Preparation and some Reactions of 6-Arylsulphonimidobenzoxazol-2(3*H*)-ones

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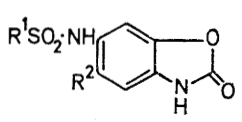
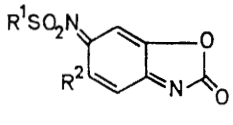
The title compounds, prepared from 6-arylsulphonamidobenzoxazol-2(3*H*)-ones by oxidation, undergo addition of hydrogen chloride, hydrazoic acid, benzenesulphinic acid, and acetylacetone to give substituted benzoxazol-2(3*H*)-ones. In contrast, piperidine and methanol cleave the heterocyclic ring.

NN'-Diarylsulphonyl- and *N*-acyl-*N'*-arylsulphonyl-1,4-benzoquinone di-imines readily undergo addition and substitution reactions to produce derivatives of *p*-phenylenediamine.[1] This paper describes similar reactions carried out on analogous di-imines in which the acyliminogroup forms part of a heterocyclic ring.



(I)



(II)

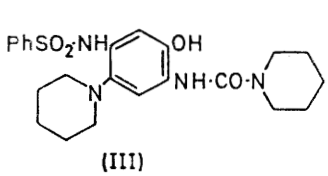
Oxidation of benzoxazol-2(3*H*)-one (I; $R^1 = p$-MeC_6H_4, $R^2 = H$) with lead tetra-acetate in a small volume of acetic acid at room temperature gave (60%) the quinone di-imine (II; $R^1 = p$-MeC_6H_4, $R^2 = H$), a derivative of the unknown oxazol-2(5*H*)-one. Its structure was supported by its spectral properties. The u.v. spectrum was similar to those of *NN'*-diphenylsulphonyl-1,4-benzoquinone di-imines.[2] The i.r. spectrum contained no NH absorption but showed a sharp peak at 1817 cm.$^{-1}$ assigned to the oxazolone carbonyl group [for compound (I; $R^1 = p$-MeC_6H_4, $R^2 = H$) $\nu_{max.}$ 1770 cm.$^{-1}$]. Its n.m.r. spectrum, detailed in the Experimental section, contained an AMX pattern corresponding to protons 4-H, 5-H, and 7-H. As in related compounds[3] there was evidence of isomerism about the C=N bond of the sulphonimido-group but one isomer was far more predominant in solution in deuteriochloroform. A similar compound (II; $R^1 =$ Ph, $R^2 = H$) was obtained by oxidation of the oxazolone (I; $R^1 =$ Ph, $R^2 = H$).

Compounds of type (II) undergo many of the normal addition reactions characteristic of quinones. Thus di-imine (II; $R^1 = p$-MeC_6H_4, $R^2 = H$) reacted readily with hydrogen chloride in benzene to give the chlorobenzoxazol-2(3*H*)-one (I; $R^1 = p$-MeC_6H_4, $R^2 = Cl$). The position of substitution was suggested by the n.m.r. spectrum which showed two sharp singlets, superimposed upon the signals from the tosyl group, at τ 2·40 and 2·74. These were assigned to the protons at positions 4 and 7 of the benzoxazolone ring. The structure of this product was confirmed by an alternative synthesis. 5-Chlorobenzoxazol-2(3*H*)-one has been reported to be nitrated at position 6, although no proof of the structure was given.[4] We have repeated this reaction and obtained a nitro-compound the n.m.r. spectrum of which shows only two sharp singlets in the low field region at τ 2·07 and 2·62, thus confirming the structure as 5-chloro-6-nitrobenzoxazol-2(3*H*)-one. This, on reduction followed by tosylation, gave a compound identical in all respects with (I; $R^1 = p$-MeC_6H_4, $R^2 = Cl$) obtained as described above. A similar oxazolone (I; $R^1 =$ Ph, $R^2 = Cl$) was also obtained by addition of hydrogen chloride to the di-imine (II; $R^1 =$ Ph, $R^2 = H$).

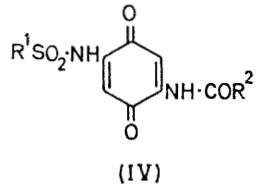
Oxidation of the chloro-compound (I; $R^1 = p$-MeC_6H_4, $R^2 = Cl$) with lead tetra-acetate gave the di-imine (II; $R^1 = p$-MeC_6H_4, $R^2 = Cl$) in good yield. The product readily underwent addition of hydrogen chloride to form 5,(4 or 7)-dichloro-6-toluene-*p*-sulphonamidobenzoxazol-2(3*H*)-one. The di-imine (II; $R^1 =$ Ph, $R^2 = Cl$) was also prepared by a similar method.

Sodium azide reacted with the di-imine (II; $R^1 = p$-MeC_6H_4, $R^2 = H$) in acetic acid solution to yield the azide (I; $R^1 = p$-MeC_6H_4, $R^2 = N_3$). Once again the position of attachment of the azido-group was suggested by the n.m.r. spectrum which contained two sharp 1H singlets at τ 2·44 and 2·90 assigned to positions 4 and 7 and this was confirmed by the direct formation of the same azide from di-imine (I; $R^1 = p$-MeC_6H_4, $R^2 = Cl$) The azide was readily reduced by alkaline sodium dithionite to the aminobenzoxazolone (II; $R^1 = p$-MeC_6H_4, $R^2 = NH_2$).

