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STANNOUS (II) TRIFLATE PROMOTED REARRANGEMENT OF β-KETO SULFOXIDES. SYNTHESIS OF 1,4-DIKETONES

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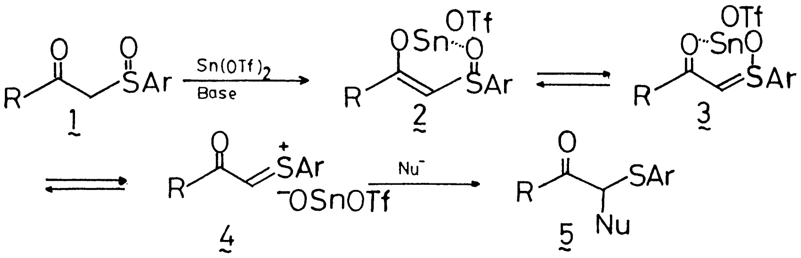
Stannous triflate promotes rearrangement of β-keto sulfoxides to generate α-thiocarbocation, which in turn react with silyl enol ethers to give 2-arylsulfenyl-1,4-diketones in good yields.

The rearrangement of β-keto sulfoxides has found useful applications in synthetic organic chemistry, e.g., the Pummerer rearrangement,[1)] however, concomitant carbon-carbon bond formation in an intermolecular fashion appears to meet with limited success.[2)]

Our continuous interests in Sn(II) promoted reactions have already brought about an excellent stereoselection in the Sn(II) enolate mediated aldol reaction,[3)] and in particular asymmetric aldol reaction effected by a coordination of Sn(II) with a diamine ligand derived from (L)-proline has opened a new area of asymmetric carbon-carbon bond forming reactions,[4)] i.e., ligand controlled asymmetric synthesis.

In the present study, we focussed our attention on a characteristic feature of Sn(II) species to form strong chelate complexes with sulfoxides.[5)]

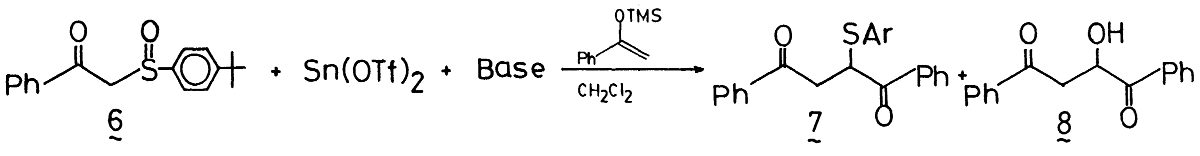


Scheme 1.

On treatment of β-keto sulfoxide 1 with stannous triflate in the presence of a tertiary amine, the enolate of the β-keto sulfoxide 2 initially formed is expected to rearrange into α-thiocarbocation 4, which in turn reacts with a suitable nucleophile at the carbon α to carbonyl to give β-arylsulfenyl ketone 5, and this process is considered to be an "umpolung" use of the stannous enolate.

Among various nucleophiles screened (alkyl enol ethers, enamines, trimethylsilyl cyamide, allyltrimethylsilane,[6)] malonate anions, silyl enol ethers[7)]), silyl enol ethers did give the addition products. A series of reactions was carried out in an effort to find the optimum reaction conditions using 2-p-t-butylphenylsulfinylacetophenone and α-trimethylsiloxystyrene, and the results are summarized in Table 1.

