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TRITYL SALTS AS EFFICIENT CATALYSTS IN THE ALDOL REACTION

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In the presence of a catalytic amount of trityl salts, such as TrOTf, $TrSbCl_6$, $TrPF_6$, $TrSnCl_5$, etc., silyl enol ethers react with aldehydes to give the corresponding aldols in good yields. The preferential formations of erythro or threo aldols become possible by the suitable choice of the counter anions of these trityl salts and the substituents on silicon of the enolates.

In the previous papers, we have shown that trityl perchlorate is an efficient catalyst in the O-$^{1)}$ and C-$^{2)}$ glycosylations, in the aldol-type reactions,$^{3)}$ and in the Michael reaction.$^{4)}$ In these reactions, we assumed that trityl cation has strong affinity toward alkoxy (or acyloxy) group of acetals, or carbonyl oxygen of aldehydes and α,β-unsaturated ketones to generate cationic species, which smoothly react with various nucleophiles. On the assumption that trityl salts other than trityl perchlorate would be also effective in these reactions, we examined the effect of several trityl salts such as TrOTf,$^{5)}$ $TrSbCl_6$,$^{6)}$ $TrPF_6$,$^{6)}$ $TrSnCl_5$,$^{6)}$ etc. in these reactions. In this communication, we wish to report the effect of various trityl salts on yields and stereochemistry of the aldol reaction between silyl enol ethers and aldehydes.

The reactions of trimethyl silyl enol ethers of cyclohexanone or 3-pentanone and benzaldehyde were chosen as models and, in the presence of a catalytic amount of trityl salts (5 mol %), reactions were carried out at -78 °C for 1 h in dichloromethane. The results are summarized in Table 1.

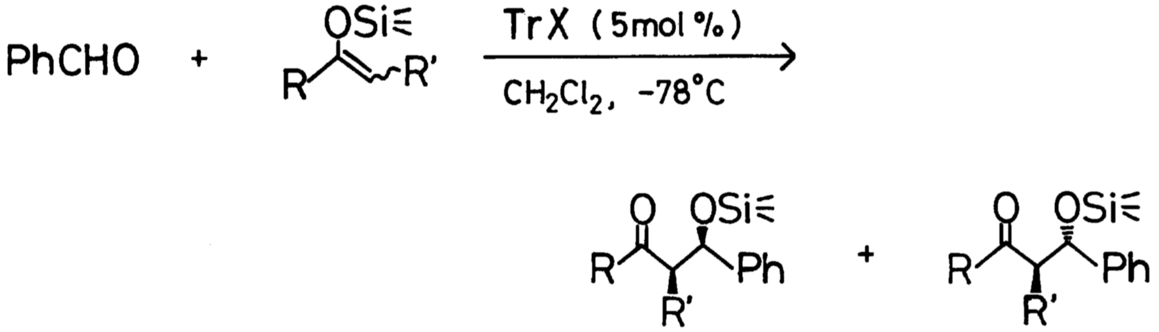
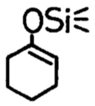
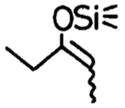
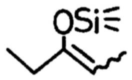


Table 1. TrX catalyzed aldol reaction

Entry	Silyl enol ether	TrX	Yield/%	Erythro : Threo[a]
1		$TrClO_4$	77	64 : 36
2		TrOTf	75	69 : 31
3		$TrSnCl_5$	80	46 : 54
4		$TrPF_6$	83	49 : 51
5		$TrSbCl_6$	81	33 : 67
6		$TrBF_4$	trace	———
7		TrCl	0	———
8	 (E/Z=76/24)	$TrClO_4$	78	48 : 52
9		TrOTf	91	71 : 29
10		$TrSnCl_5$	78	39 : 61
11		$TrPF_6$	64	38 : 62
12		$TrSbCl_6$	78	36 : 64
13		$TrBF_4$	trace	———
14		TrCl	0	———
15	 (E/Z=6/94)	$TrClO_4$	89	58 : 42
16		TrOTf	78	73 : 27
17		$TrSnCl_5$	74	46 : 54
18		$TrPF_6$	87	47 : 53
19		$TrSbCl_6$	86	46 : 54
20		$TrBF_4$	trace	———
21		TrCl	0	———

a) Diastereomeric ratios determined by ^1H NMR.

