

EFFICIENT FORMATION OF PINACOLS FROM ALDEHYDES OR KETONES MEDIATED BY
SAMARIUM DIIODIDE

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Summary

Samarium diiodide is an excellent reagent for aldehyde or ketone coupling. With aromatic aldehydes, reactions are very fast with a complete selectivity versus substituents such as cyano, carboxyl or nitro groups.

As shown in (1-3), samarium diiodide is a powerful electron-donor able to promote various reactions. Reduction of aldehydes or ketones was achieved in THF in presence of a small amount of methanol, reduction being much faster for aldehydes than for ketones (1), and the formation of pinacol being frequently negligible. The growing interest for SmI_2 in organic synthesis (4,5) leads us to describe the selective synthesis of pinacols using SmI_2 as the reducing agent.

We found that aromatic aldehydes or aromatic ketones couple within a few seconds if put in the presence of one equimolar amount of SmI_2 , at room temperature in THF in the absence of water or alcohols. A few hours are needed for aliphatic aldehydes, and one day is needed for aliphatic ketones. No alcohol was produced by competitive carbonyl reduction. The main results are collected in Table I. For example, benzaldehyde (212 mg, 2 mmol) dissolved in 5 ml of THF is added at room temperature under nitrogen, to 20 ml of 0.1 M SmI_2 in THF (2 mmol). The typical color of SmI_2 immediately turns to orange. After stirring for 10 min. a yellow precipitate appears. Hydrolysis with 0.1 N HCl followed by ether extraction and washing with sodium thiosulfate and saturated NaCl solution gives 203 mg of 1,2-diphenyl ethanediol (95 % yield).

The method, because of the high yields and its rapidity, makes it competitive with many other ways of pinacol formation (6-9). The high yields obtained in the coupling of aromatic aldehydes parasubstituted by a CN, CO_2H or NO_2 group are of special interest.

We are further investigating extent of intermolecular or intramolecular pinacol formation using SmI_2 as a reagent.

Acknowledgements

We thank CNRS for its financial support (ATP Chimie Fine n°000104).

TABLE I : Coupling of aldehydes or ketones by SmI_2 ^a

$$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}' \xrightarrow[2) \text{H}_3\text{O}^+]{1) 2 \text{SmI}_2} \text{R}-\overset{\text{R}'}{\underset{\text{OH}}{\text{C}}}-\overset{\text{R}'}{\underset{\text{OH}}{\text{C}}}-\text{R}$$

R	R'	Reaction time ^b	Yield ^{c,d}
H	C_6H_5	0.5 min.	95 %
H	p- $\text{NO}_2-\text{C}_6\text{H}_4$	0.5 min.	95 %
H	p- $\text{CN}-\text{C}_6\text{H}_4$	0.5 min.	95 %
H	p- $\text{COOH}-\text{C}_6\text{H}_4$	0.5 min.	66 %
H	p- $\text{CH}_3\text{O}-\text{C}_6\text{H}_4$	1 min.	90 %
H	p- $(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_4$	0.5 min.	90 % ^e
H	2,4,6- $(\text{CH}_3)_3-\text{C}_6\text{H}_2$	0.5 min.	95 %
H	n- C_7H_{15}	3 h	85 %
H	Cyclohexyl	4 h	95 %
H	CH_3	1 min.	0 % ^f
CH_3	n- C_6H_{13}	24 h	80 %
CH_3	C_6H_5	0.5 min.	95 %

a 2 mmol of substrate, 2 mmol of SmI_2 in 25 ml of THF at room temperature under nitrogen. For other details see the text.

b Measured by the change of color from deep-blue green (Sm^{2+}) to yellow-orange (Sm^{3+}).

c Isolated yields. Spectral data (IR and ^1H nmr) are in agreement with the structure.

d The pinacol is formed as a dl-meso mixture which was analysed only in the case of benzaldehyde (dl/meso = 56/44).

e Hydrolysis under neutral conditions. In acidic ones the product remains in the aqueous phase as a soluble ammonium salt.

f In this case, ethyl acetate is the major product. A reaction of the Tischchenko type is probably a competitive process.

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(Received in France 13 December 1982)