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Research Article

Comparative Studies on Conventional and Ultrasound-Assisted Synthesis of Novel Homoallylic Alcohol Derivatives Linked to Sulfonyl Dibenzene Moiety in Aqueous Media

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Novel homoallylic alcohols incorporating sulfone moieties were synthesized by the treatment of different carbonyl compounds with allylic bromides in aqueous media *via* sonochemical Barbier-type reaction conditions. Sulfonation of α-bromoketones with sodium benzenesulfinate in presence of CuI/2,6-lutidine rapidly gave β-keto-sulfones in good yields. In general, ultrasound irradiation offered the advantages of high yields, short reaction times, and simplicity compared to the conventional methods. The structures of all the compounds were confirmed by analytical and spectral data.

1. Introduction

Ultrasonic assisted organic synthesis as a green synthetic approach is a powerful technique that is being used more and more to accelerate organic reactions [1–5]. A large number of organic reactions can be carried out in higher yields, shorter reaction times, or milder conditions under ultrasound irradiation. This can be considered as a processing aid in terms of energy conservation and waste minimization compared to conventional heating. Many metal-mediated organic reactions have been accelerated using ultrasound irradiation [6–10]. However, increased temperatures will also increase reaction rates. While making molecules with several sulfone moieties, we compared the effect of ultrasound to conventional heating for improved yields and reaction rates.

The aryl sulfone moiety has been found in numerous biologically interesting compounds. These compounds include antifungal, antibacterial, or antitumor agents [11, 12] and inhibitors for several enzymes such as cyclooxygenase-2 (COX-2) [13], HIV-1 reverse transcriptase [14, 15], integrin VLA-4 [16], and the ATPase [17]. New compounds incorporating aryl sulfone moieties are likely to display interesting biological activity.

Nucleophilic additions to carbonyl groups are one of the cornerstones of organic chemistry. Carbonyl allylation forms homoallylic alcohols which are versatile subunits that can easily be converted to a number of other useful functions [18, 19]. Synthetic protocols have been developed for allylation of carbonyl compounds in the Barbier reaction including the use of metals such as zinc [20], tin [21], samarium [22], gallium [23], and indium [24]. In particular, indium has been shown to be an effective metal in allylations [25–29]. In the past few decades, indium has become a popular metal due to the ability of organoindium intermediates to tolerate functionality and ambient conditions along with indium being nontoxic [3, 30–33]. In addition, indium-mediated allylation reactions in aqueous media often proceed smoothly at room temperature without any additive, while other metals usually require additives and anhydrous organic solvents [34–40].

α-Haloketones have been attracting increasing attention in view of their high reactivity as building blocks for the preparation of compounds of various classes due to their selective transformations with different reagents [41]. The sulfonation of α-haloketones involves the displacement reaction of halogens with sulfinic acid salts. The reaction proceeds thermally [42] or under phase-transfer catalysis conditions [43] but more conveniently directly from sodium sulfinate under microwave radiation [44]. As microwave technology was unavailable for us and we knew that CuI under basic conditions can catalyze C–N, C–O, C–S, and C–C bond formation reactions [45–47], we investigated the use of CuI/2,6-lutidine as a catalyst for the reaction of aromatic α-bromoketone with sodium benzenesulfinate.

Herein, we report the results of the allylation reactions of aldehyde and ketone derivatives containing a sulfone moiety by indium in aqueous media under ultrasound irradiation compared to conventional methods. We also report that CuI/2,6-lutidine catalyzes the sulfonation of α-bromoketone at room temperature in DMSO, but even better with sonication.

2. Experimental Section

The chemicals used in this work were obtained from Fluka and Merck and were used without purification. Indium powder was obtained from Sigma-Aldrich Company as 99.99% pure, but containing 1% Mg as anticaking agent. Melting points were determined on a Bibby Sterilin ltd electrothermal melting point apparatus and are uncorrected. Sonochemical reactions were carried out in a Branson B1510 DTH ultrasound cleaning bath (50 kHz, 245 W). The reactions were monitored by thin layer chromatography using Fluka GF254 silica gel plates with a fluorescent indicator; detection by means of UV light at 254 and 360 nm. The IR spectra were recorded on KBr disks on a Perkin Elmer 2000 FTIR spectrometer. The NMR spectra were recorded on a Varian Mercury VX-300 NMR spectrometer at 300.13 and 75.47 MHz. ^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated chloroform ($CDCl_3$) or dimethyl sulphoxide (DMSO-d6) using TMS as the internal standard. ^{13}C chemical shifts were related to that of the solvent. Mass spectra were recorded on ESI-MS Thermo LTQ Orbitrap XL, infusion 5 uL/min, resolution: 100 000 at m/z 400, ca. 10 scans/sample averaged. The aryl sulfones **1a,b** were prepared according to the literature [48].

