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Two expedient 'one-pot' methods for synthesis of β-aryl-β-mercaptoketones over anhydrous potassium carbonate or amberlyst-15 catalyst

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Abstract. Two expedient one-pot methods have been developed for synthesis of β-aryl-β-mercaptoketones using acetophenones, benzaldehydes and thiols as starting materials. The methods involve microwave irradiation (5 min) of 1:1 mixtures of acetophenones and benzaldehydes over neutral alumina supported anhydrous potassium carbonate or amberlyst-15 in the first step, and that is followed by addition of thiol to the resulting material and keeping at room temperature for 1.5 h.

Keywords. β-aryl-β-mercaptoketones; anhydrous potassium carbonate; amberlyst-15; chalcones; thia-Michael addition.

1. Introduction

The chemistry of thia-Michael addition is being explored since a long period[1] due to its versatile applications in biosynthesis[2] and for obtaining compounds having biological activities such as tumour inhibitors,[2] γ-secretase inhibitors,[3] etc. In order to carry out such reactions, a good number of methodologies involving a variety of catalysts or catalytic systems have been developed so far; the important ones include different Lewis acids such as CdI_2,[4] $InBr_3$,[5] $Zn(ClO_4)_2.6H_2O$,[6] molecular iodine,[7,8] $Bi(NO_3)_3$[9] and $VO(OTf)_2$,[10] etc. The process can also be catalysed by organic bases, both of synthetic and natural origin,[11–16] complexes of different transition metals,[17,18] ionic liquids,[19–22] solid supports,[23–26] phosphorus doped with other element or chemical species,[27,28] polyethylene glycol,[29] porphyrin rings,[30] etc. However, the above mentioned methods involve some limitations such as use of expensive catalysts, long reaction time, etc. Besides, preparation of the Michael acceptors needs a separate step in all cases. These limitations led us to develop a new efficient methodology for a one-pot synthesis of β-aryl-β-mercaptoketones (**1**), particularly because of recent success of our group and also of others in synthesis of 2,4-diarylthiochromans (**2**) utilizing them as useful intermediates (scheme 1).[31,32]

A domino process usually refers to successive occurrence of different reactions in the same reaction vessel without separation or purification of reactive intermediates.[33,34] Survey of literature showed a growing trend in utilization of domino sequential one-pot aldol-thia-Michael process for synthesis of some important β-aryl-β-mercaptoketones (**1**). However, reports on such processes are very limited.[35,36] Herein, we report the development of two domino sequential one-pot aldol-thia-Michael processes using inexpensive catalysts such as anhydrous K_2CO_3 or amberlyst-15 (a sulphonated polystyrene resin).

2. Experimental

Melting points were recorded on a Köfler block and are uncorrected. Infrared (IR) spectra were recorded on a Perkin Elmer Fourier Transform Infrared Spectrophotometer (Spectrum BX II) as KBr pellets. ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were obtained in $CDCl_3$ on a Bruker AV-300 (300 MHz) spectrometer using tetramethylsilane as an internal standard. Mass spectrum was acquired on a Waters QTOF Micro YA263 Mass Spectrometer. Analytical samples were dried *in vacuo* at room temperature. Microanalytical data were recorded on two Perkin-Elmer 2400 Series II C, H, N analysers. An unmodified domestic household microwave oven (LG, DMO, Model No.-556P, 900 watt) equipped with inverter technology, which provides a realistic control

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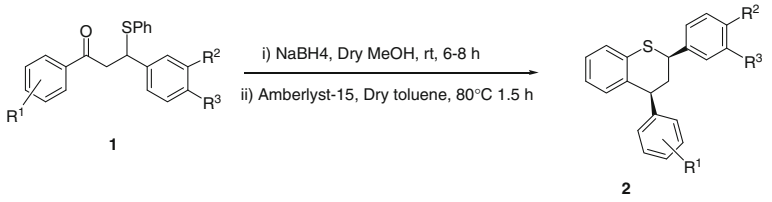


Scheme 1. Conversion of β-aryl-β-mercaptoketones (**1**) to *cis*-2,4-diarylthiochromans (**2**).

of the microwave power to the desired level (20–100%) was used for microwave heating. Column chromatography was performed on silica gel (100–200 mesh) using petroleum ether (60–80°C) and petroleum ether-ethyl acetate mixtures as eluents. Thin layer chromatography was done with silica gel G.

