible; b) isolated carbon-carbon double bonds are not reduced; c) phenyl and furyl groups are not affected; d) the operation is very simple (filtration of the reaction solution through Celite and evaporation give almost pure products).

Table 1. Reduction of α,β-unsaturated carbonyl compounds by NaHTe[a)]

Run	Carbonyl Compound	Product	Yield (%)[b)]
1			>99
2			>99
3			>99
4			>99
5			>99
6			>99
7			>99
8			36
9	$H_5C_2OCO-CH=CH-COOC_2H_5$[c)]	$H_5C_2OCO-CH_2CH_2-COOC_2H_5$	5

a) At room temperature for 4-5 h under argon. b) Determined by GLC.
c) Diethyl maleate.

As to the stereochemistry of the reaction, (-)-carvone was converted selectively into (+)-dihydrocarvone (Run 6).[4)] This shows that (I) attacks (-)-carvone exclusively from the sterically less hindered site.

1,4-Dicarbonyl compounds such as diethyl maleate and *p*-quinone were also reduced (Runs 8 and 9), but the yields were low.[5)] Scope and limitation of this reaction are now under investigation.

References and Notes

1) M. Smith in "Reduction," R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1968, p 95.

2) R. Noyori, I. Umeda, and T. Ishigami, *J. Org. Chem.*, 37, 1542 (1972), and the references cited therein.

3) D. H. R. Barton and S. W. McCombie, *J. Chem. Soc. Perkin I*, 1975, 1574.

4) (+)-Isodihydrocarvone, diastereomer of (+)-dihydrocarvone, was not detected by GLC.

5) The remainder consisted mainly of the starting material. Side reactions were negligible.

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