2.1. Typical Procedure for Reactions

2.1.1. Conventional Reactions

General Procedure for Indium-Mediated Barbier-Type Reactions. The carbonyl compound (**1a,b** or **6a,b**) (1 mmol) and the corresponding bromide (3 mmol) in a mixture of THF and H_2O (3 + 1 mL) were treated with indium (2 mmol). The mixture was vigorously stirred at 50°C for approximately 12 h. The progress of the reaction was monitored by TLC. After completion of the reaction the resulting, mixture was filtered and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution and brine, dried over anhydrous magnesium sulfate, and further dried under reduced pressure. The residue afforded the corresponding homoallylic alcohols (**2a,b**; **3a,b**; **7a,b**; **8a,b**). The product was purified by column chromatography (SiO_2; ethyl acetate/petroleum ether, 1 : 4).

General Procedure for Synthesis of 1-Substituted 2-(Phenylsulfonyl)ethanones. A mixture of 2-bromo-1-substituted ethanone **5a–e** (1 mmol), sodium benzenesulfinate (1.5 mmol), CuI (0.2 mmol), 2,6-lutidine (2.0 mmol) in DMSO (10 mL) was vigorously stirred at 25–30°C for 8 h. After completion of the reaction, the resulting suspension was partitioned between ethyl acetate and water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate twice. The combined organic layers were washed with $NaHCO_3$ solution and brine, dried over $MgSO_4$, and concentrated in vacuo to give the crude *1-substituted 2-(phenylsulfonyl)ethanones* (**6a–e**), which were separated by column chromatography (SiO_2; ethyl acetate/petroleum ether, 1 : 3).

2.1.2. Sonicated Reactions

General Procedure for Synthesis of 2-Bromo-1-Substituted Ethanones. Bromine (1 mmol) was added dropwise to a solution of 1 mmol of the aryl methyl ketone derivatives (**1b,4**) in glacial acetic acid (10 mL) in a 50 mL Erlenmeyer flask. The mixture was subjected to ultrasonic irradiation at 25–30°C for the appropriate time until completion of the reaction (monitored by TLC), then poured over crushed ice. The solid product so-formed was filtered off, washed with water, dried, and recrystallized from ethanol to afford 2-bromo-1-substituted ethanones (**5a,b**).

General Procedure for Synthesis of 1-Substituted 2-(Phenylsulfonyl)ethanones. A mixture of 2-bromo-1-substituted ethanone **5a–e** (1.0 mmol), sodium benzenesulfinate (1.5 mmol), CuI (0.2 mmol), 2,6-lutidine (2.0 mmol), and DMSO (10 mL) was added to a 50 mL Erlenmeyer flask. The mixture was subjected to ultrasonic irradiation at 25–30°C for the appropriate time. After the completion of the reaction, the resulting suspension was filtered. The filtrate was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution and brine, dried over anhydrous magnesium sulfate, and filtered. The ethyl acetate was evaporated under reduced pressure to give the crude 1-substituted 2-(phenylsulfonyl)ethanones (**6a–e**), which were separated by column chromatography (SiO_2; ethyl acetate/petroleum ether, 1 : 3). The yields of the products are summarized in Table 2, and the spectral data are given in the following.

Following this procedure 2.0 mmol of other bases Et_3N, K_2CO_3, piperidine, and no base, were used in place of 2,6-lutidine to screen the conditions. The yields are summarized in Table 3. The sulfonation of **5a** to **6a** with 2,6-lutidine in absence of CuI by this procedure gave no reaction.

General Procedure for Indium-Mediated Barbier-Type Reactions. A 50 mL Erlenmeyer flask was charged with the desired

Table 1: Synthesis of homoallylic alcohols by allylation of **1a,b** with allylbromide (alcohols **2a,b**) and cinnamyl bromide (alcohols **3a,b**) as outlined in Scheme 1.

Compound	R	Ultrasonic irradiation		Conventional heating, 50°C	
		Time (h)	Yield (%)	Time (h)	Yield (%)
2a	H	3	92	12	75
2b	CH_3	3	90	12	70
3a	H	5	93	24	73
3b	CH_3	5	89	24	70

Table 2: Synthesis of 2-bromo-1-substituted ethanones **5a,b** by bromination, and 1-substituted 2-(phenylsulfonyl) ethanones **6a–e** by CuI catalyzed sulfonation as outlined in Scheme 3.

Compound	R	Ultrasonic irradiation		Stirred at room temperature	
		Time (min)	Yield (%)	Time (h)	Yield (%)
5a	Ph SO_2	60	92	4	80
5b	F	30	95	3	82
6a	$PhSO_2$	60	93	8	79
6b	F	60	94	8	83
6c	Br	60	95	8	86
6d	CH_3	90	90	8	75
6e	H	60	92	8	78
6a[a]	$PhSO_2$	12 h	0[a]	24	0[a]

[a]Reaction in the absence of CuI and 2,6-lutidine.

Table 3: Sulfonation of **5a** to **6a** (second reaction in Scheme 3) with CuI, but screened for different bases under ultrasound irradiation.

