A Novel Route for the Synthesis of Unsaturated Oxo Sulfones and Bissulfones

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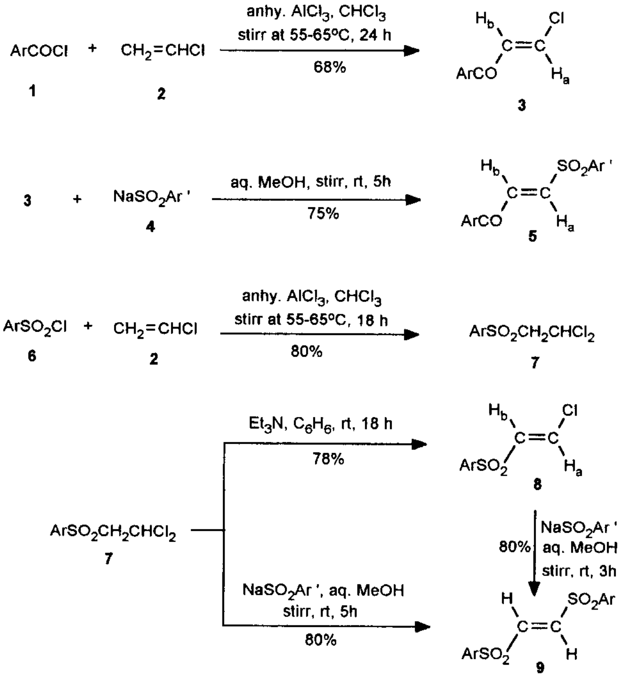
Abstract: The reaction between vinyl chloride and aroyl/arylsulfonyl chloride under Friedel–Craft's reaction conditions was the basis for the synthesis of unsaturated oxo sulfones and bissulfones.

Key words: oxo sulfones, bissulfones, Friedel–Crafts reaction, aroylsulfonyl chlorides

The development of efficient and expedient methodologies for the synthesis of activated alkenes remains a worthwhile task. Improvement and design of a new reaction system is a fundamental approach for any synthetic organic chemist. Over the years our research group has been actively involved in this area. In fact, we reported an unusually simple approach for the synthesis of *E,Z*-bis(styryl)sulfones in one of our communications.[1] In continuation of our interest in the activated alkenes,[2] the reaction of vinyl chloride with acyl, aroyl and arylsulfonyl chlorides under Friedel–Craft's conditions has been attempted and this provides an alternative to the previously mentioned method.

Indeed, different routes are available for the synthesis of unsaturated oxo sulfones and bissulfones. Unsaturated oxo sulfones result from heating an alcoholic solution of β,β-dibromopropiophenone with sodium benzenesulfinate in the presence of potassium acetate or by the dehydrohalogenation of the dibromo derivative of saturated oxo sulfone.[3] On the other hand, the unsaturated bissulfones have been reported by the reaction of thiophenol with 1,2-dichloroethene[4] or 2-chloro-1-thiophenylethene[5] followed by oxidation with 30% hydrogen peroxide in acetic acid or by the reaction of 2-chloro-1-phenylsulfonylethene with phenylsulfonic acid[6] or by the dimerization of phenylsulfonyldiazomethane[7] or by the rearrangement of 1,1-bisphenylsulfonylethene.[8]

In our present approach, the synthesis of unsaturated oxo sulfones and bissulfones was envisaged by a common route which is new, novel and simple. When vinyl chloride gas was passed into the solution of acetyl chloride in chloroform in the presence of anhydrous aluminium chloride, instead of 1-acetyl-2-chloroethene, a trimerized product, 1,3,5-triacetylbenzene was obtained.[9] But under similar conditions, when vinyl chloride gas (**2**) was passed into the solution of aroyl chloride **1**, the expected 1-aroyl-2-chloroethene **3**[10] was formed. The latter, on condensation with arylsodium sulfinates **4** in aqueous alcohol, resulted in 1-aroyl-2-arylsulfonylethenes **5**. On the other hand, when **2** was passed into a solution of arylsulfonyl chloride **6** addition products, 1-arylsulfonyl-2,2-dichloroethanes **7** were obtained.[11] However, when the latter were treated with triethylamine in benzene at room temperature, dehydrohalogenation took place with the formation of 1-arylsulfonyl-2-chloroethenes **8**. Compounds **8**, on condensation with **4** in aqueous alcohol, furnished 1,2-diarylsulfonylethenes **9**. As well as this, the latter were also obtained in a one-pot reaction by the condensation of **7** with two equivalents of **4** in aqueous alcohol (see Scheme and Tables 1 and 2).



