506. *The Preparation of Diaryl Sulphones.*

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An improved procedure has been developed for the preparation of diaryl sulphones by the Friedel–Crafts reaction. A number of new sulphones has been prepared. The mechanism of the reaction is discussed.

When an aromatic sulphonyl chloride ($Ar{\cdot}SO_2Cl$) is added to a stirred methylene or ethylene dichloride suspension of aluminium chloride, one molecular proportion of the latter (formulated as $AlCl_3$) dissolves. Decantation of the clear solution of the aluminium chloride–sulphonyl chloride complex from undissolved aluminium chloride into a solution of a benzene derivative (Ar′H) in methylene or ethylene dichloride affords hydrogen chloride and an oxonium complex of diaryl sulphone and aluminium chloride from which the sulphone is liberated by the addition of water:

$$Ar{\cdot}SO_2Cl,AlCl_3 + Ar'H \longrightarrow HCl + ArAr'SO_2,AlCl_3$$

Reaction proceeds at room temperature or below, and in homogeneous solution. The success of the method, which is analogous to that reviewed by Baddeley[1] for the preparation of aromatic ketones using acyl halides and aluminium halides, depends on the high solubility of the sulphonyl chloride–aluminium chloride complex and the low solubility of the aluminium chloride in methylene or ethylene dichloride. This ensures that the sulphonylating agent is obtained in its most reactive form and free from excess of aluminium chloride. An excess of this reagent is undesirable since it may isomerise the benzene derivative[2] before its reaction with the sulphonyl chloride.

Table 1.

Sulphonyl chloride	Benzene derivative	Orientation of substituents	Yield (%)	M. p.	Ref.
$C_6H_5{\cdot}SO_2Cl$	C_6H_6	—	90	128°	*a*
,,	C_6H_5Me	2-, 4-	5·5	81	*b*
			74	126	*a*
,,	C_6H_5Et	4-	81	92—93	*a*
,,	$1,3\text{-}C_6H_4Me_2$	2,4-	98	87·5	*c*
,,	$1,4\text{-}C_6H_4Me_2$	2,5-	92	111—112	
,,	$1,2,4\text{-}C_6H_3Me_3$	2,4,5-	76	136—137	
,,	$1,3,5\text{-}C_6H_3Me_3$	2,4,6-	70	80—81	*d*
,,	$1,4\text{-}C_6H_4Et_2$	2,5-	53	87—88	
,,	$1,2,4\text{-}C_6H_3Et_3$	2,4,5-	32	84—85	
,,	$1,4\text{-}C_6H_4Pr^n{}_2$	2,5-	61	58—59	
,,	C_6H_5Cl	4-	80	95	*a*
p-$C_6H_4Me{\cdot}SO_2Cl$	C_6H_6	4-	81	126	*a*
,,	C_6H_5Me	4,4′-	72	157—158	*a*
,,	$1,3\text{-}C_6H_4Me_2$	2,4,4′-	70	51—52	*e*
,,	$1,4\text{-}C_6H_4Me_2$	2,5,4′-	80	108—110	*e*
,,	$1,3,5\text{-}C_6H_3Me_3$	2,4,6,4′-	72	119—120	*f*
p-$C_6H_4Et{\cdot}SO_2Cl$	C_6H_6	4-	67	92—93	*a*
$2,4\text{-}C_6H_3Me_2{\cdot}SO_2Cl$	C_6H_6	2,4-	43	87·5	*c*
$2,5\text{-}C_6H_3Me_2{\cdot}SO_2Cl$	C_6H_6	2,5-	79	111—112	
$3,5\text{-}C_6H_3Me_2{\cdot}SO_2Cl$	C_6H_6	3,5-	58	97—98	
$2,4,5\text{-}C_6H_2Me_3{\cdot}SO_2Cl$	C_6H_6	2,4,5-	34	136—137	
$2,4,6\text{-}C_6H_2Me_3{\cdot}SO_2Cl$	C_6H_6	—	—		
,,	$1,3,5\text{-}C_6H_3Me_3$	2,4,6,2′,4′,6′-	75	204	*g*
,,	$C_6H_5{\cdot}OMe$	2,4,6,4′-		136	
		+ isomer		168	
$4\text{-}C_6H_4(OMe){\cdot}SO_2Cl$	$1,3,5\text{-}C_6H_3Me_3$	2,4,6,4′-	60	136	
$3,4,5\text{-}C_6H_2Me_3{\cdot}SO_2Cl$	C_6H_6	3,4,5-	67	161—162	

a Buehler and Masters, *J. Org. Chem.*, 1939, **4**, 262. *b*, Ullmann and Lehner, *Ber.*, 1905, **38**, 734. *c*, Steinkopf and Hübner, *J. prakt. Chem.*, 1934, **141**, 193. *d*, Truce, Ray, Norman, and Eickmeyer, *J. Amer. Chem. Soc.*, 1958, **80**, 3625. *e*, Burton and Praill, *J.*, 1955, 887. *f*, Bourne, Stacey, Tatlow, and Tedder, *J.*, 1951, 718. *g*, Maclean and Adams, *J. Amer. Chem. Soc.*, 1933, **55**, 4683.

