Reaction of Arenesulphonyl Halides with Free Radicals. Part 2[1]

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The generation of arenesulphonyl radicals by halogen abstraction from arenesulphonyl bromides and iodides is described. The relative reactivities of halogen abstraction by phenyl, 1-cyano-1-methylethyl, and benzyl radicals in benzene solution at 60° are reported. These relative reactivities are almost independent of the nature of the substituents on the benzene ring of $ArSO_2Br$. Sulphonyl iodides are more reactive towards phenyl radicals than bromides which in turn are more reactive than the corresponding chlorides (relative reactivities 602 : 192 : 1).

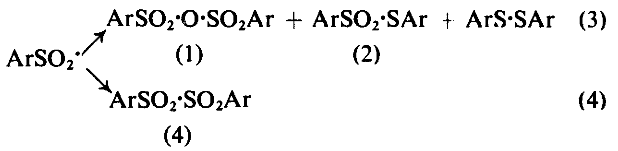
The relative reactivities of addition of arenesulphonyl iodides to substituted styrenes (M)[2] and substituted phenylacetylenes[3] have been measured for competition reactions by assuming the displacement process (2) to be very fast compared with the addition process (1). The present work was

$$ArSO_2^{\cdot} + M \longrightarrow ArSO_2{\cdot}M^{\cdot} \qquad (1)$$

$$ArSO_2{\cdot}M^{\cdot} + ArSO_2I \longrightarrow ArSO_2{\cdot}M.I + ArSO_2^{\cdot} \qquad (2)$$

carried out in order to study the effects of arenesulphonyl radical substituents on the rate of the displacement process (2).

The generation of sulphonyl radicals by halogen abstraction from sulphonyl halides has been performed with phenyl,[1] 1-cyano-1-methylethyl,[4] and triethylsilyl[5] free radicals. Arenesulphonyl radicals generated by several methods [1,4,6] in aprotic solvents (carbon tetrachloride and benzene) react to yield chiefly products of disproportionation (1)—(3) and only small amounts of dimer (4).



$$ArSO_2^{\cdot} \nearrow \underset{(1)}{ArSO_2{\cdot}O{\cdot}SO_2Ar} + \underset{(2)}{ArSO_2{\cdot}SAr} + ArS{\cdot}SAr \qquad (3)$$

$$ArSO_2^{\cdot} \searrow \underset{(4)}{ArSO_2{\cdot}SO_2Ar} \qquad (4)$$

The fact that the relative reactivities of addition of *p*-substituted arenesulphonyl radicals to *p*-methylstyrene and styrene, measured at 0°,[7] are hardly affected by the nature of the substituent (and are almost the same as in the case of $MeSO_2^{\cdot}$) was interpreted[7] as an indication of the very small delocalization of the unpaired electron over the aromatic ring. The rate constants of chlorine abstraction from arenesulphonyl chlorides by copper(I) chloride at 110° [equation (5)] are strongly affected by the nature of the substituent present in $ZC_6H_4SO_2Cl$.[8] The Hammett equation holds very

$$ZC_6H_4SO_2Cl + CuCl \longrightarrow ZC_6H_4SO_2^{\cdot} + CuCl_2 \qquad (5)$$

well for this type of reaction to give ρ^+ values of 0.565. The results are explained[8] in terms of polar effects, since 'substituents cannot be expected to exert an appreciable stabilizing influence on the resulting sulphonyl radical, in view of the poor conjugation of the sulphonyl group with the benzene ring.'[8]

The study of the relative reactivities of the addition of arenesulphonyl iodides to substituted styrenes[2] has led to ρ^+ values which are affected by the nature of the substituent in the sulphonyl radical ring (ρ^+ changes from -0.35 to -0.88 when the substituent changes from *p*-methoxy to *m*-nitro).

