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Reactions of the Free Toluene-p-sulphonyl Radical. Part I. Diagnostic **Reactions of Free Radicals**

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The free ρ ·CH₃·C₆H₄·SO₂ radical is easily produced by the thermolysis or photolysis of ρ ·Me·C₆H₄·SO₂·I; copper powder assists the removal of iodine and so do radicals R2C(CN). Evidence is presented to show that $p \cdot Me \cdot C_6 H_4 \cdot SO_2 \cdot I$ adds homolytically to olefins and that free $p \cdot Me \cdot C_6 H_4 \cdot SO_2 \cdot I$ radicals tend to disproportionate according to the equation:

 $6 \operatorname{Me} \cdot \operatorname{C}_{6} \operatorname{H}_{4} \cdot \operatorname{SO}_{2} \cdot \longrightarrow 2 (\operatorname{Me} \cdot \operatorname{C}_{6} \operatorname{H}_{4} \cdot \operatorname{SO}_{2})_{2} O + \operatorname{Me} \cdot \operatorname{C}_{6} \operatorname{H}_{4} \cdot \operatorname{SO}_{2} \cdot \operatorname{C}_{6} \operatorname{H}_{4} \cdot \operatorname{Me}$

 $p \cdot Me \cdot C_6 H_4 \cdot SO_2 \cdot radicals$ add to the oxygen atoms of quinones giving the ditoluene-p-sulphonate esters of quinols. Arylsulphinyl radicals do not appear to have a similar reactivity; they merely dimerise to thiolsulphonate esters Ar·S·SO₂·Ar.

FREE arylsulphonyl radicals can be produced by three general routes: (a) by addition of aryl radicals to sulphur dioxide, 1 (b) by the one-electron oxidation of arenesulphinic acids,² and (c) by the homolysis of arenesulphonyl halides.

Route (a) has limitations arising from the need first to produce active aryl radicals, but it gives a good indication of the relative reactivities of typical aryl, alkyl, and are nesulphonyl free radicals. Route (b), though the most suitable for the study of the e.s.r. spectra of arenesulphonyl radicals, has the least general applicability, partly because it is restricted to reactions in water and partly because it is impossible by this route to prevent rapid subsequent oxidation and self-coupling reactions of the initially formed radicals. Route (c) has the widest scope, but it is desirable to make diagnostic tests to establish that homolytic and not heterolytic reactions of arenesulphonyl halides are indeed being studied.

Arenesulphonyl iodides undergo spontaneous homolysis in aprotic solvents at room temperature, their decomposition being accelerated by illumination, and so the most convenient way to produce free arenesulphonyl radicals is to warm these iodides in benzene or carbon tetrachloride with the addition of a metal such as copper to remove iodine as soon as it has been liberated. In this paper we describe reactions of toluene-p-sulphonyl iodide that are diagnostic of free toluene-p-sulphonyl radicals. Our attempts to produce and study arenesulphinyl radicals, Ar·SO·, by a similar route have not been successful.

The Homolysis of Arenesulphonyl Iodides.—Following the initial work of Kharasch and Mosher,³ Skell,⁴ Cristol⁵ and their colleagues have shown that a number

¹ J. M. Squire and W. A. Waters, J. Chem. Soc., 1962, 2068. ² M. McMillan and W. A. Waters, J. Chem. Soc. (B), 1966, 422.

³ M. Kharasch and R. A. Mosher, J. Org. Chem., 1952, 17, 453.

⁴ P. Skell and J. H. McNamara, J. Amer. Chem. Soc., 1957, 79, 85; P. Skell, R. C. Woodworth, and J. H. McNamara, *ibid.*, p. 1253.
 ⁵ S. J. Cristol and J. A. Reeder, J. Org. Chem., 1961, 26, 2182;

S. J. Cristol and D. I. Davies, ibid., 1964, 29, 1282.

of are nesulphonyl halides can be added to various olefins in the presence of peroxide catalysts or of u.v. light and this reaction can also be effected with some alkanesulphonyl chlorides.⁶

Toluene-p-sulphonyl iodide is reactive enough to combine directly with many olefins in daylight, without the addition of a catalyst and the products easily lose hydrogen iodide. Though the course for this addition to an olefin R·CH:CH₂ is that expected for a homolytic addition in which the toluene-p-sulphonyl radical (Ts) is the chain carrier (1, 2), it could also be the course of

$$R \cdot CH: CH_2 + Ts \cdot \longrightarrow R \cdot CH \cdot CH_2 Ts \cdot (1)$$

$$R \cdot CH \cdot CH_2 Ts + Ts \cdot I \longrightarrow R \cdot CH I \cdot CH_2 Ts + Ts \cdot (2)$$

heterolytic addition following the ionisation of the iodide (3) to give a reactive arenesulphonyl cation. We have

$$\operatorname{Ar} \cdot \operatorname{SO}_2 \cdot \operatorname{I} \Longrightarrow \operatorname{Ar} \cdot \operatorname{SO}_2^+ + \operatorname{I}^- \tag{3}$$

established that heterolytic reactions are not involved by showing (a) that there is little addition of toluenep-sulphonyl iodide to vinyl cyanide or butadiene in the dark, (b) that in daylight the additions to α -methylstyrene and vinyl cyanide are markedly retarded by the addition of quinol, and (c) that the cation Ts⁺ formed by treating toluene-p-sulphonyl chloride with silver perchlorate or aluminium chloride does not add to α -methylstyrene or vinyl cyanide.

