Reaction of Toluene-*p*-sulphonyl Iodide with Free Phenyl Radicals [1]
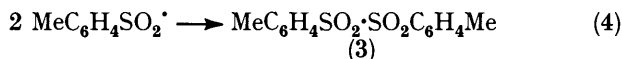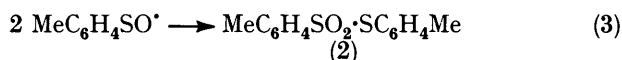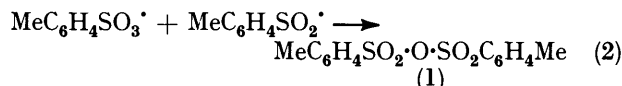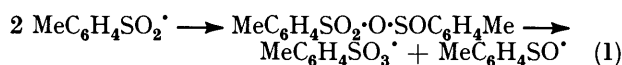
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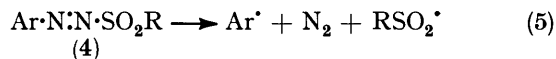
Trapping of phenyl radicals produced by thermal decomposition of phenylazo *p*-tolyl sulphone (4a) by toluene-*p*-sulphonyl iodide is an effective way to generate toluene-*p*-sulphonyl radicals uncomplicated by the presence of phenyl radicals.

THE formation of free sulphonyl radicals from sulphonyl halides was proposed some years ago as the result of studies concerning its addition to unsaturated compounds.[2] The copper-promoted decomposition of toluene-*p*-sulphonyl iodide and bromide in aprotic solvents (carbon tetrachloride and benzene), that was studied by Corrêa and Waters [3] and yields toluene-*p*-sulphonic anhydride (1), *S*-*p*-tolyl toluene-*p*-thiosulphonate (2), and small amounts of the expected dimer, di-*p*-tolyl disulphone (3), provides a convenient way to generate aryl sulphonyl radicals and to study their chemistry uncomplicated by that of other radicals produced by homolysis of the sulphur–halogen bond.[4]

We have now been able to show that sulphonyl radicals, produced from toluene-*p*-sulphonyl iodide and phenyl radicals, yield similar amounts of disproportionation and dimerization products, and the addition of sulphonyl radicals to benzene is not important [equations (1)—(4)].
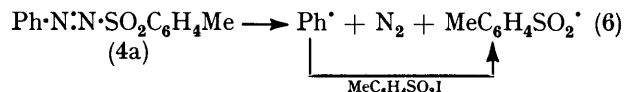
$$2 \text{ MeC}_6\text{H}_4\text{SO}_2{}^{\bullet} \longrightarrow \text{MeC}_6\text{H}_4\text{SO}_2{\cdot}\text{O}{\cdot}\text{SOC}_6\text{H}_4\text{Me} \longrightarrow$$
$$\text{MeC}_6\text{H}_4\text{SO}_3{}^{\bullet} + \text{MeC}_6\text{H}_4\text{SO}^{\bullet} \quad (1)$$

$$\text{MeC}_6\text{H}_4\text{SO}_3{}^{\bullet} + \text{MeC}_6\text{H}_4\text{SO}_2{}^{\bullet} \longrightarrow$$
$$\text{MeC}_6\text{H}_4\text{SO}_2{\cdot}\text{O}{\cdot}\text{SO}_2\text{C}_6\text{H}_4\text{Me} \quad (2)$$
$$(1)$$

$$2 \text{ MeC}_6\text{H}_4\text{SO}^{\bullet} \longrightarrow \text{MeC}_6\text{H}_4\text{SO}_2{\cdot}\text{SC}_6\text{H}_4\text{Me} \quad (3)$$
$$(2)$$

$$2 \text{ MeC}_6\text{H}_4\text{SO}_2{}^{\bullet} \longrightarrow \text{MeC}_6\text{H}_4\text{SO}_2{\cdot}\text{SO}_2\text{C}_6\text{H}_4\text{Me} \quad (4)$$
$$(3)$$