We have now started an analysis of the reaction of arenesulphonyl halides with free radicals, by studying the reaction products and relative rates of halogen abstraction from ring-substituted arenesulphonyl halides. In this paper we report the results of the reaction of phenyl and benzoyloxyl radicals with toluene-*p*-sulphonyl halides and the values of the relative reactivities of halogen abstraction from arenesulphonyl halides by phenyl, 2-cyano-1-methylethyl, and benzyl radicals. Radicals have been generated by thermal decomposition of phenylazotriphenylmethane (PAT), phenylazo *p*-tolyl sulphone, benzoyl peroxide, azobisisobutyronitrile (AIBN), and t-butyl phenylperacetate.

Results and Discussion

*Reaction of Phenylazotriphenylmethane (PAT) with Toluene-*p*-sulphonyl Halides (Bromides and Iodides).*—Phenyl radicals produced by thermal decomposition of PAT, in boiling carbon tetrachloride, react with arenesulphonyl halides (bromides and iodides) by abstracting halogen atoms and so producing arenesulphonyl radicals [equation (7)]. Most of the phenyl radicals are involved in halogen abstraction. Although sulphonyl radicals yield disproportionation products [equation (8)] they react in good yield (30—40%) with triphenylmethyl radicals [equation (9)] yielding a cross-combination product, *p*-tolyl triphenylmethyl sulphone. No products of combination of $ArSO_2^{\cdot}$ (and $ArSO_3^{\cdot}$) radicals with $Ph^{\cdot}$ could be detected.

$$Ph{\cdot}N_2{\cdot}CPh_3 \xrightarrow{\Delta} Ph^{\cdot} + N_2 + Ph_3C^{\cdot} \qquad (6)$$

$$Ph^{\cdot} + ArSO_2X \longrightarrow PhX + ArSO_2^{\cdot} \qquad (7)$$

$$ArSO_2^{\cdot} \longrightarrow ArSO_2{\cdot}O{\cdot}SO_2Ar + ArSO_2{\cdot}SAr \qquad (8)$$

$$Ph_3C^{\cdot} + ArSO_2^{\cdot} \longrightarrow Ph_3C{\cdot}SO_2Ar \qquad (9)$$

$$ArSO_2^{\cdot} + CCl_4 \longrightarrow ArSO_2Cl + CCl_3^{\cdot} \qquad (10)$$

$$Ph^{\cdot} + CCl_4 \longrightarrow PhCl + CCl_3^{\cdot} \qquad (11)$$

$$Ph^{\cdot} + Ph_3C^{\cdot} \longrightarrow Ph_4C + \ldots \qquad (12)$$

$$Ar = p\text{-}MeC_6H_4$$

Chlorine abstraction by phenyl [equation (11)] and toluene-*p*-sulphonyl radicals [equation (10)] from the solvent (CCl_4) also occurred since $MeC_6H_4SO_2Cl$ and PhCl were formed. The combination of phenyl and triphenyl radicals [equation (12)] could be detected but the yield of tetraphenylmethane and similar products was not determined; it was quite small. No products containing the trichloromethyl group could be detected in the reaction mixtures. The results are summarized in Table 1.

Table 1. Products of the thermal reaction of PAT with $MeC_6H_4SO_2X$ (molar ratio 1 : 2) in boiling CCl_4 under N_2

Reaction product	Reaction with $MeC_6H_4SO_2Br$	Reaction with $MeC_6H_4SO_2I$
	Yield (%) based on PAT	
PhCl	6	1
PhBr	67	
PhI		82
$MeC_6H_4SO_2{\cdot}CPh_3$	56	78
	Yield (%) based on $MeC_6H_4SO_2I$	
$MeC_6H_4SO_2Cl$	<2	<2
$MeC_6H_4SO_2{\cdot}SC_6H_4Me$	6	9
$MeC_6H_4SO_2{\cdot}SO_2C_6H_4Me$	0	0
$MeC_6H_4SO_2{\cdot}O{\cdot}SO_2C_6H_4Me$	0	8
$MeC_6H_4SO_2{\cdot}CPh_3$	28	39

