

## Reaction of Arenesulphonyl Halides with Free Radicals. Part 3.<sup>1</sup>

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The decomposition of azoisobutyronitrile (AIBN) and *t*-butyl phenylperacetate in the presence of toluene-*p*-sulphonyl bromide and iodide were studied; results are explained on the basis of free radical reactions.

The relative reactivities of several alkane- and arene-sulphonyl chlorides towards phenyl, benzyl, and trichloromethyl radicals were measured in competition experiments. Results are rationalized on the grounds of a balance between polar effects in the initial and in the transition state.

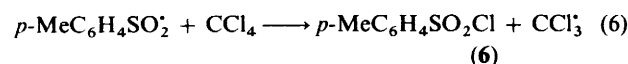
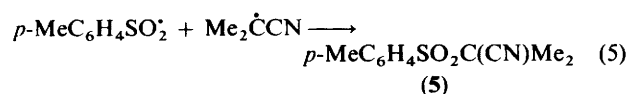
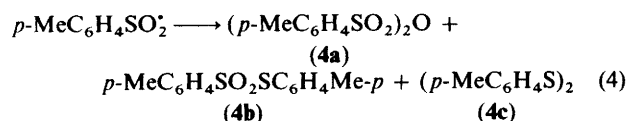
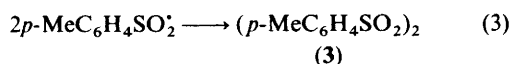
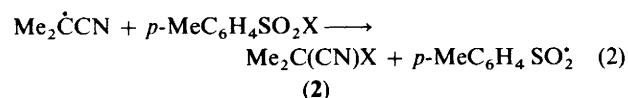
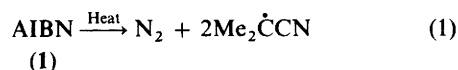
In previous papers<sup>1,2</sup> we reported the generation of arene-sulphonyl radicals resulting from halogen abstraction from arenesulphonyl bromides and iodides by phenyl, 1-cyano-1-methylethyl, and benzyl radicals in benzene and carbon tetrachloride solutions. The relative reactivities of halogen abstraction are almost independent of the nature of the substituents on the benzene ring, although the nature of the halogen strongly influences the rate of halogen abstraction (I:Br:Cl = 602:192:1).

In this paper we report the results of the decomposition of AIBN and *t*-butyl phenylperacetate in the presence of sulphonyl bromides and iodides as well as the study of relative reactivities of halogen abstraction by phenyl, benzyl, and trichloromethyl radicals towards arene- and alkane-sulphonyl chlorides.

### Results and Discussion

**Decomposition of AIBN in the Presence of Toluene-*p*-sulphonyl Iodide and Bromide.**—AIBN was allowed to decompose in boiling CCl<sub>4</sub> under nitrogen in the presence of toluene-*p*-sulphonyl iodide and bromide. The results are summarized in Table 1.

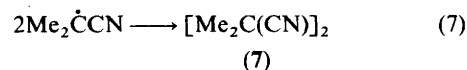
The reaction products may be rationalized on the basis of homolytic processes initiated by halogen abstraction from sulphonyl halides by 1-cyano-1-methylethyl radicals [equations (2)–(7)].



**Table 1.** Products of the thermal reaction of AIBN with *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>X (molar ratio 1:1) in boiling CCl<sub>4</sub> under N<sub>2</sub>

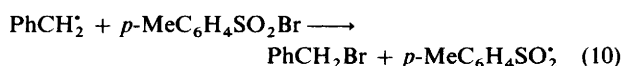
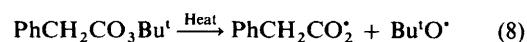
Reaction product	Reaction with <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> I (% yield)	Reaction with <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Br (% yield)
Me <sub>2</sub> C(CN)I	94 <sup>a</sup>	
Me <sub>2</sub> C(CN)Br		63 <sup>a</sup>
[Me <sub>2</sub> C(CN)] <sub>2</sub>	21 <sup>a</sup>	20 <sup>a</sup>
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> C(Me) <sub>2</sub> CN	3 <sup>a</sup>	12 <sup>a</sup>
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> C(Me) <sub>2</sub> CN	3 <sup>b</sup>	12 <sup>b</sup>
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Cl	5 <sup>b</sup>	2 <sup>b</sup>
( <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> ) <sub>2</sub>	9 <sup>b</sup>	2 <sup>b</sup>
( <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> ) <sub>2</sub> O	10 <sup>b</sup>	1 <sup>b</sup>
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> SC <sub>6</sub> H <sub>4</sub> Me- <i>p</i>	9 <sup>b</sup>	9 <sup>b</sup>
( <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> S) <sub>2</sub>	8 <sup>b</sup>	0.3 <sup>b</sup>
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> X		36 <sup>b</sup>

