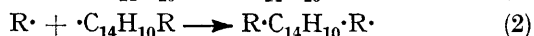
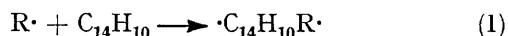


## Reactions of the Free Toluene-*p*-sulphonyl Radical. Part II.<sup>1</sup> Reactions with Polycyclic Aromatic Hydrocarbons

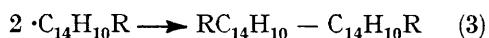
By C. M. M. da Silva Corrêa and William A. Waters,\* The Dyson Perrins Laboratory, Oxford University

Toluene-*p*-sulphonyl iodide, in the presence of copper powder, adds  $p\text{-Me}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot$  radicals to the *meso*-positions of both anthracene and 2,3-benzanthracene: there is no reaction with phenanthrene or 1,2-benzanthracene. In the absence of copper some *meso*-substitution of anthracene also occurs. With both 9-methyl and 9,10-dimethyl-anthracene side-chain substitution of hydrogen by  $p\text{-Me}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot$  occurs at a *meso*-methyl group. These reactions are interpreted in relation to the partial polar character of toluene-*p*-sulphonyl free radicals.

FREE radicals react with aromatic compounds by addition (eqn. 1) to the  $\pi$ -electron system. With hydrocarbons of the anthracene series this attack occurs very easily at *meso*-positions, additions of phenyl,<sup>2</sup> methyl,<sup>3</sup> benzyl,<sup>4,5</sup> 2-cyano-2-propyl,<sup>6</sup> benzoyloxy,<sup>7</sup> and of a number of thiyl<sup>8</sup> radicals having been reported. Fol-



(giving *meso*-disubstituted 9,10-dihydroanthracenes)

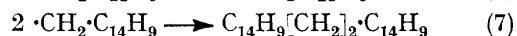
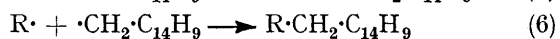


(giving di-substituted-tetrahydrobianthryls)



(giving *meso*-mono-substituted anthracenes)

lowing the initial addition, three reactions (2–4) are possible. With strongly electrophilic (*i.e.*, oxidising) radicals such as benzoyloxy<sup>7</sup> the aromatisation (4) is favoured, but with more nucleophilic radicals, such as benzyl,<sup>4,5</sup> 2-cyano-2-propyl,<sup>6</sup> or thiyl,<sup>8</sup> with which reducing ( $\text{R}\cdot \longrightarrow \text{R}^+ + \text{e}$ ) rather than oxidising ( $\text{R}\cdot + \text{e} \longrightarrow \text{R}^-$ ) reactions are favoured, the additions (2) and (3) are dominant, one or other of these preponderating according to the relative concentrations of the radicals  $\text{R}\cdot$  and  $\cdot\text{C}_{14}\text{H}_{10}\text{R}$  in the system. With 9-methylanthracene, as with toluene, another initial reaction (5) is possible and this can lead either to side-chain substitution (6) or to dimerisation (7) to a compound of bibenzyl type. Again it is with strongly electrophilic

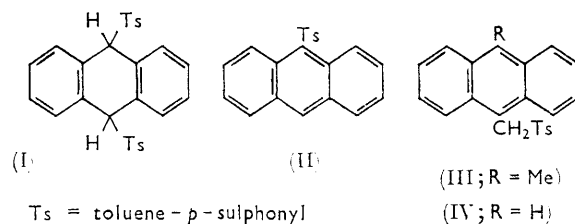


radicals (*e.g.*,  $\text{Br}\cdot$ ,  $\text{PhCO}\cdot\text{O}$ ) that reaction (5) is favoured in comparison with (1).

Since the study of the reactivity of a free radical towards hydrocarbons of the anthracene series gives information concerning its partial polar character it has been of interest to discover whether the strongly dipolar  $\text{SO}_2$  group of the toluene-*p*-sulphonyl free radical, would

endow it with electrophilic properties, similar to that of the benzoyloxy-radical rather than with the nucleophilic properties shown by thiyl radicals,  $\text{R}\cdot\text{S}\cdot$ .

