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The Trityl Cation Catalyzed Michael Type Reaction of Stannylated Nucleophiles with Ethylthioketene Dithioacetals

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In the presence of a catalytic amount of trityl salt, allylstannanes and stannylated enolates smoothly react with 2-(2-ethylthioalkylidene)-1,3-dithiolane, synthetic equivalent of α,β-unsaturated ester, to afford the corresponding adducts in good yields, respectively.

In the preceding paper,1) a new and efficient Michael reaction equivalent by employing silylated carbon nucleophiles and ethylthioketene dithioacetals was described. Functionalized ketene dithioacetals produced in this reaction are synthetically valuable compounds because further transformations can be made from their ketene dithioacetal function.2) In this communication, we wish to describe results of the reaction of 2-(2-ethylthioalkylidene)-1,3-dithiolane (1) with stannylated carbon nucleophiles. These nucleophiles smoothly react with the cationic species as ethylthioketene dithioacetals by the use of only a catalytic amount of trityl salt as an activator.

As mentioned in the preceding paper,1) almost no desired reaction occured with an ethylthioketene dithioacetal and allyltrimethylsilane. This may be attributed to the lower reactivity of allylsilanes compared to silyl enol ethers or ketene silyl acetals, and therefore, more reactive allylating reagents were explored.

Allylstannanes are known to be more reactive nucleophiles than allylsilanes and several interesting synthetic reactions using allylstannanes have appeared in recent literature.3) However, examples of the Michael type reaction by means of allylstannanes are few.4) So, we tried first the reaction of allyltriphenylstannane and 2-(2-ethylthiopropylidene)-1,3-dithiolane (1a) by the use of an equimolar amount of trityl tetrafluoroborate as an activator. In this case, in contrast to the result with allylsilane, the desired adduct was obtained in 61% yield. Further, it was clarified that a catalytic amount (7 mol%) of trityl salt was enough to complete this reaction. Survey of catalysts, nucleophiles, etc.,

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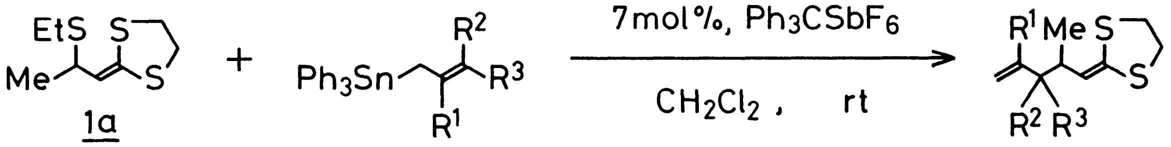


Table 1. Reaction of 1a with Allylstannanes[a)]

Entry	R^1	R^2	R^3	Yield/%	
1	H	H	H	91	
2	H	(Me , H)[b)]		80	c)
3	Me	H	H	69	d)
4	H	Me	Me	57	

a) All new compounds gave satisfactory spectroscopic data.
b) E:Z=7:1 (determined by ^{13}C-NMR).
c) anti:syn[5)]=72:28 (determined by GC).
d) Reaction temperature: 0 °C.

showed that triphenylallylstannanes gave the highest yield in the presence of 7 mol% of trityl hexafluoroantimonate(V). The results of the reaction with various allylstannanes are summarized in Table 1.

Even the sterically hindered (3-methyl-2-butenyl)triphenylstannane smoothly gave the adduct in a moderate yield (entry 4). It should be pointed out that trityl salts such as perchlorate, tetrafluoroborate, and trifluoromethanesulfonate were also effective as well as hexafluoroantimonate(V), while neither trityl hexachloroantimonate(V) nor triphenylstannyl trifluoromethanesulfonate was effective. On the other hand, it is already known that trityl tetrafluoroborate was inactive as a catalyst in the aldol type reaction between silyl enol ethers and aldehydes or acetals, whereas trityl hexachloroantimonate(V) can be actively employed.[7)] The difference could be explained by considering the respective affinities of silicon and tin toward halide ion; when trityl tetrafluoroborate was used in the aldol reaction, the catalytic cycle was broken by the generation of trimethylsilyl fluoride from intermediate trimethylsilyl tetrafluoroborate because silicon atom has a strong affinity toward fluoride ion. Since tin has a strong affinity toward chloride ion rather than fluoride, trityl tetrafluoroborate could be effective as in the present method, while hexachloroantimonate(V) was not.

The following is a typical procedure for the allylation reaction: To a dichloromethane (1 ml) solution of trityl hexafluoroantimonate(V) (8.5 mg, 0.018 mmol) was added 2-(2-ethylthiopropylidene)-1,3-dithiolane (1a, 53 mg, 0.26 mmol) and allyltriphenylstannane (110 mg, 0.28 mmol) in 3 ml of dichloromethane at room temperature. The reaction was completed within 1 h and quenched by adding aqueous sodium hydrogencarbonate. After extracted with dichloromethane, the organic layer was dried with potassium carbonate and thin layer chromatographed to give 2-(2-methyl-4-pentenylidene)-1,3-dithiolane (41 mg, 0.22 mmol) in 86% yield.

