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Addition of Organosamarium Reagents to α, β−Unsaturated Esters

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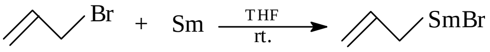
Abstract: Allylsamarium bromide reacts with α, β-unsaturated esters and α-alkyloxy carbonyl α, β-unsaturated esters to give 1,2-addition and 1,4-addition products respectively.

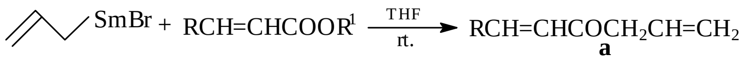
Keywords Samarium, Grignard reagent, conjugate addition, α, β–unsaturated esters.

Compared to the extensive use of samarium diiodide in organic synthesis[1], little reports appeared on the application of samarium metal in organic synthesis. As early as 1971 Evans and co-workers had prepared phenylsamarium iodide from iodo-benzene and samarium metal[2]. But they found that samarium is not so active as ytterbium. In 1986 Fukuzawa also prepared the organosamarium intermediate similar to Grignard reagent[3]. It was Curran who firstly proved and named the samarium Grignard reaction in 1991[4]. In exploring the application of samarium in organic synthesis, we found that allylsamarium bromide is easy to prepare and the results of its reaction with some substrates were satisfactory. Our group has explored the reaction of allylsamarium bromide with some substrates, such as N-(2-aminoalkyl) benzotriazoles[5], imines[6], nitriles[7], diorgano diselenides[8], disulfides[9], isocyanates and isothiocyanates[10] *etc.* to give homoallylamines, allylselenides, allylsulfides, butenamides and thiobutenamides *etc*.

Addition of Grignard reagents to α, β−unsaturated esters is an old but interesting subject. In the case of magnesium Grignard reagents, both 1,2- and 1,4-additions were possible[11, 12], the orientation depended on some effects such as the bulk of the substrates and reagents. Although many researches have been carried out on the subject by different authors no absolute conclusion can be reached[12].

Herein we wish to report the results of reactions of allylsamarium bromide with α, β−unsaturated esters. It is found that the 1,2-addition is specific for monocarboxylated esters:





The reaction could stop at the stage of ketones if the molar ratio of the substrates to reagent is 1 to1 and the allyl and substituted-vinyl ketones were the main products (see **Table** below). Though the samarium ion in the reaction was considered to be divalent, it did not initiate the troubles such as reduction or coupling of the substrates or products. Whereas for substrates of α-alkoxycarbonyl β-aryl- or alkyl-substituted α, β –unsaturated esters the reaction underwent fully through 1,4-addition route:

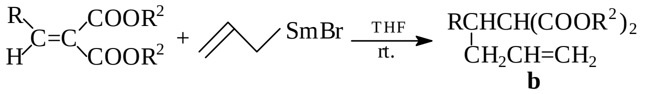


Table Products and Yields

Entry	R	R^1	R^2	Yield(%)*
1a	Ph	CH_3		69
2a	Ph	C_2H_5		67
3a	H	n- C_4H_9		58
4a	Ph	$CH_2C(CH_3)_3$		54
1b	Ph		CH_3	82
2b	Ph		C_2H_5	80
3b	*p*-ClC_6H_4-		C_2H_5	82
4b	*p*-ClC_6H_4-		CH_3	83
5b	*p*-$CH_3C_6H_4$-		CH_3	78
6b	*p*-$CH_3C_6H_4$-		C_2H_5	75
7b	*p*-$CH_3OC_6H_4$-		CH_3	66
8b	*p*-$CH_3OC_6H_4$		C_2H_5	68
9b	*p*-$O_2NC_6H_4$-		CH_3	48
10b	$CH_3(CH_2)_5$		C_2H_5	62
11b	$PhCH_2$		CH_3	65
12b	$PhCH_2$		C_2H_5	62
13b	*p*-$CH_3OC_6H_4$		Isopropylidene	58
14b	*m*-$CH_3C_6H_4$-		Isopropylidene	55

* *Isolated yields.*

The results are summarized in **Table**. Both aryl and alkyl substrates could undergo the reaction. The yields for most of the β–aryl-substituted diester were satisfactory. The bulk of R has little influence on the yield. But for the cyclic derivatives of isopropylidene malonate only moderate yields were obtained. Because β-diesters were easy to hydrolyze and decarboxylate to monocarboxylic acids the reaction may be an alternative route to synthesize δ, ε–unsaturated carboxylic acids or esters.

General Procedure

Samarium powder (0.33g, 2.2 mmol) was placed in a three-necked round bottom flask with a magnetic stirring bar. The flask was flushed with nitrogen several times. Tetrahydrofuran (20 mL, anhydrous) and then allyl bromide (0.36g, 3 mmol) were added. After the mixture was stirred for 3 h at room temperature and the solution became deep-purple the substrate (2 mmol) was added. The resulting solution was stirred for 2 h and then reaction was quenched with a little water. After a little dilute hydrochloric acid was added the mixture was extracted with diethyl ether (2×30 mL), washed with saturated aqueous NaCl solution (15 mL), dried over $MgSO_4$. After filtration and removal of the solvent, the crude product was purified by column chromatography (silica gel) using cyclohexane/ethyl acetate (10/1-20/1) as eluent. The products were fully characteried by H NMR, IR and MS spectrometers[13].

Acknowledgments

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13. Typical H NMR data are as follows. **1a**: 2.32 (d, 2 H, *J* = 6.8 Hz), 4.80-5.13 (m, 2 H), 5.47-6.03 (m, 1 H), 6.08 (d, 1H, *J* = 16 Hz), 6.55 (d, 1H, *J* = 16 Hz), 7.07-7.31 (m, 5 H); **6b**:

0.90 (t, 3 H, *J* = 7.0 Hz), 1.20 (t, 3 H, *J* = 7.0 Hz), 2.23 (s, 3 H), 2.23-2.40 (m, 2 H, CH_2), 3.23-3.53 (m, 2 H, CH, CH), 3.77 (q, 2 H, *J* = 7.0 Hz), 4.10 (q, 2 H, *J* = 7.0 Hz), 4.62-4.97 (m, 2 H), 5.15-5.78 (m, 1 H), 6.92 (s, 4 H).

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