Table 1. Examination of Reaction Conditions[a)]

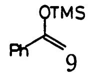
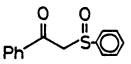
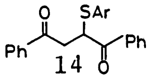
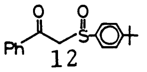
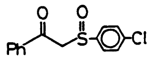
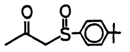
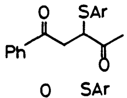
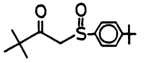
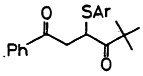
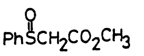
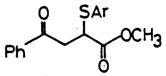
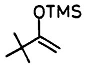
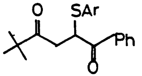
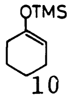
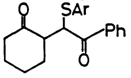
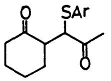
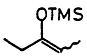
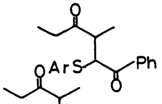
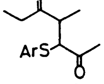
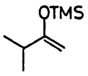
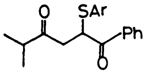


Entry	6 (equiv.)	Base (equiv.)		Sn(OTf)$_2$ (equiv.)	Yield of 7/%	8/%
1	1.0	NEP[b)]	1.0	1.0	38	16
2	2.0	NEP	2.0	2.0	51	15
3	1.0	DBU[c)]	1.0	1.0	37	12
4	1.0	LDA[d)]	1.0	1.0	0	0
5	1.0	NTMSI[e)]	1.0	1.0	47	0
6	2.0	NTMSI	2.0	2.0	68	0
7	2.0	NTMSI	1.0	2.0	43	0
8	2.0	NTMSI	4.0	2.0	0	0
9	2.0	BSA[f)]	2.0	2.0	62	0
10	4.0	BSA	4.0	4.0	82	0
11	2.0	BSTFA[g)]	2.0	2.0	53	0
12	3.0	NTMSI	3.0	3.0	71	0
13	4.0	NTMSI	4.0	4.0	82	0

a) The reaction was carried out in CH$_2$Cl$_2$ at 0 °C.
b) N-Ethylpiperidine.
c) 1,8-Diazabicyclo[5.4.0]undec-7-ene.
d) Lithium diisopropylamide and the reaction in THF.
e) N-Trimethylsilylimidazole.
f) O,N-Bis(trimethylsilyl)acetamide.
g) O,N-Bis(trimethylsilyl)trifluoroacetamide.

As shown in Table 1, the use of N-ethylpiperidine which gave the best result in the stannous triflate promoted aldol reaction[3)] afforded the desired product 7 in moderate yield along with the aldol type product 8. A satisfactory result was obtained when N-trimethylsilylimidazole or O,N-bis(trimethylsilyl)-acetamide was used as the base and the reaction was carried out with an excess of the β-keto sulfoxide. A variety of 2-arylsulfenyl-1,4-diketones were prepared under the optimum conditions found for the above model reaction. Table 2 summarizes the results.

Table 2. Preparation of 2-Arylsulfenyl-1,4-diketones[a)]

Entry	Silyl enol ether	β-Keto sulfoxide	Product[b)]	Yield/%[c)]
1	 9		 14	78
2	9	 12	14	82
3	9		14	65
4	9	 13		91
5	9			65
6	9	 $PhS(O)CH_2CO_2CH_3$		23
7		12		73
8	 10	12		75[d)]
9	10	13		66[d)]
10	 11	12		74[d)]
11	11	13		52[d)]
12		12		58

a) The reaction was carried out with stannuos triflate β-keto sulfoxide, NTMSI, and silyl enol ether (4:4:4:1). b) All compounds gave satisfactory spectral data. c) Isolated yields. d) A mixture of diastereomers (ca. 1:1) were obtained.

As far as arylsulfinyl moiety is concerned, a p-t-butylphenylsulfinyl group facilitated the reaction most effectively, whereas chlorophenylsulfinyl derivative decreased the yield of the desired product. In the cases with cyclohexanone and diethylketone silyl enol ethers, the reactions gave two diastereomers in ca. 1:1 ratio.

