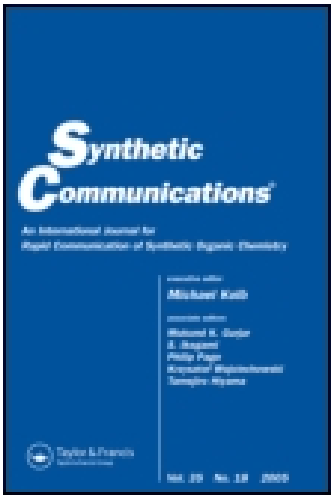

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Mono Halogenation of β-Keto Sulfides. Synthesis of β-Keto-α-phenylthio p-Tolyl Sulfones

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MONO HALOGENATION OF β -KETO SULFIDES. SYNTHESIS OF β-KETO- α-PHENYLTHIO p-TOLYL SULFONES.

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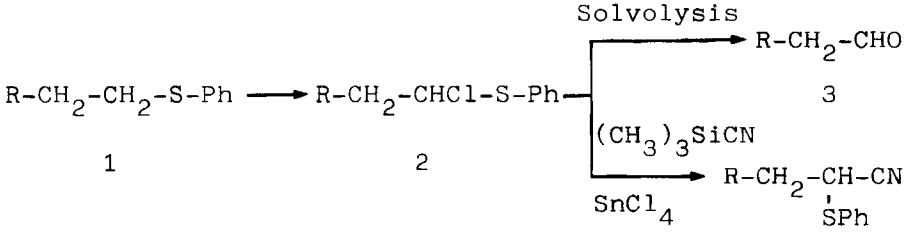
Abstract: β-Keto- α-Phenylthio p-Tolyl sulfones are obtained from β-keto-alkyl phenyl sulfides by halogenation with NCS followed by treatment with sodium p-toluene sulphinate.

Alkyl phenyl sulfides (1) are halogenated with one mole of N-chloro succinimide to α-chloro alkyl phenyl sulfides (2). These intermediates can be converted into aldehydes[1] (3) or α-phenylthio nitriles[2] (4).



* To whom correspondence should be addressed

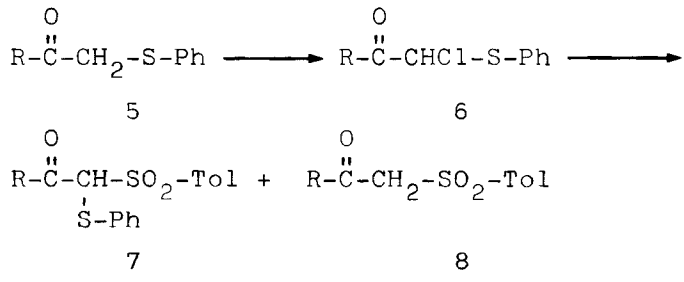
Table 1. Synthesis of β-keto-α-phenylthio p- toluene sulfones (7).

Entry	R	Yield %[a]
7a	t-C_4H_9	59
7b	n-C_6H_{13}	55
7c	n-C_8H_{17}	61
7d	C_6H_5	60

a) Isolated yields based on the starting β-keto sulfides.

In our studies to develop new synthetic applications for(1)we have found that a carbonyl group in the β position is consistent with the halogenation step. Therefore the corresponding β-keto alkyl phenyl sulfides (5) halogenated with one mole of NCS, in carbon tetrachloride, at room temperature, for 2 hours to β-keto-α-phenylthio alkyl phenyl sulfides (6) which are themselves interesting synthetic intermediates.

They can be converted on treatment with sodium p-toluene sulphinate to β-keto-α-phenyltio p-toluene sulfones(7) in reasonable yields (see Table 1). These compounds have been converted to aldehydes, ketones[3] and esters[4].



5 6 7 8

The quantity of side products, the β-keto alkyl p-toluene sulfones (8), was reduced but not eliminated after careful studies of the reaction time, temperature and solvents. They can be easily separated from the desired product (7) by column chromatography on silica gel eluting with pet. ether/5% ethyl acetate followed by dichloromethane.

Therefore the present method represents a good alternative method for the synthesis of these type of compounds, synthesized previously by acylation of methylthio methyl p-toluene sulfone[5].

EXPERIMENTAL SECTION

IR spectra were recorded with a Perkin-Elmer 237 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Varian EM-390 and FT-80A spectrophotometer respectively. Mass spectra were performed on a Kratos AEI MS50 spectrometer.

Abbreviations: TMS: tetramethyl silane, s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet.

Synthesis of β-Keto α-Chloro Sulfides (5). General Procedure.

6.6 mmol of N-Chloro succinimide was added to 6.0 mmol of β-keto alkyl phenyl sulfides (5) in 50ml of CCl_4 at $0^{o}C$. After 2 hours the mixture was filtrated and the solvent removed in a rotatory evaporator. The product obtained was practically pure and used in the next step without any purification.

