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AN EFFECTIVE ACTIVATION OF ALLYL METHYL ETHERS BY A CATALYTIC AMOUNT OF TRITYL PERCHLORATE IN THE ALLYLATION OF SILYL ENOL ETHERS

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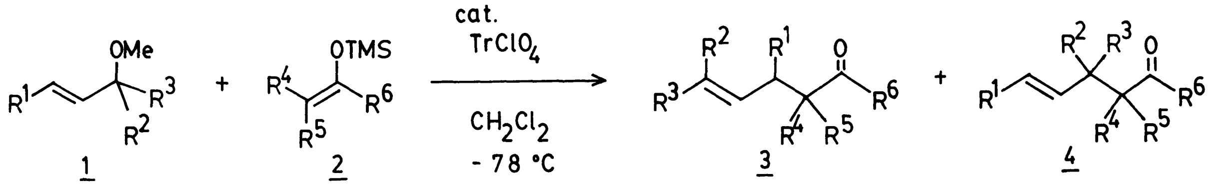
In the presence of a catalytic amount of trityl perchlorate, secondary and tertiary allyl methyl ethers smoothly react with silyl enol ethers to afford the corresponding γ,δ-unsaturated carbonyl compounds in good yields. By the combination of this reaction with the trityl perchlorate catalyzed allylation of acetals γ,δ-unsaturated ketones are synthesized from α,β-unsaturated acetals by a one-pot procedure.

Allyl ethers are rarely employed as allylating reagents in the carbon-carbon bond forming reactions,$^{1,2)}$ because it is difficult to activate allyl ethers for the reaction with carbon nucleophiles. When a catalytic amount of promoter is used, only allyl phenyl ethers are successfully employed as allylating reagents.$^{2)}$ Therefore, exploration of an efficient method for the activation of allyl alkyl ethers by a catalytic use of promoter is of synthetic value.

In the course of our investigation on new synthetic reactions using trityl cation,$^{3)}$ the catalytic reactions of the carbon-carbon bond formation, such as the aldol reactions,$^{4)}$ the Michael reaction$^{5)}$ and the allylation of acetals$^{6)}$ have been developed. These reactions are based on the ability of trityl cation to activate the oxygen-containing functional groups such as acetal and carbonyl compounds.

These facts prompted us to investigate the activation of allyl methyl ethers by trityl perchlorate for the reaction with silyl enol ethers. And it was found that, in the presence of a catalytic amount of trityl perchlorate, secondary and tertiary allyl methyl ethers smoothly react with silyl enol ethers to afford the corresponding γ,δ-unsaturated carbonyl compounds in good yields. In addition, by the combination of this reaction with the trityl perchlorate catalyzed allylation of acetals, γ,δ-unsaturated ketones are easily prepared from α,β-unsaturated acetals by a one-pot procedure.

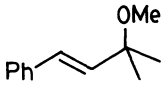
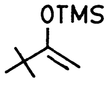
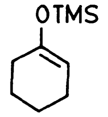
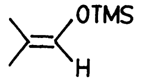
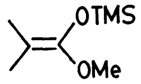
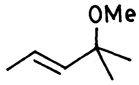
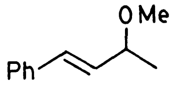
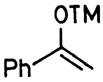
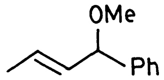
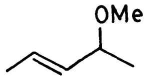
At first, 3-methoxy-1-phenylpropene, a primary allyl methyl ether, was treated with the silyl enol ether of acetophenone in the presence of a catalytic amount of trityl perchlorate at -78 °C in CH_2Cl_2, but only a trace of the desired product was obtained. On the other hand, the reactions of secondary or tertiary allyl methyl ethers (1) with silyl enol ethers (2) smoothly proceeded under the same conditions to give the corresponding γ,δ-unsaturated carbonyl compounds (3 and 4) in good yields (Scheme 1). Thus, it was proved that trityl perchlorate effectively activates secondary or tertiary allyl methyl ethers in the reaction with silyl enol ethers. Then, the reaction between various secondary or tertiary allyl methyl ethers and silyl enol ethers was examined and the results are summarized in Table 1.



Scheme 1. Tr = Ph_3C TMS = Me_3Si

According to this method, allyl methyl ether reacted smoothly with ketene silyl acetal as well as silyl enol ether of ketone or aldehyde, and γ,δ-unsaturated ester was obtained in good yield (Entry 4). In the cases of the reactions of tertiary allyl methyl ethers with silyl enol ethers of ketones or aldehydes, the allylation took place regioselectively at the γ-position of allyl methyl ethers (Entries 1-3,5). However, the regioselectivities of the reactions of secondary allyl methyl ethers were rather low (Entries 6-8).