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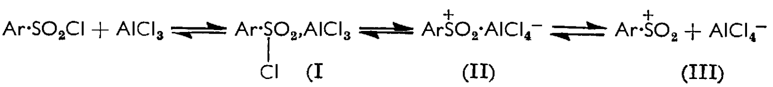
[1] Baddeley, *Quart. Rev.*, 1954, **8**, 355.

[2] Baddeley, Holt, and Voss, *J.*, 1952, 100.

The sulphones obtained by this procedure are listed in Table 1. In general the yields are better than those previously recorded.

The position of the alkyl groups in 2,5-diethyl- and 2,5-di-n-propyl-diphenyl sulphone was established by oxidation with nitric acid. Both compounds provided 2,5-dicarboxydiphenyl sulphone, which with diazomethane afforded a diester identical with that obtained by a similar procedure from 2,5-dimethyldiphenyl sulphone. 2,4,6-Trimethyldiphenyl sulphone, obtained by oxidation of the known 2,4,6-trimethyldiphenyl sulphide,[3] proved to be identical with the product of interaction of benzenesulphonyl chloride and mesitylene. The m. p. of this product (80—81°) accords with that obtained by Truce and his co-workers,[4] and substantiates the error in Meyer's m. p.[5] of 116°. 2,4,5-Trimethyldiphenyl sulphone (m. p. 136—137°) was prepared by the action both of benzenesulphonyl chloride on 1,2,4-trimethylbenzene and of 2,4,5-trimethylbenzenesulphonyl chloride on benzene. The m. p. (160°) claimed by Meyer [5] for 2,4,5-trimethyldiphenyl sulphone is, therefore, in error.

By comparison with the formation of the acyl chloride–aluminium chloride complex, that of the sulphonyl chloride–aluminium chloride complex is only feebly exothermic. This suggests that the bonding of aluminium to oxygen is relatively weak in the sulphonyl chloride–aluminium chloride complex. The almost complete recovery of sulphonyl chlorides when the addition complexes with aluminium chloride are treated with water indicates that the cation shown in (III) can be present only in traces and that addition compounds of this type are to be represented by (I):



$$\mathrm{Ar{\cdot}SO_2Cl} + \mathrm{AlCl_3} \rightleftharpoons \underset{\mathrm{Cl}\quad (\mathrm{I}}{\mathrm{Ar{\cdot}SO_2,AlCl_3}} \rightleftharpoons \underset{(\mathrm{II})}{\mathrm{Ar\overset{+}{S}O_2{\cdot}AlCl_4^-}} \rightleftharpoons \underset{(\mathrm{III})}{\mathrm{Ar{\cdot}\overset{+}{S}O_2} + \mathrm{AlCl_4^-}}$$

On the other hand, the observation that 2,4,6-trimethylbenzenesulphonyl chloride is not sterically hindered in its reactions with mesitylene and with anisole suggests that the cation and not the oxonium complex is the effective electrophilic reagent. These findings are consistent with the observations by Jensen and H. C. Brown [6] that benzenesulphonylation of chlorobenzene proceeds by free ions (III), that of toluene by the addition compound (I) or the ion pair (II), and that of benzene by both paths simultaneously.

In view of its ready reaction with mesitylene and anisole, the failure of mesitylenesulphonyl chloride to react with benzene cannot be attributed to steric effects. The results listed in Table 2 demonstrate that methyl groups *ortho* and *para* to the SO_2Cl group have a marked retarding influence on the reaction rate. This effect has also been observed in the acylation reaction and has been attributed [7] to a reduction in the electrophilic character of the reagent consequent on the inductive effect of *o*- and *p*-alkyl groups. Conversely, increasing alkylation of the hydrocarbon facilitates attack by a given electrophile, and the rate of reaction of benzenesulphonyl chloride with alkylbenzenes is in the expected order mesitylene > *m*-xylene > benzene.

TABLE 2. *Action of alkylbenzenesulphonyl chlorides on benzene.*

Sulphonyl chloride	Sulphone isolated (%) after 72 hr.	Sulphonyl chloride	Sulphone isolated (%) after 72 hr.
2,4,6-$C_6H_2Me_3$-	0	2,5-$C_6H_3Me_2$-	79
2,4,5-$C_6H_2Me_3$-	34	4-C_6H_4Me-	81 (after 60 hr.)
2,4-$C_6H_3Me_2$-	43	C_6H_5-	90 (after 24 hr.)
3,4,5-$C_6H_2Me_3$-	67		

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[3] Bourgeois, *Ber.*, 1895, **28**, 2322.