Table 2. Products of the thermal reaction of $MeC_6H_4SO_2I$ with $(PhCO_2)_2$ (molar ratio 1 : 1) in boiling benzene in the presence of O_2

Reaction product	First expt.	Second expt.
	Yield (%) based on $MeC_6H_4SO_2I$	
$MeC_6H_4SO_2{\cdot}O{\cdot}SO_2C_6H_4Me$	20	22
$MeC_6H_4SO_2{\cdot}SC_6H_4Me$		1
$MeC_6H_4SO_2{\cdot}SO_2C_6H_4Me$		1
$MeC_6H_4SO_3Ph$	0	0
$MeC_6H_4SO_2Ph$	8	1
$MeC_6H_4SO_3^-$	1	1
	Yield (%) based on $(PhCO_2)_2$	
PhI	28	42
Ph·Ph	0	0
$PhCO_2H$	40	39
$PhCO_2Ph$	32	38

*Decomposition of Benzoyl Peroxide in the Presence of Toluene-*p*-sulphonyl Iodide.*—The decomposition of benzoyl peroxide in aromatic solvents in the presence of iodine led to products in which the benzoyloxy-group remains intact in relatively high yields. It was demonstrated by Hammond[9] that the reaction of benzoyloxyl radicals with iodine is fast enough to prevent reaction with the solvent or decarboxylation in the primary process of thermal decomposition of the peroxide. In benzene solution, in the presence of iodine, the only products of the decomposition were iodobenzene, benzoic acid, phenyl benzoate, and carbon dioxide. It was suggested the formation of benzoyl hypoiodite which reacted very rapidly with benzene in non-radical reactions catalysed by iodine, yielding $PhCO_2H$ and $PhCO_2Ph$.

We have now studied the products of thermal decomposition of benzoyl peroxide in benzene solution in the presence of toluene-*p*-sulphonyl iodide and oxygen (air not excluded). The reaction of phenyl radicals with the solvent was completely suppressed (no biphenyl was detected) and the usual disproportionation and dimerization products (1)—(4) of arenesulphonyl radicals were isolated. The other products of reaction were iodobenzene, benzoic acid, phenyl benzoate, toluene-*p*-sulphonic acid, and phenyl *p*-tolyl sulphone. The results are summarized in Table 2.

When the reaction was carried out with a larger excess of solvent (benzene), the yield of $MeC_6H_4SO_2Ph$ decreased. This shows that the sulphone was not formed by reaction with the solvent. The improved yield of PhI was the result of improved analytical conditions (see Experimental section).

The results show that, as in the presence of iodine, no significant decarboxylation occurs in the presence of $MeC_6H_4SO_2I$. This may be the result of iodine abstraction from the sulphonyl iodide [equation (13)] or from molecular iodine [equation (16)]. In any case, the presence of toluene-*p*-sulphonyl iodide causes a dramatic change in the reaction products of the decomposition of benzoyl peroxide in benzene, as illustrated in Table 3.

$$PhCO_2^{\cdot} + MeC_6H_4SO_2I \longrightarrow PhCO_2I + MeC_6H_4SO_2^{\cdot} \quad (13)$$

$$MeC_6H_4SO_2I \longrightarrow MeC_6H_4SO_2^{\cdot} + I^{\cdot} \quad (14)$$

$$2\,I^{\cdot} \longrightarrow I_2 \quad (15)$$

$$PhCO_2^{\cdot} + I_2 \longrightarrow PhCO_2I + I^{\cdot} \quad (16)$$

The formation of disproportionation and dimerization products ($MeC_6H_4SO_2{\cdot}O{\cdot}SO_2C_6H_4Me$, $MeC_6H_4SO_2{\cdot}SC_6H_4Me$, and $MeC_6H_4SO_2{\cdot}SO_2C_6H_4Me$) is a good indication of formation of toluene-*p*-sulphonyl radicals, $MeC_6H_4SO_2^{\cdot}$. Iodobenzene may arise from the decomposition of benzoyl hypoiodite, since its yield is much smaller than that obtained when phenyl radicals were generated directly in solution by decomposition of PAT (see Tables 1 and 2).

