

Mono-Allylation of Gem-Diacetates with Allylsamarium Bromide

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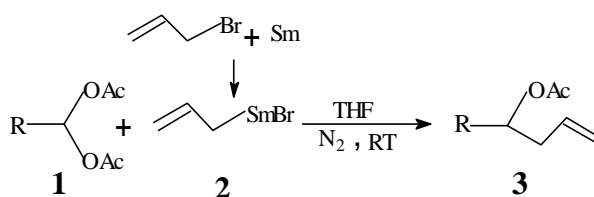
Abstract: The substitution reaction between gem-diacetates and allylsamarium bromide was investigated, and homoallylic alcohol acetates were obtained in moderate to good yields.

Keywords: Gem-diacetates, substitution, monoallylation, allylsamarium bromide.

Our group have explored the reaction of allylsamarium bromide with a variety of substrates, such as N-(2-aminoalkyl)benzotriazoles¹, imines², nitriles³, diorgano diselenides⁴, disulfides⁵, isocyanates⁶ and nitroalkenes⁷. Here we wish to report the monoallylation of gem-diacetates with allylsamarium bromide.

Gem-diacetates are stable in neutral and basic media, thus they are frequently used to protect aldehydes⁸. However, the presence of two leaving groups at the same carbon may make carbon nucleophiles displace one of the acetoxy group affording the substitution products⁹. To the best of our knowledge, only a few substitution reactions of the gem-diacetates by organometallic reagents have been investigated. Sydnes and Sandberg have studied systematically the substitution of diacetates with organolithium and Grignard reagents¹⁰. Heerden *et al.* reported Pd (0) catalyzed substitution of allylic 1,1-diacetates by tributylvinyltin and allyltributyltin¹¹. Very recently, Yadav *et al.*¹² reported the indium mediated allylation of gem-diacetates to homoallylic acetates. Here we describe the results of our study on the substitution reactions between allylsamarium bromide and gem-diacetates (**Scheme 1**).

Scheme 1



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Our study shows that allylsamarium bromide can substitute one acetoxy group of the diacetates to afford homoallylic acetates at room temperature. No double allylated product was detected. When R is *m*-nitrophenyl or *p*-nitrophenyl, the reaction failed to give the desired homoallylic acetate, probably due to the reductive potential of divalent samarium species (here it refers to allylsamarium bromide), which was destroyed by the nitro group attached on the aromatic ring. In the case of the gem-diacetates of α , β -unsaturated aldehydes, the yield is relatively low, but no 1, 4-addition product was detected. The results are shown in the **Table 1**.

Table 1 Mono-allylation of gem-diacetates with allylsamarium bromide

Entry	R	T/°C	t/min	Yield (%)
a	C ₆ H ₅	20	10	85
b	<i>p</i> -CH ₃ C ₆ H ₄	20	8	82
c	<i>P</i> -ClC ₆ H ₄	20	15	70
d	<i>p</i> -CH ₃ OC ₆ H ₄	20	15	80
e	3,4-(OCH ₂ O)C ₆ H ₄	20	20	72
f	(<i>E</i>)-C ₆ H ₅ CH=CH	20	30	42
g	(<i>E</i>)-CH ₃ CH=CH	20	30	48

a. Isolated yields based on gem-diacetates.

General procedure

Under an inert atmosphere of nitrogen, powdered samarium (0.18 g, 1.25 mmol) was placed in a 50 mL three-necked flask and a solution of allylbromide (0.2 g, 1.5 mmol) in 1 mL THF was added by syringe. The mixture was magnetically stirred for 1 h at room temperature to obtain a purple suspension. Then a solution of gem-diacetates (1 mmol) in 0.5-1 mL THF was added to the suspension in one portion by syringe. Completion of the reaction was monitored by TLC. The reaction was quenched with saturated ammonium chloride aqueous solution (5 mL) and extracted with ether (3×10 mL). The organic layer was washed with brine, dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by preparative TLC on silica gel (cyclohexane/acetate as eluent) to give colorless to light yellow oil.

References and notes

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Received 27 March, 2001