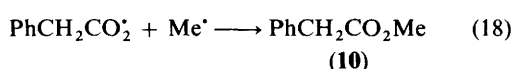
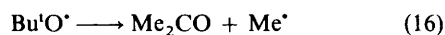
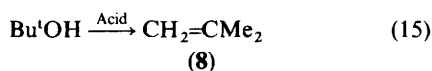
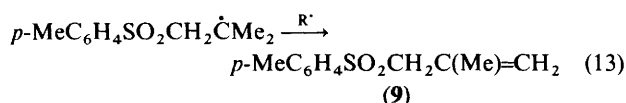
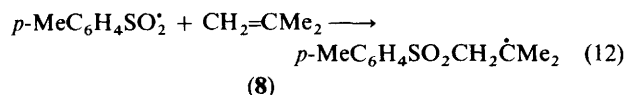
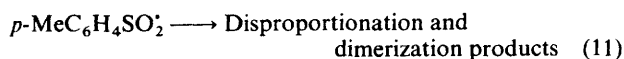
<sup>a</sup> Yield based on AIBN. <sup>b</sup> Yield based on *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>X.



About 50% (and 30%) of Me<sub>2</sub>ĊCN radicals are involved in iodine (and bromine) abstraction from the sulphonyl halide. The increase in the S–X bond strength is compatible with the decreased yield of (2) and increased yield of (5). Either of the sulphonyl halides or radicals is reactive enough to trap most of the Me<sub>2</sub>Ċ(CN) radicals that escape from the solvent cage, and 20% is a plausible yield for dimerization within the cage.<sup>3</sup> Sulphonyl radicals exhibit the usual tendency to disproportionate to compounds (4), yielding smaller amounts of dimerization products (3).

**Decomposition of *t*-Butyl Phenylperacetate in the Presence of Toluene-*p*-sulphonyl Bromide.**—Benzyl radicals produced by the thermal decomposition of PhCH<sub>2</sub>CO<sub>3</sub>Bu<sup>t</sup> in C<sub>6</sub>H<sub>6</sub> under N<sub>2</sub> at 70 °C react with toluene-*p*-sulphonyl bromide by abstraction of bromine atoms to produce toluene-*p*-sulphonyl radicals, that follow the usual pattern of disproportionation and dimerization.<sup>4</sup> Several other products were also isolated (Table 2). The results may be rationalized on the basis of free radical reactions [equations (8)–(18)].





The sulphone (9) may be formed according to equations (12) and (13) in a manner similar to the reaction of sulphonyl radicals with  $\alpha$ -methylstyrene.<sup>4</sup> The alkene 2-methylpropene

**Table 2.** Products of the thermal reaction of  $\text{PhCH}_2\text{CO}_3\text{Bu}^\cdot$  with  $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{Br}$  (molar ratio 1:1) in  $\text{C}_6\text{H}_6$  under  $\text{N}_2$ , at  $70^\circ\text{C}$

Reaction product	Yield (%)
$\text{PhCH}_2\text{Br}$	23 <sup>a</sup>
$\text{PhCH}_2\text{CO}_2\text{Me}$	10 <sup>a</sup>
$\text{PhCH}_2\text{CO}_2\text{H}$	31 <sup>a</sup>
$(\text{PhCH}_2)_2$	Trace
$p\text{-MeC}_6\text{H}_4\text{SO}_2\text{CH}_2\text{C}(\text{Me})=\text{CH}_2$	33 <sup>b</sup>
$p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}$	23 <sup>b</sup>
$(p\text{-MeC}_6\text{H}_4\text{SO}_2)_2$	6 <sup>b</sup>
$p\text{-MeC}_6\text{H}_4\text{SO}_2\text{SC}_6\text{H}_4\text{Me-}p$	1.5 <sup>b</sup>
$(p\text{-MeC}_6\text{H}_4\text{S})_2$	0.5 <sup>b</sup>
$(p\text{-MeC}_6\text{H}_4\text{SO}_2)_2\text{O}$	Not detected
$\text{Bu}^\cdot\text{OH}$	8 <sup>c</sup>
$\text{Me}_2\text{CO}$	2 <sup>c</sup>

<sup>a</sup> Based on  $\text{PhCH}_2\text{CO}_3\text{Bu}^\cdot$ . <sup>b</sup> Based on  $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{Br}$ . <sup>c</sup> Based on  $\text{Bu}^\cdot\text{O}^\cdot$ .

