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Preliminary communication

SELECTIVE 1,2-ADDITION OF ORGANOCERIUM(III) REAGENTS TO α,β-UNSATURATED CARBONYL COMPOUNDS

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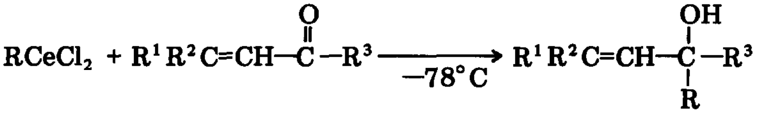
Summary

Organocerium(III) reagents react with α,β-unsaturated carbonyl compounds to afford 1,2-addition products in higher regioselectivity in comparison with organolithiums and the Grignard reagents. This selective 1,2-addition of organocerium reagents is considered to proceed through a polar pathway.

Previously we reported that organocerium(III) reagents were conveniently generated by the reaction of anhydrous cerium(III) chloride with organolithium reagents [1]. The reagents reacted smoothly with easily enolizable ketones to afford the addition products in good to excellent yields. The results revealing the low basicity and strong carbonylophilicity of the reagents prompted us to study the reaction of the reagents with α,β-unsaturated carbonyl compounds, in that the exclusive formation of 1,2-addition products should be anticipated*. This expectation was readily demonstrated by our preliminary experiments. Thus, the butylcerium reagent reacted cleanly with such simple α,β-enones as 2-cyclohexenone and 4-phenyl-3-buten-2-one in tetrahydrofuran (THF) at −78°C for 2—3 h to afford the corresponding 1,2-addition products in essentially quantitative yields.

$$\mathrm{RLi + CeCl_3 \xrightarrow[-78^\circ C]{THF} RCeCl_2 + LiCl}$$



$$\mathrm{RCeCl_2 + R^1R^2C{=}CH{-}\overset{\overset{\large O}{\|}}{C}{-}R^3 \xrightarrow[-78^\circ C]{} R^1R^2C{=}CH{-}\underset{\underset{\large R}{|}}{\overset{\overset{\large OH}{|}}{C}}{-}R^3}$$

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*Recently it was reported that divalent organolanthanoid σ-complexes, prepared by the reaction of lanthanoid metal with iodobenzene or iodomethane, reacted with α,β-enones to give 1,2-addition products in high selectivity [2,3].

In order to obtain the mechanistic aspect of this 1,2-addition reaction, as well as to demonstrate its synthetic utility, we studied the reactivities of cerium reagents toward new probes, (*E*)- and (*Z*)-1-(*p*-methoxyphenyl)-3-phenyl-2-propen-1-one (I*E* and I*Z**), since α,β-enones conjugating with an aryl group are known to be readily susceptible to 1,4-addition with Grignard reagents [4]. The reactions with I*E* or I*Z* were carried out at —78° C, and furthermore the corresponding lithium and the Grignard reagents were allowed to react with these probes under the same conditions for comparison. The results are summarized in Table 1.