2.1 *General procedure for synthesis of β-aryl-β-mercaptoketones (**1**)*

A mixture of acetophenone (**3**, 1 mmol) and aromatic aldehyde (**4**, 1 mmol) was thoroughly ground over neutral alumina (4 g) with added anhydrous K_2CO_3 (1 mmol) or amberlyst-15 (80 mg) and the resulting powder was subjected to microwave irradiation at 540 W for 5 min (120–125°C). After cooling the mass to room temperature, thiol (**5**, 1.3 mmol) was added and thoroughly mixed and then the mixture was kept at room temperature for 1.5 h under closed condition. The solid was then washed thoroughly with dichloromethane and the concentrate of the washings was subjected to column chromatography over silica gel using petroleum ether-ethyl acetate mixtures as eluents to get **1** in pure state.

The same method was followed for synthesis of **7** and **8** also.

2.2 *Analytical and spectral data of some selected β-aryl-β-mercaptoketones and related compounds*

2.2a *3-(4-Methylphenyl)-1-phenyl-3-phenylsulphanylpropan-1-one **1b***: Colourless crystals, IR (KBr) υ_{max} = 1668 (C=O), 1597, 1440, 1329, 1233, 1176, 1112, 994, 811, 728 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 3H, -CH_3), 3.50–3.70 (m, 2H, -CH_2), 4.94 (t, 1H, J = 7.0 Hz, H-2), 7.06 (d, 2H, J = 7.8 Hz), 7.22–7.26 (m, 4H), 7.32–7.35 (m, 2H), 7.42 (t, 2H, J = 7.2 Hz), 7.50–7.59 (m, 2H), 7.87 (d, 2H, J = 7.2 Hz); Anal. Calcd. for $C_{22}H_{20}OS$ (332.46): C, 79.48; H, 6.06. Found: C, 79.33; H, 6.22.

2.2b *3-(3-Nitrophenyl)-1-phenyl-3-phenylsulphanylpropan-1-one **1e***: Light yellow crystals, IR (KBr) υ_{max} = 1671 (C=O), 1531, 1347, 1224, 987 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.68 (d, 2H, J = 7.2 Hz, -CH_2), 5.00 (t, 1H, J = 7.2 Hz, H-2), 7.23–7.34 (m, 5H), 7.37–7.48 (m, 3H), 7.55–7.63 (m, 2H), 7.88–7.91 (m, 2H), 8.02–8.07 (m, 1H), 8.17 (t, 1H, J = 2.4 Hz); Anal. Calcd. for $C_{21}H_{17}NO_3S$ (363.43): C, 69.40; H, 4.71; N, 3.85. Found: C, 69.22; H, 4.93; N, 3.98.

2.2c *3-(4-Nitrophenyl)-1-phenyl-3-phenylsulphanylpropan-1-one **1f***: Light yellow crystals, IR (KBr) υ_{max} = 1678 (C=O), 1514, 1346, 1228, 984, 825 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.67 (d, 2H, J = 7.2 Hz, -CH_2), 4.97 (t, 1H, J = 7.0 Hz, H-2), 7.23–7.31 (m, 5H), 7.42–7.58 (m, 4H), 7.60–7.87 (m, 1H), 7.89 (dd, 2H, J = 8.1 and 1.2 Hz), 8.08 (d, 2H, J = 8.7 Hz); Anal. Calcd. for $C_{21}H_{17}NO_3S$ (363.43): C, 69.40; H, 4.71; N, 3.85. Found: C, 69.52; H, 4.63; N, 4.01.