(8) may be formed by acid-catalysed dehydration of  $\text{Bu}^\cdot\text{OH}$  (Equation 15), since no sulphone (9) is obtained when the decomposition is carried out in the presence of magnesium oxide.

**Relative Reactivities of Arene- and Alkane-sulphonyl Chlorides towards Free Radicals.**—The relative reactivities of halogen abstraction from arenesulphonyl iodides and bromides were reported in a previous paper.<sup>1</sup> These relative reactivities are almost independent of the nature of the substituent on the benzene ring of  $\text{ArSO}_2\text{Br}$ . The  $\sigma$ -character of arenesulphonyl radicals<sup>5</sup> and the 'early' transition state of the bromine removal may be the reason for the absence of resonance and polar effects in the reaction, whereas the less exothermic reactions of sulphonyl chlorides, which have less reactant-like transition states, may exhibit these effects.

The relative reactivities were measured in competition experiments as referred to previously,<sup>1</sup> the results of which are summarized in Table 3. The absolute rate constant of bromine abstraction from  $\text{CBr}_4$  by phenyl radicals was measured by Lorand and co-workers<sup>6</sup> and is about  $5 \times 10^9 \text{ mol}^{-1} \text{ l s}^{-1}$  ( $45^\circ\text{C}-\text{CCl}_4$ ). At  $60^\circ\text{C}$ ,  $\text{PhSO}_2\text{Cl}$  and  $\text{C}_{10}\text{H}_7\text{SO}_2\text{Cl}$  are about  $10^3$  times less reactive than  $\text{CBr}_4$ , showing that chlorine abstraction is still a very fast reaction. However, toluene- $p$ -sulphonyl iodide is only 1.5 times less reactive than  $\text{CBr}_4$  towards phenyl radicals, at  $45^\circ\text{C}$ .

Benzyl radicals show similar lack of selectivity towards benzene- and naphthalene-sulphonyl chlorides. This is because the resonance effects in the transition state of halogen abstraction from arenesulphonyl halides is relatively unimportant. The results obtained with methane- and hexadecane-sulphonyl chlorides show that the size of the alkyl chain is not important.

The importance of polar effects is evident with benzyl and trichloromethyl radicals. Benzyl radicals react slower with arenesulphonyl chlorides carrying on electron-donor sub-

**Table 4.** Polar effects in the initial state ( $PE^0$ ) and transition state ( $PE^\ddagger$ ). The Hammett  $\rho$  values for halogen abstraction from sulphonyl halides

Bond	Radical	Expected signal of $\rho^\ddagger$ based on		Observed $\rho^\ddagger$	Overall effect
		$PE^0$	$PE^\ddagger$		
S-Br	$\text{PhCH}_2^\cdot$	—	+	-0.11	$PE^0$
	$\text{Me}_2\dot{\text{C}}\text{CN}$	—	—	-0.17	$PE^0 + PE^\ddagger$
S-Cl	$\text{PhCH}_2^\cdot$	—	+	+0.31	$PE^\ddagger$
	$\text{Cl}_3\text{C}^\cdot$	—	—	-1.1	$PE^0 + PE^\ddagger$

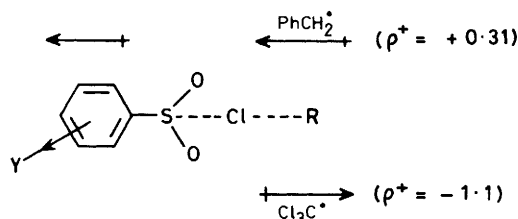
**Table 3.** Relative reactivities of halogen abstraction from arene- and alkane-sulphonyl chlorides