Scheme

In summary, we have developed an effective and simple route for the synthesis of ethylenic oxo sulfones and bissulfones.

Melting points were determined on a Mel-Temp apparatus and are uncorrected. IR spectra (KBr disc) were recorded on a Beckmann IR-18 spectrophotometer. NMR spectra were recorded in CDCl$_3$/DMSO-d_6 using 120 MHz on a varian EM-360 spectrophotometer, all chemical shifts are reported in ppm from TMS as an internal standard. The mass spectra were recorded on Jeol JMS-D 300 instrument at 70 eV. Elemental analyses were obtained from the University of Poona, Pune, India.

Table 1 Selected Physical and Spectroscopic Data of **3, 7** and **8**

Product[a]	Ar	Yield (%)	mp or bp (°C) (°C/mm)	IR ν (cm^{-1})	^{1}H NMR ($CDCl_3$) δ, J (Hz)	M$^+$
3a	C_6H_5	68	122–125/16[b]	1670, 1592	6.85 (d, 1 H, Hb, J = 14), 7.05–7.92 (m, 6 H, Ha, 5 H_{arom})	–
3b	4-ClC_6H_4	74	145–147/15	1664, 1597	6.87 (d, 1 H, Hb, J = 13.8), 7.12–8.02 (m, 5 H, Ha, 4 H_{arom})	201, 203 (m + 2), 205 (m + 4)
3c	4-$NO_2C_6H_4$	71	150–153/18	1673, 1601, 1382	6.82 (d, 1 H, Hb, J = 13.8), 7.14–7.98 (m, 5 H, Ha, 4 H_{arom})	211, 213 (m + 2)
7a	C_6H_5	80	78–79[c]	1296, 1136	4.01 (d, 2 H, CH_2, J = 6.0), 6.22 (t, 1 H, $CHCl_2$), 7.55–8.15 (m, 5 H_{arom})	–
7b	4-$CH_3C_6H_4$	85	59–60	1301, 1152	2.02 (s, 3 H, CH_3), 3.98 (d, 2 H, CH_2, J = 6.1), 6.24 (t, 1 H, $CHCl_2$), 7.49–8.12 (m, 4 H_{arom})	253, 255 (m + 2), 257 (m + 4)
7c	4-ClC_6H_4	74	95–96	1304, 1126	4.06 (d, 2 H, CH_2, J = 6.0), 6.15 (t, 1 H, $CHCl_2$), 7.50–8.17 (m, 4 H_{arom})	273, 275 (m + 2), 277 (m + 4), 279 (m + 6)
8a	C_6H_5	78	47–49[d]	1598, 1305, 1130	6.60 (d, 1 H, Hb, J = 12), 7.45–8.12 (m, 6 H, Ha, 5 H_{arom})	–
8b	4-$CH_3C_6H_4$	83	45–46[e]	1601, 1294, 1126	2.10 (s, 3 H, CH_3), 6.64 (d, 1 H, Hb, J = 12.0), 7.32–8.10 (m, 5 H, Ha, 4 H_{arom})	–
8c	4-ClC_6H_4	80	90–92[f]	1605, 1302, 1135	6.63 (d, 1 H, Hb, J = 12.2), 7.48–8.10 (m, 5 H, Ha, 4 H_{arom})	–