Relative Reactivities of Arenesulphonyl Halides towards Free Radicals.—The relative reactivities were measured by competition experiments based on reactions (17) and (18) (where

$$YC_6H_4SO_2X + R^{\cdot} \xrightarrow{k} RX + YC_6H_4SO_2^{\cdot} \quad (17)$$

$$MeC_6H_4SO_2I + R^{\cdot} \xrightarrow{k_I} RI + MeC_6H_4SO_2^{\cdot} \quad (18)$$

$R = Ph^{\cdot}$, $Me_2\dot{C}CN$, or $Ph{\cdot}CH_2^{\cdot}$; X = Br or Cl) by using equation (19). The concentrations [RX] and [RI] were measured by g.l.c.

$$k/k_I = \log(1-[RX]/[ArSO_2X]_0)/\log(1-[RI]/[ArSO_2I]_0) \quad (19)$$

Toluene-*p*-sulphonyl iodide is about three times as reactive as the corresponding bromide and the bromide is *ca.* 200 times as reactive as the corresponding chloride (see Table 4). This is the result of the relative strength of sulphur–halogen bonds.

The relative reactivities are very similar when the same sulphur–halogen bond is broken independently of the nature of the substituent present in the aromatic sulphonyl halide ring (see Table 4).

Although phenyl radicals are quite insensitive to polar effects in hydrogen abstraction from substituted toluenes,[10] important polar effects have been found for iodine abstraction from substituted iodobenzenes,[11] aliphatic iodides,[12] bridgehead iodides,[13] and heterocyclic iodides.[14]

Experiments with the more selective 1-cyano-1-methylethyl radical generated by thermal decomposition of AIBN at 70° in benzene solution also demonstrated similar and non-regular relative reactivities when the substituents in the $ArSO_2Br$ ring were changed (see Table 5).

Benzyl radicals (generated by thermal decomposition of t-butyl phenylperacetate at 70° in benzene solution) behave similarly. The sulphonyl iodide could not be used in the presence of the perester since iodine was rapidly formed when the reactants were mixed. Chlorotriphenylmethane was used as reference compound for the competition reactions (20)

Table 3. Effect of the presence of iodine and $MeC_6H_4SO_2I$ on the decomposition of $(PhCO_2)_2$

	Yield (%) based on $(PhCO_2)_2$			
Reaction	Ph·Ph	$PhCO_2Ph$	$PhCO_2H$	PhI
$(PhCO_2)_2 + C_6H_6$ [a]	130	0	47	
$(PhCO_2)_2 + C_6H_6 + I_2$ [b]	0	58	16	39
$(PhCO_2)_2 + C_6H_6 + I_2$ [c]	0	41	106	33
$(PhCO_2)_2 + C_6H_6 + MeC_6H_4SO_2I$ [d]	0	32—38	39—40	28—42

[a] Peroxide (10.2 mmol) in benzene (50 cm^3) for 22.5 h. [b] Peroxide (10.2 mmol) in boiling benzene (50 cm^3) in the presence of iodine (10.2 mmol) for 13 h. [c] Peroxide (78 mmol) in benzene (245 cm^3) at 79° in the presence of iodine (78 mmol) for 33 h.[9] [d] Peroxide (10.8—17.1 mmol) in boiling benzene (75 cm^3) in the presence of $MeC_6H_4SO_2I$ (21.1—34.0 mmol) for 17—19 h.