Reaction of Phenylazo p-*Tolyl Sulphone with Toluene-* p-*sulphonyl Iodide.*—Although arylazo *R*-sulphones (4) may be decomposed under free radical conditions (in the presence of MgO and pyridine) to yield sulphonyl radicals [5] complications arise from the presence of aryl radicals (equation 5). Reported products from the

$$\text{Ar}{\cdot}\text{N}\!\!:\!\!\text{N}{\cdot}\text{SO}_2\text{R} \longrightarrow \text{Ar}^{\bullet} + \text{N}_2 + \text{RSO}_2{}^{\bullet} \quad (5)$$
$$(4)$$

decomposition of (4) under free radical conditions do not include sulphonic anhydrides, $(\text{RSO}_2)_2\text{O}$, although sulphonic acids and aryl sulphonic esters (RSO_3H and RSO_3Ar) have been isolated.

In our work we have found that in the thermal decomposition of phenylazo *p*-tolyl sulphone (4a) in presence of toluene-*p*-sulphonyl iodide (plus magnesium oxide or pyridine) (equation 6) most of the phenyl radicals are involved in abstracting iodine from the sulphonyl iodide, the attack on the solvent (benzene and carbon tetrachloride) being a very secondary

reaction. An increase in the concentration of sulphonyl radicals leads to formation of the disproportionation and dimerization products (1)—(3).

$$\underset{(4a)}{\text{Ph}{\cdot}\text{N}\!\!:\!\!\text{N}{\cdot}\text{SO}_2\text{C}_6\text{H}_4\text{Me}} \longrightarrow \text{Ph}^{\bullet} + \text{N}_2 + \text{MeC}_6\text{H}_4\text{SO}_2{}^{\bullet} \quad (6)$$

$$\underset{\text{MeC}_6\text{H}_4\text{SO}_2\text{I}}{\vert\text{———————}\uparrow}$$

The results of the experiments are summarized in the Table.

Products of the thermal reaction of $\text{MeC}_6\text{H}_4\text{SO}_2\text{I}$ with Ph·N꞉N·SO$_2$C$_6$H$_4$Me (molar ratio 1 : 1) in boiling carbon tetrachloride and boiling benzene

| | In CCl$_4$ | | | In C$_6$H$_6$ |
Reaction products	1*st* expt. (MgO)	2*nd* expt. (MgO)	3*rd* expt. (Pyridine)	4*th* expt. (MgO)
% Yields based on Ph$^{\bullet}$				
PhCl	2	2	2	
PhI	55	50	36	78
Ph·Ph	0	0	0	2
% Yields based on TolSO$_2{}^{\bullet}$				
MeC$_6$H$_4$SO$_2$Cl	4	7	4	
MeC$_6$H$_4$SO$_2$Ph		1	3	2
MeC$_6$H$_4$SO$_3$Ph	8	8	10	3
MeC$_6$H$_4$SO$_2$·SC$_6$H$_4$Me		10	10	17
MeC$_6$H$_4$SO$_2$·SO$_2$C$_6$H$_4$Me	4	1		2
MeC$_6$H$_4$SO$_2$·O·SO$_2$C$_6$H$_4$Me		15	22	17
MeC$_6$H$_4$SO$_3{}^-$	18	6		10

MeC$_6$H$_4$SO$_2{}^-$, Ph·N꞉N·Ph, MeC$_6$H$_4$S·SC$_6$H$_4$Me, and MeC$_6$H$_4$·Ph were not detected in the reaction mixture.

Most of the phenyl *p*-tolyl sulphone formed must come from cage combination of phenyl and toluene-*p*-sulphonyl radicals, since the yield of sulphone is approximately the same whether the reaction is carried out in benzene or carbon tetrachloride.

The presence of phenyl toluene-*p*-sulphonate is not the result of addition of toluene-*p*-sulphonyloxy radicals to benzene, since its yield is not increased when the solvent is changed from carbon tetrachloride to benzene. In accordance with this, sulphonate is not formed when toluene-*p*-sulphonyl iodide is decomposed in benzene.