[a] Satisfactory microanalysis obtained: C ± 0.23, H ± 0.12
[b] Lit.[10] bp 125–127 °C/18 mm
[c] Lit.[11] mp 80–82 °C
[d] Lit.[6] mp 49–50 °C
[e] Lit.[6] mp. 48 °C.
[f] Lit.[6] mp 96–97 °C

1-Aroyl-2-chloroethenes 3; General Procedure
Into the solution of aroyl chloride (5 mmol) in $CHCl_3$ (50 mL) kept at 10–15 °C, anhyd $AlCl_3$ (5 mmol) was added portionwise. The temperature of the mixture was slowly raised to 55–65 °C and vinyl chloride gas (an equimolar mixture of 1,2-dichloroethane and alc. KOH) was passed through the mixture for 24 h. Stirring was continued for an additional period of 30 min and the contents were poured onto crushed ice and extracted with $CHCl_3$. The combined extracts were washed with sat. $NaHCO_3$ and H_2O, dried (Na_2SO_4) and the solvent was distilled off. The syrupy liquid obtained was distilled under reduced pressure to get pure 1-aroyl-2-chloroethene. The physical and spectroscopic data are given in Table 1.

1-Aroyl-2-arylsulfonylethenes 5; General Procedure
To a solution of 1-aroyl-2-chloroethene (5 mmol) in MeOH (20 mL), **4**[12] (5.5 mmol) in H_2O (20 mL) was added dropwise with stirring at r.t. for 5 h. The crystallized solid was filtered, washed with H_2O, dried (Na_2SO_4) and recrystallized from MeOH. The physical and spectroscopic data are given in Table 2.

1-Arylsulfonyl-2,2-dichloroethanes 7; General Procedure
Into a well stirred solution of arylsulfonyl chloride (5 mmol) in $CHCl_3$ (100 mL) kept at 10–15 °C was added gradually anhyd $AlCl_3$ (5 mmol). The temperature of the mixture was slowly raised to 55–65 °C and vinyl chloride gas was passed for 18 h. Stirring was continued for an additional period of 30 min and the resulting mixture was poured onto crushed ice. The organic layer was separated, washed with H_2O, dried (Na_2SO_4) and the solvent was removed under vacuum. The solid obtained was recrystallized from pet.ether/EtOAc. The physical and spectroscopic data are given in Table 1.

1-Arylsulfonyl-2-chloroethenes 8; General Procedure
Et_3N (1 mmol) in benzene (20 mL) was added dropwise to an ice cold solution of 1-arylsulfonyl-2,2-dichloroethane (1 mmol) in benzene (50 mL) over 45 min and kept aside for 16–18 h. The precipitated triethylamine hydrochloride was filtered off. The filtrate was neutralised with 6M HCl. The organic layer was separated, dried and solvent was removed under vacuum to get **8**, which was purified by filtration through a column of silica gel (60–120) mesh, BDH with hexane/EtOAc, 3:2 as eluent). The physical and spectroscopic data are given in Table 1.

1,2-Diarylsulfonylethenes 9; General Procedure
Method A: A solution of 1-arylsulfonyl-2-chloroethene (1.2 mmol) in MeOH (20 mL) was added dropwise to **4** (1.2 mmol) in H_2O (10 mL) and stirred at r.t. for 3 h. The crude compound separated was filtered and recrystallized from MeOH to get **9**.

Method B: A mixture of 1-arylsulfonyl-2,2-dichloroethane (1.2 mmol) and **4** (2.4 mmol) in MeOH (20 mL) in H_2O (10 mL) was stirred at r.t. for 5 h. The solid obtained was filtered, dried and recrystallized from MeOH to get **9**. The physical and spectroscopic data are given in Table 2.

