3500 J. Org. Chem. 1994, 59, 3500-3502

The Reaction of Sodium Hydrogen Telluride with α,β-Unsaturated Carbonyl Compounds[1]

Masakazu Yamashita,* Yoshifumi Tanaka,
Akishi Arita, and Minoru Nishida

Department of Applied Chemistry, Faculty of Engineering, Doshisha University, Kamikyo-ku, Kyoto 602, Japan

Received November 23, 1993

In the context of investigations on the reactivity of tellurium compounds toward functional substrates,[2] we have studied reductions using sodium hydrogen telluride (1) as a stoichiometric reductant.[3] Recently, this reagent has been employed for several chemoselective reductions.[4]

On the other hand, the selective reduction of α,β-unsaturated carbonyl compounds (ketones, aldehydes, esters, lactones, etc.) is one of the most important organic reactions, and a number of new hydride reducing reagents have been investigated recently.[5] Our interest in the area of metal-mediated reductions has also led us to develop a new method for effecting conjugate reduction of α,β-enals and α,β-enones using 1.[6] We report here a detailed study of this stoichiometric reduction which appears somewhat attractive for general applicability. In addition, the reaction of 1 to α,β-carbon–carbon triple bond carbonyl compounds is described.

Results and Discussion

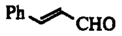
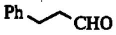
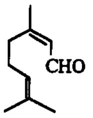
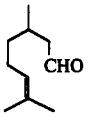
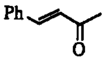
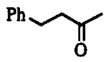
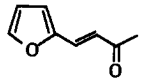
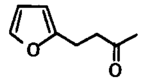
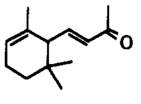
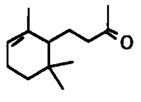
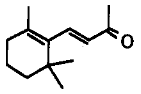
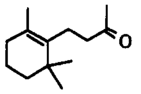
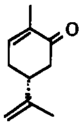
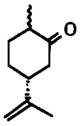
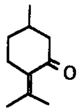
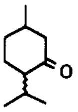
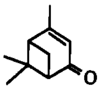
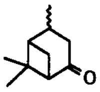
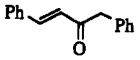
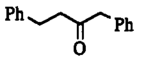
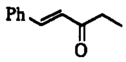
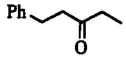
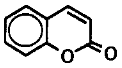
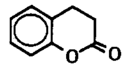
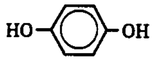
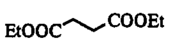
Reduction of Conjugated Enals and Enones. For example, sodium hydrogen telluride (1) reacted with cinnamaldehyde in ethanol at room temperature under argon atmosphere to give 3-phenylpropanal in almost quantitative yield (Table 1, run 1). In this reaction, the carbon–carbon double bond of the α,β-unsaturated carbonyl compound was reduced exclusively and the carbonyl group remained unchanged (Scheme 1).

Scheme 1

$$R^1C(O)CH{=}CHR^2 \xrightarrow{\text{NaHTe (1)}} R^1C(O)CH_2CH_2R^2$$

The other results are summarized in Table 1. As shown in Table 1, this reaction is applicable to a wide variety of α,β-unsaturated carbonyl compounds including aldehydes, ketones, esters, and lactones.[7]

Table 1. Reduction of α,β-Unsaturated Carbonyl Compounds

run	substrate	product	yield,[a] %
1			>98
2			>98
3			>98
4			>98
5			>98 (89)
6			>98 (87)
7		 (*trans:cis* = 98:2)	>98
8		 (*trans:cis* = 90:10)	>98
9		 (*trans:cis* = 81:19)	>98 (72)
10			>98
11			>98
12			>98
13			(62)
14			(5)

[a] Yields were determined by GLC. Numbers in parentheses indicate the isolated yield.

In the reduction of some components of essential oils, such as (−)-carvone, pulegone, α-ionone, β-ionone, citral, and verbenone, only the carbon–carbon double bond of the α,β-unsaturated carbonyl moiety was reduced, respectively, despite the presence of unconjugated carbon–carbon double bond(s). With respect to coumarin belonging to α,β-unsaturated cyclic esters, the result was similar to those described above (run 5). 1,4-Dicarbonyl compounds such as diethyl maleate and *p*-benzoquinone were also found to be reduced (runs 6 and 7), but the conversion was rather low. The remainder mainly consisted of the starting material, and byproducts were negligible.

The present procedure possesses the following characteristics: (a) 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

---

[1] Organic reactions using sodium hydrogen telluride. 3. For parts 1 and 2, see refs 3 and 6.