[4] Truce, Ray, Norman, and Eickmeyer, *J. Amer. Chem. Soc.*, 1958, **80**, 3625.

[5] H. Meyer, *Annalen*, 1923, **433**, 327.

[6] Jensen and Brown, *J. Amer. Chem. Soc.*, 1958, **80**, 4042.

[7] Baddeley and Voss, *J.*, 1954, 418.

Fractional crystallisation of the crude product obtained by the interaction of benzenesulphonyl chloride and toluene in ethylene dichloride solution afforded 4-methyldiphenyl sulphone (74%) and the 2-isomer (*ca.* 5%). Attempts to bring about a more efficient separation of the isomers by chromatography were unsuccessful. Recent infrared spectroscopic studies [8] have indicated that in the benzenesulphonylation of toluene in benzenesulphonyl chloride solution the isomer distribution is *o*- 29·4, *m*- 8·7, *p*- 62·9%. Even when allowance is made for the relatively inefficient separation of isomers by fractional crystallisation, it appears that the use of ethylene dichloride as solvent affords a mixture in which the *ortho* : *para*-ratio is lower than that found with benzenesulphonyl chloride as solvent. The interaction of mesitylenesulphonyl chloride, aluminium chloride, and anisole provided mesityl 4-methoxyphenyl sulphone together with a small amount of isomeric product, possibly the 2-isomer.

The reaction between equimolecular proportions of *p*-diethylbenzene and benzenesulphonyl chloride–aluminium chloride complex provided mixtures from which crystalline 2,5-diethyldiphenyl sulphone could be isolated in only 25% yield based on the sulphonyl chloride. This yield was increased to 53% by the use of two molecular proportions of *p*-diethylbenzene. In the latter case, investigation of the one molecular proportion of hydrocarbon unconsumed showed that it contained both di- and tri-ethylbenzene. Further, apart from unconsumed hydrocarbon, the crude product consisted of a mixture of sulphones. It therefore appears that *p*-diethylbenzene had isomerised and disproportionated before reacting with the sulphonylating complex. The results obtained when benzenesulphonyl chloride–aluminium chloride complex reacts with *p*-di-n-propylbenzene and with 1,2,4-triethylbenzene may be explained along similar lines. The accepted order of mobility of alkyl groups Me $<$ Et $<$ Pr^n no doubt serves to explain why such complications did not arise in the sulphonylation of methylbenzenes.

EXPERIMENTAL

Preparation of Sulphones.—The following general procedure was employed. To freshly powdered aluminium chloride (1·25 moles), in ethylene dichloride (500 ml.), was added the sulphonyl chloride (1·0 mole). The mixture was kept at room temperature for 30 min. and the clear solution was decanted from undissolved aluminium chloride into a solution of the aromatic hydrocarbon (1·1 moles) in ethylene dichloride (500 ml.). After the selected time, usually overnight, the solution was poured into ice and dilute hydrochloric acid and the mixture was steam-distilled until oily drops no longer passed over. The residual sulphone rapidly crystallised, and was separated. When this procedure failed to provide crystalline sulphone, the mixture was decomposed by ice and dilute hydrochloric acid, and the ethylene dichloride layer was separated and dried after being washed successively with water, dilute sodium hydroxide solution, and water again. The oily sulphone obtained on removal of the solvent, the last traces under reduced pressure, rapidly solidified. The diphenyl sulphones prepared by this general procedure are listed in Table 1. The following new *diphenyl sulphones* were prepared: 3,5-*dimethyl*- (Found: C, 68·2; H, 5·7; S, 12·5. $C_{14}H_{14}O_2S$ requires C, 68·3; H, 5·7; S, 13·0%), 2,4,5-*trimethyl*- (Found: C, 69·2; H, 6·2; S, 12·4. $C_{15}H_{16}O_2S$ requires C, 69·2; H, 6·2; S, 12·3%), 3,4,5-*trimethyl*- (Found: C, 69·3; H, 6·6; S, 12·5%), 2,5-*diethyl*- (Found: C, 69·8; H, 6·4; S, 11·5. $C_{16}H_{18}O_2S$ requires C, 70·1; H, 6·6; S, 11·7%), 2,5-*di-n-propyl*- (Found: C, 71·3; H, 7·3; S, 10·5. $C_{18}H_{22}O_2S$ requires C, 71·5; H, 7·4; S, 10·6%), 2,4,5-*triethyl*- (Found: C, 71·5; H, 7·3; S, 10·7. $C_{18}H_{22}O_6S$ requires C, 71·5; H, 7·4; S, 10·6%), 4′-*methoxy*-2,4,6-*trimethyl*- (Found: C, 66·3; H, 6·0; S, 10·8. $C_{16}H_{18}O_3S$ requires C, 66·3; H, 6·2; S, 11·0%).