2.2d *3-(4-N,N-Dimethylphenyl)-1-phenyl-3-phenylsulphanylpropan-1-one **1g***: Yellow crystals, IR (KBr) υ_{max} = 1679 (C=O), 1525, 1360, 1229, 948, 806, 756 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.91 (s, 6H, -$N(CH_3)_2$), 3.48–3.69 (m, 2H, -CH_2), 4.93 (dd, 1H, J = 8.4 and 5.8 Hz, H-2), 6.67 (d, 2H, J = 7.8 Hz), 7.17–7.26 (m, 4H), 7.35 (dd, 2H, J = 7.8 and 1.8 Hz), 7.41 (t, 2H, J = 7.5 Hz), 7.53 (t, 2H, J = 6.9 Hz), 7.86 (d, 2H, J = 7.2 Hz); Anal. Calcd. for $C_{23}H_{23}NOS$ (361.50): C, 76.42; H, 6.41; N, 3.87. Found: C, 76.18; H, 6.20; N, 3.91.

2.2e *3-(3,4-Methylenedioxyphenyl)-1-phenyl-3-phenylsulphanylpropan-1-one **1h***: Colourless crystals, IR (KBr) υ_{max} = 1678 (C=O), 1596, 1581, 1489, 1255, 1038, 934, 744 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.48–3.67 (m, 2H, -CH_2), 4.92 (t, 1H, J = 6.8 Hz, H-2), 5.89 (s, 2H, -CH_2-) 6.65 (d, 1H, J = 7.8 Hz), 6.77 (d, 1H, J = 7.8 Hz), 6.92 (s, 1H) 7.24 (d, 3H, J = 5.4 Hz), 7.35–7.45 (m, 4H), 7.53 (d, 1H, J = 6.6 Hz), 7.88 (d, 2H, J = 7.2 Hz); Anal. Calcd. for $C_{22}H_{18}O_3S$ (362.44): C, 72.90; H, 5.01. Found: C, 72.61; H, 4.82.

2.2f *3-Phenyl-1-(4-methylphenyl)-3-phenylsulphanylpropan-1-one **1i***: Colourless crystals, IR (KBr) υ_{max} = 1674 (C=O), 1605, 1440, 1338, 1231, 1180,

976, 812 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 3H, -CH_3), 3.56–3.61 (m, 2H, -CH_2), 4.94 (dd, 1H, J = 7.8 and 6.3 Hz, H-2), 7.17–7.22 (m, 4H), 7.23 (d, 2H, J = 1.8 Hz), 7.26 (s, 2H), 7.30–7.34 (m, 4H), 7.77 (d, 2H, J = 8.1 Hz); Anal. Calcd. for $C_{22}H_{20}OS$ (332.46): C, 79.48; H, 6.06. Found: C, 79.64; H, 6.22.

2.2g *3-(4-Methoxyphenyl)-1-(4-methylphenyl)-3-phenylsulphanylpropan-1-one* ***1j***: Colourless crystals, IR (KBr) υ_{max} = 1676 (C=O), 1597, 1460, 1338, 1251, 1036, 976, 812 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 3H, -CH_3), 3.52–3.60 (m, 2H, -CH_2), 3.75 (s, 3H, -OCH_3), 4.92 (dd, 1H, J = 8.3 and 5.8 Hz, H-2), 6.78 (d, 2H, J = 8.4 Hz), 7.20–7.34 (m, 9H), 7.77 (d, 2H, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): 21.6, 44.7, 47.7, 55.2, 113.8, 127.4, 128.2, 128.8, 129.3, 132.6, 133.2, 134.3, 134.5, 144.1, 158.7, 196.8; TOF MS ES$^+$ (M+Na)$^+$: Calcd. 385.1238. Found 385.1237; Anal. Calcd. for $C_{23}H_{22}O_2S$ (362.48): C, 76.21; H, 6.12. Found: C, 75.98; H, 5.94.

2.2h *3-(4-Chlorophenyl)-1-(4-methylphenyl)-3-phenylsulphanylpropan-1-one* ***1k***: Colourless crystals, IR (KBr) υ_{max} = 1656 (C=O), 1564, 1492, 1332, 1184, 1012, 988, 817 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 3H, -CH_3), 3.48–3.63 (m, 2H, -CH_2), 4.90 (t, 1H, J = 7.1 Hz, H-2), 7.18–7.31 (m, 11H), 7.77 (d, 2H, J = 8.1 Hz); Anal. Calcd. for $C_{22}H_{19}ClOS$ (366.90): C, 72.02; H, 5.22. Found: C, 72.21; H, 4.98.