Products and yields of reaction products are listed in Table 1. The absence of polymers indicates that reaction (2) must be very fast.

TABLE 1 Direct addition of toluene-*p*-sulphonyl iodide to olefins in daylight

Olefin	Products isolated			Yields (%)	
Styrene	Ph•CHI•CH₂Ts	trans- Ph•CH:CHTs	93		
α-Methyl- stvrene		Ph·C(:CH ₂)·CH ₂ Ts	s	59	
1,1-Ďiphenyl- ethylene		trans- Ph ₂ C:CHTs		50	
Vinyl cyanide	TsCH ₂ ·CHI·CN	trans-	87		
Butadiene	TsCH. CH:CH.CH.I	Is CH.CH.CN	87 89	_	
Cyclohexene	Adduct (unstable)	$1-TsC_6H_9$ co	a. 58		

Since the formation of free iodine and often of hydrogen iodide in direct reactions between arenesulphonyl iodides and organic molecules tends to obscure the reactions of the arenesulphonyl radicals themselves, we have more generally effected the homolysis of toluenep-sulphonyl iodide in the presence of a halogen-trapping reagent. Our studies show that free arenesulphonyl radicals undergo reactions other than dimerisation and substantiate early studies of reactions of naphthalene2-sulphinic acid and of naphthalene-2-sulphonyl iodide made by Otto, Rössing, and Tröger.⁷ The thermal decomposition of toluene-p-sulphonyl iodide in carbon tetrachloride under nitrogen in the presence of either copper or silver powders yielded mainly toluenep-sulphonic anhydride and p-tolyl toluene-p-thiolsulphonate in accord with the disproportionation (4),

$$6 \text{ Ts} \rightarrow 2 \text{Ts}_{2} O + \text{Ts} \cdot \text{S} \cdot C_{6} H_{4} Me \qquad (4)$$

whilst the production of di-p-tolyl disulphone, Ts·Ts, could not be established. Even the irradiation of a solution of toluene-p-sulphonyl iodide in benzene in the absence of a metal gave only 5% of di-p-tolyl disulphone compared with 23% of toluene-p-sulphonic anhydride. Again when the iodide is warmed in benzene or carbon tetrachloride with either azobisisobutyronitrile or 1,1-azobis-(1-cyanocyclohexane) then the free alkyl radicals, $R_2C(CN)$ ·, liberated from the azo-compounds abstract iodine ⁸ but do not combine easily with the toluene-p-sulphonyl radicals. The latter give only small amounts of di-p-tolyl disulphone, but high yields of toluene-p-sulphonic anhydride as shown in Table 2. Aniline is

TABLE 2

$\begin{array}{ccc} Percentage \ yields \ of \ products \ of \ reactions \ between \\ p\cdot Me \cdot C_6H_4 \cdot SO_2 \cdot I \ and \ azo-compounds, \ R \cdot N_2 \cdot R \\ & Me_2C(CN) \cdot N_2 \cdot CMe_2 \cdot CN \ C_8H_{10}(CN) \cdot N_2 \cdot C_6H_{10} \cdot CN \\ Product \ In \ C_6H_6 \ In \ CCl_4 \ In \ C_6H_6 \\ R_2C(CN) \cdot I \ \dots \ 35 \ 32 \ 13 \\ R_2C(CN) \cdot CR_2 \cdot CN \ - \ 29 \ 3^{3} \cdot 7 \end{array}$

27

 $3 \cdot 0$

54

1

4.6

a good reagent for the estimation of this anhydride, since its toluene-p-sulphonate (reaction 5) is insoluble in nonpolar solvents.

37

18

<u>Ts₂O</u>

Ts•Ts

$$2PhNH_2 + Ts_2O \longrightarrow Ph\cdot NHTs + PhNH_3, OTs^-$$
 (5)

We have checked that di-p-tolyl disulphone is stable in boiling carbon tetrachloride in the presence of copper. Moreover the heterolytic reactions (6) and (7) would have

$$2 \operatorname{Cu} + \operatorname{Ts} \cdot \mathbf{I} \longrightarrow \operatorname{Ts}^{-} \operatorname{Cu}^{+} + \operatorname{Cu} \mathbf{I} \quad (6)$$

$$Ts^{-}Cu^{+} + Ts \cdot I \longrightarrow Ts \cdot Ts + CuI$$
 (7)

yielded disulphone and not disproportionation products, since no sulphonate is formed in the reaction between toluene-p-sulphonyl iodide and sodium toluene-p-sulphinate, which gives the disulphone. We therefore suggest that toluene-p-sulphonyl radicals, which are mesomeric (8) combine either as in (9) or (preferably) as in (10) and from the latter reaction can disproportionate as shown in (11)--(13).