[2] For recent reviews, see: Petragnani, N.; Comasseto, J. V. *Synthesis* 1991, 793 and 897. Petragnani, N.; Comasseto, J. V. *Rev. Heteroatom. Chem.* 1990, *2*, 40. Engman, L. *Phosphorus Sulfur* 1988, *38*, 105.

[3] Yamashita, M.; Kadokura, M.; Suemitsu, R. *Bull. Chem. Soc. Jpn.* 1984, *57*, 3359.

[4] Barton, D. H. R.; Bohe, L.; Lusinchi, X. *Tetrahedron* 1990, *46*, 5273. Barrett, A. G. M.; Read, R. W.; Barton, D. H. R. *J. Chem. Soc., Perkin Trans. 1* 1980, 2191. Barrett, A. G. M.; Barton, D. H. R.; Read, R. W. *J. Chem. Soc., Chem. Commun.* 1979, 645. Shobana, N.; Amirthavalli, M.; Deepa, V.; Shanmugam, P. *Indian J. Chem., Sect. B* 1988, *27B*, 965. Ramesh, M.; Shanmugam, P. *Ibid.* 1983, *22B*, 617. Ramasamy, K.; Kalyanasundaram, S. K.; Shanmugam, P. *Synthesis* 1978, 311. Suzuki, H.; Kawaguchi, T.; Takaoka, K. *Bull. Chem. Soc. Jpn.* 1986, *59*, 665. Suzuki, H.; Takaoka, K. *Chem. Lett.* 1984, 1733 and references cited therein.

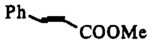
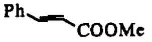
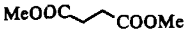
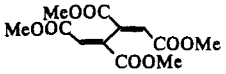
[5] Hudlicky, M. *Reduction in Organic Chemistry*; Ellis Horwood Limited: Chichester, 1984; p 119.

[6] Yamashita, M.; Kato, Y.; Suemitsu, R. *Chem. Lett.* 1980, 847.

[7] Reduction of cinnamic acid derivatives to 3-phenylpropanoic acid derivatives using 1 has been reported: Ramasamy, K.; Kalyanasundaram, S. K.; Shanmugam, P. *Synthesis* 1978, 545.

0022-3263/94/1959-3500$04.50/0

Table 2. Reaction of NaHTe (1) with Acetylenic Compounds

run	substrate	substrate:1	product (yield, %)[a]	
1	PhC≡CCOOMe	1:1		(62)
2	PhC≡CCOOMe	1:2.5	 	(54) (35)
3	MeOOCC≡CCOOMe	1:1	 	(24) (45)
4	MeOOCC≡CCOOMe	1:2.5		(82)
5	PhC≡CPh	1:2.5	b	
6	PrC≡CH	1:2	b	

[a] Isolated yields. [b] No reaction.

of the reaction solution through Celite and concentration give almost pure products); and (e) yields of the products are almost quantitative.

In order to investigate the stereoselectivity of this reduction, the reaction of (−)-carvone with 1 was conducted. As shown in Table 1, (−)-carvone was found to be converted into (+)-dihydrocarvone selectively with only a trace amount of isodihydrocarvone.

As mentioned above, 1 was found to be a selective reducing agent of α,β-carbon–carbon double bonds conjugated with carbonyl group of ketones, aldehydes, or esters. However, among the compounds examined, isophorone and jasmones were not reduced. Therefore, further investigation on the limitation of this reduction is necessary.

Reaction of 1 with Carbon–Carbon Triple Bonds. The reaction of 1 with acetylenic carbonyl compounds was examined. The results are shown in Table 2. In the reaction of methyl phenylpropiolate with 1 molar equiv of 1 (run 1, Table 2), methyl *trans*-cinnamate (4) was obtained in 42% yield, and the remainder was the starting material. However, when 2.5 equiv of 1 was used with the ester, methyl 3-phenylpropionate (5) was formed in 54% yield along with 35% of the cinnamate 4 (run 2).

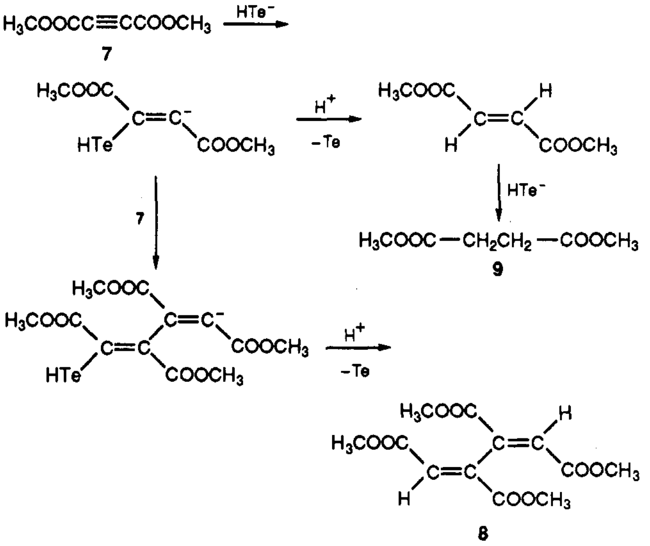
On the other hand, interestingly, in the reaction of dimethyl acetylenedicarboxylate (7) with equimolar 1, tetramethyl (*E*,*E*)-1,3-butadiene-1,2,3,4-tetracarboxylate (8) was obtained as a yellow oil in 45% yield along with the expected dimethyl succinate (9) (run 3). It is notable that no stereoisomers of 8[8] and dimethyl fumarate were detected.

