

A Novel Cyclodimerization of α,β -Unsaturated Carbonyl Compounds promoted by Ytterbium Metal

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Ytterbium metal has been used to promote cyclodimerization of α,β -unsaturated ketones and esters, leading to cyclopentanol, cyclopentanone, or cyclohexanone derivatives, regio- and stereo-selectively.

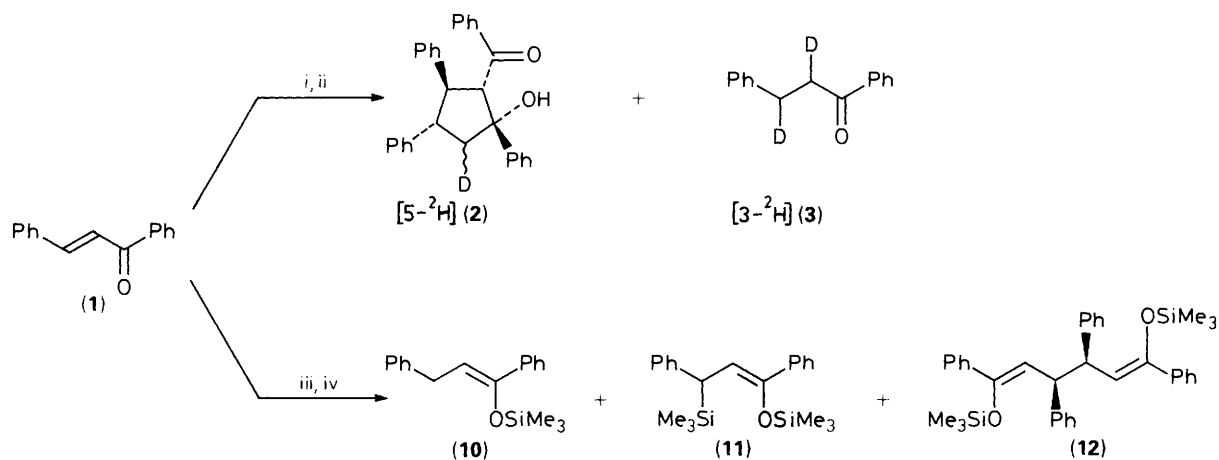
We have previously demonstrated that diaryl ketones are readily unpoled by ytterbium metal to react with various electrophiles such as carbonyl compounds, epoxides, and diphenylacetylene.¹ Carbon-carbon double bonds conjugated with aromatic rings are also reduced by Yb metal in the presence of methanol.² In order to evaluate the reducing ability of the metal, we investigated the reaction of α,β -unsaturated carbonyl compounds, expecting selective reduction of the alkenic moiety as with $\text{SmI}_2\text{-MeOH}$ ³ or the carbonyl group as with $\text{CeCl}_3\text{-NaBH}_4$.⁴

When chalcone (**1**) (2.5 equiv.) was treated with ytterbium metal (40 mesh) in THF-HMPA (4:1) (THF = tetrahydrofuran, HMPA = hexamethylphosphoramide) at room temperature, the mixture changed to green then to dark red, and the reaction was quenched with water after 3.5 h to give

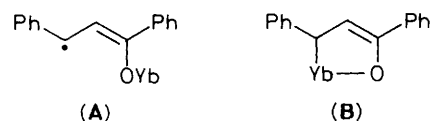
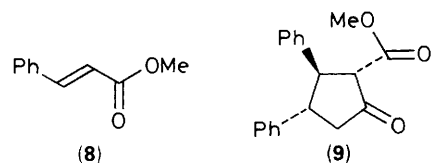
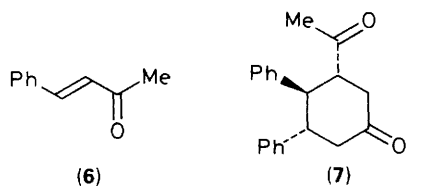
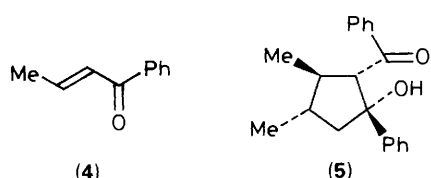
(1*R**,2*S**,3*R**,4*S**)-2-benzoyl-1,3,4-triphenylcyclopentanol (**2**)[†] and benzylacetophenone (**3**) in 73 and 35% yields,[‡] respectively. Other regio- and stereo-isomers, corresponding to (**2**), were not detected. Similar cyclodimerizations of