Table 4. Relative reactivities of halogen abstraction from arenesulphonyl halides by Ph· radicals in benzene at 60°

	Ph· from PAT			Ph· from $Ph{\cdot}N_2{\cdot}SO_2C_6H_4Me$		
$YC_6H_4SO_2X$	Relative reactivity	Standard deviation	Runs	Relative reactivity	Standard deviation	Runs
X = I, Y = *p*-Me	1			1		
X = Br, Y = *p*-Me	0.35	0.02 (6%)	9	0.32	0.02 (6%)	8
X = Br, Y = H	0.35	0.01 (3%)	9	0.32	0.02 (6%)	8
X = Br, Y = *p*-Cl	0.36	0.009 (3%)	9	0.33	0.01 (3%)	8
X = Br, Y = *p*-MeO	0.33	0.007 (3%)	9	0.30	0.01 (3%)	8
X = Cl, Y = *p*-Me	1					
X = Br, Y = *p*-Me	192	27 (14%)	5			
X = I, Y = *p*-Me	602	130 (22%)	6			

Table 5. Relative reactivities of halogen abstraction from arenesulphonyl bromides by $Me_2\dot{C}CN$ and $PhCH_2{\cdot}$ radicals in benzene at 70°

	Reaction with $Me_2\dot{C}CN$			Reaction with $PhCH_2{\cdot}$		
Y in $YC_6H_4SO_2Br$	k/k_I [a]	Standard deviation	Runs	k/k_{Cl} [b]	Standard deviation	Runs
p-MeO	0.13	0.03 (22%)	10	29.2	5.3 (18%)	9
p-Me	0.15	0.01 (7%)	7			
H	0.08	0.01 (12%)	6			
p-Cl	0.11	0.02 (18%)	12	23.0	4.1 (18%)	7
m-NO_2				19.8	3.5 (18%)	9

[a] $ArSO_2Br$ and $MeC_6H_4SO_2I$ in competition. [b] $ArSO_2Br$ and Ph_3CCl in competition.

and (21). The relative reactivities were determined by equation

$$ArSO_2Br + PhCH_2{\cdot} \xrightarrow{k} ArSO_2{\cdot} + PhCH_2Br \quad (20)$$

$$Ph_3CCl + PhCH_2{\cdot} \xrightarrow{k_{Cl}} Ph_3C{\cdot} + PhCH_2Cl \quad (21)$$

(22). The concentrations of $PhCH_2Br$ and $PhCH_2Cl$ were

$$k/k_{Cl} = \log(1-[PhCH_2Br]/[ArSO_2Br]_0)/(1-[PhCH_2Cl]/[Ph_3CCl]_0) \quad (22)$$

determined by g.l.c. The results are summarized in Table 5.

The absence of an effect on the relative reactivities when the substituent of the ring is changed may result from a very fast displacement reaction (23), where the ' early ' transition state

$$YC_6H_4SO_2Br + R{\cdot} \longrightarrow \left[YC_6H_4\overset{\delta\cdot}{S}O_2 \cdots \overset{(1-\delta)\cdot}{Br} \cdots R\right]^{\ddagger} \longrightarrow YC_6H_4SO_2{\cdot} + BrR \quad (23)$$

has very little developed radical character. The σ-character of arenesulphonyl radicals [15] may also contribute to the absence of interaction between the substituent Y and the unpaired electron which is associated with sulphur in the transition state. Under these circumstances, the strength of the S–Br bond is not affected by resonance stabilization of the incipient radical.

Although the strength of the S–Br bond may be increased by electron-withdrawing substituents in the ring (retarding the abstraction reaction), polar effects may neutralize bond strength effects since electron-withdrawing substituents Y should assist reaction (24). All these facts are consistent with

$$\overset{\longleftarrow\!\!+}{Y{-}C}_6H_4{-}SO_2Br + R{\cdot} \longrightarrow \left[\overset{\longleftarrow\!\!+}{Y{-}C}_6H_4SO_2 \cdots \overset{\longleftarrow\!\!+}{Br \cdots R}\right] \longrightarrow \text{Products} \quad (24)$$

a very fast transfer reaction.