Interaction of Benzenesulphonyl Chloride, Aluminium Chloride, and Aromatic Hydrocarbon in Ethylene Dichloride.—p-*Diethylbenzene.* After a reaction time of 4 hr. at room temperature the oily organic product of reaction contained only a trace of benzenesulphonyl chloride and of *p*-diethylbenzene. The whole of the crude sulphone distilled in the range 175—180°/0·3 mm.

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[8] Jensen and H. C. Brown, *J. Amer. Chem. Soc.*, 1958, **80**, 4046.

The distillate, which failed to solidify, was extracted with light petroleum (b. p. 60—80°). On storage at 0°, the extracts deposited 2,5-diethyldiphenyl sulphone (25%; m. p. 84—86°). The remainder of the crude sulphone did not crystallise. When the above experiment was repeated with excess of *p*-diethylbenzene (1·0 mol.), free hydrocarbon (0·9 mol.) was recovered. The latter was distilled through a short column and gave fractions (i) b. p. 64—70°/14 mm., and (ii) b. p. 70—100°/14 mm. Fraction (i) (diethylbenzenes) yielded an oily sulphonamide which could not be separated into pure components. Fraction (ii) was brominated by Norris and Ingram's procedure.[9] The crude bromo-derivatives, after repeated crystallisation from ethanol, afforded a product which did not depress the m. p. of 2,4,6-tribromo-1,3,5-triethylbenzene (m. p. 102—103°). Extraction with light petroleum (b. p. 60—80°) of the crude sulphone from the reaction provided crystalline 2,5-diethyldiphenyl sulphone (53%) and an uncrystallisable oil (34%).

p-*Di-n-propylbenzene.* The reaction of the benzenesulphonyl chloride–aluminium chloride complex (1·0 mol.) and *p*-di-n-propylbenzene (1·0 mol.) gave a crude sulphone from which 2,5-di-n-propyldiphenyl sulphone (25%; m. p. 58—60°) was obtained by extraction with light petroleum (b. p. 60—80°). Doubling the molecular ratio of the hydrocarbon increased the yield of pure sulphone to 53% based on sulphonyl chloride.

Toluene. The crude sulphone (94%; m. p. 86—106°), obtained from benzenesulphonyl chloride and toluene, on fractional crystallisation from benzene–light petroleum (b. p. 60—80°), afforded 4-methyldiphenyl sulphone (74%; m. p. 125—126°) and the 2-isomer (5·5%; m. p. 80—81°). The latter did not depress the m. p. of authentic 2-methyldiphenyl sulphone which was obtained by oxidation of the corresponding sulphide. This sulphide (65%; b. p. 150—152°/8·0 mm.) was obtained from thiophenol and diazotised *o*-toluidine by Ziegler's method.[10]

Interaction of 2,4,6-*Trimethylbenzenesulphonyl Chloride, Aluminium Chloride, and Anisole in Ethylene Dichloride.*—The crude product on crystallisation from ethanol provided both plates and needles. The former (72%) did not depress the m. p. of 4′-methoxy-2,4,6-trimethyldiphenyl sulphone (m. p. 136°). The needles (*ca.* 5%), m. p. 167—169° (Found: C, 65·9; H, 6·2; S, 10·8. $C_{16}H_{18}O_3S$ requires C, 66·3; H, 6·2; S, 11·0%), were an isomeric *sulphone.*

Oxidation of Alkylated Diphenyl Sulphones.—2,5-Dimethyldiphenyl sulphone (1 g.), concentrated nitric acid (10 ml.), and water (15 ml.) were heated in a sealed tube at 160° for 6 hr., affording 2,5-dicarboxydiphenyl sulphone (70%), m. p. 263—264°. By the action of diazomethane the acid was converted into its *dimethyl ester*, m. p. 108—109° (Found: C, 57·0; H, 4·6; S, 9·4. $C_{16}H_{14}O_6S$ requires C, 57·5; H, 4·2; S, 9·6%). This ester was identical with that given by 2,5-diethyl- and 2,5-di-n-propyl-diphenyl sulphone under similar conditions.

3,5-Dimethyl- and 3,4,5-trimethyl-benzenesulphonic acids were obtained by fusion of the 2,5- and 2,4,6-isomers respectively with aluminium chloride at 180°. Details are to be provided in a later paper.

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[9] Norris and Ingram, *J. Amer. Chem. Soc.*, 1938, **60**, 1422.
[10] Ziegler, *Ber.*, 1890, **23**, 2472.