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Table 2 Selected Physical and Spectroscopic Data of **5** and **9**

Product[a]	Ar	Ar′	Yield (%)	mp (°C)	IR ν (cm^{-1})	^{1}H NMR ($CDCl_3$) δ, J (Hz)	M$^+$
5a	C_6H_5	C_6H_5	75	113–114[b]	1669, 1592, 1326, 1147	7.38 (1 H, Hb, J = 18.0), 7.45–8.15 (m, 11 H, Ha and 10 H_{arom})	272
5b	C_6H_5	4-CH_3 C_6H_4	80	123–124	1665–1598, 1330, 1125	2.44 (s, 3 H, CH_3), 7.24 (d, 1 H, Hb, J = 18.1), 7.39–8.00 (m, 10 H, Ha and 9 H_{arom})	286
5c	C_6H_5	4-OCH_3 C_6H_4	78	127–128	1659, 1592, 1327, 1125	3.82 (s, 3 H, OCH_3), 7.29 (d, 1 H, Hb, J = 18.2), 7.45–8.21 (m, 10 H, Ha and 9 H_{arom})	–
5d	C_6H_5	4-Cl C_6H_4	78	120–121	1675, 1600, 1325, 1131	7.35 (d, 1 H, Hb, J = 18.0), 7.43–8.16 (m, 10 H, Ha and 9 H_{arom})	306, 308 (m + 2)
5e	C_6H_5	4-Br C_6H_4	79	118–120	1670–1594, 1330–1154	–	–
5f	C_6H_5	3,4-Cl_2 C_6H_3	75	123–124	1674, 1598, 1315, 1142	–	–
5g	4-Cl C_6H_4	C_6H_5	81	115–116	1680, 1592, 1334, 1128	7.31 (d, 1 H, Hb, J = 18.0), 7.48–8.23 (m, 10 H, Ha and 9 H_{arom})	306, 308 (m + 2)
5h	4-Cl C_6H_4	4-CH_3 C_6H_4	83	120–121	1669, 1584, 1320, 1140	2.42 (s, 3 H, CH_3), 7.36 (d, 1 H, Hb, J = 18.1), 7.42–8.00 (m, 9 H, Ha and 8 H_{arom})	–
5i	4-Cl C_6H_4	4-OCH_3 C_6H_4	82	127–128	1668, 1596, 1340, 1125	3.82 (s, 3 H, OCH_3), 7.32 (d, 1 H, Hb, J = 18.1), 7.48–8.12 (m, 9 H, Ha and 8 H_{arom})	336, 338 (m + 2)
5j	4-Cl C_6H_4	4-Cl C_6H_4	85	123–124	1672, 1587, 1332, 1145	–	–
5k	4-Cl C_6H_4	4-Br C_6H_4	80	116–117	1665, 1592, 1328, 1127	–	–
5l	4-Cl C_6H_4	3,4-Cl_2 C_6H_3	79	123–124	1674, 1601, 1325, 1127	–	–
5m	4-NO_2 C_6H_4	C_6H_5	78	150–151	1665, 1592, 1380, 1336, 1125	7.28 (d, 1 H, Hb, J = 18.2), 7.50–8.17 (m, 10 H, Ha and 9 H_{arom})	317
5n	4-NO_2 C_6H_4	4-CH_3 C_6H_4	80	125–126	1672, 1600, 1382, 1325, 1142	–	–
5o	4-NO_2 C_6H_4	4-OCH_3 C_6H_4	72	132–133	1664, 1585, 1365, 1332, 1130	3.82 (s, 3 H, OCH_3), 7.26 (d, 1 H, Hb, J = 18.1), 7.45–8.01 (m, 9 H, Ha and 8 H_{arom})	–
5p	4-NO_2 C_6H_4	4-Cl C_6H_4	77	118–119	1667, 1590, 1385, 1342, 1136	7.34 (d, 1 H, Hb, J = 18.2), 7.53–8.12 (m, 9 H, Ha and 8 H_{arom})	351, 353 (m + 2)
5q	4-NO_2 C_6H_4	4-Br C_6H_4	70	140–141	1660, 1587, 1370, 1336, 1125	–	–
5r	4-NO_2 C_6H_4	3,4-Cl_2 C_6H_3	68	123–125	1666, 1594, 1375, 1328, 1140	–	–
9a	C_6H_5	C_6H_5	80	223–225[c]	1324, 1142	7.40 (s, 2 H_{olef}), 7.55–8.00 (m, 10 H_{arom})	308
9b	C_6H_5	4-CH_3 C_6H_4	86	218–220	1335, 1146	2.40 (s 3 H, CH_3), 7.36 (s, 2 H_{olef}), 7.49–7.94 (m, 9 H_{arom})	322
9c	C_6H_5	4-OCH_3 C_6H_4	82	225–227[d]	1330, 1150	3.78 (s, 3 H, OCH_3), 7.39 (s, 2 H_{olef}), 7.45–7.92 (m, 9 H_{arom})	–
9d	C_6H_5	4-Cl C_6H_4	78	>240[e]	1327, 1145	7.42 (s, 2 H_{olef}), 7.57–8.05 (m, 9 H_{arom})	342, 344 (m + 2)