Radical (Temperature/ $^\circ\text{C}$ )	Sulphonyl chloride	Relative reactivity	Standard deviation (%)	Runs
$\text{Ph}^\cdot$ <sup>a</sup>	2-Naphthalene	1.1	13	9
(60)	Benzene	(1) <sup>b</sup>	19	7
$\text{PhCH}_2^\cdot$ <sup>c</sup>	$p$ -Methoxybenzene	0.56	18	10
(70)	$p$ -Tolyl	0.72	21	7
	Benzene	(1) <sup>d</sup>	8	8
	$p$ -Chlorobenzene	1.02	11	8
	2-Naphthalene	1.00	8	8
	Methane	0.52	10	8
	Hexadecane	0.62	20	6
$\text{CCl}_3^\cdot$ <sup>e</sup>	$p$ -Methoxybenzene	8.34	20	7
(70)	$p$ -Chlorobenzene	(1)		
	$m$ -Nitrobenzene	0.19	11	6

<sup>a</sup> Decomposition of  $\text{PhN}_2\text{CPh}_3$ . <sup>b</sup>  $\text{ArSO}_2\text{Cl}$  and  $\text{CBr}_4$  in competition. <sup>c</sup> Decomposition of  $\text{PhCH}_2\text{CO}_3\text{Bu}^\cdot$ . <sup>d</sup>  $\text{RSO}_2\text{Cl}$  and  $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{Br}$  in competition. <sup>e</sup> Decomposition of  $\text{CBrCl}_3$  under visible light (250 W Philips lamp, HP/T).

stituents in the benzene ring ( $\rho^+ = +0.31$ ),\* according with the usual nucleophilic behaviour of these radicals. Trichloromethyl radicals show an opposite behaviour, reacting faster with arenesulphonyl chlorides carrying on electron-donor substituents ( $\rho^+ = -1.1$ ).

The smaller reactivity of alkanesulphonyl chlorides compared with benzene- and naphthalene-sulphonyl chlorides may also be attributed to the smaller electronegativity of the  $sp^3$  carbon atoms compared with  $sp^2$  atoms. The results now obtained and those reported previously<sup>1</sup> can be rationalized on the basis of a balance between polar effects in the initial ( $PE^0$ ) and in the transition state ( $PE^\ddagger$ ),<sup>7</sup> as shown in Table 4. If electron-donating substituents in the benzene ring of  $ArSO_2X$  lower the bond dissociation energy (BDE) of the S-X bond (polar effects in the initial state,  $PE^0$ ) as has been found for hydrogen abstraction from benzylic C-H bonds,<sup>8</sup> negative  $\rho$  values for halogen abstraction should be expected independent of the electrophilicity or nucleophilicity of the abstracting radicals. If polar effects in the transition state,  $PE^\ddagger$ , are dominant, negative  $\rho$  values for halogen abstraction by electrophilic radicals (such as  $Cl_3C^\cdot$ ), and positive  $\rho$  values for nucleophilic radicals (such as  $PhCH_2^\cdot$ ) should be expected. It is very important to note that



benzyl radicals appear to be nucleophilic towards arenesulphonyl chlorides ( $\rho^+ > 0$ ) but electrophilic towards arenesulphonyl bromides ( $\rho^+ < 0$ ). This behaviour is the result of the relative importance of  $PE^0$  and  $PE^\ddagger$ . When  $PE^0$  is dominant (weaker S-X bond)  $\rho^+ < 0$ ; if  $PE^\ddagger$  are more important (stronger S-X bond; later transition state),  $\rho^+ > 0$  (for nucleophilic radicals, such as  $PhCH_2^\cdot$ ).

## Experimental

**Materials.**—Most of the materials were prepared and purified as described previously.<sup>1</sup> Bromotrichloromethane, benzyl chloride, benzyl bromide, and methanesulphonyl chloride were commercial products (BDH), as were methylallyl chloride (Merck), *p*-chlorobenzenesulphonyl chloride (Aldrich), hexadecanesulphonyl chloride (ICN Pharmaceuticals), and 2-naphthalenesulphonyl chloride (Aldrich), and were used after distillation or recrystallization, as necessary.

2-Iodo- and 2-bromo-2-methylpropanenitrile (**2**) were prepared as described by Ford and Waters.<sup>9</sup> 2,2,3,3-Tetramethylbutanedinitrile (**7**),<sup>10</sup> di-*p*-tolyl disulphide (**4c**),<sup>11</sup> methyl phenylacetate (**10**),<sup>12</sup> *m*-nitrobenzenesulphonyl chloride,<sup>13</sup> and *p*-methoxybenzenesulphonyl chloride<sup>14</sup> were prepared by literature procedures.

