111. *The Use of Phenylmagnesium Bromide for the Preparation of Phenyl Aryl Sulphides, Sulphoxides, and Sulphones.*

By H. Burton and W. A. Davy.

Phenyl aryl sulphides are obtained in moderate yields from diaryl disulphides and phenylmagnesium bromide (I). In agreement with Gilman and Fothergill (*J. Amer. Chem. Soc.*, 1929, **51**, 3501), phenyl aryl sulphones or sulphoxides are formed from arysulphonyl chlorides and (I) according to the experimental conditions; when the arylsulphonyl chloride (*e.g.*, thiophen-2-sulphonyl chloride) is relatively unstable, a preponderating reaction appears to be the formation of diphenyl sulphoxide. The same side-reaction occurs to a very minor extent with the stable *p*-toluenesulphonyl chloride.

THE limited applicability of the usual methods for the synthesis of aryl 2-thienyl sulphones (Burton and Davy, preceding paper) prompted us to explore the possibility of using the Grignard reagent for this purpose, more especially since little work has been reported in this field. We have reported (*loc. cit.*) that phenylmagnesium bromide (I) and 2 : 2'-dithienyl disulphide gave a moderate yield of phenyl 2-thienyl sulphide, and we have found that phenyl *p*-tolyl sulphide is formed in similar yield using di-*p*-tolyl disulphide and (I). Preliminary work using 4 : 4'-dinitrodiphenyl and 4 : 4'-diacetamidodiphenyl disulphides showed that whilst the former reacted vigorously with (I) the product was a black tar (a similar product was obtained also using *p*-nitrobenzenesulphenyl chloride), whereas the diacetamido-compound was recovered unchanged, even when the reaction was carried out in a large volume of anisole to effect solution. *p*-Acetamidobenzenesulphenyl chloride and (I) gave an almost quantitative yield of 4 : 4'-diacetamidodiphenyl disulphide.

The interaction of various arylsulphonyl chlorides with Grignard reagents has been studied chiefly by Hepworth and Clapham (*J.*, 1921, **119**, 1188), Wedekind and Schenk (*Ber.*, 1921, **54**, 1604), and Gilman and Fothergill (*J. Amer. Chem. Soc.*, 1929, **51**, 3501). The last-named authors criticised the findings of the earlier workers and postulated the following reactions to account for the results :

$$
\text{(i)}\quad \text{Ar·SO}_2\text{Cl} + \text{MgPhBr} \longrightarrow \text{Ar·SO}_2\text{Ph} + \text{MgBrCl};
$$
$$
\text{(ii)}\quad \text{Ar·SO}_2\text{Cl} + \text{MgPhBr} \longrightarrow \text{Ar·SO}_2\text{·MgBr} + \text{PhCl};
$$
$$
\text{(iii)}\quad \text{Ar·SO}_2\text{·MgBr} + \text{MgPhBr} \longrightarrow \text{Ar·SOPh} + (\text{MgBr})_2\text{O}.
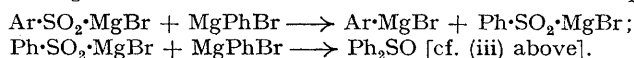$$
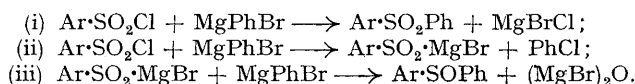
Reactions (i) and (ii) occur in the cold, but in the hot (ii) followed by (iii) takes place. We have confirmed that these changes do occur in the reaction between *p*-toluenesulphonyl chloride and (I); in particular we have shown that phenyl *p*-tolyl sulphoxide is formed from *p*-toluenesulphinic acid and (I). We prefer to postulate reaction (iii) thus :

$$
\text{Ar·SO}_2\text{·MgBr} + \text{MgPhBr} \longrightarrow \text{Ar·SPh(OMgBr)}_2 \longrightarrow \text{Ar·SPh(OH)}_2 \longrightarrow \text{Ar·SOPh} + \text{H}_2\text{O}.
$$

The reactions of *p*-toluenesulphinyl chloride with (I) appear to run parallel with those of the sulphonyl chloride and give phenyl *p*-tolyl sulphoxide and sulphide.

