

Synthesis of Sulphones from Sulphonyl Fluorides and Organometallic Compounds

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Sulphones, Organometallic Compounds

The reaction between sulphonyl fluorides and arylmagnesium bromides was investigated. The good yields of sulphones obtained demonstrates the potentialities of this reaction as a synthetic method for sulphones.

Cadmium reagents were found to be unreactive toward the same sulphonyl fluorides.

Introduction

Recently, β -disulphones were synthesised in high yields from sulphonyl fluorides by interaction with alkylmagnesium bromides [1]. It is assumed that this reaction proceeds through the formation of a monosulphone which undergoes α -metallation followed by further reaction with the sulphonyl fluoride to produce β -disulphone. Since aromatic sulphones cannot be metallated at the α -position, it seemed of interest from the synthetic and mechanistic points of view to investigate the reaction of sulphonyl fluorides with Grignard's reagents of the aromatic type. Moreover, this study extends our previous investigations on the reactions of sulphonyl chlorides with organocadmium reagents [2-4].

Results and Discussion

Previous reports from our laboratories showed that sulphonyl chlorides react smoothly with

organocadmium reagents to form sulphones (among other products) in moderate to poor yields. Unlike sulphonyl chlorides, sulphonyl fluorides were found to be inactive towards organocadmium reagents. For example, when benzenesulphonyl fluoride was allowed to react with diphenylcadmium under the conditions reported earlier [3] for sulphonyl chlorides, diphenyl sulphone was obtained in only 5-7% yield and most of the sulphonyl fluoride was recovered unreacted. Extension of the reaction time to 12 h under reflux in benzene gave no reaction. Also, adding a catalyst such as ferric chloride or aluminum chloride or using different solvents such as dimethyl sulphoxide at different temperatures, failed to push the reaction forward and most of the sulphonyl fluoride was recovered at the end of the reaction.

Unlike the cadmium reagents, the more reactive Grignard reagents were found to react smoothly with sulphonyl fluorides to give aromatic sulphones in high yields. The reaction was carried out in ether under reflux for one hour and the products were isolated and purified. The selectivity and generality of this reaction are suggested by the examples shown in Tables I, II and III. The products recorded in

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Table I. Reaction of Grignard reagents with benzenesulphonyl fluoride.

Ex.	Grignard Reagent	Sulphone	Yield ^a [%]	Conversion ^b [%]
1	Phenylmagnesium bromide	Diphenyl sulphone	82	86
2	<i>p</i> -Tolylmagnesium bromide	Phenyl <i>p</i> -tolyl sulphone	78	82
3	<i>p</i> -Anisylmagnesium bromide	<i>p</i> -Anisyl phenyl sulphone	75	52
4	α -Naphthylmagnesium bromide	α -Naphthyl phenyl sulphone	44.7	45
5	β -Naphthylmagnesium bromide	β -Naphthyl phenyl sulphone	62	—
6	Benzylmagnesium bromide	Benzyl phenyl sulphone	46	62.2
7	β -Phenylethylmagnesium bromide	β -Phenylethyl phenyl sulphone	5 ^c	37.8
8	<i>p</i> -Chlorophenylmagnesium bromide	<i>p</i> -Chlorophenyl phenyl sulphone	79	82

^a Average of duplicate runs, based on the sulphonyl fluorides consumed. ^b Based on the recovered unreacted sulphonyl fluoride. ^c β -Disulphone was obtained in 80% yield.

Table II. Reaction of Grignard reagents with *p*-toluenesulphonyl fluoride.

Ex.	Grignard Reagent	Sulphone	Yield ^a [%]	Conversion [%]
1	Phenylmagnesium bromide	Phenyl <i>p</i> -tolyl sulphone	79	79
2	<i>p</i> -Tolylmagnesium bromide	<i>p,p'</i> -Ditolyl sulphone	65.7	59
3	<i>p</i> -Anisylmagnesium bromide	<i>p</i> -Anisyl <i>p</i> -tolyl sulphone	36	17
4	α -Naphthylmagnesium bromide	α -Naphthyl <i>p</i> -tolyl sulphone	20	43
5	Benzylmagnesium bromide	Benzyl <i>p</i> -tolyl sulphone	15.4	47.8

^a Based on the sulphonyl fluoride which is actually participated in the reaction.