**Decomposition of AIBN.**—(a) *In the presence of toluene-*p*-sulphonyl iodide.* A solution of AIBN (10.02 g, 61.0 mmol) and toluene-*p*-sulphonyl iodide (18.05 g, 64.0 mmol) in carbon tetrachloride (200 ml) was heated under nitrogen for 9 h at reflux temperature. The solution, after storage at 0 °C, deposited a crystalline mixture of (*p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)<sub>2</sub>O (2.03 g) and (*p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)<sub>2</sub> (1.81 g) whose composition was established by i.r., t.l.c., and transformation of the sulphonic anhydride into the

derivative  $PhNH_3^+$ ,  $p$ -MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>−</sup> by reaction with aniline in benzene.

The cold filtrate was diluted to 250 ml and a portion (150 ml) was evaporated under reduced pressure, at 40–45 °C, and the liquid residue, after having been cooled, was extracted with light petroleum (b.p. 60–80 °C). The petroleum extract gave a mixture of Me<sub>2</sub>C(CN)I and [Me<sub>2</sub>C(CN)]<sub>2</sub>. The liquid residue (1.4 g) was analysed by preparative t.l.c. on Kieselgel G-60 (Merck) using benzene as the eluant and gave (*p*-MeC<sub>6</sub>H<sub>4</sub>S)<sub>2</sub>, *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>Me-*p*, [Me<sub>2</sub>C(CN)]<sub>2</sub> and *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>C(Me)<sub>2</sub>CN. All compounds were characterized by comparison of their i.r. and <sup>1</sup>H n.m.r. spectra with those of authentic samples.

The remaining portion (100.0 ml) of the cold filtrate was used for quantitative g.l.c. analysis using PhBr as an internal standard. The total yields were Me<sub>2</sub>C(CN)I (11.14 g), [Me<sub>2</sub>C(CN)]<sub>2</sub> (1.72 g), *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl (0.62 g), *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>C(Me)<sub>2</sub>CN (0.42 g), (*p*-MeC<sub>6</sub>H<sub>4</sub>S)<sub>2</sub> (1.21 g), and *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>Me-*p* (1.52 g).

(b) *In the presence of toluene-*p*-sulphonyl bromide.* A solution of AIBN (10.50 g, 64.0 mmol) and toluene-*p*-sulphonyl bromide (15.05 g, 64.0 mmol) in carbon tetrachloride (200 ml) was heated under N<sub>2</sub> for 9 h at reflux temperature. The reaction mixture was worked up as described in reaction (a) to yield (*p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)<sub>2</sub>O (0.21 g), (*p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)<sub>2</sub> (0.43 g), Me<sub>2</sub>C(CN)Br (6.02 g), [Me<sub>2</sub>C(CN)]<sub>2</sub> (1.74 g), *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>C(CN)<sub>2</sub>CN (1.72 g), *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl (0.27 g), *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Br (5.36 g), (*p*-MeC<sub>6</sub>H<sub>4</sub>S)<sub>2</sub> (0.05 g), and *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>Me-*p* (1.61 g).

**1-Cyano-1-methylethyl *p*-Tolyl Sulphone (5).**—A mixture of toluene-*p*-sulphonyl iodide (19.7 g, 70 mmol), 2-iodo-2-methylpropanenitrile (13.6 g, 70 mmol), copper bronze (8.9 g, 140 mmol), and carbon tetrachloride (150 ml) was stirred and heated under N<sub>2</sub> for 6 h at reflux temperature. The mixture was filtered whilst hot and the filtrate was left in refrigerator for 2 days. The cold solution deposited white crystals of (*p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)<sub>2</sub>O and (*p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)<sub>2</sub> which were removed by filtration. The filtrate was concentrated to ca. 40 ml and analysed by chromatography on silica gel with light petroleum (b.p. 40–60 °C; 400 ml), light petroleum–benzene (1:1; 450 ml), and benzene (350 ml) as eluants, to yield *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl, Me<sub>2</sub>C(CN)I, *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>Me-*p* and the expected sulphone *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>C(Me)<sub>2</sub>CN (1.1 g, 7.1%), m.p. 114–115 °C (Found: C, 59.3; H, 5.9; N, 6.5; S, 14.4. C<sub>11</sub>H<sub>13</sub>NO<sub>2</sub>S requires C, 59.2; H, 5.9; N, 6.3; S, 14.4%).  $\nu_{max}$  (Nujol), 2 240m (CN), 1 320s, 1 305s, 1 290s, 1 160s, and 1 135s cm<sup>−1</sup> (SO<sub>2</sub>);  $\delta_H$  (90 MHz; CDCl<sub>3</sub> + CCl<sub>4</sub>; internal standard Me<sub>4</sub>Si) 1.68 (6 H, s, 2 × Me), 2.49 (3 H, s, Me), 7.38 (2 H, d, *J* 9 Hz, C<sub>6</sub>H<sub>4</sub>), and 7.86 (2 H, d, *J* 9 Hz, C<sub>6</sub>H<sub>4</sub>); *m/z* (relative intensity) 223 (*M*<sup>+</sup>, 8%), 155 (53), 139 (3), 91 (100), 65 (20), 41 (11), and 28 (47).

