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Trityl Salts Catalyzed Aldol-Type Reaction of Alkyl Enol Ethers with Acetals

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β-Alkoxy ketones are synthesized in good yields by the reaction of alkyl enol ethers with acetals in the presence of a catalytic amount of trityl salts. Of enol ethers, methoxymethyl (MOM) enol ether exhibits an enhanced reactivity as a nucleophile.

Previously, we have reported a number of communications on trityl salt catalyzed carbon-carbon bond forming reactions.[1)] In most of these reactions, silyl nucleophiles such as silyl enol ether and allylsilane are used. Therefore, silyl ester such as Me_3SiClO_4, originated from trityl perchlorate, could be involved in a catalytic reaction cycle as a similar promoter. In this communication, we wish to report the trityl salt catalyzed aldol-type reaction of alkyl enol ethers with acetals to demonstrate the possible catalytic cycle free from an in situ formed silyl ester of strong acid.

Firstly, methyl enol ethers were treated with dimethyl acetal of benzaldehyde (1) in the presence of a catalytic amount of trityl salts and the corresponding aldol products were obtained in good yields. However, methyl enol ethers did not react with acetals derived from aliphatic aldehydes showing that methyl enol ethers are less nucleophilic than the corresponding silyl enol ethers. Then, methoxymethyl (MOM) enol ether (2), which should be more active than methyl enol ethers, was prepared[2)] and good results were obtained as expected (Table 1).

Typical experimental procedure is as follows: To a CH_2Cl_2 solution (1 ml) of $TrClO_4$ (9.5 mg, 0.028 mmol) were successively added a CH_2Cl_2 solution (1.5 ml) of 2,2-dimethoxypropane (28 mg, 0.27 mmol) and a CH_2Cl_2 solution (1.5 ml) of 1-(methoxymethyloxy)-1-phenylpropene (55 mg, 0.31 mmol) at -78 °C. After stirring 1 d at that temperature, a few drops of pyridine were added and the yellow color of trityl cation soon disappeared. The solvent was evaporated and the residue was purified by TLC (silica gel) affording the desired aldol product (46 mg, 83%).

The reaction of acetals with alkyl enol ethers has been extensively studied[3)] by the use of boron trifluoride etherate,[4)] ferric chloride,[5)] zinc chloride,[6)] or acidic montmorillonite clay[7)] as a promoter, since it provides an easy access to α,β-unsaturated aldehydes. Because of facile occurrence of polymerization, however, about 3 mole equivalents of acetal to enol ether are usually required in order to obtain the desired aldol product in a moderate yield. Compared with these results, the present reaction has the following advantages; (i) the desired

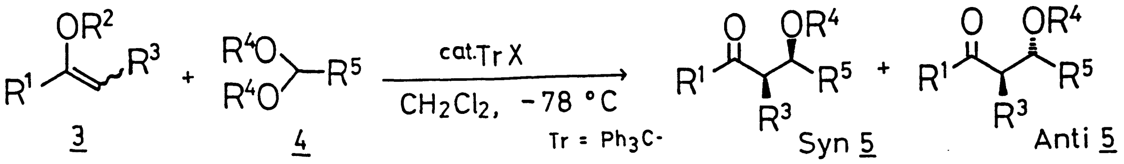
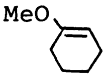
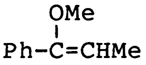
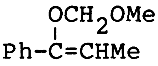


Table 1. The Synthesis of β-Alkoxyketones

Entry	3	4	TrX	Time/h	Yield/%	Syn:Anti
1	 6	$PhCH(OMe)_2$ 1	$TrClO_4$	1	77	27:73
2	6	1	$TrSbCl_6$	1	78	30:70
3	6	1	TrOTf	1	80	27:73
4	 $Ph\text{-}\overset{OMe}{C}\text{=}CHMe$	1	$TrClO_4$	1	86	79:21
5	 $Ph\text{-}\overset{OCH_2OMe}{C}\text{=}CHMe$ 2	1	$TrClO_4$	1	73	75:25
6	2	$i\text{-}PrCH(OMe)_2$	$TrClO_4$	24	93	88:12
7	2	$Me_2C(OMe)_2$	$TrClO_4$	24	83	——

1:1 adducts are obtained in good yields by the use of equimolar amounts of enol ethers and acetals; (ii) the reaction is effectively promoted at low temperature by a catalytic amount of trityl salts.

It should be noted that the above mentioned result clearly indicates that acetals are actually activated only by trityl salts in the present aldol-type reaction.

References

1) T. Mukaiyama, S. Kobayashi, and M. Murakami, Chem. Lett., 1984, 1759; T. Mukaiyama, S. Kobayashi, and M. Murakami, ibid., 1985, 447; M. Ohshima, M. Murakami, and T. Mukaiyama, ibid., 1985, 1871; T. Mukaiyama, H. Nagaoka, M. Ohshima, and M. Murakami, ibid., 1986, 1009; T. Mukaiyama, M. Tamura, and S. Kobayashi, ibid., 1986, 1817, and references cited therein.

2) MOM enol ether (2) was prepared by treatment of the corresponding MOM allylic ether with t-BuOK in DMSO at rt: bp 130 °C (133 Pa); Z:E= 9:1.

3) F. Effenberger, Angew. Chem., Int. Ed. Engl., 8, 295 (1969).

4) R. I. Hoaglin and D. H. Hirsh, J. Am. Chem. Soc., 71, 3468 (1949); D. R. Hall, P. S. Beevor, R. Lester, R. G. Poppi, and B. F. Nesbitt, Chem. Ind. (London), 1975, 216.

5) S. M. Makin, S. M. Gabrielyan, A. S. Chebotarev, E. K. Vladimirskaya, and N. M. Morlyan, Zh. Org. Khim., 10, 2044 (1974) [Chem. Abstr., 82, 3721q (1975)].

6) O. Isler and P. Schudel, Adv. Org. Chem., 14, 115 (1963), and references cited therein.

7) D. Fishman, J. T. Klug, and A. Shani, Synthesis, 1981, 137.

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