Table III. Reaction of phenylmagnesium bromide with arenesulphonyl fluorides.

Ex.	Arenesulphonyl fluoride	Sulphone	Yield ^a [%]	Conversion [%]
1	Benzenesulphonyl fluoride	Diphenyl sulphonyl	82	86
2	β -Naphthalenesulphonyl fluoride	β -Naphthyl phenyl sulphone	80	84
3	<i>p</i> -Toluenesulphonyl fluoride	Phenyl <i>p</i> -tolyl sulphone	79	79
4	<i>p</i> -Anisolesulphonyl fluoride	<i>p</i> -Anisyl phenyl sulphone	56	32
5	β -Phenylethanesulphonyl fluoride	β -Phenylethyl phenyl sulphone	60	71
6	<i>p</i> -Bromobenzenesulphonyl fluoride	<i>p</i> -Bromophenyl phenyl sulphone	91	92

^a Based on the sulphonyl fluoride which is actually participated in the reaction.

these Tables are all known compounds and their identities were confirmed by superposition of properties with recorded values and/or by direct comparison with authentic samples.

The data shown in Table I suggest that the presence of electron withdrawing or electron donating groups on the benzene nucleus carrying the magnesium atom have no or little effect on the yield of the sulphone (compare runs 3 and 8). However, the consumption of only 48% of the sulphonyl fluoride in the reaction of *p*-anisylmagnesium bromide with benzenesulphonyl fluoride indicates that electron donating groups may retard the reaction. On the other hand, substitution of electron donating groups on the benzene ring of the sulphonyl fluoride not only lowered the percentage of conversion but also decreased the yield of the sulphone (*cf.* Table III run 4). Electron withdrawing groups have the opposite effect. Substitution of an electron donating group on both the sulphonyl fluoride and the Grignard reagent seriously decreased the rate of conversion. For example, when *p*-toluenesulphonyl fluoride was allowed to react with *p*-anisylmagnesium bromide under our general conditions, only 17% of the sulphonyl fluoride reacted after 24 h and 83% were recovered unreacted.

The relatively low yield of α -naphthyl phenyl sulphone (45%) from α -naphthylmagnesium bromide and benzene sulphonyl fluoride may be attributed to steric hindrance. This is supported by the higher yield of β -naphthyl phenyl sulphone from the reaction of the less hindered β -naphthylmagnesium bromide with benzenesulphonyl fluoride. This sulphone, however, was obtained in even higher yield from the reaction of β -naphthalenesulphonyl fluoride and phenylmagnesium bromide. Of course, the latter result is expected since the reaction site in this case is further away from the bulky naphthalene ring.

Experimental

General procedure

The Grignard reagents were prepared from bromoarenes (0.055 mole) according to the published procedure [5]. To a cold solution of this reagent in dry ether, there was added in one portion a solution of 0.055 mole of the sulphonyl fluoride in 20 ml dry ether and the reaction mixture was heated under reflux for one hour. The flask was cooled in an ice bath, decomposed with ice-cold hydrochloric acid and the organic layer was extracted with ether. The solvent was removed by distillation and the residue was subjected to steam distillation.

Separation and identification of the different reaction products will be described under each individual run.

Action of benzenesulphonyl fluoride on phenylmagnesium bromide

Phenylmagnesium bromide (prepared from 8.6 g bromobenzene and 1.35 g magnesium) reacted with 6.75 g benzenesulphonyl fluoride according to the general procedure described above. From the steam-nonvolatile portion 6.3 g (82%) of diphenyl sulphone was obtained by recrystallisation from ethanol, m.p. 129 °C and was not depressed by mixing, lit. [6] m.p. 129 °C.

Action of benzenesulphonyl fluoride on p-tolylmagnesium bromide

The reaction was carried out as usual to give finally 1.2 g (18%) of unreacted benzenesulphonyl fluoride as a steam distillable fraction and 6.0 g (78.80%) of *p*-tolyl phenyl sulphone as a steam-nondistillable product, m.p. 125 °C and was not depressed by mixing; lit. [7] m.p. 124.5 °C.

Action of benzenesulphonyl fluoride on p-anisylmagnesium bromide

The reaction was carried out according to the general procedure, but the final reflux period was extended over night. The steam-distillable fraction was unreacted benzenesulphonyl fluoride (3.2 g, 48%).