2.2i *3-Phenyl-1-(4-methoxyphenyl)-3-phenylsulphanylpropan-1-one* ***1l***: Colourless crystals, IR (KBr) υ_{max} = 1670 (C=O), 1601, 1573, 1423, 1338, 1233, 1173, 1024, 984, 845 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.47–3.65 (m, 2H, -CH_2), 3.85 (s, 3H, -OCH_3), 4.95 (dd, 1H, J = 7.8 and 6.0 Hz, H-2), 6.89 (d, 2H, J = 8.7 Hz), 7.15–7.34 (m, 10H), 7.87 (d, 2H, J = 6.9 Hz); Anal. Calcd. for $C_{22}H_{20}ClO_2S$ (348.46): C, 75.83; H, 5.79. Found: C, 75.91; H, 5.84.

2.2j *3-(4-Methoxyphenyl)-1-(4-methoxyphenyl)-3-phenylsulphanylpropan-1-one* ***1m***: Colourless crystals, IR (KBr) υ_{max} = 1672 (C=O), 1607, 1515, 1256, 1179, 1030, 822, 733 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.44–3.62 (m, 2H, -CH_2), 3.75 (s, 3H, -OCH_3), 3.84 (s, 3H, -OCH_3), 4.94 (dd, 1H, J = 8.1 and 6.0 Hz, H-2), 6.77 (d, 2H, J = 8.7 Hz), 6.89 (d, 2H, J = 8.7 Hz), 7.18–7.35 (m, 7H), 7.85 (d, 2H, J = 8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): 44.4, 47.8, 55.2, 55.5, 113.7, 113.8, 127.3, 128.8, 128.9, 129.9, 130.4, 132.6, 133.3, 134.6, 158.7, 163.6, 195.6; TOF MS ES$^+$(M+Na)$^+$: Calcd. 401.1187. Found 401.1188; Anal. Calcd. for $C_{23}H_{22}O_3S$ (378.48): C, 72.99; H, 5.86. Found: C, 72.71; H, 5.74.

2.2k *3-(4-Chlorophenyl)-1-(4-methoxyphenyl)-3-phenylsulphanylpropan-1-one* ***1n***: Colourless crystals, IR (KBr) υ_{max} = 1603 (C=O), 1574, 1492, 1328, 1256, 1176, 1025, 982, 818 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.51–3.55 (m, 2H, -CH_2), 3.85 (s, 3H, -OCH_3), 4.90 (t, 1H, J = 7.0 Hz, H-2), 6.90 (d, 2H, J = 8.4 Hz), 7.18–7.31 (m, 9H), 7.86 (d, 2H, J = 7.8 Hz); Anal. Calcd. for $C_{22}H_{19}ClO_2S$ (382.90): C, 69.01; H, 5.00. Found: C, 69.22; H, 4.83.

2.2l *3-(4-Chlorophenyl)-1-phenyl-3-(4-methylphenylsulphanyl)propan-1-one* ***1o***: Colourless crystals, IR (KBr) υ_{max} = 1678 (C=O), 1492, 1325, 1226, 1093, 814 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.30 (s, 3H, -CH_3) 3.50–3.65 (m, 2H, -CH_2), 4.83 (t, 1H, J = 7.0 Hz, H-2), 7.04 (d, 2H, J = 7.8 Hz), 7.13–7.26 (m, 6H), 7.43 (t, 2H, J = 7.5 Hz.), 7.55 (br. t, 1H, J = 7.3 Hz), 7.87 (br. d, 2H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): 21.1, 44.5, 48.1, 128.1, 128.5, 128.7, 129.2, 129.8, 129.9, 132.9, 133.4, 133.7, 136.7, 138.1, 140.0, 196.8; Anal. Calcd. for $C_{22}H_{19}ClOS$ (366.08): C, 72.02; H, 5.22. Found: C, 72.25; H, 5.36.

