C–C Bond Cleavage and Deoxygenation of Chalcone by the Organo-ytterbium σ-Complex PhYbI

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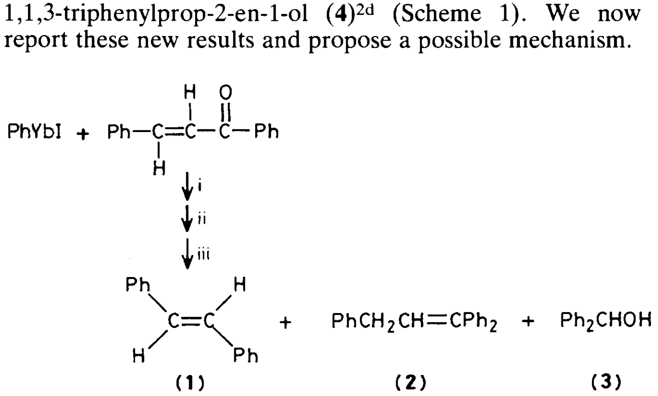
Reaction of excess of the organo-ytterbium σ-complex PhYbI with chalcone gives *trans*-stilbene (**1**), the C–C bond cleavage product and 1,1,3-triphenylpropene (**2**) together with diphenylmethanol (**3**); a possible mechanism of the reaction is proposed.

We have recently reported that organolanthanoid σ-complexes (RLnI), which are prepared *in situ* from lanthanoid metals (Ln) and organic iodides (RI),[1] react with a variety of substrates and show unique reactivity.[2] These include the selective 1,2-addition of an equimolar amount of RLnI to α,β-unsaturated carbonyl compounds.[2d] Beletskaya *et al.* reported that a different reaction occurred to give propene derivatives when the reaction system contained an excess of RLnI.[3] In a continuing study of this reaction, we have found that in the reaction with an excess of PhYbI with chalcone, *trans*-stilbene (**1**) and 1,1,3-triphenylpropene (**2**) are formed with diphenylmethanol (**3**) instead of the 1,2-addition product 1,1,3-triphenylprop-2-en-1-ol (**4**)[2d] (Scheme 1). We now report these new results and propose a possible mechanism.



Scheme 1. *Reagents:* i, excess of PhYbI, THF, −30 °C, 1 h; ii, room temp., 18 h; iii, 2 M HCl.

A typical reaction was carried out as follows. Yb metal (40-mesh; 3.5 mg-atom) was placed in a 50 ml centrifuge tube which was then sealed with a serum cap and pure nitrogen passed through. After the metal in the tube had been dried by heating under the stream of nitrogen, tetrahydrofuran (THF; 2 ml), which had been freshly distilled under nitrogen from sodium benzophenone ketyl, was added by syringe. The tube was then cooled to −30 °C, and PhI (3 mmol) in THF (2 ml) was added in drops during 10—20 min. After the red-brown complex PhYbI had formed, further THF (4 ml) was added. Chalcone (1 mmol) in THF (2 ml) was then added dropwise to the solution and the mixture was stirred at −30 °C for 1 h and then at room temperature overnight. After usual work-up, the products were identified by comparison with authentic samples. The results are summarized in Table 1. As shown in Table 1, the reaction of an equimolar amount of PhYbI with chalcone gives the 1,2-addition product (**4**) selectively (run 1),[2d] but as the ratio of PhYbI to chalcone increases, *trans*-stilbene (**1**) or triphenylpropene (**2**) becomes the main product instead of (**4**) (runs 2—4). If the reaction is carried out only at −30 °C without heating up to room temperature, (**4**) is still formed exclusively, although excess of PhYbI is present

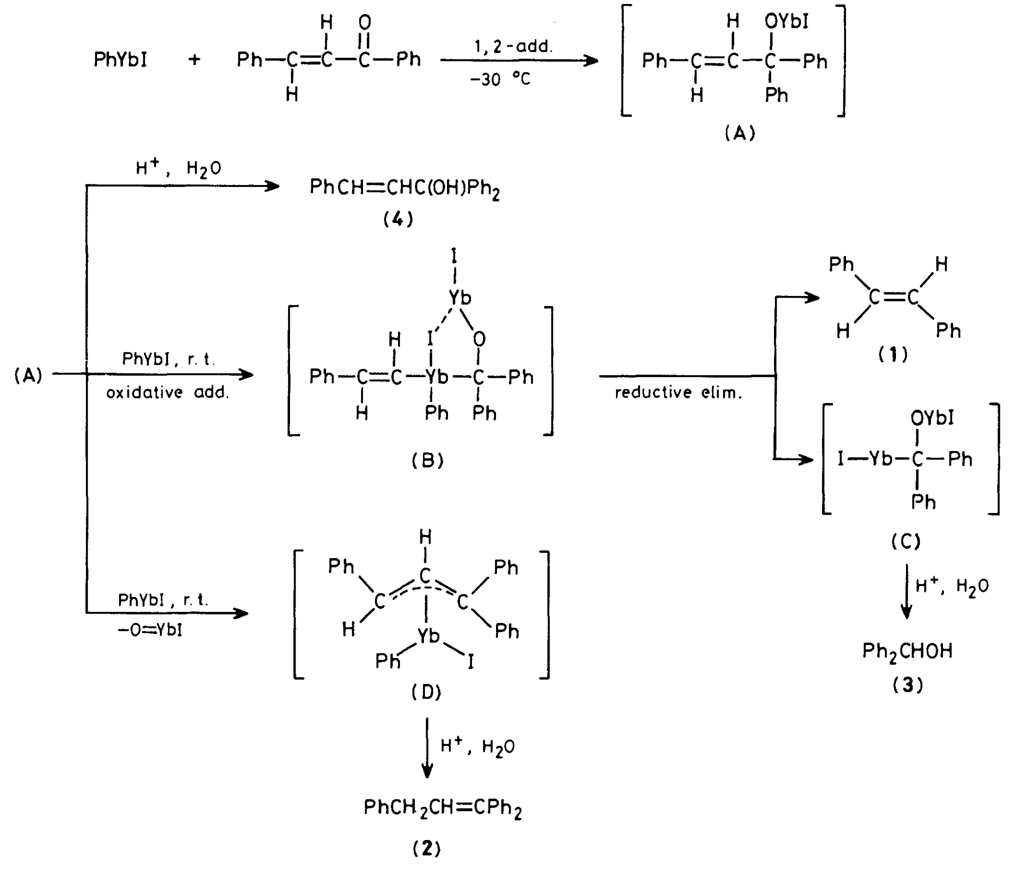
$$\text{PhYbI} + \text{PhCH=CHC(OH)Ph}_2 \xrightarrow{\text{i}}\xrightarrow{\text{ii}} (\mathbf{1}) + (\mathbf{2}) + (\mathbf{3})$$