The steam-nonvolatile fraction was chromatographed on a 60 cm × 1 cm column packed with silica gel and 3.9 g (75%) of *p*-anisyl phenyl sulphone was eluted with pet. ether (60–80)-benzene mixture (2:3), m.p. 90 °C, and was not depressed by mixing; lit. [8] 90–91 °C.

Action of benzenesulphonyl fluoride on α-naphthylmagnesium bromide

α-Naphthylmagnesium bromide was treated with benzenesulphonyl chloride according to our general procedure to give naphthalene (2.2 g, 30%) and unreacted benzenesulphonyl fluoride (3.5 g, 55.7%).

The non-steam distillable fraction was chromatographed on a 60 cm × 1 cm column packed with silica gel and 2.4 g (44.7%) of α-naphthyl phenyl sulphone was eluted with petroleum-ether (60 to 80 °C) benzene mixture (3:2), m.p. 99 °C, lit. [9] 97–99 °C and the mixed m.p. was not depressed.

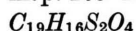
Action of benzenesulphonyl fluoride on β-naphthylmagnesium bromide

The products of this reaction were separated in the same way as in the preceding reaction. The following compounds were obtained: naphthalene (0.8 g, 11%) and 3.5 g (72%) of β-naphthyl phenyl sulphone, m.p. 115–116 °C and mixed m.p. 116 °C.

Action of benzenesulphonyl fluoride on benzylmagnesium bromide

Benzylmagnesium bromide (prepared from 9.49 g benzyl bromide and 1.35 g magnesium turnings) was allowed to react with benzenesulphonyl fluoride

(6.75 g) and the product was extracted with ether according to the general procedure. When the ethereal solution was cooled in an ice bath, a solid product was precipitated, recrystallisation from ethanol gave 2.0 g (53%) of *α,α*-bis(benzenesulphonyl)toluene(disulphone) m.p. 207 °C, lit. [10] m.p. 205–207 °C.



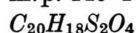
Calcd S 17.20,

Found S 17.09.

The original ethereal solution was evaporated and the residue was subjected to steam distillation. The steam-distillable fraction gave 2.5 g (37.8%) of unreacted benzenesulphonyl fluoride and 1.0 g (13%) of dibenzyl. The steam-nondistillable product was separated by filtration, recrystallised from ethanol to give 2.7 g (46%) of benzyl phenyl sulphone, m.p. 146 °C, mixed m.p. 146 °C and lit. [11] m.p. 148 °C.

Action of benzenesulphonyl fluoride on β-phenylethylmagnesium bromide

The reaction was worked up as in the preceding reaction. The following compounds were obtained: β,β-bis(benzenesulphonyl)ethylbenzene (2.5 g, 50%), m.p. 140–142 °C.



Calcd S 16.58,

Found S 16.49.

Unreacted benzenesulphonyl fluoride 2.5 g (37.8%) and β-phenylethyl phenyl sulphone (0.12 g, 1.0%), m.p. 58 °C, lit. [12] m.p. 57.5–58.5 °C.

Action of benzenesulphonyl fluoride on p-chlorophenylmagnesium bromide

p-Chlorophenylmagnesium bromide (prepared from 10.5 g *p*-chlorobromobenzene) was allowed to react with benzenesulphonyl fluoride (6.75 g) according to the general procedure. The steam distillable fraction gave 1.0 g (18%) of unreacted benzenesulphonyl fluoride. Recrystallization of the steam non distillable residue from ethanol gave 7.9 g (79%) of *p*-chlorophenyl phenyl sulphone, m.p. 88 °C, lit. [13] 91 °C.

Action of p-toluenesulphonyl fluoride on phenylmagnesium bromide

This reaction was similar to the preceding one and the following products were obtained: unreacted *p*-toluenesulphonyl fluoride (2.01 g, 21%) and 7.6 g (79%) of phenyl *p*-tolyl sulphone, m.p. 123.0 °C, lit. [7] m.p. as well as the mixed m.p. was 124.5 °C.