Table 2 (continued)

Product[a]	Ar	Ar′	Yield (%)	mp (°C)	IR ν (cm^{-1})	^{1}H NMR (CDCl$_3$) δ, J (Hz)	M$^+$
9e	C_6H_5	4-Br C_6H_4	79	>240	1332, 1143	–	–
9f	C_6H_5	3,4-Cl$_2$ C_6H_3	72	210–212	1337, 1145	7.45 (s, 2 H$_{olef}$), 7.59–8.04 (m, 8 H$_{arom}$)	–
9g	4-CH$_3$ C_6H_4	C_6H_5	78	235–237	1345, 1126	–	322
9h	4-CH$_3$ C_6H_4	4-CH$_3$ C_6H_4	80	237–239[f]	1338, 1140	2.42 (s, 6 H, 2 CH$_3$), 7.38 (s, 2 H$_{olef}$), 7.45–7.98 (m, 8 H$_{arom}$)	336
9i	4-CH$_3$ C_6H_4	4-OCH$_3$ C_6H_4	76	215–217	1327, 1145	–	–
9j	4-CH$_3$ C_6H_4	4-Cl C_6H_4	80	230–232	1330, 1127	2.38 (s, 3 H, CH$_3$), 7.38 (s, 2 H$_{olef}$), 7.46–8.12 (m, 8 H$_{arom}$)	–
9k	4-CH$_3$ C_6H_4	4-Br C_6H_4	79	232–234	1328, 1150	–	–
9l	4-CH$_3$ C_6H_4	3,4-Cl$_2$ C_6H_4	81	213–215	1335, 1147	–	–
9m	4-Cl C_6H_4	C_6H_5	79	217–219	1327, 1145	7.40 (s, 2 H$_{olef}$), 7.50–8.14 (m, 9 H$_{arom}$)	342, 344 (m + 2)
9n	4-Cl C_6H_4	4-CH$_3$ C_6H_4	82	214–216	1342, 1127	–	–
9o	4-Cl C_6H_4	4-OCH$_3$ C_6H_4	75	219–221	1345, 1127	3.85 (s, 3 H, OCH$_3$), 7.37 (s, 2 H$_{olef}$), 7.49–8.12 (m, 8 H$_{arom}$)	372, 374 (m + 2)
9p	4-Cl C_6H_4	4-Br C_6H_4	79	>240	1338, 1154	–	–
9q	4-Cl C_6H_4	4-Cl C_6H_4	83	230–232	1345, 1142	7.43 (s, 2 H$_{olef}$), 7.55–8.17 (m, 8 H$_{arom}$)	–
9r	4-Cl C_6H_4	3,4-Cl$_2$ C_6H_3	82	>240	1344, 1132	–	–

[a] Satisfactory microanalysis obtained: C ± 0.24, H ± 0.11

[b] Lit.[3] mp 114°C

[c] Lit.[6] mp 227–228°C; Lit.[4] mp 219–220°C

[d] Lit.[6] mp 192–193°C

[e] Lit.[6] mp 275–276°C

[f] Lit.[6] mp 229–230°C

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