**Decomposition of *t*-Butyl Phenylperacetate in the Presence of Toluene-*p*-sulphonyl Bromide.**—*t*-Butyl phenylperacetate (1.12 g, 6.0 mmol), toluene-*p*-sulphonyl bromide (1.41 g, 6.0 mmol), and benzene (15 ml) were allowed to react for 40 h at 70 °C under N<sub>2</sub> in the absence of light. After having been stored at room temperature the benzene solution deposited crystals of *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H (233 mg).

Preparative g.l.c. of the benzene filtrate gave Bu<sup>o</sup>OH, PhCH<sub>2</sub>Br, PhCH<sub>2</sub>CO<sub>2</sub>H, PhCH<sub>2</sub>CO<sub>2</sub>Me, and *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>CH<sub>2</sub>C(Me)=CH<sub>2</sub> (when the reaction was carried out in the presence of MgO this sulphone was not obtained). All compounds were characterized by comparison of their i.r. and <sup>1</sup>H n.m.r. spectra with those of authentic samples.

In a second experiment, *t*-butyl phenylperacetate (0.7516 g, 3.6 mmol), toluene-*p*-sulphonyl bromide (0.8467 g, 3.6 mmol), and benzene (8.0 ml) reacted as described before. The benzene

\*  $\rho^+ = f(\sigma^+)$ .

solution, after separation of *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H (140 mg), was diluted to 25 ml. No toluene-*p*-sulphonic anhydride could be detected in the reaction mixture (test with PhNH<sub>2</sub>). A portion (10 ml) of the benzene filtrate was evaporated under reduced pressure and the residue was treated with CCl<sub>4</sub> (5 ml). On being allowed to stand, (*p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)<sub>2</sub> separated as white solid (25 mg). Another portion (5.0 ml) of the benzene filtrate was analysed by quantitative g.l.c. using *p*-dichlorobenzene as an internal standard. Total yields were Me<sub>2</sub>CO (4.0 mg), Bu<sup>o</sup>OH (20.5 mg), PhCH<sub>2</sub>Br (139.7 mg), PhCH<sub>2</sub>CO<sub>2</sub>Me (51.6 mg), PhCH<sub>2</sub>CO<sub>2</sub>H (153.0 mg), *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>CH<sub>2</sub>C(Me)=CH<sub>2</sub>, (249.1 mg), (*p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)<sub>2</sub> (4.3 mg), and *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>Me-*p* (14.9 mg).