Scheme 2. *Reagents:* i, PhYbI (3 mmol) and PhCH=CHC(OH)Ph$_2$ (1 mmol) in THF (10 ml), room temp., 18 h; ii, 2 M HCl.

Table 1. Reactions of excess of RYbI with chalcone.

Run	R	RYbI : Chalcone	Reaction conditions	Product and yield, %[a] (1)	(2)	(4)
1	Ph	1 : 1	−30 °C, 1 h then r.t.,[i] 18 h	tr.[i]	tr.	62
2	Ph	1.5 : 1	"	12[b]	5	40
3	Ph	2 : 1	"	22[b]	36	tr.
4	Ph	3 : 1	"	31[b]	30	tr.
5	Ph	3 : 1	−30 °C, 18 h	tr.	tr.	41
6	Ph	3 : 1	−30 °C, 1 h then r.t., 3 h	21[b]	16	24
7	Ph	3 : 1	−30 °C, 1 h then 60 °C, 3 h	21[b]	9	tr.
8	Ph	3 : 1	−30 °C, 1 h then r.t., 18 h	10[b,c]	35	tr.
9	Ph	3 : 1	"	24[b,d]	7	39
10	p-MeC$_6$H$_4$	3 : 1	"	—[e]	—[f]	—[g]
11	p-BrC$_6$H$_4$	3 : 1	"	—	—	—[h]

[a] Based on chalcone and determined by g.c. [b] Diphenylmethanol (**3**) was also formed in almost equimolar amounts with respect to (**1**). [c] Hexamethylphosphoric triamide (HMPA) was used as cosolvent. [d] Diethyl ether was used as cosolvent. [e] *trans*-*p*-Methylstilbene and phenyl-*p*-tolylmethanol were each formed in 19% yield. [f] 1,3-Diphenyl-1-*p*-tolylprop-1-ene was formed in 15% yield. [g] 1,3-Diphenyl-1-*p*-tolylprop-2-ene-1-ol was formed in 13% yield. [h] 1,3-Diphenyl-1-*p*-bromophenylprop-2-ene-1-ol was formed in 60% yield. [i] r.t. = room temperature; tr. = trace.



Scheme 3. Possible mechanism.

(run 5). The decrease in yield in the case of the reaction at 60 °C might be due to the decomposition of the complex PhYbI at this temperature (run 7). In the reaction of p-MeC$_6$H$_4$YbI with chalcone (run 10), the methyl-substituted stilbene PhCH=CHC$_6$H$_4$Me-*p* was obtained and (**1**) was not detected indicating that one phenyl group of the stilbene (**1**) was derived from the complex PhYbI and not from chalcone in the reaction of PhYbI with chalcone. In any reaction where *trans*-stilbene (**1**) was obtained, an equimolar amount of diphenylmethanol (**3**) was also formed. This type of reaction did not occur in the case of p-BrC$_6$H$_4$YbI (run 11).

It was also found that the reaction of excess of PhYbI with 1,1,3-triphenylprop-2-en-1-ol gave products (**1**), (**2**) and (**3**) in 22, 48, and 19% yields, respectively (Scheme 2).

These results could be explained by the mechanism in Scheme 3. First, one molecule of PhYbI attacks chalcone regioselectively at the 1- and 2-positions to give the intermediate (A) which after hydrolysis leads to the usual

1,2-addition product (**4**).[2d] With excess of PhYbI present at room temperature, oxidative addition of another molecule of PhYbI to the C–C bond of (A) would occur to give the intermediate (B)† which would undergo reductive elimination to give (**1**) and the Yb complex (C). Hydrolysis of the intermediate (C) would give diphenylmethanol (**3**). This accounts for the formation of almost equimolar amounts of (**1**) and (**3**). With excess of PhYbI, (A) also undergoes C–O bond cleavage and electron transfer from PhYbI to give the π-complex (D) which would give (**2**) after hydrolysis.

This C–C bond cleavage of an α,β-unsaturated ketone and allyl alcohol by RYbI complexes has not been reported before, and the reaction of excess of PhYbI with other substrates is being studied.

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† Although intermediate (B) contains the unusual tetravalent Yb^{IV}, the cyclic structure would decrease its positive charge stabilizing the intermediate. The formation of the deuteriated $HOCD(Ph)_2$ in 11% yield together with PhHC=CHPh (14%) and $PhCDHCH=CPh_2$ (56%) from the reaction of (**4**) with PhYbI on quenching with D_2O also supports the mechanism.