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A Novel Synthesis of Allyl Sulfides by Organosamarium Reagents†

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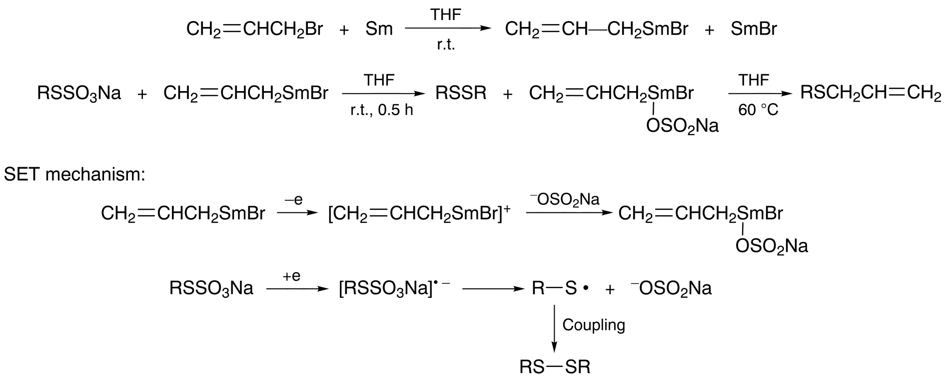
Organosamarium reagents react with sodium alkyl thiosulfates to afford allyl sulfides; a reaction mechanism involving organosamarium(II) and organosamarium (III) intermediates is suggested.

Intensive studies have been carried out on the role of SmI_2 in organic synthesis.[1–3] In general, the reactivity of samarium(II) iodide is characterized by the single electron transfer (SET) from samarium(II) to a suitable substrate. Recently, the use of samarium metal in organic synthesis has stimulated great interest.[4–7] Curran first reported the Grignard reaction of alkylsamarium(III) reagents.[8] S. H. Wu *et al.* reported the Barbier-type allylation of ketones[9] and carboxylic esters[10] with samarium metal and allyl bromide and an allylsamarium(II) intermediate reaction mechanism has been suggested. Our group have studied the reaction of allylsamarium(II) with imine,[11] the synthesis of allyl selenides by allylsamarium(II) reagents[12] and homoallylamines by the addition of allylsamarium(II) reagents to nitriles,[13] and the synthesis of allyl sulfides by treating allylsamarium(II) reagents with disulfides.[14]

Up until now, no reaction mechanism involving both the organosamarium(III) and the organosamarium(II) intermediate has been suggested. The organosamarium(III) intermediate is more stable than the corresponding organosamarium(II) intermediate. In some reactions, the organosamarium(II) intermediate may act as a reductive reagent rather than a general organometallic reagent. Recently, there has been an increase in the interest on the application of organosamarium reagents in organic synthesis which prompted us to investigate the reaction mechanism of organosamarium intermediates. Here we report the reaction of allylsamarium(II) reagents with sodium alkyl thiosulfates to afford allyl sulfides. In our experiments, mixtures of sodium alkyl thiosulfates and allylsamarium(II) reagent, prepared as described in the Experimental section, were stirred for 0.5 h at room temperature. Only alkyl disulfides (no allyl sulfides) were obtained. However, allyl sulfides were obtained when the reaction was carried out at 60 °C. Considering the experimental facts mentioned above and according to our previous work that samarium diiodide reductively cleaves the S—S bond of sodium alkyl thiosulfates to give the corresponding disulfides,[15] we suggest that the reaction may occur *via* single electron transfer from the allylsamarium(II) intermediate to the sodium alkyl thiosulfates to yield an allylsamarium(III) intermediate and alkyl disulfide, which further react to form allyl sulfides at 60 °C.



Sulfides are a class of useful synthetic intermediates, and many syntheses have been reported for their preparation, for example, the alkylation of thiols,[16] the reaction of alkyl halide with sodium sulfide,[17] addition of hydrogen sulfide to alkene,[18] reduction of disulfides with copper in the presence of halide,[19] reduction of sulfoxides with titanium(II) chloride,[20] deoxygenation of sulfoxides with triphenylphosphine–iodide–sodium iodide,[21] and the synthesis of allyl sulfides *via* allyldialkyltelluronium salts.[22] The advantages of this present method are readily available starting materials, simple operation, mild and neutral conditions, as well as good yield. The results are summarized in Table 1.

Experimental

Typical procedure.—Samarium (0.33 g, 2.2 mmol), THF (20 ml) and allyl bromide (0.30 g, 2.5 mmol) were added to a three necked flask with stirring at room temperature under nitrogen. When the mixture turned purple, the stirring was continued for 1 h until the samarium powder disappeared. Sodium alkyl thiosulfates were then added to the solution. The solution turned brownish red within a few seconds and the mixture was further stirred for 2.5 h at room temperature under nitrogen and then at 60 °C for a given time. Water (10 ml) was then added and the resulting mixture extracted with diethyl ether (3 × 40 ml) and the ether layer separated. The ethereal solution was washed with water (3 × 40 ml) and the organic layer dried ($MgSO_4$). The solvent was removed by evaporation under reduced pressure and the crude product obtained purified by preparative TLC on silica gel (cyclohexane and ethyl acetate as

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Table 1 Reaction conditions, products and yields

		Reaction conditions		
Entry	Products	t/h	T/°C	Yield (%)[a]
1	$\mathrm{PhCH_2SCH_2CH{=}CH_2}$	1.5	60	86
2	p-$\mathrm{ClC_6H_4CH_2SCH_2CH{=}CH_2}$	1.5	60	84
3	n-$\mathrm{C_{16}H_{33}SCH_2CH{=}CH_2}$	2	60	80
4	n-$\mathrm{C_{12}H_{25}SCH_2CH{=}CH_2}$	2	60	84
5	n-$\mathrm{C_{10}H_{21}SCH_2CH{=}CH_2}$	2	60	80
6	n-$\mathrm{C_8H_{17}SCH_2CH{=}CH_2}$	2	60	81
7	n-$\mathrm{C_7H_{15}SCH_2CH{=}CH_2}$	2	60	78
8	n-$\mathrm{C_6H_{13}SCH_2CH{=}CH_2}$	2	60	76

[a]Yield of isolated product.

eluent). The products were characterized by ^{1}H NMR, MS and IR.

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