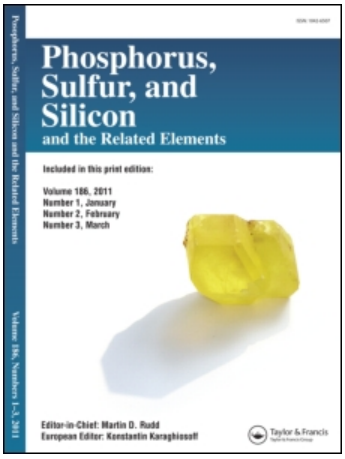

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Benzyltriphenylphosphonium peroxodisulfate $(PhCH_2PPh_3)_2S_2O_8$ (1) is readily prepared as an white solid from benzyltriphenylphosphonium chloride, performs conversion of α-sulfinyl oximes (2) and α-sulfinyl hydrazones (4) to the corresponding β-keto sulfoxides (3) in high yields and high enantiomeric purity.

Keywords: α-Sulfinyl oximes; α-Sulfinyl hydrazones; β-Keto sulfoxides Benzyltriphenylphosphonium peroxodisulfate; Chiral non-racemic synthesis; High enantiomeric purity

INTRODUCTION

β-Keto sulfoxides are very important starting materials in asymmetric synthesis,[1,2] and can be synthesis by the cleavage of the C=N bonds of α-sulfinyl oximes and α-sulfinyl hydrazones. These compounds prepared via the addition of aryl methyl sulfoxides to aryl *N*-oxides[3] or addition of lithiated *N, N*-dimethyl hydrazones to menthyl sulfinate esters[4] respectively. The hydrolysis of C=N double bond of α-sulfinyl oximes (2) and

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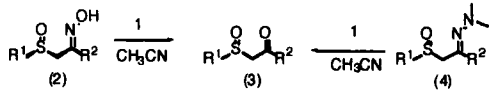
α-sulfinyl hydrazones (4) by classical method[5] was attempted but the optical purity and yield by this method were low (ee <35 and yield <50 %).

RESULTS AND DISCUSSION

We found that the cleavage of C=N double bond of α-sulfinyl oximes (2) and α-sulfinyl hydrazones (4) by benzyltriphenylphosphonium peroxodisulfate ($PhCH_2PPh_3)_2S_2O_8$ (1) in acetonitrile under reflux is rapid (45–80 min). The reaction is very fast and almost quantitative with high optical purity from ^1H NMR analysis in the presence of chemical shift reagent (>95) (Table I and Table II). The general reaction is detailed in Scheme 1. In all case, the crude product was judged to be of >95% purity based on ^1H NMR and TLC analysis as shown in Table I and II. Because of the mildness of the reagent (1) the corresponding sulfones are not formed in these reactions. At this stage the mechanism of the reaction is not clear to us. The enantiomeric purity of (3) was determined to be >97 from ^1H NMR chiral shift studies using (-)-(R)-*N*-(3,3-dinitrobenzoyl)-α-phenylethylamine (5) as a chiral shift reagent[1] and comparing the optical rotation of the products with known compounds.[1–5] To determine the enantiomeric purity of (3) we mixed it with one equivalent of chiral shift reagent (5) in a NMR tube.

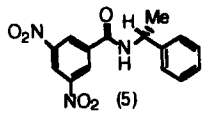


(2) (3) (4)

a R^1 = phenyl, R^2 = phenyl
b R^1 = phenyl, R^2 = 3,4-dimethoxyphenyl
c R^1 = *p*-tolyl, R^2 = phenyl
d R^1 = *p*-tolyl, R^2 = 3,4-dimethoxyphenyl
e R^1 = *2-methoxy-1-naphthyl*, R^2 = phenyl
f R^1 = *2-methoxy-1-naphthyl*, R^2 = 3,4-dimethoxyphenyl
g R^1 = *p*-tolyl, R^2 = 2,4,6-trimethylphenyl
h R^1 = *p*-tolyl, R^2 = 2,4,6-trimethyl-3,5-dichlorophenyl
I R^1 = *p*-tolyl, R^2 = 4-methoxyphenyl

a R^1 = phenyl, R^2 = phenyl
b R^1 = phenyl, R^2 = 3,4-dimethoxyphenyl
c R^1 = *p*-tolyl, R^2 = phenyl
d R^1 = *p*-tolyl, R^2 = 3,4-dimethoxyphenyl
e R^1 = *2-methoxy-1-naphthyl*, R^2 = phenyl
f R^1 = *2-methoxy-1-naphthyl*, R^2 = 3,4-dimethoxyphenyl
g R^1 = *p*-tolyl, R^2 = H
h R^1 = *p*-tolyl, R^2 = Me
I R^1 = *p*-tolyl, R^2 = Et

