Reductive Removal of the *tert*-Hydroxy Group in α,β-Unsaturated γ-*tert*-Hydroxyketones with Chlorotrimethylsilane-Sodium Iodide. An Alternative to Zinc–Acetic Acid Reduction

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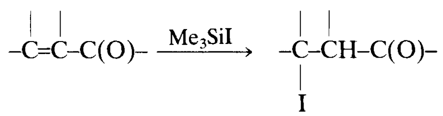
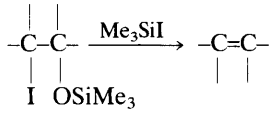
Chlorotrimethylsilane–sodium iodide effects reductive removal of the *tert*-hydroxy group in the α,β-unsaturated γ-*tert*-hydroxyketones (**1**), (**3**), (**5**), and (**7**).

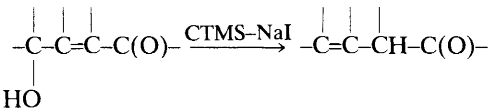
Reactions of iodotrimethylsilane with α,β-unsaturated ketones have been reported to give β-iodoketones[1] [equation (1)] and with iodo trimethylsiloxanes, the corresponding olefins are obtained in excellent yields[2] [equation (2)]. We reasoned, therefore, that the reaction of α,β-unsaturated γ-hydroxyketones with chlorotrimethylsilane (CTMS)–NaI should yield β,γ-unsaturated ketones[3] [equation (3)].



$$-\overset{|}{C}=\overset{|}{C}-C(O)- \xrightarrow{Me_3SiI} -\overset{|}{\underset{\underset{I}{|}}{C}}-\overset{|}{C}H-C(O)- \qquad (1)$$



$$-\overset{|}{\underset{\underset{I}{|}}{C}}-\overset{|}{\underset{\underset{OSiMe_3}{|}}{C}}- \xrightarrow{Me_3SiI} -\underset{|}{C}=\underset{|}{C}- \qquad (2)$$

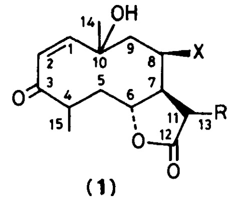


$$-\overset{|}{\underset{\underset{HO}{|}}{C}}-\overset{|}{C}=\overset{|}{C}-C(O)- \xrightarrow{CTMS-NaI} -\overset{|}{C}=\overset{|}{C}-\overset{|}{C}H-C(O)- \qquad (3)$$

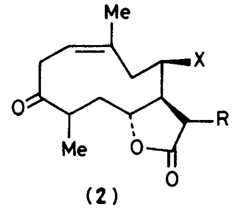
Table 1.[a]

Substrate	Product	Reaction time/min (% Yield)
(**1a**—**c**)	(**2a**—**c**)	10 (90)
(**3**)	(**4**)	30 (40)
(**5**)[b]	(**6**)	10 (60)
(**7**)	(**8**)	5 (60)

[a] Zinc–acetic acid reduction of compounds (**1**), (**3**), and (**5**) furnished (**2**), (**4**), and (**6**), respectively in 70—80% yield whereas (**7**) furnished (**8**) with a 10,1 *trans* double bond (ref. 7). [b] Compound (**5**) on reaction with CTMS–NaI gave a mixture of α,β- and β,γ-unsaturated ketones (by n.m.r. spectroscopy) owing to facile migration of the 10,1 double bond. However during purification by t.l.c. the mixture was fully converted into (**6**).

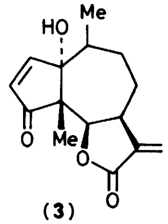


(**1**)

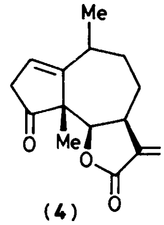


(**2**)

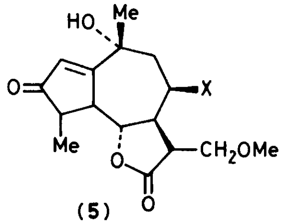
a; R = ═CH$_2$
b; R = —Me
c; R = —CH$_2$OMe



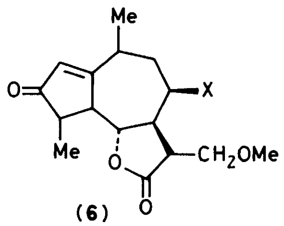
(**3**)



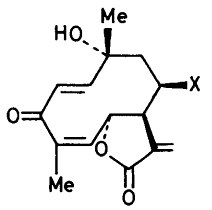
(**4**)



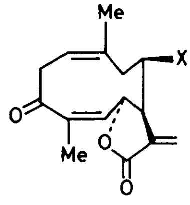
(**5**)



(**6**)

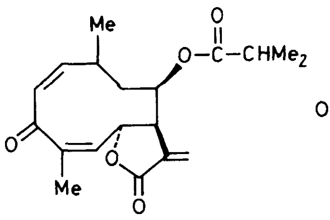


(**7**)

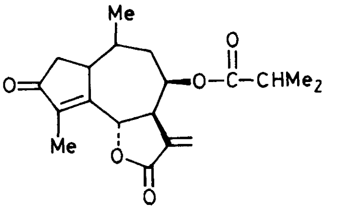


(**8**)

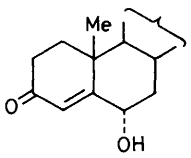
X = –O–C(O)–CHMe$_2$



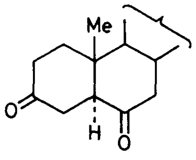
(9)



(10)



(11)



(12)

The results of the application of this principle to compounds (**1a**—**c**), (**3**), (**5**), and (**7**) are presented in Table 1. In a typical experiment a solution of 0.5 mmol of compound (**1a**) in 4 ml of dry acetonitrile was treated with 2.0 mmol of NaI and 1.0 mmol of CTMS with stirring at room temp., and the reaction was monitored by t.l.c. The usual work-up procedure followed by purification by SiO_2 t.l.c. furnished (**2a**).[4]

When the reaction of substrate (**7**) with CTMS–NaI was allowed to continue for 1 h, compounds (**9**) and (**10**) were obtained as the only major products.

It is evident from Table 1 that this method constitutes a useful alternative to zinc–acetic acid reduction, especially for the reductive removal of a *tert*-hydroxy group.[5]

Extension of this technique to 6α-hydroxycholest-4-en-3-one (**11**) furnished cholestane-3,6-dione (**12**) in quantitative yield.[6] Before the carbonium ion at C-5 is trapped by iodide, a probable elimination of a proton from C-6 (or a hydride shift from C-6 to C-5) takes place resulting in the formation of (**12**).

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