To substantiate reaction (13) we have prepared both benzenesulphinyl chloride and toluene-*p*-sulphinyl chloride by Barnard's method⁹ and, in accord with

⁸ Cf. M. C. Ford and W. A. Waters, J. Chem. Soc., 1952, 2240.
⁹ D. Barnard, J. Chem. Soc., 1957, 4673; cf. Org. Synth., 1954, 34, 93.

Org.

⁶ H. Goldwhite, M. S. Gibson, and C. Harris, *Tetrahedron*, 1965, **21**, 2743.

⁷ R. Otto, A. Rössing, and J. Tröger, J. prakt. Chem., 1893, 47, 94.

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his reaction with zinc, find that when refluxed in carbon tetrachloride with copper powder they yield the corresponding thiolsulphonates. Our attempts to add arenesulphinyl radicals to olefins have not been successful: this accords with the finding of Kice and Pawlowski¹⁰



$$MeC_{6}H_{4} \xrightarrow{[]}{} + \cdot O \xrightarrow{[]}{} C_{6}H_{4}Me \xrightarrow{} \\O O O \\MeC_{6}H_{4} \xrightarrow{} O \xrightarrow{} O \xrightarrow{} C_{6}H_{4}Me \quad (10)$$

$$MeC_{6}H_{4} \xrightarrow{O}_{O} \xrightarrow{S}_{O} \xrightarrow{O}_{6}H_{4}Me \xrightarrow{}$$

$$MeC_{6}H_{4} \xrightarrow{O}_{O} \xrightarrow{O}_{O} \xrightarrow{O}_{O} + \cdot \overset{O}{\overset{O}_{O}} \xrightarrow{O}_{O} + \cdot \overset{O}{\overset{O}_{O}} \xrightarrow{O}_{O} \xrightarrow{O}_$$

$$2 \operatorname{MeC}_{6}\operatorname{H}_{4} \xrightarrow{\overset{\circ}{\longrightarrow}} \operatorname{MeC}_{6}\operatorname{H}_{4} \xrightarrow{\overset{\circ}{\longrightarrow}} \operatorname{S} \xrightarrow{\overset}{\xrightarrow}} \operatorname{S} \xrightarrow{\overset{\circ}{\longrightarrow}} \operatorname{S} \xrightarrow{} \operatorname{S} \xrightarrow{$$

who decomposed arenesulphinyl sulphones, Ar·SO₂·SOAr, in the presence of 1,1-diphenylethylene and effected the addition of the arenesulphonyl radicals only to the olefin, obtaining merely thiolsulphonate dimers from the sulphinyl radicals. Other attempts to produce Ar·SO· radicals have had a similar outcome ¹¹ so that reaction

¹⁰ J. L. Kice and N. E. Pawlowsky, J. Amer. Chem. Soc., 1964,

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(13) must be much faster than additions of Ar·SO· radicals to other molecules.

Reactions of Arenesulphonyl Radicals with Quinones.— Free radicals of carbon, R_3C_{\cdot} , combine with quinones by addition at oxygen to give quinol ethers,^{12,13} addition at carbon being much less favoured. In contrast, nucleophiles (e.g., PhNH₂, RSO₂⁻) add, as to $\alpha\beta$ -unsaturated ketones, to carbon centres. Since the S=O bonds of arenesulphonyl radicals necessarily make them strongly dipolar entities the course of their reactions with quinones could not safely be predicted and its has been interesting to find that there is a close parallel between the behaviour of toluene-p-sulphonyl radicals and of cyanoisopropyl radicals.¹³ In each case attack occurs at oxygen, the ditoluene-p-sulphonate esters of the corresponding quinols being formed (14).

$$2T_{s} + 0 \longrightarrow T_{s} O \longrightarrow T_{s} O$$

From the reaction between toluene-p-sulphonyl iodide, copper powder, and p-benzoquinone in hot carbon tetrachloride the bulk of the quinol ditoluene-p-sulphonate separated when the filtered solution was cooled, but examination of the filtrate established the formation also of toluenesulphonic anhydride and of p-tolyl toluene-p-thiolsulphonate, the expected products of selfcoupling of toluene-p-sulphonyl radicals (reactions 10— 13). Similar mixtures were obtained with the other quinones. No addition reaction occurred in the absence of copper powder.