Toluene-*p*-sulphonic acid (in the sulphonate form) may be formed from the reaction of toluene-*p*-sulphonic anhydride with magnesium oxide, but the yield of sulphonate anion is not increased when the reaction is carried out in benzene, showing that abstraction of hydrogen from radicals of the type $\text{RC}_6\text{H}_6{}^{\bullet}$ must here be

$$\text{RC}_6\text{H}_6{}^{\bullet} + \text{MeC}_6\text{H}_4\text{SO}_3{}^{\bullet} \longrightarrow$$
$$\text{RC}_6\text{H}_5 + \text{MeC}_6\text{H}_4\text{SO}_3\text{H} \quad (7)$$
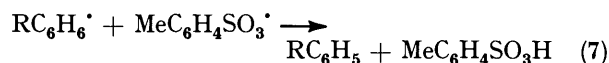
unimportant (equation 7) although sulphonyloxy radicals are very effective hydrogen abstractors.[6]

In carbon tetrachloride, toluene-*p*-sulphonyl chloride was isolated. This means that toluene-*p*-sulphonyl radicals are reactive enough to abstract chlorine from the solvent.

EXPERIMENTAL

General Procedures.—(a) *Reaction in carbon tetrachloride.* In a typical experiment toluene-*p*-sulphonyl iodide [7] (7.61 g, 27.0 mmol) and phenylazo *p*-tolyl sulphone [8] (7.02 g, 27.0 mmol) in carbon tetrachloride (60 cm³) were stirred with magnesium oxide (6.0 g, 150 mmol) for 48 h at reflux temperature under nitrogen. The hot mixture was filtered and the solid (MgO) was extracted with hot benzene (Soxhlet) and then water. The benzene extract gave 0.20 g of di-*p*-tolyl disulphone, m.p. 192—195° (lit.,[9] 220—221°); the aqueous extract, when treated with *S*-benzylisothiouronium chloride, gave 3.2 g of the corresponding toluene-*p*-sulphonate, m.p. 181—182° (lit.,[10] 182°).

The carbon tetrachloride filtrate, on storage at 0 °C, deposited crystals of toluene-*p*-sulphonic anhydride (2.14 g), m.p. 99—101° (lit.,[11] 128—129.5°). All compounds were characterized by comparison of their i.r. and n.m.r. spectra with those of authentic specimens.

Part of the carbon tetrachloride filtrate, on column and thin layer chromatography (t.l.c.) (as described later), gave iodobenzene (5), phenyl *p*-tolyl sulphone (6), *S*-*p*-tolyl toluene-*p*-thiosulphonate (2), and phenyl toluene-*p*-sulphonate (7), all characterized by comparison of their i.r. and n.m.r. spectra, g.l.c. retention times, and t.l.c. R_F values with those of authentic samples.

Toluene-*p*-sulphonyl chloride (8) was isolated by g.l.c. (nitrogen flow rate 250 cm³ min⁻¹) using a Varian–Aerograph chromatograph, model 1740 (serial 1700) equipped with an effluent splitter and microsample collector and a 5% SE-30 column (3 m × 3/8 in) on Chromosorb (60—80 mesh, acid washed) at 170 °C. Retention time was 2.5 min.

Yields of compounds (2), (5), (6), (7), and (8) were determined by quantitative g.l.c. analysis using *p*-bromochlorobenzene as internal standard, as described later.

(b) *Reaction in benzene.* Phenylazo *p*-tolyl sulphone (11.0 g, 42.3 mmol), toluene-*p*-sulphonyl iodide (12.0 g, 42.5 mmol), and magnesium oxide (9.5 g, 238 mmol) in benzene (80 cm³) were allowed to react for 24 h as described above. The reaction mixture was cooled (ice) and filtered. The solid (MgO) was extracted with hot benzene (Soxhlet) and then water. The benzene extract gave 0.40 g of di-*p*-tolyl disulphone; the aqueous extract gave 1.50 g of toluene-*p*-sulphonate anion. Extraction with sodium hydrogen carbonate gave no sulphinate anion.