Experimental

Materials.—PAT was prepared by oxidation of the corresponding hydrazine [16] in benzene for 24 h. Toluene-*p*-sulphonyl iodide (and bromide) was prepared from the corresponding sodium sulphinate and iodine (or bromine) [17] in aqueous media. Other arenesulphonyl bromides were prepared from a stirred suspension of the corresponding sodium sulphinate in benzene.[18] Azobisisobutyronitrile (B.D.H.) was recrystallized from benzene. t-Butyl phenylperacetate was obtained [19] from phenylacetyl chloride [20] and t-butyl hydroperoxide.[21] Benzoyl peroxide (B.D.H.) was purified by cold recrystallization from $CHCl_3$–MeOH.[22] Toluene-*p*-sulphonyl chloride (B.D.H.) and chlorotriphenylmethane [23] were recrystallized from light petroleum (b.p. 60—80°). Carbon tetrachloride (B.D.H.) was washed with H_2SO_4, dried ($CaCl_2$), and distilled. Benzene (B.D.H., AnalaR) was dried over sodium.

Preparation of p-*Tolyl Triphenylmethyl Sulphone*.—A mixture of toluene-*p*-sulphonyl iodide (17.1 g, 60 mmol), triphenylmethyl chloride (16.8 g, 60 mmol), copper bronze (7.6 g, 120 mmol), and carbon tetrachloride (150 cm^3) was stirred and heated for 5 h at reflux temperature under nitrogen. The hot mixture was filtered and the filtrate, on cooling at 0°, yielded the sulphone (6.43 g), m.p. 170° (from benzene–ether) (lit.,[24] 173°). The compound was characterized by comparison of its i.r. spectrum with that of an authentic specimen (we thank Professor M. Kobayashi, Tokyo Metropolitan University, for the i.r. spectrum), $\tau(CDCl_3)$ 7.70 (s, Me), 3.02 (d, C_6H_4, J 7.7 Hz), and 2.42—2.90 (m, CPh_3 and C_6H_4). The solid (CuI + Cu) was extracted with hot benzene (Soxhlet); the benzene extract gave more sulphone (6.06 g). The total yield was 53%.

The sulphone, when analysed by g.l.c. or t.l.c., decomposes giving triphenylmethanol, toluene-*p*-sulphonic acid, and other products (not identified). Similar behaviour was reported earlier by Kobayashi *et al.*[24]

Decomposition of PAT in the Presence of Toluene-p-*sulphonyl Halides*.—(a) *Reaction with toluene*-p-*sulphonyl bromide*. A solution of PAT (5.85 g, 16.7 mmol) and toluene-*p*-sulphonyl bromide (8.02 g, 34.0 mmol) in carbon tetrachloride (50 cm^3) was heated under nitrogen for 30 h in the absence of light. The solution, after storage for 48 h at 0°, deposited crystals of *p*-tolyl triphenylmethyl sulphone (3.5 g). The filtrate, after being diluted to 100.0 cm^3, was analysed by g.l.c. and preparative t.l.c. on Kieselgel G-60 (Merck) using $CHCl_3$ as eluant. Preparative t.l.c. gave *S*-*p*-tolyl toluene-*p*-thiosulphonate, tetraphenylmethane, triphenylmethanol, and unchanged toluene-*p*-sulphonyl bromide. All compounds were characterized by comparison of their i.r. and ^1H n.m.r. spectra with those of authentic samples. Quantitative g.l.c. analysis gave the following results: PhCl (0.18 g), PhBr (1.78 g), and $MeC_6H_4SO_2{\cdot}SC_6H_4Me$ (0.59 g).

(b) *Reaction with toluene*-p-*sulphonyl iodide*. The reaction was conducted in a similar manner to (a) using PAT (5.96 g, 17.0 mmol), toluene-*p*-sulphonyl iodide (8.02 g, 34.0 mmol), and carbon tetrachloride (50 cm^3). The reaction mixture, after storage for 20 h at 0°, deposited a solid (5.26 g) which was a mixture of *p*-tolyl triphenylmethyl sulphone and toluene-*p*-sulphonic anhydride, with traces of the dimer di-*p*-tolyl disulphone. The relative proportions of products were calculated from ^1H n.m.r., giving $MeC_6H_4SO_2{\cdot}CPh_3$ (83.1%, 4.4 g) and $MeC_6H_4SO_2{\cdot}O{\cdot}SO_2C_6H_4Me$ (16.9%, 0.90 g). The filtrate of the reaction mixture, after dilution to 100.0 cm^3, was analysed by quantitative g.l.c. as previously giving the following results: PhCl (0.022 g), PhI (2.86 g), and $MeC_6H_4SO_2{\cdot}SC_6H_4Me$ (0.82 g). $MeC_6H_4SO_2{\cdot}CPh_3$ (0.50 g) was determined from its solubility in CCl_4.