It is conceivable that a slight degree of reduction of the quinone to quinol might have occurred in the above reaction, in which case reactions (15) and (16) could perhaps have occurred also. But when toluene-p-

$$2 \operatorname{Ts} \cdot I + \operatorname{HO} \cdot C_{6} \operatorname{H}_{4} \cdot \operatorname{OH} \longrightarrow$$

$$2 \operatorname{HI} + \operatorname{Ts} \cdot \operatorname{O} \cdot C_{6} \operatorname{H}_{4} \cdot \operatorname{O} \cdot \operatorname{Ts} \quad (15)$$

$$O: C_{6} \operatorname{H}_{4}: O + 2 \operatorname{HI} \Longrightarrow \operatorname{HO} \cdot C_{6} \operatorname{H}_{4}: \operatorname{OH} + I_{6} \quad (16)$$

sulphonyl iodide was refluxed in dry benzene with copper powder and an equimolar amount of quinol the only identifiable reactions product was 2-toluenep-sulphonylquinol (A), the normal product of the attack of toluene-p-sulphinates on p-benzoquinone.¹⁴ Whether (A) is indeed formed by heterolytic reactions is uncertain but the sequence (15)—(18) is rational.

$$TsI + HI \longrightarrow TsH + I_2$$
 (17)

$$T_{sH} + O:C_{6}H_{4}:O \longrightarrow Carbon adduct, A$$
 (18)

Again when toluene-p-sulphonic anhydride was refluxed in dry carbon tetrachloride with an equimolar amount of p-benzoquinone the anhydride was recovered in over 90% yield even if copper powder was added to the mixture.

 A. F. Bickel and W. A. Waters, J. Chem. Soc., 1950, 1764.
 F. J. Lopez Aparicio and W. A. Waters, J. Chem. Soc., 1952, 4666.

¹⁴ J. Walker, J. Chem. Soc., 1945, 633.

^{86, 4898.} ¹¹ R. M. Topping and N. Kharasch, J. Org. Chem., 1962, 27,

1877

All these tests support the occurrence of the free-radical addition (14).

TABLE 3

Reaction of toluene-*p*-sulphonyl radicals with quinones

	D	iester of quinol	Ts₂O	Methyl affinity	Redox potential of
	Yield		Yield	of	quinone
Quinone	(%)	М. р.	(%)	quinone	(V)
<i>b</i> -Benzoquinone	46	162163°	12	1.00	0.711
Toluquinone	28	152 - 153 *	22	0.68	0.653
p-Xvloquinone	12	191	38	0.41	0.597
Thymoquinone	$2 \cdot 8$	160 - 162	47		0.589
<i>m</i> -Xvloquinone	0.7	160-162 *	48		0.600
Chloranil	$2 \cdot 4$	227-228 *		0.02	0.703
9.10-Phenanthra-					
guinone	$2 \cdot 4$	200-201 *		0.046	0.471
Duroquinone	0			_	0.466
Anthraquinone	0	_		<u> </u>	0.120
Acenaphthaquinone	0				

* Not reported in literature hitherto.

Table 3, which is closely comparable with that published by Lopez Aparicio and Waters ¹³ for the reactions between quinones and 2-cyano-2-propyl radicals, shows that Tol·SO₂· radicals are electron donors rather than electron acceptors since they react preferably with quinones of high redox potential. The close correlation between the percentage yields of quinol diesters and the ' methyl affinities ' of quinones as measured by Rembaum and Szwarc ¹⁵ merits comment first because it shows up the effect of steric hindrance with chloranil and secondly because the correlation is quite rational if it is accepted that methyl radicals attack oxygen atoms and not carbon centres in quinones as they supposed.

Attempts to add toluene-p-sulphinyl radicals to benzoquinone yielded only p-tolyl toluene-p-thiolsulphonate (reaction 13).

EXPERIMENTAL

Toluene-p-sulphonyl iodide, m.p. 90—91° (decomp.) after crystallisation from carbon tetrachloride, was prepared from sodium toluene-p-sulphinate ¹⁶ and iodine as described by Whitmore and Thurman.¹⁷

Additions of Toluene-p-sulphonyl iodide to Olefins.— (i) α -Methylstyrene (5.0 g.) and toluene-p-sulphonyl iodide (9.0 g.), in ether (250 ml.) were kept for 14 hr. in a flask without protection from light. The brown solution was then washed with alkaline aqueous sodium thiosulphate (10%), dried (Na₂SO₄), and evaporated. The residue, after crystallisation from light petroleum (b.p. 60—80°)-carbon tetrachloride (6:1) gave 4.9 g. (57%) of 3-toluene-p-sulphonyl-2-phenylpropene, CH₂:CPh·CH₂·SO₂·C₆H₄·Me, m.p. 101° (Found: C, 70.0; H, 5.8; S, 11.5. C₁₈H₁₆O₂S requires C, 70.6; H, 5.9; S, 11.7%). Both the i.r. and the n.m.r. spectra were in accord with this structure; the CH₂:C protons had τ 4.40 and 4.75. Ozonolysis of 1 g. in ethyl acetate (50 ml.) yielded benzoyl toluene-p-sulphonylmethane, $Me \cdot C_6 H_4 \cdot SO_2 \cdot CH_2 \cdot CO \cdot Ph$ (0.95 g.), m.p. 105— 107°, unchanged after admixture with an authentic specimen prepared from phenacyl chloride and sodium toluene*p*-sulphinate.

