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Reaction of α-methylstyrene with arylsulfonyl chlorides: spontaneous dehydrochlorination against the Zaitsev rule

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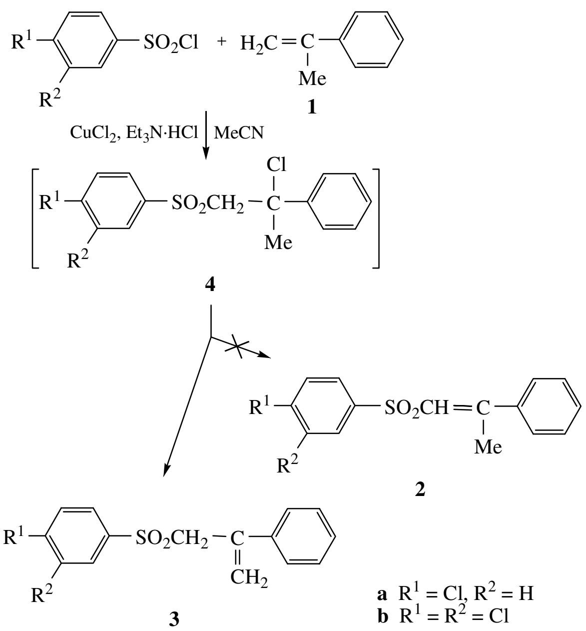
The free-radical addition of arylsulfonyl chlorides to α-methylstyrene in the presence of copper chloride is accompanied by the dehydrochlorination of the adducts formed.

The free radical addition of alkyl and arylsulfonyl chlorides to various alkenes and alkadienes in the presence of copper chlorides was first studied in detail by Asscher and Vofsi.[1] Subsequently, this general and convenient method for the synthesis of β-halosulfones and α,β-unsaturated sulfones after dehydrohalogenation of the latter was extensively developed. The addition of sulfonyl chlorides and iodides to activated and non-activated alkenes, conjugated dienes and trienes, allenes, acetylenes, styrenes with different substituents in the aromatic rings, β-methylstyrene, *etc.* was described.[1–10] However, there is no published data on the use of α-methylstyrene in these reactions.

We studied the addition of arylsulfonyl chlorides to α-methylstyrene **1** under standard conditions commonly used to obtain adducts of sulfonyl chlorides with alkenes, in particular, with substituted styrenes.[3,4] The reaction was carried out with an equimolar ratio of the reagents in acetonitrile in the presence of copper(II) chloride and triethylamine hydrochloride. (The role of the latter is to convert copper salts to more soluble complex compounds).[†] We encountered some unexpected results in this reaction (Scheme 1).



Scheme 1

First, the addition of arylsulfonyl chlorides to α-methylstyrene is accompanied by the simultaneous dehydrochlorination of the β-chlorosulfone formed. Hydrogen chloride is liberated throughout the entire reaction, giving an unsaturated sulfone as the only end product. In almost all the studies reported, the dehydrochlorination stage is carried out as a separate process, *e.g.*, by treatment with triethylamine in benzene at room temperature.[1–4]

Second, the dehydrohalogenation of arylsulfonyl chloride adducts with α-methylstyrene does not obey the Zaitsev rule. Less substituted allyl sulfones **3a**,**b** are formed instead of expected vinyl sulfones **2a**,**b** with a higher degree of substitution. This is confirmed by ^{1}H NMR and IR spectroscopic data. The ^{1}H NMR spectra of products **3a**,**b** contain singlets of two protons of the terminal double bond at δ 5.62 and 5.21 (**3a**) and at 5.57 and 5.30 (**3b**). The protons of the CH_2SO_2 group manifest themselves in the spectrum as singlet signals at δ 4.65 (**3a**) and 4.54 (**3b**). The presence of absorption bands at 1623.6 [ν(C=C)], 1417.8 [$\delta_{(planar)}$(>C=CH$_2$)] and 897.8 cm^{-1} [$\delta_{(nonplanar)}$(>C=CH$_2$)] in the IR spectra of the products and the absence of bands in the region 980–960 cm^{-1} (–C=C–) suggests that each of these compounds contains a terminal double bond.

The final products were obtained in the yields of 88.3% (**3a**) and 91.3% (**3b**); their melting points are 117–118 and 123–125 °C, respectively.

By shortening the synthesis time of sulfone **3a** from 3 to 0.5 h and reducing the reaction temperature from 85 to 60 °C, we obtained a product which, according to its ^{1}H NMR spectrum, consisted of sulfone **3a** and adduct **4a** in the ~2:1 ratio. The methyl protons of adduct **4a** manifest themselves in the spectrum as a singlet signal at δ 1.63 ppm, while the methylene protons form two doublets at δ 3.75 and 3.87 ppm. The multiplicity and the positions of proton signals of compounds **3a** and **4a** are in good agreement with simulated spectra. The presence of compound **4a** in the product of the uncompleted reaction suggests that it actually occurs *via* an intermediate adduct of sulfonyl chloride with α-methylstyrene. The spectrum of the product does not contain the signals of protons of sulfone **2a**.

