CHEMISTRY LETTERS, pp. 727-728, 1988.

A Novel Synthesis of Alkyl Aryl Sulfones via the Telluride Ion-Assisted Coupling of Arenesulfonyl Chlorides with Alkyl Halides

Hitomi SUZUKI,* Yoshinobu NISHIOKA, Seetharama Iyer PADMANABHAN,
and Takuji OGAWA*
Department of Chemistry, Faculty of Science, Ehime University,
Bunkyo-cho, Matsuyama 790

Arenesulfonyl chlorides undergo a facile one-pot coupling reaction with primary alkyl iodides and benzyl halides through the telluride ion-induced polarity reversal, giving the corresponding alkyl aryl sulfones in acceptable yields.

Alkyl aryl sulfones are compounds of increasing synthetic importance; carbanions stabilized by the sulfonyl group may be reacted with various electrophiles to afford α-substituted sulfones, from which the sulfonyl group is replaced by hydrogen or eliminated as sulfinate, thus providing convenient routes to a wide variety of eventually sulfur-free compounds.

The most commonly used methods for the preparation of alkyl aryl sulfones involve the oxidation of sulfides with peracid or treatment of alkyl halides with alkali metal salts of arenesulfinates.1) These methods are, however, not always free from some drawbacks such as unpleasant odor, long reaction times, competing side reactions, or insufficient conversion.

We have found that arenesulfonyl chlorides (1) are transformed into the corresponding alkyl aryl sulfones (3) in moderate yields via the telluride-mediated reaction with alkyl halides (2) according to the following equation:

$$\underset{\underline{1}}{\mathrm{ArSO_2Cl}} \quad + \quad \underset{\underline{2}}{\mathrm{RX}} \quad \xrightarrow[\mathrm{-Te,\ -Cl^-,\ -X^-}]{\mathrm{Te^{-2}}} \quad \underset{\underline{3}}{\mathrm{ArSO_2R}}$$

The coupling reaction is based on the reactivity inversion of arenesulfonyl chlorides, where the formerly electrophilic sulfonyl group is converted to nucleophilic sulfinate ion through the transfer of electrons from telluride ion.

Smooth reaction was observed for primary alkyl iodides and benzyl chlorides; little or no O-alkylation products were obtained under the conditions employed (see Table). Alkyl bromides were less satisfactory and alkyl chlorides were not appropriate as alkylating agent. As expected, secondary alkyl halides preferentially underwent β-elimination to olefins. Use of phase-transfer agent generally suppressed competing formation of tellurides, thus improving the yields of sulfones to an appreciable extent.2)

The present procedure was also applicable to alkanesulfonyl chloride; a similar reaction of octanesulfonyl chloride with ethyl iodide led to ethyl octyl

Table 1. Alkyl aryl sulfones obtained from the cross-coupling of arenesulfonyl chlorides with alkyl halides[a)]

Ar	RX	Reaction time/h	Reaction temp/°C	Yield/%[b)]
4-$CH_3C_6H_4$	C_2H_5I	10	60	71
4-$CH_3C_6H_4$	C_2H_5Br	10	60	31[c)]
4-$CH_3C_6H_4$	n-C_4H_9I	10	60	43
4-$CH_3C_6H_4$	n-$C_8H_{17}I$	10	60	41
4-$CH_3C_6H_4$	$C_6H_5CH_2Cl$	5	90	74[c)]
4-$CH_3C_6H_4$	4-$ClC_6H_4CH_2Cl$	5	90	51[c)]
4-BrC_6H_4	C_2H_5I	5	90	48
4-BrC_6H_4	$C_6H_5CH_2Cl$	5	90	58[c)]
1-$C_{10}H_7$	C_2H_5I	10	60	51
1-$C_{10}H_7$	$C_6H_5CH_2Cl$	5	60	49[c)]
2-$C_{10}H_7$	C_2H_5I	10	60	62
2-$C_{10}H_7$	$C_6H_5CH_2Cl$	5	60	45[c)]

a) Structures of all products were confirmed by IR, ^1H-NMR, mass spectra, and elemental analyses or by direct comparison with authentic specimens.

b) Yields refer to the isolated compounds and are not optimized.

c) Reactions were performed in the presence of benzyltriethylammonium chloride.

sulfone in 74% yield.

The typical procedure is as follows: A wine-colored solution of sodium telluride,[3)] prepared by heating a mixture of powdered tellurium (1 mmol), Rongalite (5 mmol) and 1 mol dm^{-3} -aqueous sodium hydroxide (15 ml), was added dropwise to a stirred solution of p-toluenesulfonyl chloride (1 mmol) and benzyltriethylammonium chloride (0.1 mmol) in THF (10 ml) at room temperature under nitrogen. An instantaneous reaction occurred and the color of the reaction mixture changed to deep black. After 5 min's stirring, benzyl chloride (5 mmol) in THF (3 ml) was added and the resulting mixture was kept at 90 °C for 5 h. After cooling, the solvent was removed under reduced pressure and the residue was treated with aqueous ammonium chloride and benzene. Organic phase was separated after filtration through a thin layer of Celite and worked up as usual to give benzyl p-tolyl sulfone in 74% isolated yield; mp 143-145 °C.

References

1) For a recent review of sulfone chemistry, see P. D. Magnus, Tetrahedron, 33, 2019 (1977).

2) Phase-transfer alkylation of sulfinate salts has been reported; G. E. Vennstra and B. Zwaneburg, Synthesis, 1975, 519; F. Manescalchi, M. Orena, and D. Savoia, ibid., 1979, 445; J. Wildeman and A.M. van Leusen, ibid., 1979, 733.

3) H. Suzuki and M. Inouye, Chem. Lett., 1985, 225.

(Received February 16, 1988)