SCHEME 1



(5)

TABLE I Conversion of (2) to the corresponding carbonyl compounds (3)

Starting Material	*Product*	*Reaction Time/min*	*Yield %*[a]	*e.e %*
2a	**3a**	45	96	97
2b	**3b**	45	95	99
2c	**3c**	58	98	100
2d	**3d**	55	95	100
2e	**3e**	45	99	100
2f	**3f**	65	97	99
2g	**3g**	55	99	96
2h	**3h**	55	96	97
2I	**3I**	70	96	97

a. Isolated yields.

TABLE II Conversion of (4) to the corresponding carbonyl compounds (3)

Starting Material	*Product*	*Reaction Time/min*	*Yield %*[a]	*e.e %*
4a	**3a**	60	98	95
4b	**3b**	65	98	96
4c	**3c**	60	95	98
4d	**3d**	60	97	98
4e	**3e**	65	97	100
4f	**3f**	80	99	100
4g	**3g**	60	96	98
4h	**3h**	55	99	95
4I	**3I**	70	98	99

a. Isolated yields.

In conclusion, we report here an efficient, rapid, mild and inexpensive method for the conversion of α-sulfinyl oximes (2) and α-sulfinyl hydrazones (4) by benzyltriphenylphosphonium peroxodisulfate $(PhCH_2PPh_3)_2S_2O_8$ (1) in acetonitrile under refluxing conditions to the corresponding β-keto sulfoxides (3). This reagent is superior to previously

reported methods in terms of selectivity, yields, purity, and high enantiomeric purity of products and short reaction time.

EXPERIMENTAL

General

All yields refer to isolated products after purification. Starting materials were synthesis by known methods.[1–5] Products were characterized by comparison with authentic samples[1–5] and by spectroscopy data (IR, NMR spectrum, tin layer chromatography, melting and boiling point). All reactions were carried out in acetonitrile. All mps. Were taken on a Gallenkamp melting apparatus and are uncorrected. Research Institute of Petroleum Industry, Tehran, I. R. IRAN performed elemental analysis. ^1H NMR spectra were recorded at 90 and 250 MHz The spectra were measured in $CDCl_3$ unless otherwise stated, relative to TMS (0.00 ppm). Optical rotations were recorded with a JASCO, DIP-370, Digital Polarimeter.

Preparation of $(PhCH_2PPh_3)_2S_2O_8$ (1)

To an aqueous solution of benzyltriphenylphosphonium chloride (8.55 g, 22 mmol, 75 ml H_2O), was added a solution of potassium peroxodisulfate (3 g, 11 mmol) in water (60 ml). The reaction mixture was stirred at room temperature for 15 min. The resulting white solid product was collected, washed with cooled distilled water (20 ml) and dried in a desiccator under vacuum over calcium chloride, to yield 9.5 g (96 %), mp 180–182 C. ^1H NMR: δ 7.93–6.87 (m, 20 H), 4.7 (d, J = 25.6 Hz, $\underline{CH_2}$-P). ^{13}C NMR: δ 133.50, 133.20, 130.20, 129.60, 129.40, 128.10, 127.70, 127.20, 117.30 (d, J = 85.5 Hz, $\underline{CH_2}$-P). IR (KBr): 1290, 1260, 1092, 1058, 700, 658, 590, 546 cm^{-1}. Anal calcd $C_{50}H_{44}O_8P_2S_2$: C, 66.80; H, 4.90; S, 7.30 %. Found; C, 66.70; H, 4.90; S, 7.40. Found S_2O_8. 21.30 %, calcd 21.38 %.[6]

Oxidation of (2) or (3) to (4). General Procedure

The α-sulfinyl oximes (2) or α-sulfinyl hydrazones (4) (1 mmol) was added to a stirred solution of the oxidant (1) (1 mmol, 0.90 g) in ace-

tonitrile (20 ml). The mixture was heated at reflux until TLC showed complete disappearance of starting material, which required 45–80 min depending on substrate (Table I and II). The mixture was cooled and 2 g of silica gel was added to the reaction mixture and the reaction mixture was stirred for 5 min. The solid was then separated by suction filtration through Celite and washed with acetonitrile (2 10 ml). Evaporation of the solvent gave the β-keto sulfoxides (4). The crude products were purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane as eluent (90:10).

Acknowledgements

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