2.2m *3-(4-Nitrophenyl)-1-(4-chlorophenyl)-3-(4-methylphenylsulphanyl)propan-1-one* ***1p***: Colourless crystals, IR (KBr) υ_{max} = 1686 (C=O), 1514, 1344, 1219, 985, 822 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.30 (s, 3H, -CH_3) 3.59–3.62 (m, 2H, -CH_2), 4.87 (t, 1H, J = 6.9 Hz, H-2), 7.05 (d, 2H, J = 7.8 Hz), 7.17 (d, 2H, J = 7.8 Hz), 7.26 (s, 1H), 7.42 (t, 3H, J = 7.5 Hz), 7.83 (d, 2H, J = 8.4 Hz), 8.09 (d, 2H, J = 8.4 Hz); Anal. Calcd. for $C_{22}H_{18}ClNO_3S$ (411.07): C, 64.15; H, 4.40. Found: C, 63.90; H, 4.31.

2.2n *3-Phenyl-1-(3-nitrophenyl)-3-phenylsulphanylpropan-1-one* ***1s***: Light yellow crystals, IR (KBr) υ_{max} = 1674 (C=O), 1536, 1349, 1236, 987 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.57–3.73 (m, 2H, -CH_2), 4.94 (t, 1H, J = 7.0 Hz, H-2), 7.21–7.39 (m, 10H), 7.64 (t, 1H, J = 8.0 Hz), 8.18 (dd, 1H, J = 7.8 and 0.9 Hz), 8.38 (dt, 1H, J = 8.1 and 0.9 Hz), 8.67 (s, 1H); Anal. Calcd. for $C_{21}H_{17}NO_3S$ (363.43): C, 69.40; H, 4.71; N, 3.85. Found: C, 69.24; H, 4.95; N, 4.02.

2.2o *(E)-1,5-diphenyl-3-(phenylthio)pent-4-en-1-one* ***7***: Colourless crystals, mp: 102–104°C. IR (KBr) υ_{max} = 1672 (C=O), 1607, 1515, 1256, 1179, 1030, 822, 733 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.40–3.43 (m, 2H, CH_2), 4.48 (m, 1H, >CH-S-), 6.16

Table 1. Optimization of reaction conditions for generation of chalcone (**6a**) by variation of MW power and irradiation time.

Entry	Power (W)	Time (min)	Yield[a] of 6 (%)	
			Anh. K_2CO_3	Amberlyst-15
1	180	10	nil	Nil
2	360	3	5	Trace
3	360	5	27	16
4	360	7	43	30
5	540	3	85	72
6	540	5	97	85
7	540	7	97	85
8	720	3	Reaction mixture charred	

[a]Isolated yield for this and all the subsequent tables

(dd, 1H, J = 15.7 and 8.0 Hz, H-4), 6.30 (d, 1H, J = 15.6 Hz, H-5), 7.19–7.33 (m, 8H, Ar-H), 7.44–7.60 (m, 5H, Ar-H), 7.92–7.94 (m, 2H, *ortho*-protons of -COPh) Anal. Calcd. for $C_{23}H_{20}OS$ (344.47): C, 80.19; H, 5.85; Found: C, 80.04; H, 6.02.

2.2p *Diastereomers of 1,3,8,10-tetraaryl-4,7-dithiadecan-1,10-dione* ***8***: Colourless crystals, melting range 118–126°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.40–2.50 (m, 4H, -S-CH_2-CH_2-S- of the major isomer), 2.60–2.68 (m, ~1.33H, -S-CH_2-CH_2-S- of the minor isomer), 3.45 (d, 4H, J = 6.9 Hz, –CO-C$\underline{H}_2$-CH< of the major isomer), 3.51 (d, ~1H, J = 6.9 Hz, –CO-C$\underline{H}_2$-CH< of the minor isomer), 4.46 (br. t, 2H, J = 6.9 Hz, –CO-C$\underline{H}_2$-CH< of the major isomer), 4.58 (br. t, ~0.5 H, J = 6.9 Hz, –CO-CH_2-C$\underline{H}$< of the minor isomer), 7.23–7.58 (m, ~12.5H, Ar-H of both the isomers), 7.86–7.89 (~5H, *ortho* protons of –COC_6H_5 of both the isomers).