Base	Time (h)	Yield (%)
None	6	11
Et_3N	6	25
K_2CO_3	6	50
Piperidine	6	39
2,6-lutidine	1	93

aldehyde or ketone **1a**,**b**–**6a**,**b** (1 mmol), corresponding bromide (3 mmol), indium (2 mmol), and THF: H_2O (3 + 1 mL). The mixture was irradiated in the water bath of an ultrasonic cleaner at 25–30°C for a period specified in Table 1 (monitored by TLC). After the completion of the reaction, the resulting suspension was filtered. The filtrate was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution and brine, dried over anhydrous magnesium sulfate, and completed under reduced pressure to give the crude homoallylic alcohols (**2a**,**b**; **3a**,**b**; **7a**,**b**; **8a**,**b**), which were separated by column chromatography (SiO_2; ethyl acetate/petroleum ether, 1 : 4). The yields of the products are summarized in Tables 1 and 2, and the spectral data are given below.

2.2. Physical and Spectral Data

1-(4-(Phenylsulfonyl)phenyl)but-3-en-1-ol (2a). mp. = 62–64°C; IR (KBr): 3494 (OH), 1304, 1152 (SO_2) cm^{-1}; ^1H NMR (300 MHz, CDCl3) δ: 2.35 (*s*, O**H**, D_2O-exchangeable), 2.38–2.45 (*m*, C**HH**–COH–), 4.78 (*t*, *J* = 6.0, C**H**OH), 5.12–5.18 (*m*, C**HH**=CH–), 5.69–5.82 (*m*, $-CH_2C\mathbf{H}=CH_2$) 7.48–7.94 (*m*, Ar**H**'s); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ: 43.8, 72.2, 119.3, 126.6, 127.5, 127.7, 129.2, 133.1, 133.4, 140.3, 141.5, 149.6; MS (ESI) *m*/*z* (rel.int.): 311.08 $[M + Na]^+$ (100); HRMS (ESI) Calc. for $C_{16}H_{16}O_3S$ + Na: 311.0712, Found 311.0713.

2-(4-(Phenylsulfonyl)phenyl)pent-4-en-2-ol (2b). mp. = 71–72°C; IR (KBr): 3501 (OH), 1308, 1156 (SO_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 1.59 (*s*, C**H**$_3$), 2.19 (*s*, O**H**, D_2O-exchangeable), 2.47 (*dd*, *J* = 8.4, 8.4, C**H**H–COH–), 2.63 (*dd*, *J* = 6.3, 6.3, CH**H**–COH–), 5.10–5.15 (*m*, C**HH**=CH–), 5.48–5.61 (*m*, $-CH_2C\mathbf{H}=CH_2$), 7.48–7.96 (*m*, Ar**H**'s); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ: 29.7, 48.2, 73.5, 120.4, 125.9, 127.6, 127.6, 129.2, 132.6, 133.1, 139.7, 141.6, 153.4; MS (ESI) *m*/*z* (rel.int.): 325.1 $[M + Na]^+$ (100); HRMS (ESI) Calc. for $C_{17}H_{18}O_3S$ + Na: 325.0869, Found 325.0868.

2-Phenyl-1-(4-(phenylsulfonyl)phenyl)but-3-en-1-ol (3a). mp. = 134–136°C; IR (KBr): 3543 (OH), 1298, 1155 (SO_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 2.51 (*s*, O**H**, D_2O-exchangeable), 3.43 (*t*, *J* = 9.0, –C**H**Ph), 4.83 (*d*, *J* = 7.2, C**H**–COH–), 5.19–5.29 (*m*, C**HH**=CH–), 6.13–6.25 (*m*, $-C\mathbf{H}=CH_2$), 6.96–7.87 (*m*, Ar**H**'s); ^{13}C NMR (75.46 MHz,

$CDCl_3$) δ: 59.3, 76.5, 119.3, 127.0, 127.3, 127.5, 128.1, 128.5, 128.8, 129.1, 133.0, 136.8, 139.5, 140.1, 141.6, 147.6; MS (ESI) *m*/*z* (rel.int.): 387.1 $[M + Na]^+$ (100); HRMS (ESI) Calc. for $C_{22}H_{20}O_3S$ + Na: 387.1025, Found 387.1022.

3-Phenyl-2-(4-(phenylsulfonyl)phenyl)pent-4-en-2-ol (3b). mp. = 80–82°C; IR (KBr): 3503 (OH), 1306, 1155 (SO_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 1.41 (*s*, CH_3), 2.14 (*s*, O**H**, D_2O-exchangeable), 3.55 (*d*, *J* = 9.0, –C**H**Ph), 4.91 (*d*, *J* = 16.5, C**HH**=CH–), 5.03 (*d*, *J* = 16.5, C**HH**=CH–), 6.00–6.12 (*m*, –C**H**=CH2), 7.07–7.94 (*m*, ArH's); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ: 28.1, 61.7, 76.2, 118.7, 126.6, 127.0, 127.1, 127.5, 128.3, 129.2, 129.4, 133.0, 136.4, 139.3, 139.5, 141.7, 152.3; MS (ESI) *m*/*z* (rel.int.): 401.1 $[M + Na]^+$ (100); HRMS (ESI) Calc. for $C_{23}H_{22}O_3S$ + Na: 401.1182, Found 401.1179.

