Reductive Coupling of Ketones or Aldehydes with Electron-deficient Alkenes Promoted by Samarium Di-iodide

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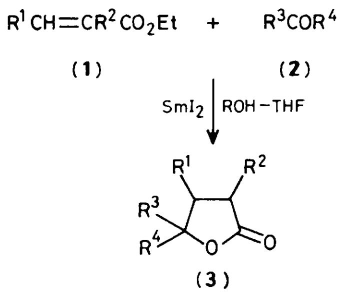
Samarium di-iodide is an efficient reagent for the reductive coupling of ketones or aldehydes and electron-deficient alkenes, whereby γ-lactones can be prepared in good yields from ethyl acrylate.

There have been several recent examples of the use of lanthanoid reagents in organic synthesis.[1] Samarium di-iodide, a strong one-electron transfer reagent, is particularly useful for carbon–carbon bond formation.[2—5] We have now found that it is effective for the reductive coupling of ketones or aldehydes with electron-deficient alkenes such as ethyl acrylate to afford γ-lactones.



When a mixture of ethyl acrylate (**1**; $R^1 = R^2 = H$) (2 mmol), acetophenone (**2**; $R^3 = Ph$, $R^4 = Me$) (2 mmol), and t-butyl alcohol (2 mmol) was added to a deep-green solution of samarium di-iodide [prepared[2b] from samarium metal and 1,2-di-iodomethane in tetrahydrofuran (THF)] in THF (0.4 M; 10 ml) under nitrogen, a mild exothermic reaction proceeded rapidly at room temperature, the colour changing to a

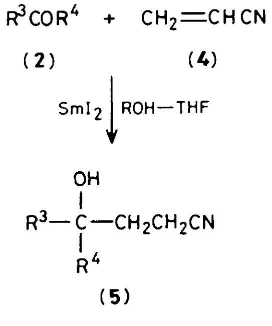
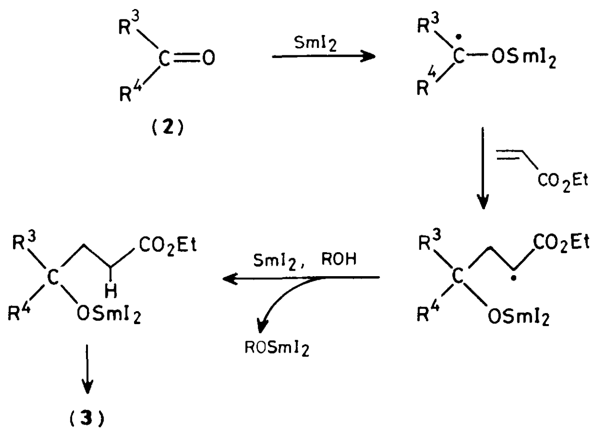


Table 1. Reductive coupling of ketones or aldehydes with electron-deficient alkenes.[a]

Alkene	Ketone or aldehyde (2) R^3	R^4	% Isolated yield of (3) or (5)
(1; R^1 = R^2 = H)	Ph	Me	70[b]
	Ph	Ph	38
	Et	Et	40
	-$[CH_2]_5$-		76
	Ph	H	82
	Pr^n	H	65[c]
	C_5H_{11}	H	28
	Pr^i	H	44
	CH_2=$CH[CH_2]_2$	Me	70
(1; R^1 = H, R^2 = Me)	Ph	Me	75[d]
	Ph	H	75[d]
	-$[CH_2]_5$-		63
(1; R^1 = Me, R^2 = H)	Ph	H	50[d]
(4)	Ph	Me	17
	C_6H_{13}	Me	20

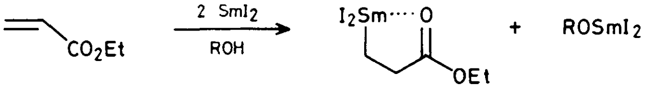
[a] See text for typical conditions. [b] 66 and 50% with MeOH and EtOH (2 mmol) respectively instead of Bu^tOH; 72 and 62% on addition of TMEDA or tetraethyleneglycol dimethyl ether (4 mmol) respectively. [c] Including γ-hydroxy ester (20%). [d] *cis* : *trans* 50 : 50.



Scheme 1

brownish yellow. After 3 h, the usual work-up gave the γ-lactone (3; R^1 = R^2 = H, R^3 = Ph, R^4 = Me) (1.4 mmol) in good yield following preparative t.l.c. (hexane–Et_2O, 1 : 1, as eluant). 2-Phenylethanol was a by-product,† but in low yield. The presence of an alcohol is essential, complex unidentified products being obtained in the absence of an alcohol; t-butyl alcohol gave more satisfactory results than methanol or ethanol. The alcohol acted as a proton donor, the use of MeOD leading to the deuteriated γ-lactone (3; R^1 = H, R^2 = D, R^3 = Ph, R^4 = Me).

The effect of addition of tetramethylethylenediamine (TMEDA) or tetraethyleneglycol dimethyl ether was examined, since their complexation with samarium might suppress the simple reduction of the ketone,[4] but the yields of (3) were not improved (Table 1).



Scheme 2

Results for other ketones and aldehydes, shown in Table 1, demonstrate that the reaction is applicable to both aliphatic and aromatic ketones or aldehydes, whereas the electrochemical method is limited to aliphatic compounds.[6] The yields of (3) were usually reasonable and the conditions are mild; *e.g.* hex-5-en-2-one gives the lactone (3; R^1 = R^2 = H, R^3 = CH_2=$CHCH_2CH_2$, R^4 = Me) in 70% yield with no side reactions.[7]

α- and β-Substituted γ-lactones were prepared from ethyl methacrylate and ethyl crotonate, respectively, as *cis*- and *trans*-isomers (R^1 and R^2 groups).‡

In the reaction of (2) with acrylonitrile (4), the γ-hydroxy nitrile derivatives (5)§ were produced, but the yields were not satisfactory (Table 1).

The reaction may proceed by a radical mechanism as in Scheme 1, although reaction *via* a samarium ester homoenolate mechanism should also be considered (Scheme 2).[8]

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† Compounds can be reduced to the corresponding alcohols by SmI_2 in the presence of an alcohol; see ref. 2b.

‡ Ratio determined by ^1H n.m.r. spectroscopy; two doublets were observed at δ 1.12 and 1.24 for the α-methyl group of the γ-lactone derived from benzaldehyde and ethyl methacrylate.

§ (5; R^3 = Ph, R^4 = Me): δ_H (60 MHz; CCl_4; Me_4Si) 1.42 (3H, s, Me), 1.8—2.1 (4H, m, CH_2CH_2), 2.68 (1 H, br. s, OH), and 7.11 (5H, m, Ph); $\nu_{max.}$ (CCl_4) 3479 (OH) and 2250 cm^{-1} (CN).