As control experiments, other Lewis acids were tested as a promotar in this type of reaction, and titanium tetrachloride, tin(IV) chloride, cupric triflate, boron trifluoride etherate did not effect the introduction of silyl enol ether, whereas trimethylsilyl triflate induced rearangement to give the desird product but in low yield (<8%) under the similar conditions employed in the present procedure.[8)]

The following example is representative: To a suspension of stannous triflate

(207 mg, 0.496 mmol) in 0.5 ml of CH_2Cl_2 was added a mixture of α-trimethylsiloxystyrene (24.0 mg, 0.124 mmol), 2-p-t-butylphenylsulfinylacetophenone (149 mg, 0.496 mmol), and N-trimethylsilylimidazole (0.073 ml, 0.496 mmol) in 1.5 ml of CH_2Cl_2 at -78 °C, and the mixture was stirred at that temperature for 5 min. After stirring at 0 °C for 30 min, phosphate buffer (pH 7, 5 ml) was added, and the mixture was extracted with CH_2Cl_2 (5 mlx3). The combined extracts were dried ($MgSO_4$) and concentrated to leave an oil. Purification on silica gel TLC (eluent:EA/Hx=1/6) gave 2-p-t-butylphenylsulfenyl-1,4-diphenyl-1,4-butandione (41.0 mg, 82%) and the recovered β-keto sulfoxide (51 mg).

Thus, stannous triflate has been found to be very effective to promote rearrangement of sulfoxides under aprotic conditions even in the presence of tertiary amine, whereas several other Lewis acids usually forms strong complexes with amines, resulting in formation of precipitates to lose Lewis acidity.

Since the arylsulfenyl moiety can be removed via either oxidative or reductive work up,$^{9)}$ leading to unsaturated 1,4-dicarbonyl or saturated 1,4-dicarbonyl compounds, respectively, the present method offers a useful addition to the existed procedures for the preparation of 1,4-diketones as well as the Pummerer type rearangement under aprotic conditions.

References

1) For a review, see: T. Numata, J. Synth. Org. Chem. Jpn., 36, 845 (1978); recent examples of cyclization via the Pummerer rearrangement, see: Y. Oikawa and O. Yonemitsu, J. Org. Chem., 41, 1118 (1976); P. Magnus, T. Gallaghre, P. Broven, and C. Huffman, J. Am. Chem. Soc., 106, 2105 (1984), and references therein.

2) Only a few examples are known. See for instance, M. Hojo, R. Masuda, T. Saeki, K. Fujimori, S. Tsutsumi, Tetrahedron Lett., 1977, 3883; Y. Tamura, H.-D. Choi, H. Maeda, and H. Ishibashi, ibid., 22, 1343 (1981).

3) T. Mukaiyama, R. W. Stevens, and N. Iwasawa, Chem. Lett., 1982, 353; R. W. Stevens and T. Mukaiyama, ibid., 1982, 1459; N. Iwasawa and T. Mukaiyama, ibid., 1982, 1083; T. Mukaiyama, T. Haga, and N. Iwasawa, ibid., 1982, 1601; R. W. Stevens and T. Mukaiyama, ibid., 1983, 595.

4) N. Iwasawa and T. Mukaiyama, Chem. Lett., 1982, 1441; 1983, 297; R. W. Stevens and T. Mukaiyama, ibid., 1983, 1799.

5) Stannous halides have been known to form complexes with sulfoxides, see: I. S. Morrison and H. M. Haendler, J. Inorg. Nucl. Chem., 29, 393 (1967).

6) Allyltrimethylsilan reacted to give the rearranged product in very low yield.

7) Silyl enol ethers have been reported to react with β-halo sulfides under the influence of Lewis acid; I. Fleming, "Some Uses of Silicon Compounds in Organic Synthesis," in "Organic Synthesis Today and Tomorrow," ed by B. M. Trost and C. R. Hutchinson, Pergamon Press, Oxford (1981), pp. 85-96; L. Duhamel, J. Chauvin, and C. Goumet, Tetrahedron Lett., 24, 2095 (1983).

8) In the absence of stannous triflate, a mixture of N-trimethylsilylimidazole, β-keto sulfoxide, and silyl enol ether did not give the desired addition product even at 110 °C.

9) See Ref. 7.

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