Decomposition of Benzoyl Peroxide in the Presence of Toluene-p-*sulphonyl Iodide*.—*First experiment*. Benzoyl peroxide (4.15 g, 17.1 mmol) and toluene-*p*-sulphonyl iodide (9.60 g, 34.0 mmol) in benzene (75 cm^3) were allowed to react for 16.5 h at reflux temperature. The cold mixture when extracted with water (2 × 30 cm^3) and the aqueous layer, when treated with *S*-benzylisothiouronium chloride, gave the corresponding toluene-*p*-sulphonate (0.06 g), m.p. 180—181° (lit.,[25] 182°). Benzoic acid (0.84 g) was extracted from the benzene layer with sodium hydrogencarbonate solution followed by acidification. No sulphinic acid could be detected in the solid. Sulphur was also absent. The benzene layer was dried ($MgSO_4$) and evaporated under reduced pressure; the residue was dissolved in hot carbon tetrachloride (35 cm^3) and the solution cooled to give a solid (2.28 g) characterized as toluene-*p*-sulphonic anhydride. The carbon tetrachloride filtrate was diluted to 100.0 cm^3 and a portion, after being concentrated, was separated by t.l.c. [20 × 20 plates, coated with Kieselgel G-60 (Merck) and using benzene–light petroleum as eluant] yielding three main fractions (decreasing R_F values): iodobenzene, phenyl benzoate, and phenyl *p*-tolyl sulphone, all characterized by comparison of their i.r. and ^1H n.m.r. spectra, g.l.c. retention times, and t.l.c. R_F values with those of authentic samples. Another portion (10.0 cm^3) of the carbon tetrachloride filtrate was analysed by quantitative g.l.c. using *p*-bromochlorobenzene as internal standard. Total yields were PhI (0.96 g), $PhCO_2Ph$ (1.07 g), and $PhSO_2C_6H_4Me$ (0.38 g).

Second experiment. In a second experiment, benzoyl peroxide (2.57 g, 10.6 mmol) and toluene-*p*-sulphonyl iodide (5.94 g, 21.1 mmol) in benzene (75 cm^3) were allowed to react for 19 h at reflux temperature. In order to minimize the loss of PhI, the benzene solution, after being extracted with water and sodium hydrogencarbonate solution, was analysed by quantitative g.l.c. yielding PhI (0.90 g), $PhCO_2Ph$ (0.80 g), $MeC_6H_4SO_2Ph$ (0.06 g), and $MeC_6H_4SO_2{\cdot}SC_6H_4Me$ (0.24 g). The main benzene solution was evaporated under reduced pressure and the residue treated with hot carbon tetrachloride. On storage at 0° the solution deposited crystals of toluene-*p*-sulphonic anhydride (1.5 g) mixed with di-*p*-tolyl disulphone (0.04 g). *S*-*p*-Tolyl toluene-*p*-thiosulphonate was isolated by using preparative t.l.c., as described before. Biphenyl and phenyl toluene-*p*-sulphonate could not be detected.

Decomposition of Benzoyl Peroxide in Benzene.—(a) *In the absence of iodine*. Benzoyl peroxide (2.47 g, 10.2 mmol) in benzene (50 cm^3) was allowed to decompose for 22.5 h at reflux temperature. On storage at room temperature the benzene solution deposited crystals of *p,p'*-quaterphenyl (0.04 g) characterized by comparison of its i.r. spectrum with that[26] of an authentic sample. Benzoic acid (0.14 g) was extracted from the benzene solution with sodium hydrogencarbonate followed by acidification. G.l.c. and t.l.c. analysis of the benzene solution showed phenyl benzoate to be absent. The yield of biphenyl (0.48 g) was determined by quantitative g.l.c.