When toluene-*p*-sulphonyl iodide reacted with anthracene in the presence of copper powder the adduct 9,10-dihydro-9,10-ditoluene-*p*-sulphonylanthracene (I) (reaction 2) was obtained in 22% yield together with another substance (perhaps a stereoisomer) which, like the adduct (I), was converted into 9-toluene-*p*-sulphonylanthracene (II) on chromatography through alumina. In the absence of copper a lower yield of (I) was obtained together with (II). In these circumstances iodine may act as the attacking radical of equation (4).



With 9,10-dimethylanthracene the side-chain substitution product (10-methyl-9-anthryl)-toluene-*p*-sulphonylmethane (III) was formed in 49% yield (reaction-5 and 6) in the presence of copper, and similarly 9-methylanthracene gave 9-anthryl-toluene-*p*-sulphonylmethane (IV). Products of similar type to (III) and (IV) are not formed with benzyl, 2-cyano-2-propyl, or thiyl radicals, so we conclude that toluene-*p*-sulphonyl radicals are more electrophilic (*i.e.*, better hydrogen abstractors) than these radicals, but less electrophilic than benzoyloxy-radicals. This accords with the strongly dipolar nature of the sulphone group of toluene-*p*-sulphonyl, provided that the unpaired electron is localised more at weakly electrophilic sulphur than at strongly electrophilic oxygen.

In the benzanthracene series, toluene-*p*-sulphonyl radicals could be added in 61% yield to the linear isomer, 2,3-benzanthracene, but no reaction could be effected with 1,2-benzanthracene. The latter, with only two *meso*-positions, is the less reactive hydrocarbon, but steric hindrance may also be involved. Phenanthrene

<sup>1</sup> Part I, C. M. M. da S. Corrêa and W. A. Waters, preceding paper.

<sup>2</sup> R. O. C. Norman and W. A. Waters, *J. Chem. Soc.*, 1958, 167.

<sup>3</sup> A. J. L. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1956, 1108.

<sup>4</sup> A. J. L. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1957, 1001.

<sup>5</sup> R. O. C. Norman and W. A. Waters, *J. Chem. Soc.*, 1957, 950.

<sup>6</sup> A. F. Bickel and E. C. Kooyman, *Rec. Trav. chim.*, 1952, **71**, 1137.

<sup>7</sup> I. M. Roitt and W. A. Waters, *J. Chem. Soc.*, 1952, 2695.

<sup>8</sup> A. J. L. Beckwith and B. S. Low, *J. Chem. Soc.*, 1961, 1304; 1964, 2571; *Austral. J. Chem.* 1963, **16**, 845; 1964, **17**, 109.

Org.

also was not attacked and neither were cumene or *m*-xylene with which side-chain reactivity (reaction 5) might have been expected.