TABLE 1

REACTION OF ORGANOCERIUM, ORGANOLITHIUM, OR THE GRIGNARD REAGENT WITH (*E*)- OR (*Z*)-$C_6H_5CH{=}CHCOC_6H_4OCH_3$-*p*

Entry	Substrate	Reagent	Conditions ^{a}		Yield of products (%) ^{b}		
			Solvent	Time (h)	II*E*	II*Z*	III
1	I*E*	CH_3CeCl_2	THF/ether(12/1)	0.5	98	0	trace
2	I*E*	CH_3Li	THF/ether(5/1)	0.5	65	0	17
3	I*E*	CH_3MgBr	THF	0.5	38	0	60
4	I*E*	n-$C_4H_9CeCl_2$	THF/hexane(8/1)	0.5	50	0	43
5	I*E*	n-C_4H_9Li	THF/hexane(2/1)	0.5	36	0	50
6	I*E*	n-C_4H_9MgBr	THF	0.5	10	0	76
7	I*E*	$C_6H_5CeCl_2$	THF/ether(8/1)	0.5	90	0	4
8	I*E*	C_6H_5Li	THF/ether(3/1)	0.5	85	0	10
9	I*E*	C_6H_5MgBr	THF	0.5	14	0	78
10	I*Z*	CH_3CeCl_2	THF/ether(12/1)	1.0	trace	97	trace
11	I*Z*	CH_3Li	THF/ether(5/1)	1.0	trace	96	trace
12	I*Z*	CH_3MgBr	THF	1.0	26	20	38
13	I*Z*	n-$C_4H_9CeCl_2$	THF/hexane(8/1)	1.0	trace	97	trace
14	I*Z*	n-C_4H_9Li	THF/hexane(2/1)	1.0	trace	70	20
15	I*Z*	n-C_4H_9MgBr	THF	1.0	20	25	50
16	I*Z*	$C_6H_5CeCl_2$	THF/ether(8/1)	1.5	trace	93	4
17	I*Z*	C_6H_5Li	THF/ether(3/1)	1.5	trace	90	4
18	I*Z*	C_6H_5MgBr	THF	1.5	25	20	45

^{a} All reactions were carried out at —78° C. ^{b} Isolated yield.

It should be noted that all cerium reagents underwent 1,2-addition exclusively except for entry 4. Another significant finding is that the reaction of I*Z* with cerium reagents afforded *Z*-allylic alcohols (II*Z*) in excellent yields (entries 10, 13, and 16). These results are in contrast to those of the reactions of the Grignard or lithium reagents, in which considerable amounts of 1,4-addition products (III) and isomeric 1,2-addition products (II*E*) were produced (entries 12, 14, 15, and 18) via radical anion intermediates [5]. The results obtained here suggest that the reaction of cerium reagents occurs exclusively by direct nucleophilic addition**.

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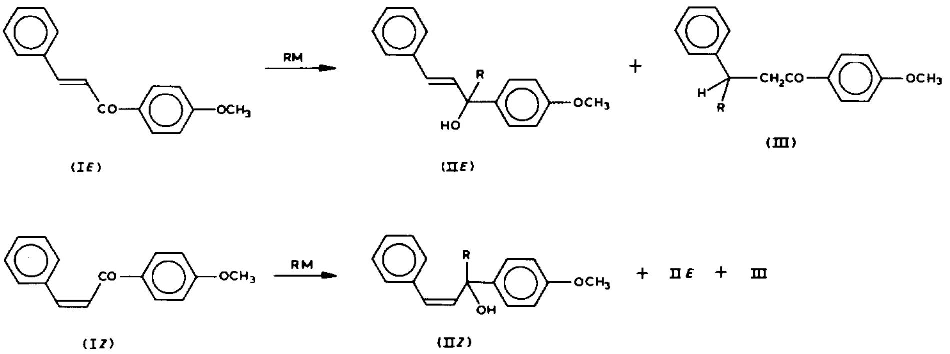
*The *Z*-isomer (I*Z*) was obtained by exposing a solution of I*E* in benzene to sunlight for 2 days, followed by repeated chromatography on silica gel. Lemon yellow oil; ^{1}H NMR (CCl_4) δ 3.75 (s, 3H), 6.45 (d, *J* 12 Hz, 1H), 6.78 (d, *J* 9 Hz, 2H), 6.88 (d, *J* 12 Hz, 1H), 7.0—7.5 (m, 5 H), 7.85 (d, *J* 9 Hz, 2H); UV (CCl_4) λ_{max} 286 nm (log ϵ 3.8).

**It is noted that this 1,2-addition of organocerium reagents formally resembles the selective 1,2-reduction of α,β-enones with the $NaBH_4/CeCl_3$ reagent system [6].



(R = CH_3, n-C_4H_9, C_6H_5. M = $CeCl_2$, Li, MgBr)

The present 1,2-addition reaction of organocerium reagents may have a potential synthetic utility, particularly for the syntheses of natural products.

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