(ii) Vinyl cyanide (3 g.) and the iodide (14 g.) were dissolved in ether (250 ml.) and kept for 20 hr. The 2-iodo-3-toluene-p-sulphonylpropionitrile (14·3 g., 87%) which had separated was crystallised from benzene and had m.p. 149—152° (decomp.) (Found: C, 35·7; H, 2·9; I, 38·2. $C_{10}H_{10}INO_2S$ requires C, 35·6; H, 3·0; I, 37·9%). When treated in ethyl acetate with triethylamine it yielded trans-1-cyano-2-toluene-p-sulphonylethylene, m.p. 131— 133° which was identified by its i.r. and n.m.r. spectra (CN band at 2250 and SO₂ bands at 1150 and 1300 cm.⁻¹; vinylic protons giving $\tau 2.73$ and 3·49; J 15·6 c./sec.).

(iii) Butadiene. Benzene (200 ml.) was saturated with butadiene and toluene-p-sulphonyl iodide (13 g.) was added with stirring. More butadiene was passed into the mixture for 30 min. After storage overnight the solution was evaporated in a vacuum and the residue, which crystallised on cooling, was triturated with light petroleum (20 ml.). The solid 4-iodo-toluene-p-sulphonylbut-2-ene which remained $(13{\cdot}6~g.,~89\%)$ was crystallised from light petroleum (b.p. 40-60°)-benzene and had m.p. 68-69° (Found: C, 38.6; H, 3.8; I, 38.2. $C_{11}H_{13}IO_2S$ requires C, 39.3; H, 4.0; I, 37.8%). Its i.r. spectrum indicated the presence of the SO2 group (bands at 1145 and 1325 cm.-1 and a trans-RCH:CHR' olefinic system (bands at 1300, 1640, and 3030 cm.⁻¹ as well as a *para*-substituted aromatic system, and this was substantiated by the n.m.r. spectrum, which had ${\bf 2}$ duplets at τ 6.12-6.23 corresponding to 2 CH₂ groups and a quintuplet at $\tau 4.14-4.36$ corresponding to the 2 vinylic protons.

(iv) Styrene (6.6 g.) when allowed to react for 2 hr. in carbon tetrachloride, gave a 93% yield of 1-iodo-1-phenyl-2-toluene-p-sulphonylethane, m.p. 138—139° (Found: C, 46.1; H, 4.1. $C_{15}H_{15}IO_2S$ requires C, 46.7; H, 3.9%), which readily lost iodine when warmed with triethylamine to give trans-1-phenyl-2-toluene-p-sulphonylethylene, m.p. 122—123° (Found: C, 69.6; H, 5.4; S, 13.0. $C_{15}H_{14}O_2S$ requires C, 69.8; H, 5.4; S, 12.4%). In the n.m.r. spectrum of this product the vinylic protons, at $\tau 2.33$ and 3.17 had J 15.4 c./sec. whilst the i.r. spectrum showed vibrations of a trans-CH:CH system at 970, 1625, and 3000 cm.⁻¹.

(v) 1,1-Diphenylethylene (8.9 g.) in carbon tetrachloride gave a 76% yield of 1,1-diphenyl-2-toluene-*p*-sulphonylethylene, m.p. 103—104° (lit.,^{10,18} 103—103.5°) (Found: C, 75.2; H, 5.4; S, 9.7. Calc. for $C_{21}H_{15}O_2S$: C, 75.4; H, 5.4; S, 9.6%). Its n.m.r. spectrum accorded with published data.¹⁰

(vi) Cyclohexene (10 g.) in carbon tetrachloride (250 ml.) gave an unstable adduct which when warmed with triethylamine yielded 1-toluene-*p*-sulphonylcyclohexene, m.p. 83—84° (lit.,¹⁹ 82—83°) (Found: C, 66·2; H, 6·8; S, 13·4%. Calc. for $C_{13}H_{16}O_2S$: C, 66·2; H, 6·8; S, 13·6%). Its i.r. spectrum showed olefinic bands at 660, 1645, and 3090 cm.⁻¹ while its n.m.r. spectrum showed 1 vinylic proton, $\tau 2\cdot9$ —3·1, distinguishable from the aromatic hydrogens with $\tau 2\cdot27$ —2·78.

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¹⁵ A. Rembaum and M. Szwarc, J. Amer. Chem. Soc., 1955, 77, 4468.