## EXPERIMENTAL

*Reactions of Toluene-*p*-sulphonyl Iodide with Anthracene.*

(i) Following a pilot experiment which showed that it was very difficult to separate unchanged anthracene from reaction products and that 9,10-dihydro-9,10-ditoluene-*p*-sulphonylanthracene (I) was converted into 9-toluene-*p*-sulphonylanthracene on chromatography in benzene through deactivated alumina, toluene-*p*-sulphonyl iodide<sup>1</sup> (34 g., 0.12 mole), anthracene (6.5 g., 0.036 mole), and copper powder (10 g., 0.15 g.-atom) and calcium carbonate (20 g.), added to maintain neutrality, were refluxed in benzene (350 ml.) for 4 hr. with vigorous stirring. The hot mixture was filtered from a grey solid and cooled; 1.5 g. of (I), m.p. 148—149° separated. Extraction of the grey solid with hot chloroform and evaporation gave a pale green solid which when washed with aqueous ammonia to remove copper salts gave a further 2.4 g. of (I), m.p. 149—150°. The cold benzene solution was concentrated, under diminished pressure, to 50 ml. and cooled to 6° whereupon 3.8 g. of white crystals, m.p. 148—149°, separated. Analysis, t.l.c., and i.r. spectrum showed that these were comprised of two compounds of very similar properties and  $R_f$ , one being (I) (the other perhaps a geometrical isomer). Evaporation of the remaining benzene solution and treatment of the residue with cold carbon tetrachloride left 1.1 g. of toluene-*p*-sulphonic anhydride, m.p. 101—103° (cf. Part I). Pure (I) when crystallised from acetic acid and then methanol had m.p. 152° (Found: C, 68.6; H, 4.7; S, 13.0.  $C_{28}H_{24}O_4S_2$  requires C, 68.8; H, 4.9; S, 13.1%). Its solution in chloroform was not fluorescent in u.v. light and had  $\lambda_{max}$  2375 Å ( $\epsilon$  15,600); its i.r. spectrum showed sulphone bands at 1180 and 1310  $cm^{-1}$  besides absorptions in the 950—1225  $cm^{-1}$  region characteristic of both 1,2- and 1,4-disubstituted benzene rings and its n.m.r. spectrum had a band at  $\tau$  7.75 (6H corr. to  $2CH_3$ ) and another at  $\tau$  5.23 (2H corr. to the *meso*-hydrogens) together with bands in the range  $\tau$  2.45—3.72 (16 aromatic H). When (I) (0.5 g.) in chloroform was passed through an alumina column (100 g.) a strong yellow band appeared and further chromatography of the yellow product followed by crystallisation from carbon tetrachloride gave 9-toluene-*p*-sulphonylanthracene (II), m.p. 190—191° (Found: C, 75.4; H, 4.6; S, 9.7.  $C_{21}H_{16}O_2S$  requires C, 75.9; H, 4.8; S, 9.6%;  $M$ , 332). Its solution in chloroform was fluorescent and had  $\lambda_{max}$  2620 ( $\epsilon$  106,000), 3650 ( $\epsilon$  5600), and 3900 Å ( $\epsilon$  6200); its i.r. spectrum showed sulphone bands at 1550 and 1320  $cm^{-1}$  and its n.m.r. spectrum a singlet at  $\tau$  7.72 ( $3H \equiv CH_3$ ), another at  $\tau$  1.34 (1 *meso*-H), bands in the  $\tau$  1.90—2.83 region (10 aromatic H), and a doublet at  $\tau$  0.57 ( $J$  ca. 8.6 c./sec.) which we tentatively assign to the *peri*-hydrogens (positions 1 and 8) of the anthracene flanking the toluene-*p*-sulphonyl group (position 9). Its mass spectrum showed a molecular-ion peak at  $m/e$  332 and major fragmentation peaks at 267 and 268 (losses of  $SO_2 + HSO_2$ ), 253, 193 and 176—178 ( $C_{14}H_8$  has  $M$  177).

(ii) Toluene-*p*-sulphonyl iodide (36 g., 0.13 mole) anthracene (15 g., 0.084 mole), and calcium carbonate (20 g.) were refluxed in benzene (350 ml.) for 8 hr. The mixture was filtered hot and the residue washed with hot benzene. From the combined solutions 4 g. of a brown solid separated

after cooling. This solid when treated with cold carbon tetrachloride and then washed with acetone yielded 2.8 g. of (I), m.p. 149—151°. The benzene solution was washed with alkaline aqueous sodium thiosulphate to remove iodine and unchanged iodide and then was dried and evaporated to give 2.4 g. of a yellow solid, m.p. 185—190°, which when crystallised from carbon tetrachloride was (II), m.p. 190—191°. Extraction of the calcium carbonate residue from the reaction with hot chloroform yielded a further 5.3 g. of (I).

*Reaction of Toluene-*p*-sulphonyl Iodide with 9,10-Dimethylantracene.*—This was carried out as above with 11 g. (0.039 mole) of iodide and 2.0 g. (0.01 mole) of hydrocarbon. The yellow product (yield 49%), after crystallisation from ethanol, had m.p. 214—215° and its solutions were fluorescent under u.v. light. The u.v. spectrum was of anthracenoid type with  $\lambda_{max}$  2630 ( $\epsilon$  95,000), 3440 ( $\epsilon$  2850), 3620 ( $\epsilon$  6000), 3700 ( $\epsilon$  11,050), and 4020 Å ( $\epsilon$  8600) and its i.r. spectrum showed sulphone bands at 1140 and 1310  $cm^{-1}$ . The n.m.r. spectrum, with bands at  $\tau$  7.70 and 6.93 ( $2CH_3$  groups) 4.60 ( $CH_2$ , shielded) and 1.64—2.94 (12 aromatic C-H) was diagnostic of (10-methyl-9-anthryl)toluene-*p*-sulphonylmethane (III) (Found: C, 76.1; H, 5.5; S, 8.9.  $C_{23}H_{20}O_2S$  requires C, 76.7; H, 5.6; S, 8.9%;  $M$ , 360). Its mass spectrum showed a molecular-ion peak at  $m/e$  360 and major fragmentation peaks at 205 (loss of  $SO_2 + C_7H_7$ ), 191, and 178.

