

SILVER TRIFLATE-PROMOTED COUPLING REACTIONS OF BENZYLIC AND ALLYLIC SULFIDES  
WITH O-SILYLATED ENOLATES OF KETONES AND ESTERS, A SYNTHESIS OF ( $\pm$ )-AR-TURMERONE

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**Summary:** Reactions of benzylic and allylic sulfides 1 having 5-mercapto-1-phenyl-1H-tetrazolyl group with O-silylated ketone and ester enolates 2 in the presence of silver triflate gave coupling products 3 in good yield. ( $\pm$ )-ar-turmerone was synthesized by this method.

Alkyl and allylic sulfides have been used widely as intermediates for the formations of carbon-carbon bonds.<sup>1)</sup> Recently, we have reported the single-step preparations of benzylic and allylic sulfides 1 having 5-mercapto-1-phenyl-1H-tetrazolyl(-ST) group from benzylic or allylic alcohols and S,S'-bis(1-phenyl-1H-tetrazol-5-yl) dithiocarbonate, and also reported that this process can be applied to the cross-coupling reaction by use of the Grignard reagent in the presence of CuBr.<sup>2)</sup> The utility of benzylic and allylic sulfides will be greatly enhanced if their coupling reactions with O-silylated ketone and ester enolates are feasible. Although, so far a few examples of coupling reactions of O-silylated enolates and sec- or t-alkyl halides in the presence of an equiv. of titanium chloride<sup>3)</sup> or a catalytic amount of zinc chloride<sup>4)</sup> have been reported, coupling reactions of benzylic or allylic sulfides with O-silylated enolates have not been reported in the literature.

Now we wish to report silver triflate-promoted coupling reactions of benzylic and allylic sulfides 1 having -ST group with O-silylated ketone and ester enolates 2. These reactions proceed under neutral conditions. The yields of coupling products 3 were high when each 2-4 equiv. mole of O-silylated compounds 2 and silver triflate were used. The following is a typical procedure for the preparation of run 2; To a mixture of 1 (R=p-methoxybenzyl)(149mg, 0.5mmol) and 2 (R<sup>1</sup>=phenyl, R<sup>2</sup>, R<sup>3</sup>=H)(192mg, 1mmol) in dry CH<sub>2</sub>Cl<sub>2</sub>(5ml) was added AgOTf(257mg, 1mmol) under argon at room temperature. After the reaction mixture was stirred for 2 hr, the reaction was quenched with 4% NaHCO<sub>3</sub> solution. Insoluble materials were filtered off, the filtrate was extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed with brine. After the extract was dried, the solvent was evaporated, and the residue was purified by preparative TLC on silica gel to give a coupling product 3(R=p-methoxybenzyl, R<sup>1</sup>=phenyl, R<sup>2</sup>, R<sup>3</sup>=H)(118mg, 98%). Some results are shown in Table. Reactions of p-methoxybenzylic sulfide and 2 equiv. of silyl enol ether or ketene silyl ether gave coupling compounds 3 in high yields(run 2 and 3). In the reaction of unsubstituted primary benzylic sulfide, each 4 equiv. of silyl enol ether and AgOTf were used under refluxing 1,2-dichloroethane(run 1). Thus, this coupling reaction could be extended even to primary benzylic sulfides. In the reaction of sec-benzylic sulfides, run 4 and 6 gave products 3 in good yields. Although, the difference in yields between run 4 and 5 may be attributable to the steric hindrance, the yield of run 5 was increased by the use of 4 equiv. mol enolate and AgOTf(run 6). Furfuryl sulfide also reacted in a good yield(run 7). On the other hand, the reaction of allylic sulfides gave the S<sub>N</sub>-type and S<sub>N'</sub>-type products(run 8 and 10). Although, run 9 gave a trans product alone, the reaction probably takes place via S<sub>N'</sub>-type.

The reaction may be explained in terms of the following mechanism.  $\alpha$ -Carbon of sulfide 1 which is activated by AgOTf reacts with  $\alpha$ -carbanion of TMS-enolate which is activated by triflate anion, and gives a coupling product 3 with elimination of sulfide (scheme 1).

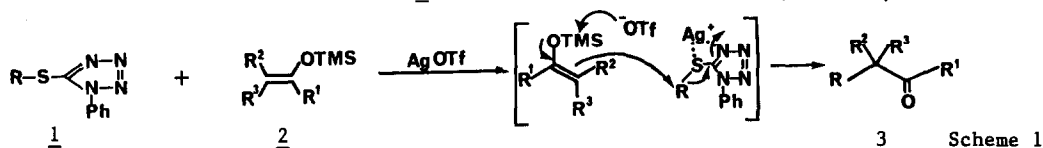
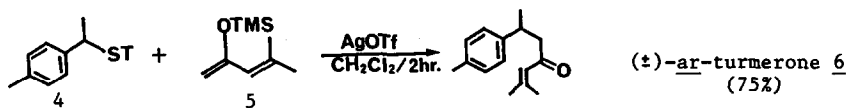


Table. Reactions of Benzylic or Allylic Sulfides 1 with O-Silylated Enolates 2

Run	Sulfide <u>1</u> <sup>a)</sup> (0.5mmol)	Enolate <u>2</u> (mmol)	AgOTf (mmol)	Product <u>3</u>	Yield (%) <sup>c)</sup>
1			(2)		62d)
2		"	(1)		98
3	"		(1)		92
4			(1)		80
5	"		(1)		50
6	"		(2)	"	90
7			(1)		70
8		"	(1)		78
9		"	(1)		87
10	"		(2)		91
11			(1)		91

a) ST: b) Estimated by NMR examinations. c) CH<sub>2</sub>Cl<sub>2</sub>/r.t./2 hr. d) 1,2-dichloroethane/reflux/6 hr.

This method constitutes a one-step synthesis of sesquiterpene ( $\pm$ )-*ar*-turmerone 6. For example, the coupling reaction of sulfide 4 (0.5mmol) and O-silylated dienolate 5 (1mmol) which was prepared from lithium enolate of mesityl oxide (LDA/THF/-78°C) and TMS-Cl gave 6 in 75% yield at room temperature for 2 hr in the presence of AgOTf (1mmol).



Thus, coupling reactions of benzylic or allylic sulfides with O-silylated enolates of ketones and esters were feasible in the presence of silver triflate under neutral conditions.

#### References

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