We then decided to explore the possibility of synthesising phenyl 2-thienyl sulphone or sulphoxide by using either thiophen-2-sulphonyl chloride (II) and (I) or, alternatively, 2-thienylmagnesium iodide and benzenesulphonyl chloride. We were finally forced to use (II) since this was the only thiophen derivative we possessed, and we could not obtain a further supply of thiophen. Interaction of (I) and (II) in boiling benzene gave a compound, m. p. 69°, which depressed the m. p. (69—70°) of phenyl 2-thienyl sulphoxide (Burton and Davy, *loc. cit.*) and contained much too little sulphur. In fact, the compound analysed as an impure specimen of diphenyl sulphoxide and did not depress the m. p. (70°) of an authentic specimen of this. The compound, m. p. 69°, was oxidised by hydrogen peroxide to a sulphone, m. p. 124°, which did not depress the m. p. of either phenyl 2-thienyl sulphone or diphenyl sulphone; genuine specimens of these sulphones do not undergo m. p. depression. We have repeated the reaction between (I) and (II) several times; on each occasion a sulphoxide, m. p. 69°, oxidisable to a sulphone, m. p. 124°, was obtained. Analytical data for these compounds, however, showed some degree of divergence but they could all be explained on the assumption that the sulphoxide, m. p. 69°, was diphenyl sulphoxide containing a small amount of phenyl 2-thienyl sulphoxide.

These results led us to examine in further detail the phenyl *p*-tolyl sulphoxide produced from *p*-toluenesulphonyl chloride and (I). Fractional crystallisation of the crude reaction product from ligroin showed the undoubted presence of a very small amount of diphenyl sulphoxide. We suggest that the following reactions would account for the formation of the diphenyl sulphoxide :

$$
\text{Ar·SO}_2\text{·MgBr} + \text{MgPhBr} \longrightarrow \text{Ar·MgBr} + \text{Ph·SO}_2\text{·MgBr};
$$
$$
\text{Ph·SO}_2\text{·MgBr} + \text{MgPhBr} \longrightarrow \text{Ph}_2\text{SO} \text{ [cf. (iii) above].}
$$

It is probable that the relative stability of the sulphonyl chloride (or sulphinic acid) may determine the amount of diphenyl sulphoxide produced in such reactions. It is hoped to present further evidence on this point later.

<p style="text-align:center">EXPERIMENTAL.</p>

*Reaction between Phenylmagnesium Bromide and Di-*p-*tolyl Disulphide.*—Di-*p*-tolyl disulphide (12·3 g.; 0·05 mol.) in benzene (100 c.c.) was added gradually with stirring to ethereal phenylmagnesium bromide (0·15 mol.). The ether was then distilled off, benzene (50 c.c.) added, and the mixture boiled for 22 hours. Decomposition with ice and ammonium chloride, separation of the benzene layer, and extraction with benzene gave, after drying and distillation, two fractions: (i) b. p. 90—100°/20 mm., (ii) up to 180°/20 mm. Fraction (i) solidified when cooled, and crystallisation from alcohol gave colourless plates (1·5 g.), m. p. 43—44°, presumably of thio-*p*-cresol. Fraction (ii) (6·5 g.) was redistilled, b. p. 170—172°/15 mm., and then oxidised with 30% hydrogen peroxide (9·5 c.c.) in acetic acid (20 c.c.) at 100° for 40 minutes; phenyl *p*-tolyl sulphone (6·1 g.), m. p. and mixed m. p. 124—125°, crystallised when the solution was cooled.

Reaction between Phenylmagnesium Bromide and p-*Toluenesulphonyl Chloride.*—(a) *In the cold.* *p*-Toluenesulphonyl chloride (57·3 g.; 0·3 mol.) in ether (200 c.c.) was added slowly with stirring to ethereal phenylmagnesium bromide (0·3 mol.) at − 10° to − 5°. After being stirred for a further 30 minutes at − 5° the mixture was decomposed with cold, dilute hydrochloric acid. The ether layer was separated and the aqueous solution extracted with ether. Dilute sodium hydroxide extracted *p*-toluenesulphinic acid (20·5 g.) from the combined ethereal extracts. The remaining ether-soluble product was steam distilled, yielding chlorobenzene (10 g.), b. p. 45°/30 mm., and diphenyl (7·5 g.) as volatile products, and phenyl *p*-tolyl sulphone (9·6 g.), m. p. and mixed m. p. 125°, as the non-volatile product. *p*-Toluenesulphinic was identified by m. p. and mixed m. p., and chlorobenzene was characterised as its 2 : 4-dinitro-derivative.

(b) *In the hot.* *p*-Toluenesulphonyl chloride (19·1 g.; 0·1 mol.) in benzene (100 c.c.) was added during 1 hour with stirring to cooled ethereal phenylmagnesium bromide (0·3 mol.). The ether was then evaporated, replaced by benzene (100 c.c.), and the mixture refluxed for 22 hours. Decomposition with dilute hydrochloric acid and extraction of the aqueous layer with ether gave a benzene–ether extract which yielded a trace of phenol when extracted with dilute sodium hydroxide. Steam distillation of the residue from this extract gave chlorobenzene (6·7 g.) and diphenyl (6·6 g.) as the volatile products, and left phenyl *p*-tolyl sulphoxide (13·5 g.; 62%), b. p. 205—207°/10 mm., m. p. and mixed m. p. 71—72° after crystallisation from ligroin (b. p. 40—60°).