3. Results and discussion

Our endeavour for synthesis of β-aryl-β-mercaptoketones (**1**) started with searching of a suitable condition for a three-component reaction. Thus, when an equimolar mixture of acetophenone (**3a**), benzaldehyde (**4a**) and thiophenol (**5a**) was subjected to microwave irradiation over neutral alumina supported potassium carbonate or amberlyst-15, instead of the desired compound **1a**, the chalcone **6a** was formed. The strong characteristic smell of thiophenol obtained by opening the microwave oven after operation clearly indicated that failure of the expected reaction was due to vaporization of thiophenol from the reaction mixture. We, therefore, chose the strategy of generating chalcones (**6**) first and then allowing them to react with thiols in the same pot under a milder condition. It may be mentioned here that microwave-assisted Michael reactions over anhydrous K_2CO_3 are known in literature.[37] The reaction condition for generation of chalcones (**6**) by microwave irradiation over neutral alumina supported anhydrous K_2CO_3[38,39] or amberlyst-15[40] was freshly optimized in the present study applying various microwave (MW) powers and irradiation times (table 1). Screening of different alkali metal carbonates and sulphonic acids for their catalytic activities was also done in this connection (tables 2 and 3). When MW irradiation was done over only neutral alumina, formation of only **6a** (yield 52%) was observed.

The results presented in table 1 clearly showed that irradiation at 540 W for 5 min was the optimum condition for the reaction. The choice of potassium carbonate

Table 2. Optimization of reaction conditions for generation of **1a** by use of different alkali metal carbonates[a].

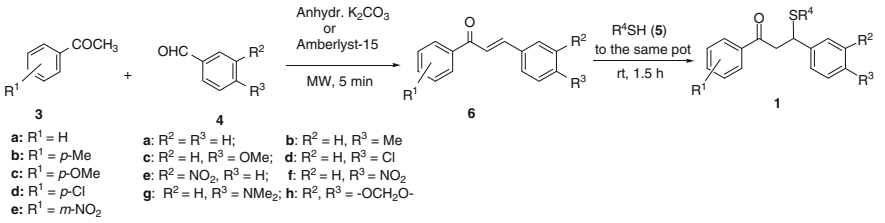
Entry	Metal carbonate	Yield (%)
1	Na_2CO_3	81
2	K_2CO_3	94
3	Cs_2CO_3	96

[a]Mol ratio of substrate to metal carbonate = 1:1 (yield optimized by use of K_2CO_3); amount of neutral alumina (solid support) = 4 g/mmol of substrate (yield optimized)

Table 3. Optimization of reaction conditions for generation of **1a** by use of different sulphonic acids[a].

Entry	Sulphonic acid	Yield (%)
1	Amberlyst-15	82
2	Camphor sulphonic acid	11
3	*p*-TsOH	52

[a]Amount of sulphonic acid = 80 mg/mmol of substrate (yield optimized by use of amberlyst-15); amount of neutral alumina (solid support) = 4 g/mmol of substrate (yield optimized)



Scheme 2. Strategy for two-step one-pot synthesis of *β*-aryl-*β*-mercaptoketones (**1**).

over other alkali metal carbonates or amberlyst-15 over other sulphonic acids was justified by the optimum yield and cost effectiveness (tables 2 and 3, respectively).

In the chosen strategy, a reaction mixture using **3a** and **4a** as starting materials (1:1 mol ratio) was allowed to cool to room temperature after microwave irradiation over anh. K_2CO_3 or amberlyst-15 and then thiophenol (**5a**) (1.3 mol ratio) was added to the same pot and allowed to stand for 1.5 h (scheme 2). TLC examination at that point indicated the formation of **1a** in high yield along with a trace amount of **6a**. From this mixture, pure **1a** could be obtained through rapid column chromatography.