2-Bromo-1-(4-(phenylsulfonyl)phenyl)ethanone (5a). mp. = 127–128°C; IR (KBr): 1705 (CO), 1318, 1156 (SO_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 4.42 (*s*, C**H**$_2$), 6.54–8.086 (*m*, Ar**H**'s); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ: 30.2, 127.9, 128.0, 129.5, 129.7, 133.7, 137.2, 140.4, 146.1, 190.1; MS (ESI) *m*/*z* (rel.int.): 362.2 $[M + Na]^+$ (100); HRMS (ESI) Calc. for $C_{14}H_{11}BrO_3S$ + Na: 362.0421, Found 362.0419.

2-Bromo-1-(4-fluorophenyl)ethanone (5b). mp. = 85–87°C; IR (KBr): 1675 (CO) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 4.41 (*s*, C**H**$_2$), 7.14–8.05 (*m*, Ar**H**'s); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ: 30.4, 115.9, 131.8, 160.1, 163.1, 185.1; MS (ESI) *m*/*z* (rel.int.): 240.1 $[M + Na]^+$ (100); HRMS (ESI) Calc. for C_8H_6BrFO + Na: 240.0303, Found 240.0312.

2-(Phenylsulfonyl)-1-(4-(phenylsulfonyl)phenyl)ethanone (6a). mp. = 193–195°C; IR (KBr): 1700 (CO), 1312, 1152 (SO_2) cm^{-1}; ^1H NMR (300 MHz, DMSO) δ: 4.52 (*s*, CH_2), 6.67–7.22 (*m*, Ar**H**'s); ^{13}C NMR (75.46 MHz, DMSO) δ: 62.5, 127.7, 128.0, 129.1, 129.2, 129.9, 130.2, 134.1, 134.2, 139.1, 139.2, 140.1, 145.2, 188.6; MS (ESI) *m*/*z* (rel.int.): 423.1 $[M + Na]^+$ (100); HRMS (ESI) Calc. for $C_{20}H_{16}O_5S_2$ + Na: 423.0331, Found 423.0329.

1-(4-Fluorophenyl)-2-(phenylsulfonyl)ethanone (6b). mp. = 123–124°C; IR (KBr): 1674 (CO), 1310, 1156 (SO_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 4.71 (*s*, C**H**$_2$), 7.15–8.00 (*m*, Ar**H**'s); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ: 63.5, 116.0, 116.3, 128.5, 129.2, 132.1, 132.31, 134.3, 138.5, 186.4; MS (ESI) *m*/*z* (rel.int.): 301.3 $[M + Na]^+$ (100); HRMS (ESI) Calc. for $C_{14}H_{11}FO_3S$ + Na: 301.0305, Found 301.0306.

1-(4-Bromophenyl)-2-(phenylsulfonyl)ethanone (6c). mp. = 130–132°C; IR (KBr): 1690 (CO), 1299, 1140 (SO_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 4.70 (*s*, C**H**$_2$), 7.27–7.90 (*m*, Ar**H**'s); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ: 63.3, 116.2, 116.4, 128.3, 129.1, 132.0, 132.4, 134.3, 138.7, 187.2; MS (ESI) *m*/*z* (rel.int.): 362.2 $[M + Na]^+$ (100); HRMS (ESI) Calc. for $C_{14}H_{11}BrO_3S$ + Na: 362.0502, Found 362.0503.

2-(Phenylsulfonyl)-1-P-tolylethanone (6d). mp. = 138–140°C; IR (KBr): 1667 (CO), 1306, 1159 (SO_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 2.40 (*s*, C**H**$_3$), 4.76 (*s*, C**H**$_2$), 7.27–7.90 (*m*, Ar**H**'s); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ: 21.6, 63.3, 128.4, 129.0, 129.3, 129.4, 133.2, 134.0, 138.8, 145.4, 187.4; MS (ESI) *m*/*z* (rel.int.): 297.3 $[M + Na]^+$ (100); HRMS (ESI) Calc. for $C_{15}H_{14}O_3S$ + Na: 297.0302, Found 297.0301.

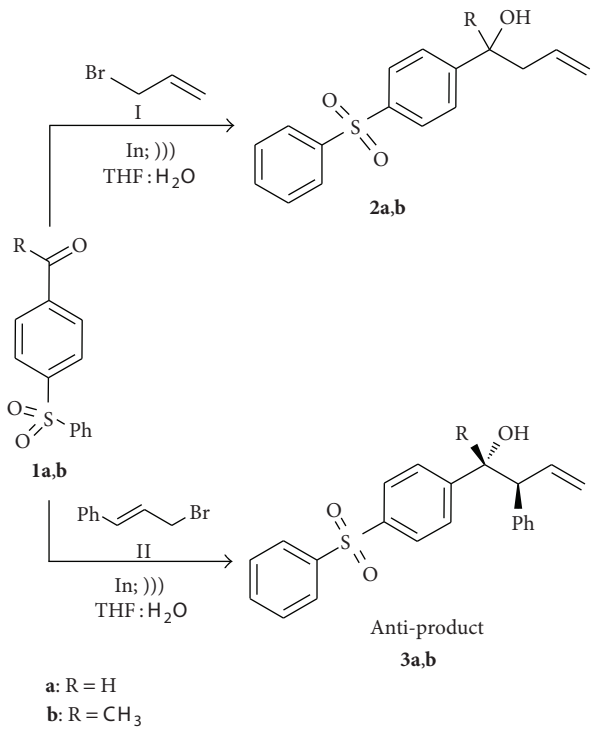
1-Phenyl-2-(phenylsulfonyl)ethanone (6e). mp. = 115–116°C; IR (KBr): 1673 (CO), 1311, 1157 (SO_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 4.74 (*s*, C**H**$_2$), 7.46–7.96 (*m*, Ar**H**'s); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ: 63.7, 128.1, 129.2, 129.5, 129.7, 133.1, 134.4, 138.5, 145.3, 186.4; MS (ESI) *m*/*z* (rel.int.): 283.1 $[M + Na]^+$ (100); HRMS (ESI) Calc. for $C_{14}H_{12}O_3S$ + Na: 283.0403, Found 283.0401.