(b) *In the presence of iodine*. Benzoyl peroxide (2.47 g, 10.2 mmol), iodine (1.29 g, 10.2 mmol), and benzene (50 cm^3) were allowed to react for 13 h at reflux temperature. The violet mixture was worked up as described in reaction (a) and analysed by quantitative g l.c. analysis using *p*-bromochlorobenzene as internal standard. Total yields were PhI (0.82 g), $PhCO_2H$ (0.20 g), and $PhCO_2Ph$ (1.18 g). No biphenyl could be detected.

Competition with Phenyl Radicals.—(a) *Relative reactivities of halogen abstraction from sulphonyl chlorides, bromides, and iodides*. Solutions (5.0 cm^3) of two arenesulphonyl halides (100—300 mg) and PAT (*ca.* 20 mg) in dry benzene were prepared. The solutions were transferred to Pyrex glass tubes, thoroughly degassed at low temperature, and sealed. Similar results were obtained when air was excluded by passing nitrogen through the solution. The reaction tubes, protected from light, were placed in a thermostat at 60° for 3.5 h. The tubes were then cooled, opened, and an internal standard solution (5.0 cm^3) of *p*-nitrotoluene in benzene was added. Quantitative analysis were performed by g.l.c. Relative reactivities were calculated by using equation (19).

(b) *Relative reactivities of bromine abstraction from arenesulphonyl bromides*. The arenesulphonyl bromide (100—300 mg) and toluene-*p*-sulphonyl iodide (100—300 mg) were allowed to react with PAT as in competition (a). When phenyl radicals were generated from phenylazo *p*-tolyl sulphone, the reaction was carried out for 30 h in the presence of suspended magnesium oxide (1.1 g) (tubes rotating in the thermostat). The relative reactivities were obtained as in (a).

Competition with 1-*Cyano*-1-*methylethyl Radicals.*—Competitions were carried out by using arenesulphonyl bromide (300—600 mg), toluene-*p*-sulphonyl iodide (70—80 mg), AIBN (*ca.* 50 mg), and benzene at 70° for 30 h. The relative reactivities were obtained as previously.

Competition with Benzyl Radicals.—Benzyl radicals were generated by thermal decomposition of t-butyl phenylperacetate. The relative reactivities were obtained from competition experiments between arenesulphonyl bromides (100—150 mg) and triphenylmethyl chloride (600—800 mg) [equations (20) and (21)] in benzene solution at 70° for 40 h.

Quantitative G.l.c. Analysis.—Yields of reaction products were determined by g.l.c. analysis (Varian Aerograph chromatograph, model 1740, equipped with hydrogen flame ionization detectors and coupled to a Varian Aerograph C.D.S. 111L integrator or to a Varian Aerograph digital integrator, model 477, with a Victor Heavy Duty Printer). The nitrogen flow rate was 17 cm^3 min^{-1}; the columns (1.5 m × 1/8 in) and temperatures (linearly programmed) were as follows: (a) PAT + ArSO$_2$X (3% SE-30 on Chromosorb W, 100—120 mesh, acid washed; 30° for 3 min, 30—200°, 20° min^{-1}); (b) reactions with (PhCO$_2$)$_2$ (3% SE-30; 70—200°, 10° min^{-1}); (c) competition experiments PAT + ArSO$_2$X (3% SE-30; 50° for 14 min, 50—220°, 20° min^{-1}); (d) competition experiments AIBN + ArSO$_2$X (3% SE-30; 20° for 6 min; 20—220°, 8° min^{-1}); (e) competition experiments PhCH$_2$CO$_3$Bu^t + ArSO$_2$X (15% Apiezon L, on Gas-Chrom P, 100—120 mesh; 90—250°, 6° min^{-1}; column 2 m × 1/8 in).

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