¹⁶ F. C. Whitmore and F. H. Hamilton, ed. H. Gilman and A. H. Blatt, Org. Synth., Coll. Vol. I, 1947, p. 492.

¹⁷ F. C. Whitmore and N. Thurman, J. Amer. Chem. Soc., 1923, **45**, 1068.

¹⁸ P. Karrer, W. Wehrli, E. Biedermann, and M. Vedova, *Helv. Chim. Acta*, 1928, **11**, 233.

¹⁹ F. G. Bordwell and R. J. Kern, J. Amer. Chem. Soc., 1955, 77, 1143.

Effect of light and inhibitors. This is shown in Table 4. The percentage of quinol added is the molar per cent relative to the toluene-*p*-sulphonyl iodide. Reactions in 'light' were effected in daylight on a laboratory bench not exposed to direct sunlight.

Attempted Reactions with Toluene-p-sulphonyl Cations.— (a) Silver perchlorate ($6\cdot 3$ g., $0\cdot 03$ mole) and calcium carbonate ($6\cdot 0$ g., $0\cdot 06$ mole) were suspended, by vigorous

TABLE 4

Effects of light and of inhibitors on additions of Toluene-*p*-sulphonyl iodide to olefins

()		
No inhibitor 2.6% Quinol 8%	8% Quinol	
$\begin{array}{c ccc} Yield & Yield \\ Conditions (\%) & Conditions (\%) & Conditions (\%) \\ 14 hr. light 57 & 18 hr. dark & 0 & 18 hr. \\ 14 hr. dark & 59 & 41 hr. dark & 0 & +23 hr. \\ & & 89 hr. dark & 0 \end{array}$	Yield tions (%) dark 0 light 25	

(B) Addition to vinyl cyanide [as (ii)]							
No inhibitor	3·4% Quinol		6.8% Quinol				
Yield Conditions (%)	Conditions	Yield (%)	Conditions	Yield (%)			
24 hr. dark $12+0.5 hr. light 42$	17 hr. dark 65 hr. dark	$3.4 \\ 16.8$	17 hr. dark 65 hr. dark	$0 \\ 12.5$			
+1.0 hr. light 58 +3.5 hr. light 63	+7 hr. light +24 hr. light	54 66	+7 hr. light +31 hr. light	$\frac{41}{55}$			

stirring, in dry benzene (100 ml.) and a mixture of toluene*p*-sulphonyl chloride (3.9 g., 0.02 mole) and α -methylstyrene (2.4 g., 0.02 mole) in benzene (25 ml.) was slowly added. After 3 hours' stirring the mixture was stored overnight, then decomposed with ice and filtered. The solids were extracted with benzene and the combined benzene solutions were evaporated. The small amount of brown oil which remained contained no sulphone (absence of i.r. SO₂ bands).

(b) Anhydrous aluminium chloride (14 g.) was added to a solution of toluene-*p*-sulphonyl chloride (10 g.) in dry ether (150 ml.) and when dissolution was complete α -methyl-styrene (7·1 g.) was added. After 18 hr. a gel had formed. It was treated with water, extracted with chloroform, and the organic layer was washed with water, dried, and evaporated. By treatment with light petroleum 8·5 g. of toluene-*p*-sulphonyl chloride, m.p. 65—67°, was recovered together with the dimer of α -methylstyrene but no sulphone.

(c) Anhydrous aluminium chloride (14 g.) was dissolved in a solution of toluene-*p*-sulphonyl chloride (10 g.) in dry ether (160 ml.) at 0° and vinyl cyanide (3 g.) in ether (40 ml.) was added slowly with stirring. On the following day the mixture was decomposed with water and the organic layer was dried and evaporated, whereupon 90% of the toluene-*p*-sulphonyl chloride was recovered. Similar results were obtained with benzenesulphonyl chloride which was used without a co-solvent.

Decomposition of Toluene-p-sulphonyl Iodide.—(a) Reaction with copper bronze powder. Toluene-p-sulphonyl iodide (17 g.) dissolved in dry (P_2O_5) redistilled carbon tetrachloride (200 ml.) was stirred for 4 hr. at reflux temperature under nitrogen with copper powder (5 g.). The mixture was filtered hot and the grey solid which remained was extracted with chloroform and then ethanol. It was

²⁰ L. Field and P. H. Settlage, J. Amer. Chem. Soc., 1954, 76, 1224.

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mainly copper iodide but extraction with water gave a pale blue solution in which a little toluene-*p*-sulphonate but no toluene-*p*-sulphinate was detected (no reaction with ferric chloride). On storage at 0° the carbon tetrachloride solution deposited crystals of toluene-*p*-sulphonic an-hydride, m.p. 99—100° (4.25 g., 69%), and mixed m.p. 98—102°, the low m.p. (lit.,²⁰ 128—129.5°) being due to contamination with some toluene-*p*-sulphonic acid (cf. Field and Settlage ²⁰). The filtrate from the above was concentrated at reduced pressure to a thick oil which when cooled and triturated with light petroleum (20 ml., b.p. 60—80°) gave *p*-tolyl toluene-*p*-thiolsulphonate (2·1 g., 72%), m.p. 75—76°, which was unchanged after admixture with an authentic specimen prepared as described by Karrer *et al.*¹⁸ Yields have been calculated from eqn. (4).