1-(Phenylsulfonyl)-2-(4-(phenylsulfonyl)phenyl)pent-4-en-2-ol (7a). mp. = 163-164°C; IR (KBr): 3438 (OH), 1307, 1156 (SO_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 2.51 (*d*, *J* = 6.3, –CHC**H**$_2$COH–), 3.70 (*d*, *J* = 15.0, C**HH**SO_2Ph–), 3.80 (*d*, *J* = 15.0, CH**H**SO_2Ph–), 4.78 (*s*, O**H**, D_2O-exchangeable), 4.98–5.10 (*m*, CHH=CH–), 5.57–5.67 (*m*, –CH_2C**H**=CH_2), 7.07–7.97 (*m*, Ar**H**'s); ^{13}C NMR (75.46 MHz, DMSO) δ: 47.1, 64.8, 73.9, 119.0, 126.5, 127.1, 127.5, 127.9, 128.6, 129.8, 132.5, 133.1, 133.8, 139.0, 140.6, 141.2, 149.6; MS (ESI) *m*/*z* (rel.int.): 465.1 $[M + Na]^+$ (100); HRMS (ESI) Calc. for $C_{23}H_{22}O_5S_2$ + Na: 465.0801, Found 465.0805.

2-(4-Fluorophenyl)-1-(phenylsulfonyl)pent-4-en-2-ol (7b). mp. = 198–200°C; IR (KBr): 3467 (OH), 1299, 1154 (SO_2) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 2.58 (*d*, *J* = 7.2, –CHCH_2COH–), 3.67 (*d*, *J* = 14.7, CHHSO_2Ph–), 3.76 (*d*, *J* = 14.7, CHHSO_2Ph–), 4.66 (*s*, OH, D_2O-exchangeable), 5.01–5.10 (*m*, CHH=CH–), 5.59–5.73 (*m*, –CH_2CH=CH_2), 6.76–7.53 (*m*, ArH's); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ: 48.3, 64.8, 74.4, 114.7, 114.7, 115.0, 119.6, 126.9, 127.1, 129.0, 131.8, 133.4, 138.0, 138.1, 140.0, 160.2, 163.4; MS (ESI) *m*/*z* (rel.int.): 343.1 $[M + Na]^+$ (100); HRMS (ESI) Calc. for $C_{17}H_{17}FO_3S$ + Na: 343.0775, Found 343.0775.

3-Phenyl-1-(phenylsulfonyl)-2-(4-(phenylsulfonyl)phenyl)pent-4-en-2-ol (8a). mp. = 170–172°C; IR (KBr): 3468 (OH), 1304, 1148 (SO_2) cm^{-1}; ^1H NMR (300 MHz, DMSO) δ: 3.11 (*d*, *J* = 15.0, –CHHSO_2Ph), 3.66 (*d*, *J* = 9.2, –CHPh), 4.45 (*d*, *J* = 15.0, CHHSO_2Ph–), 4.50 (*d*, *J* = 10.2, CHH=CH–), 4.70 (*d*, *J* = 10.2, CHH=CH–), 5.52 (*s*, OH, D_2O-exchangeable), 5.81–5.93 (*m*, –CH_2CH–CHPh), 6.88–8.01 (*m*, ArH's); ^{13}C NMR (75.46 MHz, DMSO) δ: 60.5, 63.7, 76.1, 117.5, 126.0, 126.7, 127.0, 127.4, 127.8, 128.2, 128.5, 129.6, 129.8, 132.8, 133.6, 136.0, 138.9, 139.1, 139.6, 147.7; MS (ESI) *m*/*z* (rel.int.): 541.1 $[M + Na]^+$ (100); HRMS (ESI) Calc. for $C_{29}H_{26}O_5S_2$ + Na: 541.1114, Found 541.1118.