The spontaneous abstraction of hydrogen chloride from adducts of arylsulfonyl chlorides with alkenes during their synthesis has previously been observed for 1,1-diphenylethene, 1-phenyl-3,4-dihydronaphthalene, 1-phenylcyclohexene, and acenaphthylene.[11] Apparently, in all of these cases including this study, the structures of the starting alkenes were such that, upon addition of sulfonyl chlorides to them, the chlorine atom was bound to the tertiary carbon atom. Probably, the resulting tertiary chloride then readily undergoes thermal dehydrochlorination by the E1 mechanism, which does not require an additional base added. (Apparently, the solvent, *i.e.*, acetonitrile, serves as a base). Incidentally, when the addition of sulfonyl chlorides to α-methylstyrene was carried out in the absence of triethylamine hydrochloride, this affected only slightly the yields of the products but not its direction. Sulfones **3a** and **3b** were obtained in the yields of 85.6 and 88.2%, respectively.

As regards the violation of the Zaitsev rule in the dehydrochlorination of adducts **4a**,**b**, we apparently encounter the situation where the formation of a less-substituted alkene is more favourable, since steric repulsion of *cis* substituents in the more substituted alkene is too high and makes the latter less stable. In fact, it is known[12] that the dehydrobromination of 2-bromo-2,4,4-trimethylpentane predominantly results in 2,4,4-trimethylpent-1-ene rather than 2,4,4-trimethylpent-2-ene as could be expected in accordance with the Zaitsev rule. This is due to the considerable steric repulsion of the methyl and *tert*-butyl groups that are *cis*-arranged in the latter isomer. In this work, an even higher steric hindrance should be expected for isomers **2a**,**b** due to the presence of more bulky substituents at the double bond. Because of this, the reaction gives only isomers **3a**,**b**. Isomers **2a**,**b** were not detected.

Note that unsaturated sulfones **3a**,**b** are considerably less reactive, *e.g.*, in the nucleophilic addition of thiols, than vinylsulfones obtained by the dehydrochlorination of adducts of sulfonyl chlorides with styrene. These vinylsulfones undergo thiylation in DMF in a few minutes at room temperature in the presence of catalytic amounts of triethylamine; the yield was virtually quantitative. Under these conditions, sulfones **3a**,**b** do not react with thiols. The reason for the lower reactivity of the double bond in allyl sulfones **3a**,**b** in comparison with vinyl sulfones is apparently that in this case the strong electronegative sulfonyl group cannot activate the double bond directly.

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[†] *Synthesis of sulfones* **3a** *and* **3b**.

A mixture of an arylsulfonyl chloride (0.01 mol), α-methylstyrene **1** (1.18 g, 0.01 mol), copper chloride (0.0135 g, 0.1 mmol), triethylamine hydrochloride (0.0207 g, 0.15 mmol) and acetonitrile (3.69 g, 0.09 mol) was refluxed for 3 h, cooled and poured into 4 ml of cold methanol. The resulting white precipitate was filtered off, dried, and recrystallised from 95% ethanol.

^{1}H NMR spectra of a 5% solution of samples in [^{2}H$_6$]DMSO were recorded on a Bruker AC-250 instrument; TMS was used as an internal standard. IR spectra were measured on a Specord 75 R in the range 300–4000 cm^{-1} using suspensions in Vaseline oil.

3a: mp 117–118 °C. ^{1}H NMR, δ: 7.67 (q, 4H, Ph), 7.41–7.24 (m, 5H, Ph), 5.62 (s, 1H, C=CH$_2$), 5.20 (s, 1H, CH$_2$), 4.65 (s, 2H, CH$_2$). Found (%): C, 63.14; H, 4.34; S, 10.44. Calc. for $C_{16}H_{13}O_2SCl$ (%): C, 63.05; H, 4.27; S, 10.51.

3b: mp 123–125 °C. ^{1}H NMR, δ: 7.25–7.45 (m, 5H, Ph), 7.50–7.95 (m, 3H, Ph), 5.57 (s, 1H, C=CH$_2$), 5.80 (s, 1H, C=CH$_2$), 4.54 (s, 2H, CH$_2$). Found (%): C, 55.13; H, 3.76; S, 9.62. Calc. for $C_{15}H_{12}O_2SCl_2$ (%): C, 55.05; H, 3.67; S, 9.79.

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