The benzene filtrate was diluted to 100 cm³ and a portion (5.0 cm³) treated with aniline (1 cm³) when phenyl-ammonium toluene-*p*-sulphonate (0.17 g), m.p. 222—225° (lit.,[12] m.p. 216—223°), separated out [corresponding to a total yield of 4.60 g of toluene-*p*-sulphonic anhydride (1)]; 20.0 cm³ were evaporated under reduced pressure and the residue was extracted with light petroleum (b.p. 60—80 °C) (10 cm³). The extract was passed through Kieselgel G-60 (50 g; Merck); elution with light petroleum gave a mixture of iodobenzene and biphenyl (9). This fraction, passed again through Kieselgel, gave *ca.* 1 cm³ of pure iodobenzene. Part of the benzene filtrate (10.0 cm³) was analysed by quantitative g.l.c., as described later.

(c) *Reaction in the presence of pyridine.* The reaction was conducted in a similar manner to reaction (a), but using pyridine (8.0 cm³) instead of magnesium oxide. The reaction mixture was cooled; on storage at 0 °C a brown hygroscopic solid was deposited; this was dissolved in water and treated with *S*-benzylisothioronium chloride (10) to give 3.60 g of the corresponding toluene-*p*-sulphonate [equivalent to 3.85 g of anhydride (1)]. In a blank experiment toluene-*p*-sulphonic anhydride (0.50 g) in benzene (10 cm³) reacted with pyridine to give an identical hygroscopic solid that when treated with (10) similarly gave the sulphonate derivative.

The carbon tetrachloride filtrate of the reaction mixture was washed with 5% hydrochloric acid, water, 10% aqueous sodium thiosulphate, and again water. After drying (CaCl₂) the solution was diluted to 100.0 cm³ and analysed by g.l.c. (as described later).

Separation of Compounds (2), (5), (6), (7), *and* (8).—The carbon tetrachloride filtrate (75 cm³) from (a) was passed through aluminium oxide (100 g) (May and Baker) and eluted with CCl₄ (450 cm³; fractions 1—22), C₆H₆ (350 cm³; 23—40); C₆H₆–CHCl₃ (2:1) (100 cm³; 41—44). CHCl₃ (200 cm³; 45—53), and MeOH (200 cm³; 54—63). Fractions 1—4 gave 0.90 g of iodobenzene (b.p. 188°; lit.,[13] 185—190°). Fractions 9—11 were evaporated under reduced pressure. To the combined residue a little ethanol was added. Upon cooling 0.62 g of white solid were obtained which was identified as a mixture of compounds (7) (0.28 g) and (2) (0.34 g). Fractions 17—26 were treated similarly and gave 0.03 g of *S*-*p*-tolyl toluene-*p*-thiosulphonate (2), m.p. 75° (lit.,[14] 76°). Fractions 29—40 gave a small amount of solid that appeared to be phenyl *p*-tolyl sulphone (6) with *S*-*p*-tolyl toluene-*p*-thiosulphonate (2) (i.r., spectrum and g.l.c. and t.l.c.). After crystallization from CCl₄ (1 cm³) the compound was identified as the sulphone (6), m.p. 125—126° (lit.,[15] 126—126.5°).

Quantitative G.l.c. Analysis.—Yields of compounds (2), (5), (6), (7), (8), and (9) from reactions (a), (b), and (c) were determined by g.l.c. analysis (Varian–Aerograph chromatograph, model 1740, serial 1700, equipped with hydrogen flame ionization detectors and coupled to a Varian–Aerograph digital integrator, model 477, with a Victor Heavy Duty Printer). Nitrogen flow rate was 16 cm³ min⁻¹; the column (1.5 m × ⅛ in) was packed with 3% SE-30 on Chromosorb W (100—120 mesh; acid washed). The temperature was linearly programmed (70—200°; 10° min⁻¹). Retention times (min) were: PhCl 1.4; PhI 3.3; MeC₆H₄SO₂Cl 8.5; MeC₆H₄SO₃Ph 15.8; MeC₆H₄SO₂Ph 17.1; MeC₆H₄SO₂·SC₆H₄Me 24.0. *p*-Bromochlorobenzene was used as internal standard.

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