2-(4-Fluorophenyl)-3-phenyl-1-(phenylsulfonyl)pent-4-en-2-ol (8b). mp. = 108–110°C; IR (KBr): 3470 (OH), 1308, 1150 (SO_2) cm^{-1}; ^1H NMR (300 MHz, DMSO) δ: 3.11 (*d*, *J* = 15.0, –CHHSO_2Ph), 3.69 (*d*, *J* = 9.30, –CHPh), 4.38 (*d*, *J* = 15.0, CHHSO_2Ph–), 4.56 (*d*, *J* = 9.9, CHH=CH–), 4.76 (*d*, *J* = 9.9, CHH=CH–), 5.29 (*s*, OH, D_2O-exchangeable), 5.86–5.98 (*m*, –CH_2CH–CHPh), 6.80–7.56 (*m*, ArH's); ^{13}C NMR (75.46 MHz, DMSO) δ: 60.5, 64.2, 75.9, 113.4, 113.7, 117.2, 126.6, 127.1, 127.7, 128.2, 128.3, 128.5, 129.8, 132.8, 136.6, 137.5, 139.6, 140.2, 159.2, 161.2; MS (ESI) *m*/*z* (rel.int.):



Scheme 1: Synthesis of homoallylic alcohols **2a,b**-**3a,b** under ultrasonic irradiation or conventional conditions.

419.1 $[M + Na]^+$ (100); HRMS (ESI) Calc. for $C_{23}H_{21}FO_3S$ + Na: 419.1088, Found 419.1091.

3. Results and Discussion

We first investigated the indium-mediated Barbier procedure for the allylation of the arylsulfonated 4-(phenylsulfonyl)benzaldehyde (**1a**) and 1-(4-(phenylsulfonyl)phenyl)ethanone (**1b**). A 50 mL Erlenmeyer flask was charged with the desired aldehyde **1a** or ketone **1b** (1 mmol), allylbromide (3 mmol), and indium (2 mmol) in a mixture of THF and H_2O (3 + 1 mL). The mixture was irradiated in the water bath of an ultrasonic cleaner at 25–30°C (Scheme 1). The bath had two obvious irradiation hotspots, and the flask was placed in the center of one of them.

The homoallylic alcohols **2a**,**b**-**3a**,**b** were formed in excellent yields using shorter reaction times compared to conventional heating conditions. The results are summarized in Table 1. The conversion rate of carbonyl allylation was notably affected by the temperature, under conventional conditions. At room temperature the reaction gave poor conversion even after days of reaction (40% yield of **2a**). At 35°C, the reaction improved. When the temperature was increased to 50°C, we got full conversion within reasonable time, but the yield was limited by some degradation. As THF has a boiling point of 65°C, further increase in temperature would demand a reflux setup. But the solvent composition would then change in the reaction on our scale. Thus, further increase in temperature was refrained.

In order to investigate the regio- and diastereoselectivities of the allylation reaction, cinnamyl bromide was used as an allylation reagent. Allylation reactions involving cinnamyl bromide can provide both an α-adduct and a γ-adduct, and the γ-adduct can be either a anti- or syn-product. Usually only the γ-adduct is formed, with a predominant antiselectivity [44–52]. This can be explained mechanistically by a Felkin-Anh transition state [53], but here it may be more appropriate to refer to the 6-ring chair-like conformation with the large groups in equatorial positions suggested in the transition state (Scheme 2) as a Zimmerman-Traxler transition state [54]. We also found that the indium-mediated allylation reaction always produced the γ-adduct with anti-selectivity. There were no traces of any syn-products under neither reaction conditions.

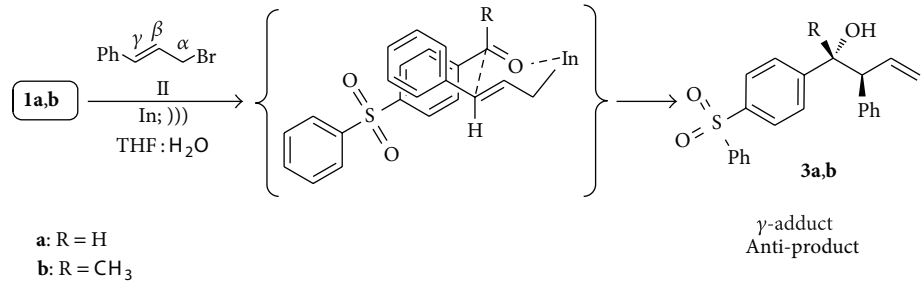
As shown in Scheme 1 and Table 1, the allylation carried out under ultrasonic irradiation gave excellent yields and shorter reaction times compared with the conventional heated reaction. For example, the product **2a** took about 12 h for completion under conventional conditions and the yield of the product was 75%. In comparison, under ultrasonic irradiation, the reaction time was 3 h and the yield 92%.

The facile reaction of the aromatic ketone **1b** was promising, so we wanted to introduce substituents to the ketone to challenge the selectivity of the allylation reaction and introduce another sulfone group. The synthesis is outlined in Scheme 3. Earlier experience with the power of ultrasound as a green chemistry technology for mediating organic synthesis [55] prompted us to explore the usefulness of ultrasound here as well. The bromination of acetyl derivatives **1b** and **4** to afford the 2-bromo-1-substituted ethanones **5a**,**b** were improved under ultrasound conditions compared to conventional stirring at 25–30°C, and gave high yields (Table 2). Most of the 2-bromo-1-arylethanone derivatives **5** were synthesized without sonication by the reaction of ketones with bromine in acetic acid with yields of 60–85% [56]. Synthesis of **5a,b** without sonication was previously also described by Cavelli et al. [49].

