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A. YANAGISAWA,* Y. TERAJIMA, K. SUGITA, K. YOSHIDA (CHIBA UNIVERSITY, JAPAN) Asymmetric Aldol Reaction of Ketones with Alkenyl Trichloroacetates Catalyzed by Dibutyltin Dimethoxide and BINAP·Silver(I) Complex: Construction of a Chiral Tertiary Carbon Center Adv. Synth. Catal. 2009, 351, 1757-1762.

Dibutyltin Dimethoxide and Ag(I)-BINAP-**Catalyzed Aldol Reactions of Ketones**

$$(R)\text{-BINAP (10 mol\%)} \\ AgOTf (20 mol\%) \\ Bu_2Sn(OMe)_2 (8 mol\%) \\ MeOH (5 equiv) \\ THF, 3 A MS, -20 °C$$
 Selected examples:
$$OMe \\ OHO \\ CO_2Me$$

$$86\% \text{ yield, dr} = 83:17, 90\% \text{ ee}$$

$$58\% \text{ yield, dr} = 97:3, 89\% \text{ ee}$$

$$38\% \text{ yield, dr} > 99:1, 93\% \text{ ee}$$
 Asymmetric aldol reaction of diketene with methyl benzoylformate:

MeOCOCCI₃

OSnBu₂(OMe)

R¹

CO₂Me

R²

$$(R)$$
-BINAP-AgOTf

Significance: The authors have reported a new asymmetric aldol reaction of alkenyl trichloroacetates with α -keto esters by using dibutyltin dimethoxide and Ag(I)-BINAP complex in the presence of methanol. The aldol products were obtained in good to excellent yields and up to 93% ee. This methodology was further extended to the reaction of diketene with methyl benzoylformate.

SYNFACTS Contributors: Hisashi Yamamoto, Cheol Hong Cheon Synfacts 2009, 11, 1227-1227 Published online: 22.10.2009 DOI: 10.1055/s-0029-1218076; Reg-No.: H12809SF

Comment: Previously, the authors reported that dibutyltin dimethoxide acts as a catalyst in the aldol reaction of alkenyl trichloroacetates with aldehydes (Tetrahedron Lett. 2003, 44, 7163). In this paper, they have extended this method to α -keto esters. It is interesting that the addition of a catalytic amount of silver(I) bidentate phosphine complex remarkably accelerated the aldol reaction.

Category

Metal-Catalyzed Asymmetric Synthesis and **Stereoselective** Reactions

Key words

aldol reaction ketones silver(I)-BINAP tin

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