(b) Photolysis. Toluene-*p*-sulphonyl iodide (17 g.) in benzene (250 ml.) was irradiated for 7 hr. with a 1 kw Hanovia u.v. lamp (type 67/36). The deep brown solution was extracted with 10% aqueous sodium thiosulphate to remove iodine and unchanged iodide and then dried. One half was evaporated under reduced pressure to leave a little white solid (0.29 g., 5%) which was di-*p*-tolyl disulphone,²¹ m.p. and mixed m.p. 218—219°. The other half was treated with aniline (3 ml.). After 15 min. phenylammonium toluene-*p*-sulphonate (0.9 g., 23%), m.p. and mixed m.p. 221—225° had separated.

(c) Toluene-*p*-sulphonyl iodide and sodium toluene*p*-sulphinate dihydrate reacted under ether or carbon tetrachloride to give only di-*p*-tolyl disulphone, m.p. 217— 220° (lit.,²¹ 221°). The latter (4 g.) was refluxed in carbon tetrachloride (100 ml.) with copper powder (2 g.) for 7 hr., then 90% of the disulphone was recovered.

(d) Reaction with 2-cyano-2-propyl radicals. Azobisisobutyronitrile (9 g., 0.05 mole) and toluene-p-sulphonyl iodide (15 g., 0.05 mole) were refluxed in dry benzene (250 ml.) for 6 hr. To 50 ml. of the cooled solution aniline (2 ml.) was added; phenylammonium toluene-p-sulphonate (0.5 g.), corresponding to a 37% yield of toluene-p-sulphonic anhydride, separated. The benzene was removed from the remainder of the solution and light petroleum (250 ml., b.p. 60-80°) was added to the residue; an orange solid separated. The light petroleum solution was fractionated and yielded 2-iodo-2-methylpropionitrile (4.0 g., b.p. 62°/15 mm.) which was identified by spectroscopic comparison with an authentic specimen 22,8 and by conversion into the amide, m.p. 181-182° (lit.,²² 183-184°). The orange solid when washed with carbon tetrachloride (20 ml.) left di-p-tolyl disulphone (1.18 g., 18%).

From a similar reaction in carbon tetrachloride, with 1.5 moles of azo-compound per mole of toluene-p-sulphonyl iodide a mixture of toluene-p-sulphonic anhydride and dip-tolyl disulphone separated on cooling (see Table 2). Evaporation of the carbon tetrachloride and treatment of the residue with light petroleum (200 ml., b.p. 40--60°) separated tetramethylsuccinonitrile (2.5 g., 29%), m.p. and mixed m.p. 161-162°. Chromatography of the residue from distillation of the 2-iodo-2-methylpropionitrile eventually separated a solid (m.p. 181-183; 0.68 g.), which from the presence of both i.r. C=O and SO₂ bands $\alpha \text{-toluene-p-sulphonylisobutyramide},$ be may mainly TolSO₂·CMe₂·CONH₂ (Found: C, 61.0; H, 6.2; S, 13.5; N, 6·1. C₁₁H₁₅NO₃S requires C, 55·5; H, 6·3; S, 13·3; N, 5.8%).

²¹ T. P. Hilditch, J. Chem. Soc., 1908, 1524.

²² M. C. Ford and W. A. Waters, J. Chem. Soc., 1957, 1853.

(e) Reaction with 1-cyanocyclohexyl radicals. On account of its greater stability 1,1-azobis-(1-cyanocyclohexane) (0.064 mole) and toluene-*p*-sulphonyl iodide (0.064 mole)were refluxed together in benzene (250 ml.) for 43 hr. The products listed in Table 2 were isolated by the procedure of section (d). The much greater relative yield of toluene*p*-sulphonic anhydride is clearly due to the very low concentration of free 1-cyanocyclohexyl radicals in the hot benzene.

Reactions of Toluene-p-sulphonyl Radicals with Quinones.— Equimolar amounts of toluene-p-sulphonyl iodide, the quinone, and copper bronze powder were refluxed together for 7 hr. in rapidly stirred carbon tetrachloride. The solutions were then filtered hot to remove copper salts and then stirred at 0° to separate any sparingly soluble organic compounds.