Carbonyl compounds **6a**–**e** incorporating another sulfone group was prepared *via* the reaction of α-haloketones with sodium benzeneulfinate under sonication (Scheme 3). The immediate success in converting **5a** to **6a** (Table 2) was followed by a screening of different bases for the reaction. Copper(I) and copper(II) catalysts has been used with a range of different bases for different bond formations including C–S bonds before [57]. But as shown in Table 3; 2,6-lutidine is the superior base together with CuI in this reaction. 2,6-lutidine as a weak and sterically hindered base has also been the superior base in reactions with sulfonyl azides [58, 59], so it may have something to do with the sulfone group. On the other hand 2,6-lutidine also improved the CuBr-catalyzed cross-coupling of arylboronic acids to alkynes [60]. That CuI is necessary as a catalyst was demonstrated by the last entry in Table 2, where the reaction was attempted in the absence of CuI. No reaction was observed even after 12 h of sonication, whereas the reaction with CuI/2,6-lutidine were completed to 93% yield in 1 h. Thus, treatment of the

Table 4: Synthesis of homoallylic alcohols by allylation of **6a,b** with allylbromide (alcohols **7a,b**) and cinnamyl bromide (alcohols **8a,b**) as outlined in Scheme 4.

Compound	R	Ultrasonic irradiation		Conventional heating, 50°C	
		Time (h)	Yield (%)	Time (h)	Yield (%)
7a	$PhSO_2$	1.5	95	12	83
7b	F	1.5	96	12	85
8a	$PhSO_2$	3	91	12	80
8b	F	3	89	12	75



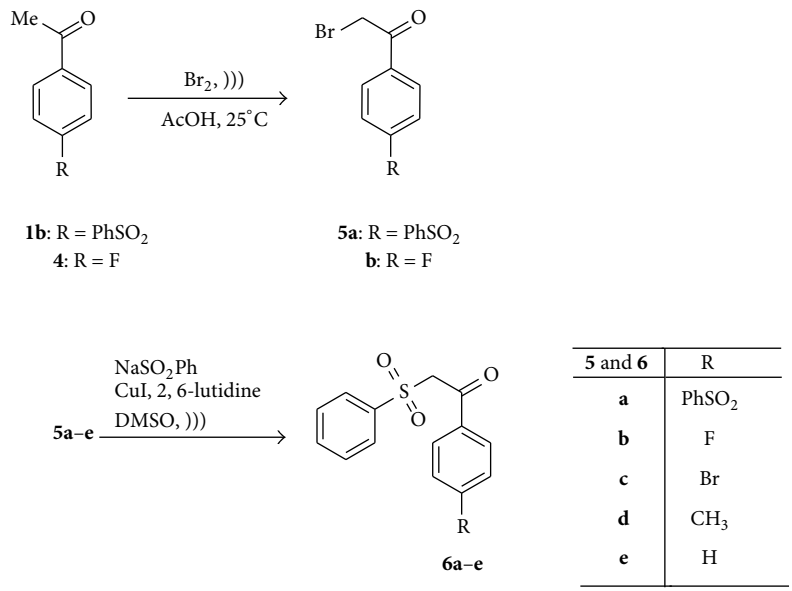
Scheme 2: The strong anti-selectivity obtained in the transformation of **1a,b** to **3a,b** may be explained by a Zimmerman-Traxler transition state.

products **5a–e** with sodium benzenesulfinate in the presence of CuI and 2,6-lutidine at room temperature in DMSO under ultrasound irradiation efficiently afforded the corresponding 6a-e (Scheme 3). In order to demonstrate the positive effect of ultrasound irradiation on the reaction, the same reactions in entries **5a**,**b**-**6a–e** in Table 2 were also investigated under conventional conditions. All reactions carried out without sonication took longer time and gave lower yields than those submitted to ultrasound irradiation. Improvement of chemical reactions by ultrasound is often ascribed to the high temperature formed when cavitations formed by the ultrasound collapses, sometimes leading to different products than those obtained without sonication. Although the energy delivered through the cleansing bath is not that high, there is still acoustic cavitation in the reaction flask. In heterogeneous systems the acoustic cavitation is known to vastly improve diffusion rates and accelerate the reactions through microjets formed from asymmetrical collapses of the bubbles, and similar effects can be achieved with high speed mechanical stirring [61]. But there are also several examples where ionic reactions are accelerated by physical effects (better mass transport) in homogenous reactions- often called "false sonochemistry" [62]. As we observed no real change of product, the improved reactivity from sonication is probably due to mechanical effects also in our homogenous reactions.