Table 1. The reaction of allyl methyl ethers with silyl enol ethers

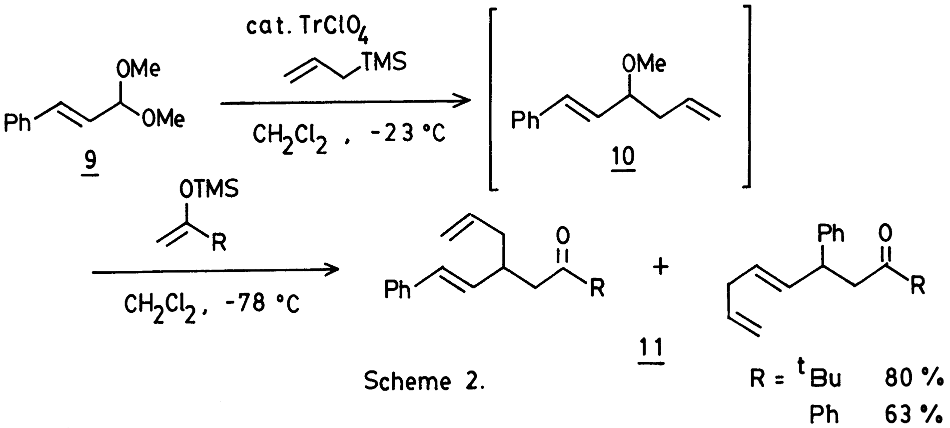
Entry	Allyl methyl ether 1	Silyl enol ether 2	Reaction time/h	Yield of 3+4/%	Ratio[a] 3:4
1	 OMe Ph 5	 OTMS 6	1	83	92: 8
2	5	 OTMS	11	93[b]	>95: 5
3	5	 OTMS H	12	80	95: 5
4	5	 OTMS OMe	11	78	42:58
5	 OMe	6	15[c]	72	>95: 5
6	 OMe Ph 7	 OTMS Ph 8	4	93	48:52
7	7	6	3	81	30:70
8	 OMe Ph	6	3	89	74:26
9	 OMe	8	12	72	——

a) The ratio was determined by ^{1}H NMR.
b) A mixture of diastereomers.
c) The reaction was carried out at -45 °C.

Typical procedure is described for the synthesis of 2,2-dimethyl-7-methyl-5-phenyl-6-octen-3-one (entry 1); under an argon atmosphere, to a CH_2Cl_2 solution (0.5 ml) of $TrClO_4$ (0.03 mmol) was added 3,3-dimethyl-2-trimethylsilyloxy-1-butene (0.27 mmol) and 3-methoxy-3-methyl-1-phenyl-1-butene (0.35 mmol) in CH_2Cl_2 (2 ml) at -78 °C. The reaction mixture was stirred for 1 h at the same temperature, then quenched with aqueous solution of sodium bicarbonate. The organic materials were extracted with CH_2Cl_2, and combined extracts were dried over Na_2SO_4. After the evaporation of the solvents, the residue was purified by preparative TLC (silica gel) to afford 2,2-dimethyl-7-methyl-5-phenyl-6-octen-3-one (0.22 mmol, 83%).

The allylation of silyl enol ethers is one of the important reactions for the synthesis of γ,δ-unsaturated carbonyl compounds, and several reactions have been developed by the use of the allylating reagents, such as allyl carbonates,[7)] allyl halides,[8)] and allyl acetates.[9)] However, there have been no report on the allylation of silyl enol ethers with allyl ethers, and the above-mentioned reaction provides a novel and useful method for the synthesis of γ,δ-unsaturated carbonyl compounds.

In the previous paper, it was shown that trityl perchlorate is an effective catalyst for the allylation of acetals with allyltrimethylsilanes.[6)] According to this reaction, allyl methyl ethers are obtained from α,β-unsaturated acetals, and it is expected that the allyl methyl ethers react further with silyl enol ethers in the presence of a catalytic amount of trityl perchlorate. Based on this consideration, we attempted the one-pot synthesis of γ,δ-unsaturated ketones (11) from α,β-unsaturated acetals (9) via allyl ethers (10) as shown in Scheme 2, and it was found that, in the presence of a catalytic amount of trityl perchlorate, the tandem reaction proceeded smoothly to afford the desired products in good yields.



Scheme 2.

R = ^{t}Bu 80%
Ph 63%

The reaction for the formation of two carbon-carbon bonds by a one-pot procedure is a very useful synthetic tool, and the above-mentioned tandem reaction enhanced the synthetic utility of the allylation of silyl enol ethers with allyl methyl ethers.

It is noted that trityl perchlorate effectively activates secondary and tertiary allyl methyl ethers in the reaction with silyl enol ethers and the present reaction provides a convenient method for the allylation of silyl enol ethers in good yields under mild conditions. Further synthetic investigation using trityl perchlorate as an activator of allyl ethers are now in progress.

References

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