Next, we examined the reaction of stannylated enolates with 2-(2-ethylthioalkylidene)-1,3-dithiolane (1). In this case, the counter anion of trityl salt had little effect on the product yield, therefore, trityl perchlorate was utilized throughout. As summarized in Table 2, α-stannylketone (entries 1, 5) can also be used as well as an O-stannylated enolate (stannyl enol ether, entry 2).[8)]

Several aldol type reactions[9)] and palladium catalyzed coupling reactions[10)] of stannylated enolates have already been studied, however, much less attention has been paid to these nucleophiles, compared to silylated enolates. The trityl cation catalyzed carbon-carbon bond forming reaction described herein with stannylated nucleophiles is thus efficient and synthetically valuable.

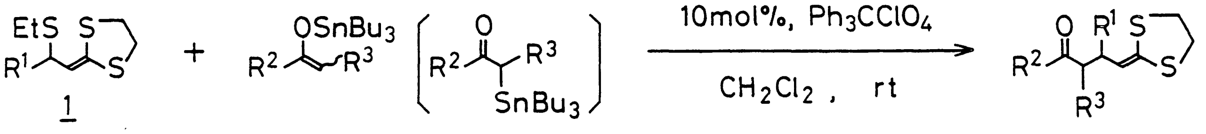
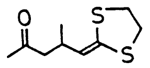
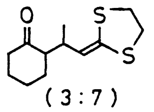
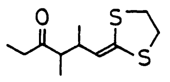
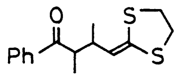
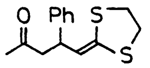


Table 2. Reaction of 1 with Stannylated Enolates[a)]

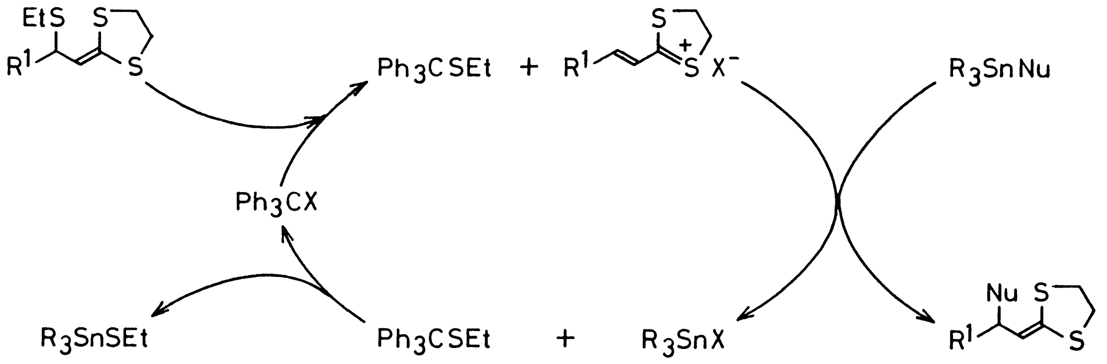
Entry	R^1	R^2	R^3	Yield/%	Product (anti:syn)
1	Me	Me	H	54	
2	Me	-$(CH_2)_4$-		85	 (3:7)
3	Me	Et	Me	78	 (1:1)
4	Me	Ph	Me	81	 (3:1)
5	Ph	Me	H	72	 b)

a) All new compounds gave satisfactory spectroscopic data.

b) Reaction temperature: 0 °C.

The mechanism of this reaction is postulated as shown in Scheme 1. It is noted that highly thiophilic nature of trialkylstannyl cation plays an important role in the step of regeneration of trityl cation, an active catalyst.

Further synthetic study using stannylated nucleophiles by the use of trityl cation catalysis is now being continued in our laboratory.



Scheme 1.

References

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3) For recently reported examples, see, G. E. Keck, D. E. Abbott, E. P. Boden, and E. J. Enholm, Tetrahedron Lett., 25, 3927 (1984); M. Shimagaki, H. Takubo, and T. Oishi, ibid., 26, 6235 (1985); G. P. Boldrini, E. Tagliavini, C. Trombini, and A. Umani-Ronchi, J. Chem. Soc., Chem. Commun., 1986, 685; G. E. Keck, S. Castellino, and M. R. Wiley, J. Org. Chem., 51, 5480 (1986).

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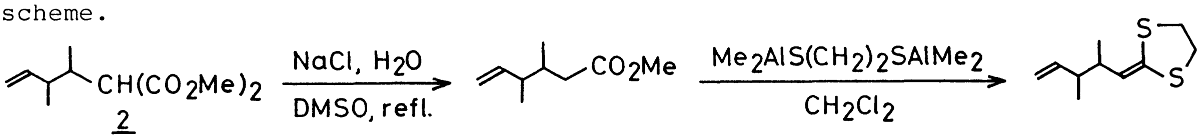
5) Stereochemistry was determined by GC comparison with authentic sample prepared from diester 2 having known stereochemistry[6] according to the following scheme.



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