Action of p-toluenesulphonyl fluoride on p-tolylmagnesium bromide

The reaction was carried out as usual to give finally, beside the unreacted *p*-toluenesulphonyl fluoride (4.0 g, 40%), *p,p'*-ditolyl sulphone, recrystal-

lized from ethanol, m.p. 158 °C, lit. [14] and mixed m.p. 158 °C.

Action of p-toluenesulphonyl fluoride on p-anisylmagnesium bromide

This reaction was carried out as usual to give finally 4.0 g (80%) *p*-toluenesulphonyl fluoride from steam distillable fraction. The non steam-distillable fraction was chromatographed using silica gel column. *p*-Anisyl *p*-tolyl sulphone (0.5 g, 36%) was eluted with petroleum ether (60–80 °C)-benzene (1:1), m.p. 108 °C, lit. [15] m.p. 108 °C.

Action of p-toluenesulphonyl fluoride on α-naphthylmagnesium bromide

α-Naphthylmagnesium bromide was treated with *p*-toluenesulphonyl fluoride according to the general procedure to give 2.8 g (28%) naphthalene and 2.6 g (27%) of *p*-toluenesulphonyl fluoride.

The non steam-distillable residue was chromatographed on a 60 cm × 1 cm column packed with silica gel and 2.2 g (20%) of α-naphthyl *p*-tolyl sulphone was eluted with petroleum ether (60–80 °C)-benzene mixture (3:2), m.p. 122 °C, lit. [16], m.p. 122–123 °C.

Action of p-toluenesulphonyl fluoride on benzylmagnesium bromide

This reaction was completed and the products were separated as in the reaction of benzenesulphonyl fluoride and benzylmagnesium bromide. The following compounds were obtained: α,α-bis(*p*-toluenesulphonyl)toluene (disulphone) (1.5 g, 29%); m.p. 179–180 °C.

$C_{21}H_{20}S_2O_4$

Calcd S 16.0,

Found S 15.2.

Also, 1.0 g (15.4%) of benzyl tolyl sulphone was obtained beside 5.0 g (52%) of unreacted *p*-toluenesulphonyl fluoride.

Action of β-naphthalenesulphonyl fluoride on phenylmagnesium bromide

The reaction was worked up as in the general procedure to give finally 1.1 g (10%) of unreacted

sulphonyl fluoride and 10.7 g (80%) of β-naphthyl phenyl sulphone, m.p. 115–117 °C, lit. [9] 115–116 °C.

Action of p-anisolesulphonyl fluoride on phenylmagnesium bromide

Phenylmagnesium bromide was allowed to react with *p*-anisolesulphonyl fluoride according to the general procedure. The steam distillable fraction gave 7.0 g (68%) of anisolesulphonyl fluoride. The steam-non volatile fraction was chromatographed on a 60 cm × 1 cm column packed with silica gel. *p*-Anisyl phenyl sulphone (2.48 g, 56%) was eluted with petroleum ether (60–80 °C)-benzene mixture (2:3), m.p. 90 °C and was not depressed by mixing; lit. [8] m.p. 90–91 °C.

Action of p-anisolesulphonyl fluoride on p-tolylmagnesium bromide

The reaction was worked up as in the preceding reaction. The following compounds were separated: unreacted *p*-anisolesulphonyl fluoride (7.4 g, 72%) and 2.2 g (52%) of *p*-anisyl *p*-tolyl sulphone, recrystallized from, m.p. 108 °C, lit. [15] m.p. 108 °C.

Action of β-phenylethanesulphonyl fluoride on phenylmagnesium bromide

Phenylmagnesium bromide (prepared from 4.3 g, 0.027 mole, bromobenzene) reacted with 5.17 g (0.027 mole) β-phenylethanesulphonyl fluoride according to the general procedure to give 1.5 g (29.5%) of unreacted sulphonyl fluoride and 3.0 g (60%) of β-phenylethyl phenyl sulphone, recrystallized from petroleum ether (40–60 °C), m.p. 57 °C, lit. [12] m.p. 58 °C.

Action of p-bromobenzenesulphonyl fluoride on phenylmagnesium bromide

The reaction was carried out as in the preceding reaction. The following compounds were separated: unreacted *p*-bromobenzenesulphonyl fluoride (0.6 g, 8%) and 6.4 g (91%) of *p*-bromophenyl phenyl sulphone, recrystallized from ethanol, m.p. 108 °C, lit. [13] 108–108.5 °C.

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