This protocol was successfully employed for synthesis of 18 other *β*-aryl-*β*-mercaptoketones (**1b-s**) by using appropriate combinations of acetophenones (**3**), benzaldehydes (**4**) and thiols (**5**) and also for synthesis of **7** by use of acetophenone (**3a**) cinnamaldehyde and thiophenol (table 4). It is noteworthy that in

Table 4. Results of one-pot synthesis of *β*-aryl-*β*-mercaptoketones (**1**) and a related compound (**7**)[a].

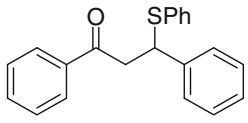
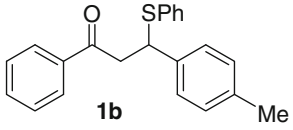
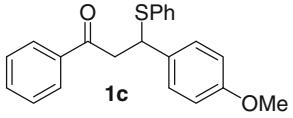
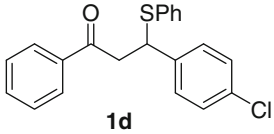
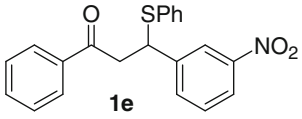
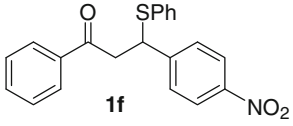
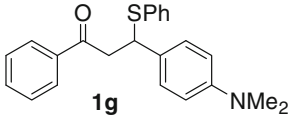
Entry	Product (**1**/**7**)	Yield (%)		Melting point (°C) [Lit.]
		Anhydr. K_2CO_3	Amberlyst-15	
1	 **1a**	94	82	94–96 [96–97][15]
2	 **1b**	94	84	72–74
3	 **1c**	90	79	84–86 [87–88][15]
4	 **1d**	95	84	74–76 [74–75][15]
5	 **1e**	94	83	108–110
6	 **1f**	92	80	100–102
7	 **1g**	84	72	152–154

Table 4. (continued)

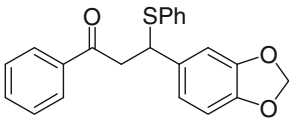
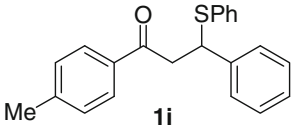
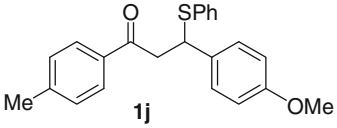
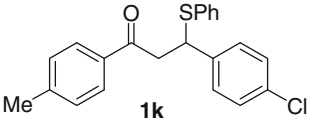
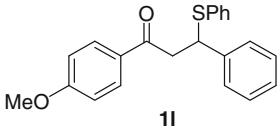
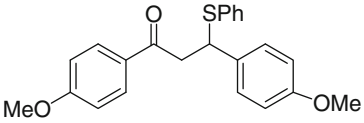
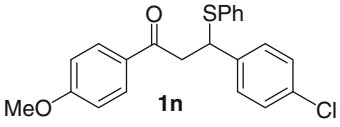
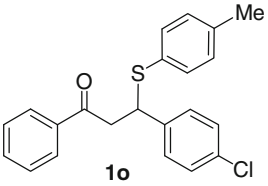
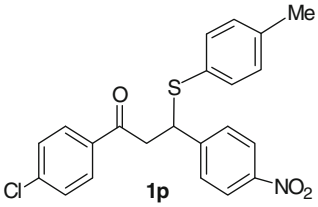
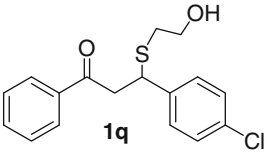
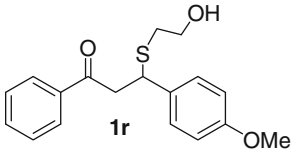
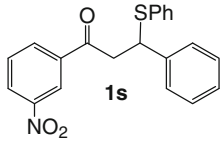
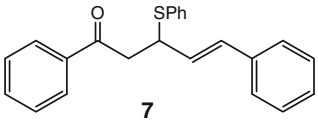
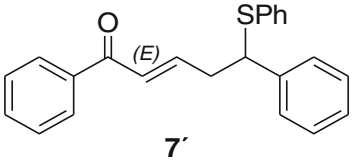
Entry	Product (**1**/**7**)	Yield (%)		Melting point (°C)
		Anhydr. K_2CO_3	Amberlyst-15	[Lit.]
8	 **1h**	87	79	66–68
9	 **1i**	93	80	60–62
10	 **1j**	88	78	112–114
11	 **1k**	94	81	90–92
12	 **1l**	91	80	118–120
13	 **1m**	89	78	110–112
14	 **1n**	90	79	96–98
15	 **1o**	83	72	118–120
16	 **1p**	85	73	126–128
17	 **1q**	88	75	60–62 [59–62][8]