[†] ¹H NMR spectroscopic data (270 MHz, CDCl₃) for (**2**): 2.73 (1H, dd, *J* 14.5, 6.1 Hz, C⁵H), 3.07 (1H, dd, *J* 14.5, 10.8 Hz, C⁵H), 3.82 (1H, ddd, *J* 10.8, 10.3, 6.1 Hz, C⁴H), 4.16 (1H, dd, *J* 11.8, 10.3 Hz, C³H), 4.57 (1H, d, *J* 11.8 Hz, C²H), 5.25 (1H, br. s, OH), 6.94–7.63 (20H, m); for (**7**): 1.65 (3H, s, Me), 2.73 (1H, dd, *J* 15.2, 4.9 Hz, C⁶H), 2.79 (1H, dd, *J* 15.4, 7.3 Hz, C²H), 3.06 (1H, dd, *J* 15.4, 5.7 Hz, C²H), 3.24 (1H, dd, *J* 15.2, 10.0 Hz, C⁶H), 3.49 (1H, dd, *J* 6.1, 5.6 Hz, C⁴H), 3.58 (1H, m, C⁵H), 3.68 (1H, m, C³H), 7.00–7.50 (10H, m).

[‡] All yields are based on Yb metal.



Scheme 1. Reagents and conditions: i, Yb, room temp.; ii, D₂O; iii, Yb, 0 °C; iv, Me₃SiCl.



α,β -unsaturated ketones and esters are summarized in Table 1. The reaction of 1-phenylbut-2-en-1-one (4) gave the cyclopentanol (5), whereas 4-phenylbut-3-en-2-one (6) was converted to 4,5-diphenyl-3-acetylcyclohexanone (7).[†] The formation of (7) is interesting, since reduction does not take place formally as with (1) and (4), however the mechanism is uncertain at present. Methyl cinnamate (8) was reductively dimerized by Yb metal to afford 3,4-diphenyl-2-methoxycarbonylcyclopentanone (9). In contrast, cinnamaldehyde was reduced to cinnamyl alcohol in 44% yield under identical conditions, but the expected 3-phenylpropionaldehyde and dimerization product were not formed.

Table 1. Cyclodimerization of α,β -unsaturated carbonyl compounds promoted by ytterbium metal.^a

Carbonyl compound	Product	% Yield ^b
(1)	(2)	73
(4)	(5)	38 (74)
(6)	(7)	44
(8)	(9)	36 (76)

^a Carbonyl compound: Yb = 2.5:1. ^b Isolated yields (GC).

Next we investigated the reaction of chalcone (1) under various conditions to determine the reaction process. Chalcone (1) was recovered unchanged in 96% yield on treatment with Yb in the presence of methanol. When the reaction of (1) with an equimolar amount of Yb was quenched with deuterium oxide, deuterated (2) and (3) were obtained in 14 and 40% yields, respectively (Scheme 1). Quenching with trimethylsilyl chloride gave (Z)-1,3-diphenyl-1-trimethylsilyloxypropene (10), (Z)-1,3-diphenyl-3-trimethylsilyloxypropene (11), and D,L-(Z)-1,6-bis(trimethylsilyloxy)-1,3,4,6-tetraphenylhexa-1,5-diene (12) in 19, 9, and 29% yields, respectively. These results suggest that electron transfer from Yb to (1) would generate the radical enolate (A) and the dianion-like (B);¹ radical cyclization of the former intermediate followed by anionic ring closure gives rise to the cyclodimerization products.

In summary, ytterbium metal promotes the cyclodimerization of α,β -unsaturated carbonyl compounds, which has not been achieved previously by other metals or electrochemistry.

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