From benzoquinone, crystals, m.p. 145-150° separated. A part of these dissolved easily in cold benzene and treatment of the benzene solution with aniline gave phenylammonium toluene-p-sulphonate, thus establishing the formation of toluene-p-sulphonic anhydride (for yields see Table 3). The cold carbon tetrachloride solution was washed with 10% sodium hydroxide to remove free phenols (none were detectable), then with 10% alkaline sodium dithionite to remove unchanged quinone, and finally with water. After drying, the carbon tetrachloride was evaporated leaving a solid, m.p. 153-158°, which was washed with a little cold benzene. Evaporation of this benzene solution gave p-tolyl toluene-p-thiolsulphonate, m.p. 74- 75° (lit., 76°) which was identified spectroscopically. The solids insoluble in cold benzene were combined and crystallised from hot benzene to give quinol ditoluene-p-sulphonate, m.p. 162-163°, unchanged after admixture with an authentic specimen prepared from quinol and toluenep-sulphonyl chloride in alkaline aqueous acetone.

The products from the other quinones were examined similarly. With *m*-xyloquinone and thymoquinone pure toluene-*p*-sulphonic anhydride crystallised directly. Some of the ditoluene-*p*-sulphonates of the 1,4-dihydroxybenzene derivatives listed in Table 3 do not seem to have been reported hitherto. Each was further characterised by satisfactory analysis and by i.r. and n.m.r. spectra.²³

In a blank experiment toluene-*p*-sulphonyl iodide and benzoquinone were refluxed for 7 hr. in carbon tetrachloride in the absence of copper. After storage at 0°, 76% of unchanged toluene-*p*-sulphonyl iodide crystallised from the solution; some benzoquinone was also recovered. Toluene*p*-sulphonic anhydride was recovered in 96% yield after reflux for 6 hr. with benzoquinone in carbon tetrachloride. Toluene-*p*-sulphonyl iodide (5 g.), quinol (2 g.), and copper powder (1.5 g.) were refluxed in benzene for 4 hr. The solution was filtered hot from copper salts and then cooled, whereupon some white crystals (0.34 g., m.p. 155—180°) separated. A test with aniline of the benzene solution showed the absence of toluene-*p*-sulphonic anhydride and, after evaporation, no di-ester of the quinol separated.

Extraction of the copper salts with hot benzene gave a further amount of the solid, m.p. 155—180°, which contained some quinol. The latter was washed out with ether, whereupon 2-toluene-p-sulphonyl quinol remained (0.6 g.), m.p. 209—211°, unchanged after admixture with an authentic specimen made from p-benzoquinone and toluene-p-sulphinic acid.¹⁴

Attempts to Produce and Study Arenesulphinyl Radicals.---Benzenesulphinyl, toluene-p-sulphinyl, and naphthalene-2-sulphinyl chlorides were prepared by treating the corresponding sulphinic acids with thionyl chloride.9 (i) Toluene-p-sulphinyl chloride (4 g.) and copper powder (3 g.) were stirred for 6 hr. in carbon tetrachloride. The mixture was left overnight, then heated and filtered. Evaporation of the filtrate in a vacuum gave a yellow residue which when crystallised from light petroleum gave p-tolyl toluene-p-thiolsulphonate (1.16 g., 36%), m.p. 74-75°, identified spectroscopically and by mixed m.p. with an authentic specimen. (ii) Toluene-p-sulphinyl chloride (10 g.), cyclohexene (5 g.), and copper powder (6 g.) were stirred for 4 hr. in carbon tetrachloride (50 ml.). The mixture was then warmed, filtered, and the filtrate concentrated to 30 ml. and cooled. Addition of light petroleum (15 ml.) caused the deposition of p-tolyl toluenep-thiolsulphonate (3.5 g., 44%), m.p. 73-76°. The remaining liquid was fractionated under reduced pressure. It gave a very small amount of yellow oil that was shown spectroscopically to contain *p*-tolyl toluene-*p*-thiolsulphonate but did not give any sulphoxide absorption band. A similar result was obtained in boiling carbon tetrachloride. Additions of toluene-p-sulphinyl chloride to styrene and ethyl cinnamate, of benzenesulphinyl chloride to cyclohexane and α -methylstyrene, and of naphthalene-2-sulphinyl chloride to styrene under u.v. irradiation again vielded only oils devoid of sulphoxide absorption bands. (iii) Toluene-p-sulphinyl chloride (6.5 g.), benzoquinone (2 g.), and copper (2.5 g.) were stirred in carbon tetrachloride (100 ml.) for 3 hr. The mixture was then stored for 2 days, warmed, filtered, and cooled whereupon a little benzoquinone separated. From part of the filtrate, by evaporation under diminished pressure followed by t.l.c., both benzoquinone and p-tolyl toluene-p-thiolsulphonate were separated, and from another part, after washing with aqueous sodium dithionite, pure p-tolyl toluene-p-thiolsulphonate was crystallised. A similar reaction was carried out in boiling carbon tetrachloride: 30% of benzoquinone and 40% of p-tolyl toluene-p-thiolsulphonate were recovered.

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²³ Full details are given by C. da S. Corrêa, D.Phil. Thesis, Oxford University, 1966.