The structure of 2-(phenylsulfonyl)-1-(4-(phenylsulfonyl)phenyl)ethanone **6a** was confirmed on the basis of its spectral data and high resolution mass analysis. The ^{1}H NMR spectrum of **6a** revealed a singlet signal at δ 4.52 (CH_2) in addition to aromatic protons as a multiplet at δ 6.67–7.22. Its ^{13}C NMR spectrum revealed a signal at δ 62.6 due to CH_2 and a signal at δ 188.7 due to C=O. The IR spectrum revealed the appearance of a carbonyl absorption band at 1700 cm^{-1} and sulfone absorption bands at 1152 and 1312 cm^{-1}. In addition, its high resolution mass spectrum revealed a peak consistent with the formula $C_{20}H_{16}O_5S_2$.

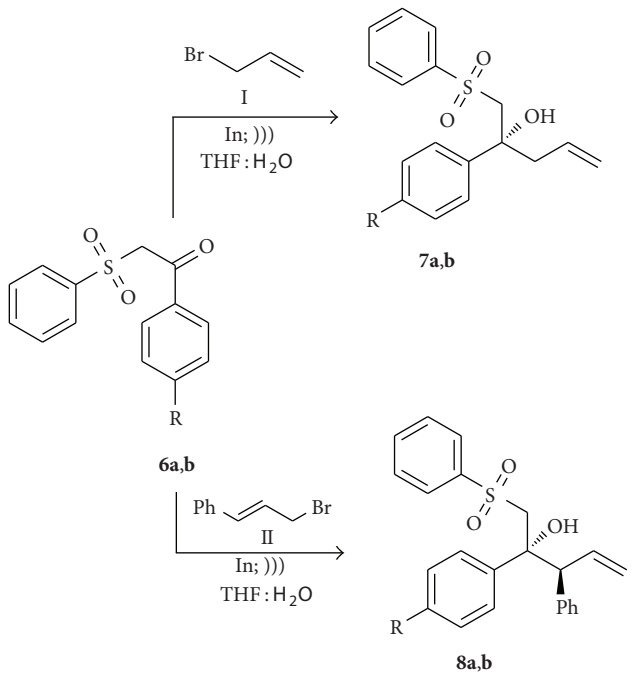
In the same manner as carried out for **1a**,**b**, the reaction of **6a**,**b** with allyl and cinnamyl bromides resulted in the corresponding homoallylic alcohols (Scheme 4) with good to excellent yields and high steroselectivity as shown as in Table 4. Again, the reactions were greatly enhanced using ultrasound irradiation compared to classical conditions with heating.

Allylation of the brominated derivatives **5a**,**b** were impractical. The conversion rate of the starting materials was poor and both allylation of the carbonyl group and substitution on the bromine occurred in different ratios forming a complex mixture of products. On the other hand, allylation of 1-substituted 2-(phenylsulfonyl)ethanone derivatives **6a**,**b** was excellent with complete conversion and great selectivity. The structures of the latter homoallylic alcohols were established on the basis of their spectral data and high resolution mass analysis. In addition, the structure of these compounds was further confirmed by 2D NMR (COSY, HETCOR and DEPT). In-depth 1D and 2D NMR spectroscopy analysis of **8b** confirmedthe ^{1}H NMR assignment: a doublet at δ 3.11 (J = 15.0 Hz) due to one proton of C**H**HSO_2Ph, δ 3.69 (J= 9.3 Hz) due to C**H**Ph, δ 4.38 (J = 15.0 Hz) due to the other proton of CH**H**SO_2Ph, δ 4.56 (J = 9.9 Hz) due to one proton of C**H**H=CH and δ 4.76 (J = 9.9 Hz) due to other proton of CH**H**=CH. The signal at δ 5.29 ppm due to O**H** was D_2O-exchangeable. Finally, there were multiplet signals



5 and 6	R
a	$PhSO_2$
b	F
c	Br
d	CH_3
e	H

Scheme 3: Synthesis of 2-bromo-1-substituted ethanones **5a,b** and 1-substituted 2-(phenylsulfonyl)ethanones **6a–e** under ultrasonic irradiation or conventional conditions.



Scheme 4: Synthesis of homoallylic alcohols **7a,b**-**8a,b** under ultrasonic irradiation or conventional conditions.

at δ 5.86–8.98 due to one proton of $-CH_2C\mathbf{H}-CHPh$ and aromatic multiplets at δ 6.80–7.56. Its high resolution mass analysis was consistent with the formula $C_{23}H_{21}FO_3S$. The IR spectrum of compound **8b** shows one band at 3470 cm^{-1} due to an OH group.

4. Conclusion

In summary, we have demonstrated that ultrasound irradiation can markedly speed up the allylation of carbonyl compounds containing sulfone moieties *via* a Barbier-type reaction. Compared to classical stirring methods even at elevated temperatures, ultrasonic irradiation is more efficient. The reaction gave products with excellent regioselectivity, favoring the γ-adduct with *anti*-selectivity when cinnamyl halides were employed as the allylation reagents. Although the indium mediated allylation were unable to differentiate between the ketone and the α-bromo group, an α-sulphone group gave no problems. Sonication also improved the reactivity in the new CuI-catalyzed sulfonation reaction to form α-phenylsulfoneketones from sulfinic acid salts and α-bromoketones.

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