Although it is only speculative at this time, a plausible mechanism is shown in Scheme 2.

When 7 was treated with 2.5 equiv of 1, 9 was obtained in 82% yield as a sole isolable product (run 4). From these results, it can be assumed that 1 was found to be capable of reducing carbon–carbon triple bonds conjugated with carbonyl group to give the corresponding enoates or saturated esters. However, unactivated alkynes such as 1-pentyne and diphenylacetylene did not react with 1.

Elucidation of the reaction mechanism and its application to organic synthesis are under study.

Scheme 2



Conclusion. Sodium hydrogen telluride (NaHTe, 1) in ethanol was found to react with α,β-unsaturated carbon–carbon double bonds or triple bonds conjugated with the carbonyl group of aldehydes, ketones, esters, and lactones. α,β-Unsaturated double bonds were reduced regio- and stereoselectively to the saturated carbonyl compounds. 1 also reacted with the conjugated carbon–carbon triple bonds to give the corresponding double bonds and then saturated ones. When dimethyl acetylenedicarboxylate was treated with 1, reductively dimerized diene, tetramethyl (*E*,*E*)-1,3-butadiene-1,2,3,4-tetracarboxylate, was obtained in addition to dimethyl succinate.

Experimental Section

Ethanol was distilled and stored over 3-Å molecular sieves. Tellurium powder and sodium borohydride were purchased from the Nacalai Chemicals as extra-pure grade and used without further purification. Sodium hydrogen telluride (1) in ethanol was prepared according to the method in the literature[9] and used for the next reaction *in situ*. The following organic compounds, cinnamaldehyde, benzyl cinnamate, coumarin, *p*-benzoquinone, diethyl maleate, (−)-carvone, α-ionone, β-ionone, citral, isophorone, and ethyl cinnamate, were commercial products of the highest available purity. Some components of essential oils, pulegone, verbenone, dihydrojasmone, and *cis*-jasmone, were donated from Ogawa Koryo Co. Benzylideneacetone and furfurylideneacetone were synthesized according to the literature directions.[10] All

---

(8) Cohen, T.; Poeth, T. *J. Am. Chem. Soc.* **1972**, *94*, 4363.

(9) Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574.

(10) Drake, N. N.; Allen, P., Jr. *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. I, p 77.

reduction experiments were carried out under argon atmosphere.

General Procedure for the Reduction of α,β-Unsaturated Carbonyl Compounds by 1. As a representative procedure, the reduction of cinnamaldehyde is described in detail. To the solution of 1 (5 mmol) in ethanol was added an ethanolic solution (2 mL) of cinnamaldehyde (2 mmol). This mixture was stirred at room temperature for 4–5 h and then filtered through Celite and concentrated. The residual liquid was almost pure 3-phenylpropanal (examined by GLC). The product was purified by distillation and identified by comparison of IR, NMR, and mass spectra with those of an authentic sample.

Reductions of the other compounds were conducted in a similar manner, and in several cases, the products were purified by TLC.

Typical Reaction Procedure of 1 with Dimethyl Acetylenedicarboxylate. To the ethanol solution of 1 (10 mmol) was added dimethyl acetylenedicarboxylate (10 mmol), and the reaction mixture was stirred at room temperature for 24 h. Then, the mixture was filtered through Celite and the solvent was removed with a rotary evaporator. The residual liquid was separated by silica gel preparative thin-layer chromatography (hexane:ethyl acetate = 7:1) to give 24% yield of dimethyl succinate and 45% of 8 as a yellow oil.

Tetramethyl (*E,E*)-1,3-butadiene-1,2,3,4-tetracarboxylate: ^{1}H NMR (CDCl$_3$) δ 3.75 (6H, s), 3.86 (6H, s), 7.37 (2H, s); IR (neat) 1720, 1675, 1310, 1230, 1200 cm^{-1}; MS *m/z* 286 (M$^+$). Anal. Calcd for $C_{12}H_{14}O_8$: C, 50.35; H, 4.93. Found: C, 50.45; H, 4.90.