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TRITYL PERCHLORATE AS AN EFFICIENT CATALYST IN THE ALDOL-TYPE REACTION

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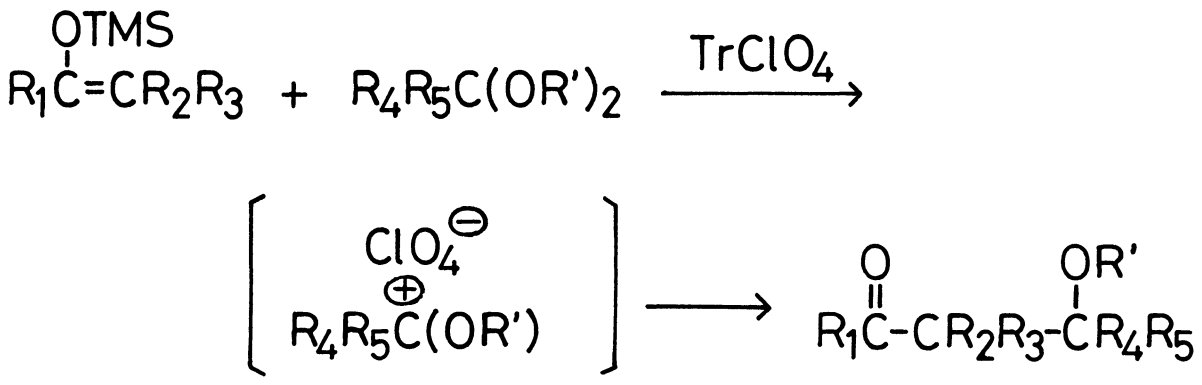
In the presence of a catalytic amount of trityl perchlorate, silyl enol ethers and ketene silyl acetals react with acetals and methyl orthoformate to give the corresponding aldol-type addition products in good yields.

In the previous papers, we have shown that, in the presence of trityl perchlorate, 1-O-acyl sugars stereoselectively react with alcohols[1] or silylated nucleophiles[2] to give the corresponding α-glycosides or α-C-ribofuranosides in good yields. In these reactions, it was shown that trityl perchlorate effectively activates acyloxy group on the anomeric center. Then we continued to investigate the use of trityl perchlorate in synthetic reactions and it was found that a catalytic amount of trityl perchlorate could also effectively activate acetals. In this communication, we wish to describe the trityl perchlorate catalyzed aldol-type reactions, which probably proceed via alkoxy-substituted carbocations stabilized by non-nucleophilic perchlorate anion.



TMS ≡ Me_3Si , Tr ≡ Ph_3C

In the first place, the reaction of trimethylsilyl enol ether of cyclohexanone with benzaldehyde dimethyl acetal was tried and the corresponding aldol was obtained in an excellent yield. In this reaction, trityl perchlorate was so effective that the reaction was complete within ten minutes at -78 °C. Thus, the reactions of silyl enol ethers derived from aldehydes, ketones, and esters with various acetals afforded the corresponding aldols in good yields. (Table 1).

According to the present reaction, erythro aldol was produced predominantly, which may be explained by the acyclic transition states.[3)]

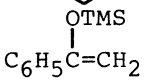
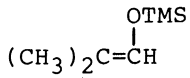
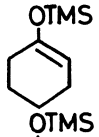
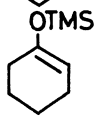
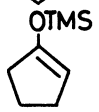
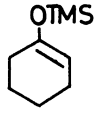
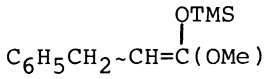
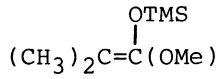
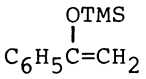
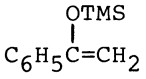
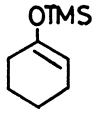
Similarly, methyl orthoformate reacts with silyl enol ethers to give β-keto acetals in good yields.

A typical procedure for the reaction of a silyl enol ether or a ketene silyl acetal with an acetal is as follows; the mixture of a silyl enol ether (1 mmol), an acetal (1 mmol), and trityl perchlorate (0.01-0.05 mmol) in CH_2Cl_2 (5 ml) was stirred at -78 °C for 10 min. Aqueous sodium hydrogen carbonate was added and extracted with CH_2Cl_2. The organic layer was dried and the solvent was removed under reduced pressure. The residue was separated by silica gel column chromatography.

Concerning the reactions of silyl enol ethers with acetals, $TiCl_4$-promoted reactions are the first example of the aldol-type reaction by employing isolable enolates.[4)] After that, there have been reported several reactions using $BF_3 \cdot OEt_2$,[5)] TMSOTf,[3)] etc. The present reaction has the advantage over these reactions in the simplicity of the procedure, such as the catalytic use of trityl perchlorate, a short reaction time, mild reaction conditions.

The most important point of this reaction is that trityl perchlorate activates an alkoxy group and the resulted intermediate carbocation is stabilized by perchlorate anion. Further investigations using these characteristic properties of trityl perchlorate are now in progress.

Table 1. The reactions of silyl enol ethers with acetals or methyl orthoformate[a)]

Silyl enol ether	Acetal or methyl orthoformate	Yield/%	(erythro/threo)[b)]
	$C_6H_5CH(OCH_3)_2$	96	(88 : 12)
	$(CH_3)_2C(OCH_3)_2$	90	
	$C_6H_5CH(OCH_3)_2$	81	
	$(CH_3)_2CHCH(OCH_3)_2$	90	(80 : 20)
	$C_6H_5(CH_2)_2CH(OCH_3)_2$	92	(71 : 29)
	$C_6H_5CH(OCH_3)_2$	88	(79 : 21)
	$C_6H_5CH(OC_2H_5)_2$	90	(88 : 12)
	$(CH_3)_2C(OCH_3)_2$	71	
	$C_6H_5CH(OCH_3)_2$	92	
	$C_6H_5CH{=}CHCH(OCH_3)_2$	90	
	$CH(OCH_3)_3$	78	
	$CH(OCH_3)_3$	70	

a) All products gave satisfactory NMR and IR spectra.

b) Each compound was separated by silica gel column chromatography.

References

1) T. Mukaiyama, S. Kobayashi, and S. Shoda, Chem. Lett., 1984, 907.

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3) S. Murata, M. Suzuki, and R. Noyori, J. Am. Chem. Soc., 99, 3248 (1980).

4) T. Mukaiyama, K. Narasaka, and K. Banno, Chem. Lett., 1973, 1011; T. Mukaiyama, K. Banno, and K. Narasaka, J. Am. Chem. Soc., 96, 7503 (1974); T. Mukaiyama and M. Hayashi, Chem. Lett., 1974, 15; T. Mukaiyama, Angew. Chem., Int. Ed. Engl., 16, 817 (1977).

5) T. Sato, M. Arai, and I. Kuwajima, J. Am. Chem. Soc., 99, 5827 (1977).

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