The sulphoxide was oxidised by 30% hydrogen peroxide in hot acetic acid to phenyl *p*-tolyl sulphone, m. p. and mixed m. p. 124—125°.

Phenyl *p*-tolyl sulphoxide was similarly obtained using benzenesulphonyl chloride and *p*-tolylmagnesium bromide.

Reaction between Phenylmagnesium Bromide and p-*Toluenesulphinic Acid.*—*p*-Toluenesulphinic acid (9·3 g.; 0·06 mol.) in ether (350 c.c.) was added slowly with stirring to cold ethereal phenylmagnesium bromide (0·18 mol.); a colourless solid separated during the addition. Benzene (400 c.c.) was added and the ether evaporated. After refluxing for 19 hours and working up in the usual manner, phenyl *p*-tolyl sulphoxide (6·6 g.; 51%) was obtained. No unchanged sulphinic acid could be isolated.

p-*Toluenesulphinyl Chloride and its Reaction with Phenylmagnesium Bromide.*—Dry *p*-toluenesulphinic acid (12 g.) was treated dropwise with freshly distilled thionyl chloride (15 g.). After the initial effervescence had ceased the mixture was heated on the steam-bath for 15 minutes and the excess of thionyl chloride removed under reduced pressure, first at room temperature and then at 50°. Extraction of the residue with boiling ligroin (b. p. 40—60°) (100 c.c.) and evaporation of the extract under reduced pressure gave an oil (12 g.) which solidified when left in a desiccator. This product gave a positive test for chlorine and was hydrolysed by water to the original sulphinic acid.

The chloride (8·75 g.; 0·05 mol.) in benzene (50 c.c.) was added slowly with stirring to cold ethereal phenylmagnesium bromide (0·15 mol.). A solid was precipitated during mixing but this redissolved on continued stirring. The ether was replaced by benzene (200 c.c.) and the mixture refluxed for 18 hours. Decomposition with ice and ammonium chloride and fractionation of the benzene-soluble product gave diphenyl (0·6 g.), phenyl *p*-tolyl sulphide, b. p. 170—175°/18 mm., and phenyl *p*-tolyl sulphoxide, b. p. 200—210°/18 mm., m. p. 69—70°. Oxidation of the total sulphide and sulphoxide fractions in the usual manner gave 4·2 and 4·5 g., respectively, of phenyl *p*-tolyl sulphone, m. p. and mixed m. p. 124—125°.

Reaction between Phenylmagnesium Bromide and Thiophen-2-sulphonyl Chloride.—Thiophen-2-sulphonyl chloride (9·1 g.; 0·05 mol.) in benzene (75 c.c.) was added slowly with stirring to cold, ethereal phenylmagnesium bromide (0·15 mol). After replacement of the ether by benzene (75 c.c.) the mixture was refluxed for 22 hours and then decomposed with ice and ammonium chloride. The dried benzene extract yielded an oil which gave the following fractions : (i) b. p. 140—150°/20 mm., m. p. and mixed m. p. 70°, consisting of diphenyl (1·1 g.), (ii) b. p. 200—205°/20 mm. Fraction (ii) solidified when cooled, and crystallised from ligroin (b. p. 40—60°) in colourless plates (3·0 g.), m. p. 69° (Found : C, 70·9; H, 5·0; S, 17·3. Calc. for $C_{10}H_8OS_2$: C, 57·7; H, 3·8; S, 30·8%. Calc. for $C_{12}H_{10}OS$: C, 71·3; H, 5·0; S, 15·8%), which depressed the m. p. of phenyl 2-thienyl sulphoxide but not that of diphenyl sulphoxide.

Another experiment gave the compound, m. p. 69° (Found : C, 70·3; H, 5·0; S, 17·2%).

Oxidation of the above " sulphoxide " (3·0 g.) with 30% hydrogen peroxide (2 c.c.) in hot acetic acid (5 c.c.) gave, on cooling, the sulphone which crystallised from aqueous alcohol in colourless plates, m. p. 124° (2·9 g.) (Found : C, 61·6; H, 4·4; S, 19·1. Calc. for $C_{10}H_8O_2S_2$: C, 53·6; H, 3·6; S, 28·6%. Calc. for $C_{12}H_{10}O_2S_2$: C, 66·1; H, 4·6; S, 14·7%), unchanged by admixture with either phenyl 2-thienyl sulphone or diphenyl sulphone.

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