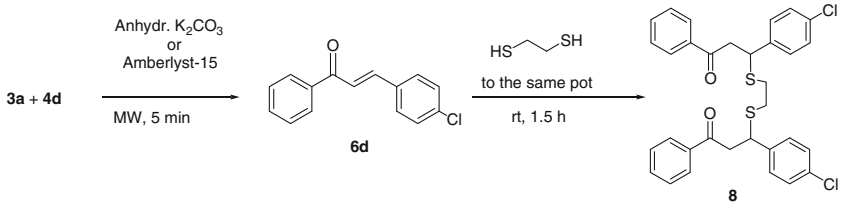
Table 4. (continued)

Entry	Product (**1**/**7**)	Yield (%)		Melting point (°C)
		Anhydr. K_2CO_3	Amberlyst-15	[Lit.]
18	 **1r**	82	73	70–72 [69–71][8]
19	 **1s**	69	55	106–108
20	 **7**	72	63	102–104

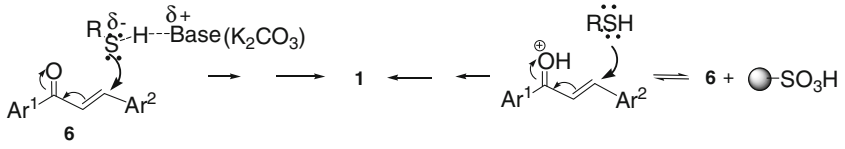
[a]The ^{1}H NMR spectral features of the product in this case (*vide* Experimental) led to the elimination of the alternative structure **7′**.



7′



Scheme 3. Synthesis of 1,3,8,10-tetraaryl-4,7-dithia-decan-1,10-dione (**8**).



Scheme 4. Plausible mechanism of formation of β-aryl-β-mercaptoketones (**1**).

the latter case, β-position of the intermediate *E*-cinnamylideneacetophenone is selectively attacked by thiophenol over δ-position.

The mentioned methodology was then extended to the combination of **3a**, **4d** and ethane-1,2-dithiol (mol ratio: 1:1:0.6), when a 1:4 (approx.) mixture of the diastereomers of **8** was obtained in 63% yield. However, attempted separation of these diastereomers by column chromatography over silica gel did not meet with success (scheme 3).

Regarding the mechanistic aspects of the thia-Michael addition, it may be pointed out that in the K_2CO_3-catalysed process, the thiols are activated, while in the amberlyst-15-catalysed process, the α,β-unsaturated ketones are activated to make the addition effective (scheme 4).

4. Conclusion

We have developed a very simple protocol for rapid, efficient and one-pot synthesis of β-aryl-β-mercaptoketones by use of tandem reactions on common inexpensive catalysts such as anhydrous K_2CO_3

and amberlyst-15. Such processes are a matter of current interest in the literature.[36]

Supplementary information

The electronic supplementary material contains ^{1}H NMR, ^{13}C NMR and mass spectra of a number of compounds of the series **1**, **7** and **8,** which can be seen in www.ias.ac.in/chemsci.

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Financial assistance from the University of Grants Commission (UGC)-Center of Advanced Studies and the Department of Science and Technology-Promotion of University Research and Scientific Excellence programmes, of the Department of Chemistry is gratefully acknowledged. The authors also acknowledge the DST-FIST programme to the Department of Chemistry, Jadavpur University for providing the NMR spectral data. CG and RM are thankful to UGC, New Delhi for their Research Fellowships.

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