*Reaction of Toluene-*p*-sulphonyl iodide with 9-Methylanthracene.*—This was carried out similarly. From the initial benzene filtrate colourless crystals, m.p. 131—135° (decomp.) separated (5%). These were too insoluble in common solvents for purification, but their i.r. spectrum in Nujol paste resembled that of (I). From the benzene solution, after concentration, fluorescent yellow 9-anthryl-toluene-*p*-sulphonylmethane (IV) was isolated in 30% yield, m.p. 212—214° (Found: C, 76.1; H, 5.3; S, 9.3.  $C_{22}H_{18}O_2S$  requires C, 76.3; H, 5.2; S, 9.3%;  $M$ , 346). Its u.v. spectrum in chloroform had  $\lambda_{max}$  2590 ( $\epsilon$  55,500), 3370 ( $\epsilon$  2360), 3530 ( $\epsilon$  5350), 3720 ( $\epsilon$  8500), and 3920 Å ( $\epsilon$  7650) and its i.r. spectrum sulphone bands at 1140 and 1310  $cm^{-1}$ . The diagnostic n.m.r. spectrum showed singlets at  $\tau$  7.73 ( $CH_3$ ), 4.62 ( $CH_2$  shielded) and 1.60 (C-H *meso*) together with bands at  $\tau$  2.9—3.1 (12 aromatic C-H). Its mass spectrum showed a molecular-ion peak at  $m/e$  346 and major fragmentation peaks at 193—190 (max at 192) again corresponding to loss of  $SO_2 + C_7H_7$  ( $C_{15}H_{12}$  has  $M$ , 192).

*Reactions of Toluene-*p*-sulphonyl Iodide with Benzanthracenes.*—The iodide (18 g.), 2,3-benzanthracene (5 g., 3 equiv.), and copper (5 g.) were refluxed in benzene for 5 hr. The mixture was filtered hot and the filtrate concentrated to 75 ml. whereafter a white solid (0.73 g.) separated on cooling. The residual solution after evaporation and treatment with light petroleum yielded a mixture of toluene-*p*-sulphonic anhydride and *p*-tolyl toluene-*p*-thiol-sulphonate (0.4 g., identified spectroscopically). Extraction with chloroform of the material insoluble in benzene gave more white solid (6.5 g.) which when crystallised from chloroform-methanol proved to be 9,10-dihydro-9,10-ditoluene-*p*-sulphonyl-2,3-benzanthracene, m.p. 190—191° (Found: C, 71.4; H, 4.8; S, 12.3.  $C_{32}H_{26}O_4S_2$  requires C, 71.4; H, 4.9; S, 11.9%). Its u.v. spectrum in chloroform had  $\lambda_{max}$  2400 ( $\epsilon$  5600), 2820 ( $\epsilon$  4065), and 2925 Å ( $\epsilon$  3575), its i.r. spectrum showed sulphone bands at 1170 and 1315  $cm^{-1}$ , whilst the n.m.r. spectrum had bands at  $\tau$  7.75 ( $CH_3$ ), 4.99 (*meso*-C-H) and 1.85—3.83 (aromatic

C-H) but the material was too sparingly soluble in  $\text{CDCl}_3$  for accurate integration of the spectrum.

A reaction, on the same scale, with 1,2-benzanthracene yielded *ca.* 3 g. of toluene-*p*-sulphonic anhydride, *ca.* 2 g. of *p*-tolyl toluene-*p*-thiolsulphonate, and unchanged hydrocarbon. In the absence of copper the recovery of 1,2-benzanthracene was 94%.

The reaction of toluene-*p*-sulphonyl iodide with copper powder in cumene at 80° also yielded only toluene-*p*-sulphonic anhydride, m.p. 101—103° and *p*-tolyl toluene-

*p*-thiolsulphonate, m.p. 73—76°. Similar negative results were obtained with solutions of phenanthrene, 2,6-dimethylnaphthalene, or *m*-xylene.

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