In the case of TrOTf, $TrPF_6$, $TrSnCl_5$, or $TrSbCl_6$, the reaction mixture assumed a yellowish color indicating the generation of trityl cation, which effectively promote the aldol reaction by catalytic use. The effect of the counter anions on the stereochemistry is observed as follows; trityl triflate favors erythro aldols and trityl hexachloroantimonate does threo ones. While trityl chloride is not effective because it is more covalently bonded than the other above mentioned trityl salts and trityl cation is not generated enough to promote the aldol reaction. In addition, it was observed that a catalytic amount of trityl tetrafluoroborate is not effective,7) unexpectedly, and this may be due to the decomposition of the reaction intermediate, silyl tetrafluoroborate, to silyl fluoride and boron trifluoride.8) Under the reaciton conditions, the promoter, trityl tetrafluoroborate, could not be regenerated.9)

Based on these results, it is assumed that erythro or threo aldols would be predominantly produced by the suitable choice of the trityl salts and the substituents on silicon of the enolates. Indeed, as shown in Table 2, erythro

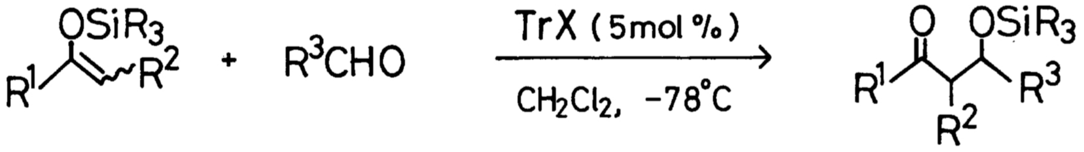
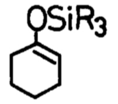
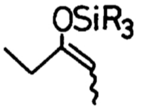
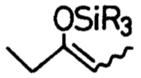


Table 2. Synthesis of erythro or threo aldols[a)]

	Silyl enol ether	Aldehyde	TrX	SiR_3	Yield/%	Erythro : Threo[b)]
1		PhCHO	TrOTf	$PhMe_2$	79	78 : 22
2			$TrSbCl_6$	$^tBuMe_2$	92	18 : 82
3	 (E/Z=76/24)	PhCHO	TrOTf	$PhMe_2$	86	71 : 29
4			$TrClO_4$	$^tBuMe_2$	89	16 : 84
5		$Ph(CH_2)_2CHO$	TrOTf	$PhMe_2$	68	63 : 37
6			$TrClO_4$	$^tBuMe_2$	79	21 : 79
7	 (E/Z=6/94)	PhCHO	TrOTf	$PhMe_2$	84	73 : 27
8			$TrClO_4$	$^tBuMe_2$	87	27 : 73
9		$Ph(CH_2)_2CHO$	TrOTf	$PhMe_2$	74	79 : 21
10			$TrClO_4$	$^tBuMe_2$	80	27 : 73

a) All products gave satisfactory NMR and IR spectra.

b) Diastereomeric ratios determined by ^1H NMR, ^{13}C NMR, and/or HPLC.

aldols are preferentially produced by the combined use of trityl triflate and dimethylphenyl silyl enol ethers, while threo aldols predominate from trityl hexachloroantimonate or trityl perchlorate[10)] and t-butyldimethyl silyl enol ethers.

Further studies toward clarification of detailed mechanism as well as other synthetic reactions utilizing the respective unique characteristics of these trityl salts are currently in progress in our laboratory.

References

1) T. Mukaiyama, S. Kobayashi, and S. Shoda, Chem. Lett., 1984, 907.
2) T. Mukaiyama, S. Kobayashi, and S. Shoda, Chem. Lett., 1984, 1529.
3) T. Mukaiyama, S. Kobayashi, and M. Murakami, Chem. Lett., 1984, 1759; 1985, 447.
4) S. Kobayashi, M. Murakami, and T. Mukaiyama, Chem. Lett., 1985, 953.
5) TrOTf was prepared from trityl chloride and silver triflate. See also T. R. Forbus, Jr. and J. C. Martin, J. Org. Chem., 44, 313 (1979).
6) Commercially available from Aldrich Chemical Company.
7) Barton et al. reported the hydrolysis of acetals under mild conditions by the use of a stoichiometric amount of trityl tetrafluoroborate. D. H. R. Barton, P. D. Magnus, G. Smith, G. Streckert, and D. Zurr, J. Chem. Soc., Perkin Trans. 1, 1972, 542.
8) For example, see I. Paterson and L. G. Price, Tetrahedron Lett., 22, 2829 (1981).
9) The aldols are obtained in moderate yields by stoichiometric use.
10) In the case of the silyl enol ethers of 3-pentanone, the combined use of trityl perchlorate and t-butyldimethyl silyl enol ethers gave better threo selectivity than that of trityl hexachoroantimonate and t-butyl dimethyl silyl enol ethers.

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