Reaction of β-Keto α-Chloro Sulfides (5) with sodium p-toluene sulphinate.

A mixture of β-keto α-chloro sulfide (6mmol) sodium p-toluene sulphinate (6mmol), tetrabutylammonium hydrogen sulphate (158mg) in 2ml of acetone and 2ml of benzene was refluxed (60°C) for 4 hours. After this period 30ml of water were added and the heterogeneous mixture extracted with ethyl ether (3x). The combined organic layers were dried over sodium sulphate and evaporated. The residue was chromatographed on silica gel eluting with pet. ether/5% ethyl acetate followed by dichloromethane.

3,3 Dimethyl β-keto α-thiophenyl butyl p-toluene sulfone (7a).

M.p. 144-145°C (ethyl alcohol). IR ν 3000, 1730, 1610, 1490, 1350, 1180, 830, 710, 690, 660, 580 cm^{-1}. ^{1}H NMR ($CDCl_3$/TMS) δ 1.2 (s, 9H, $3CH_3$), 2.5 (s, 3H, CH_3), 5.3 (s, 1H, CH), 7.3-8.2 (m, 9H, aromatics). ^{13}C NMR($CDCl_3$/TMS) δ 21.66 (CH_3), 26.17 ($3CH_3$), 47.34 (quaternary C), 72.80 (CH), 129.09, 129.25, 129.44, 131.03, 132.42, 132.81, 137.41, 145.44 (aromatics), 204.14 (CO). MS m/e 362(M^+), 278, 207, 179, 139, 123, 110, 57 (base peak). HRMS m/e for $C_{19}H_{22}S_2O_3$:calcd 362.1003; found 362.1004.

β-Keto α-phenylthio hexyl p-toluene sulfone (7b).

M.p. 65-67°C (ethyl alcohol). IR ν 2920, 1720, 1410, 1340, 1170, 770, 730, 580 cm^{-1}. ^{1}H NMR($CDCl_3$/TMS) δ 0.93 (t, 3H, CH_3), 1.10-1.80 (m, 4H, $2CH_2$), 2.50 (s,3H,CH_3), 2.85 (q, 2H, CH_2), 4.96 (s, 1H, CH), 7.4-7.7 (m, 7H, aromatics), 8.00-8.20 (m, 2H, aromatics). ^{13}C NMR($CDCl_3$ /TMS) δ 13.79(CH_3), 21.73(CH_3), 22.03(CH_2), 25.61(CH_2),

42.06(CH_2), 79,65(CH), 129.08, 129.55, 130.12, 132.31 , 132.92 (aromatics), 198.02 (CO). MS m/e 362 (M^+), 278, 207(base peak), 139, 123, 110. HRMS m/e for $C_{19}H_{22}S_2O_3$: calcd 362.1003; found 362.1003.

β -Keto α-phenylthio octyl p-toluene sulfone (7c).

M.p. 82-84°C (ethyl alcohol). IR ν 2960, 2860, 1710, 1580, 1340, 1150, 740, 560 cm^{-1}. ^1H NMR ($CDCl_3$/TMS) δ 0.9 (t, 3H, CH_3), 1.4 (m, 8H, $4CH_2$), 2.35 (s, 3H ,CH_3), 2.60(q, 2H, CH_2), 4.70 (s, 1H, CH), 7.1-7.8 (m, 9H, aromatics). ^{13}C NMR ($CDCl_3$/TMS) δ 13.29 (CH_3), 14.00 (CH_3), 21.69 (CH_2), 23.44 (CH_2), 29.49 (CH_2), 31.30 (CH_2), 42.37 (CH_2), 79.49 (CH), 129.04, 129.47, 129.59, 130.04, 132.02, 133.68, 145.76 (aromatics), 198.91(CO). MS m/e 390(M^+), 275, 235, 155, 139, 123 (base peak) . HRMS m/e for $C_{21}H_{26}S_2O_3$: calcd 390.1315;found 362.1314.

β -Keto α-thiophenyl β-phenyl ethyl p-toluene sulfone (7d).

M.p. 88-90°C (ethyl alcohol). IR ν 2950, 1690, 1600, 1440, 1320, 1140, 810, 730, 680, 650, 560 cm^{-1}. ^1H NMR ($CDCl_3$/TMS) δ 2.4 (s, 3H, CH_3), 6.7 (s, 1H, CH),7.1-8.0 (m, 14H, aromatics). ^{13}C NMR ($CDCl_3$/TMS) δ 21.59 (CH_3), 75.31 (CH), 128.77, 129.07, 129.19, 129.32, 129.66, 130.53, 132.06, 133.35, 133.89, 134.21, 135.06, 145.54 (aromatics), 189.25 (CO), MS m/e 382 (M^+), 227, 210, 199, 149, 105 (base peak). HRMS m/e $C_{21}H_{18}S_2O_3$: calcd 382.0691; found 382.0701.

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