**2-Methylprop-2-enyl *p*-Tolyl Sulphone (9).**—A solution of toluene-*p*-sulphonyl iodide (5.1 g, 18 mmol) and methallyl chloride (2.3 g, 25 mmol) in benzene (30 ml) was heated for 2 h at reflux temperature. The cold solution was washed with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (10%) and water. After having been dried (CaCl<sub>2</sub>) the solvent was removed and the crude residue [(5.86 g) an oil with an n.m.r. spectra compatible with 3-chloro-2-iodo-2-methylpropyl *p*-tolyl sulphone] was treated with zinc in ethanol according to Haszeldine<sup>15</sup> to give 2-methylprop-2-enyl *p*-tolyl sulphone (2.46 g, 65%) of m.p. 66–68 °C [71–72 °C, after recrystallization from light petroleum (b.p. 40–60 °C)] (Found: C, 63.1; H, 6.8; S, 15.25. C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>S requires C, 62.8; H, 6.7; S, 15.25%);  $\nu_{\max}$  (Nujol) 1305, 1280, 1160, and 1125 cm<sup>-1</sup> [all strong (SO<sub>2</sub>)];  $\delta_{\text{H}}$  (90 MHz; CCl<sub>4</sub>: Me<sub>4</sub>Si) 7.63 (2 H, d, *J* 8 Hz, C<sub>6</sub>H<sub>4</sub>), 7.20 (2 H, d, *J* 8 Hz, C<sub>6</sub>H<sub>4</sub>), 4.88 (1 H, m, CHH), 4.55 (1 H, m, =CHH), 3.59 (2 H, d, *J* 0.7 Hz, CH<sub>2</sub>), 2.40 (3 H, s, MeAr), and 1.84 (3 H, m, MeC=C); *m/z* (relative intensity) 210 (*M*<sup>+</sup>, 6%), 155 (23), 146 (26), 131 (20), 91 (66), 65 (16), 55 (100), and 39 (13).

The sulphone was also prepared from sodium toluene-*p*-sulphonate and methallyl chloride following the method used by Shriner<sup>16</sup> for other sulphones.

**Competition Experiments.**—Reactions with 1-cyano-1-methylethyl and benzyl radicals have been described previously.<sup>1</sup> Trichloromethyl radicals were generated by photolysis of bromotrichloromethane in benzene solution (0.01M) at 70 °C for 40 h under visible light (Philips lamp, HP/T-250 W) and the relative reactivities were obtained from competition experiments between two arenesulphonyl chlorides (*ca.* 0.02M), whose disappearance was accurately measured. It was assumed that no ArSO<sub>2</sub>Cl was regenerated by the reaction of arenesulphonyl radicals with bromotrichloromethane since (a) the amount of ArSO<sub>2</sub>Cl formed when arenesulphonyl radicals were generated in CCl<sub>4</sub> under similar conditions<sup>2</sup> did not exceed 5% of the sulphonyl radicals involved (see also Table 3) and (b) bromine abstraction from BrCCl<sub>3</sub> is much more likely than chlorine abstraction (for phenyl radicals,  $k_{\text{BrCCl}_3}/k_{\text{CCl}_3}$  is *ca.* 10<sup>3</sup>, at 45 °C).<sup>6</sup>

**Quantitative G.l.c. Analysis.**—Yields of reaction products or unchanged arenesulphonyl chlorides were determined by g.l.c. analysis (Varian Aerograph 1740 and 3700, and Tracor 565

chromatographs, equipped with hydrogen flame ionization detectors and coupled to electronic integrators – Varian Aerograph model 477, Perkin Elmer M-2, and Hewlett Packard 3390 A.

The columns (1.5 m × 1/8 in) and temperatures (linearly programmed) were as follows: (a) AIBN + ArSO<sub>2</sub>X (3% SE-30 on Chromosorb W, 100–120 mesh, acid washed; 50 °C for 6 min, 50–205 °C, 12 °C min<sup>-1</sup>); (b) PhCH<sub>2</sub>CO<sub>2</sub>Bu<sup>t</sup> + ArSO<sub>2</sub>Br + Ph<sub>3</sub>CCl (15% Apiezon L on Gas-Chrom P, 100–120 mesh; 90–250 °C, 6 °C min<sup>-1</sup>); (c) PhCH<sub>2</sub>CO<sub>2</sub>Bu<sup>t</sup> + ArSO<sub>2</sub>Cl + *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Br (3% OV 1, on Supelcoport, 80–100 mesh; 80 °C for 8 min, 80–200 °C, 10 °C min<sup>-1</sup>; glass column, 6' × 4 mm i.d.); (d) PhCH<sub>2</sub>CO<sub>2</sub>Bu<sup>t</sup> + RSO<sub>2</sub>Cl + *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl (5% OV 101, on Chromosorb G.H.P., 100–120 mesh; 36 °C for 35 min, 36–200 °C, 2 °C min<sup>-1</sup>; column 50 cm × 3 mm i.d.); (e) CBrCl<sub>3</sub> + ArSO<sub>2</sub>Cl (3% OV 1, on Supelcoport, 80–100 mesh; 60 °C for 5 min, 60–150 °C, 20 °C min<sup>-1</sup>; glass column, 6' × 4 mm i.d.).

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