Analogous addition products (I; $R^1 =$ Ph, $R^2 = SO_2Ph$) and (I; $R^1 = p$-MeC_6H_4, $R^2 = SO_2Ph$) were obtained from the di-imines (II; $R^1 =$ Ph, $R^2 = H$) and (II; $R^1 = p$-MeC_6H_4, $R^2 = H$) respectively by reaction with sodium benzenesulphinate in acetic acid solution. Further, treatment of the latter di-imine with acetylacetone in methanolic sodium methoxide[5] gave the benzoxazol-2-one (I; $R^1 = p$-MeC_6H_4, $R^2 = CHAc_2$). The structures of these products were assigned by n.m.r. spectroscopy and by analogy with the azido- and chloro-compounds discussed earlier.



(III)



(IV)

[1] For a review see R. Adams and W. Reifschneider, *Bull. Soc. chim. France*, 1958, 23.

[2] R. Adams and J. L. Anderson, *J. Amer. Chem. Soc.*, 1950, **72**, 5154.

[3] I. Baxter and D. W. Cameron, *J. Chem. Soc.* (*C*), 1968, 1747.

[4] P. Friedlander, *Fortschritte der Teerfarbenfabrikation und verwandter Industriezweige*, vol. 15, 1545, through Beilstein.

[5] *Cf.* R. Adams and D. C. Blomstrom, *J. Amer. Chem. Soc.*, 1953, **75**, 3403.

A number of examples have also been observed in which nucleophilic addition to the 5-position of the di-imines (II) was accompanied by other products including those formed by opening of the heterocyclic ring. For example, when a benzene solution of compound (II; R^1 = Ph, R^2 = H) was added to one of piperidine, the i.r. spectrum of the almost colourless crude product obtained contained no absorption in the 1700—1800 $cm.^{-1}$ region indicating the absence of the benzoxazol-2-one system. Two compounds were isolated from this reaction product, although t.l.c. investigation indicated traces of several other components. The major product was assigned structure (III). Its i.r. spectrum showed, in addition to –OH and –NH groups, an absorption at 1635 $cm.^{-1}$ consistent with a urea carbonyl group. Its n.m.r. spectrum contained two 1H singlets in the aromatic region and indicated the presence of two piperidino-groups in different environments.

The yellow, minor product was postulated to have structure (IV; R^1 = Ph, R^2 = $\overline{CH_2 \cdot [CH_2]_4 \cdot N}$). Its i.r. spectrum confirmed the presence of phenylsulphonamido- and ureido-groups as well as a quinonoid component. Its n.m.r. spectrum indicated that it contained a piperidino-group and two uncoupled quinonoid protons at τ 3·54 and 2·81.

The formation of these two products can be rationalised in terms of nucleophilic attack by piperidine at the carbonyl group of the heterocyclic ring and position 5 of the quinonoid system. The quinone (IV; R^1 = Ph, R^2 = $\overline{CH_2 \cdot [CH_2]_4 \cdot N}$) arises from compound (III) by oxidation either during the reaction or upon work up. Cleavage of the heterocyclic ring of benzoxazol-2-ones by amines under forcing conditions has been reported.[6]

Opening of the five-membered ring of compound (II; R^1 = *p*-MeC_6H_4, R^2 = H) also occurred on reaction with methanol in the presence of boron trifluoride–ether. The i.r. spectrum of the only product isolated showed that it contained two –NH groups, one urethane group and a quinone nucleus. The n.m.r. spectrum confirmed the presence of a methoxy- and two isolated quinonoid protons. On the basis of this information structure (IV; R^1 = *p*-MeC_6H_4, R^2 = OMe) is suggested for this product.

EXPERIMENTAL

Unless otherwise stated u.v. spectra were measured in 95% ethanol, i.r. spectra in potassium bromide, and n.m.r. spectra in trifluoroacetic acid. All integrations were consistent with the assignments.

6-*Toluene*-p-*sulphonamidobenzoxazol*-2(3H)-*one* (I; R^1 = *p*-MeC_6H_4, R^2 = H).—This was prepared from 6-aminobenzoxazol-2(3*H*)-one hydrochloride [7] (2·5 g.) and toluene-*p*-sulphonyl chloride (2·8 g.) in pyridine (50 ml.) at 0°. The *sulphonamide* (3·4 g.), isolated by pouring the reaction mixture into ice-cold hydrochloric acid, crystallised from aqueous ethanol and had m.p. 208—209° (Found: C, 55·1; H, 3·8; N, 9·2. $C_{14}H_{12}N_2O_4S$ requires C, 55·3; H, 4·0; N, 9·2%); $\lambda_{max.}$ 227 and 286 nm. (log ε 4·19 and 3·77), $\lambda_{infl.}$ 235 nm. (log ε 4·17); $\nu_{max.}$ 3310, 3260, 1770, and 1630 $cm.^{-1}$; τ 7·60 (s, CH_3Ar), 2·97 (dd, *J* 8 and 2 c./sec., 5-H), 2·83br (s, 4-H and 7-H) and 2·34 and 2·67 (AA′BB′, *J* 7 c./sec., tosyl).

6-*Benzenesulphonamidobenzoxazol*-2(3H)-*one* (I; R^1 = Ph, R^2 = H).—This was prepared as described above from the amine (4·8 g.), benzenesulphonyl chloride (4·2 ml.), and pyridine (45 ml.). The *sulphonamide* (5·5 g.) had m.p. 193° (methanol) (Found: C, 53·5; H, 3·8; N, 9·5. $C_{13}H_{10}N_2O_4S$ requires C, 53·8; H, 3·5; N, 9·6%); $\lambda_{max.}$ 241, 268, and 287 nm. (log ε 4·07, 3·65, and 3·75), $\lambda_{infl.}$ 276 nm. (log ε 3·69); $\nu_{max.}$ 3270, 3210, and 1750 $cm.^{-1}$.

6-*Toluene*-p-*sulphonimidobenzoxazol*-2(3H)-*one* (II; R^1 = *p*-MeC_6H_4, R^2 = H).—A mixture of the oxazolone (I; R^1 = *p*-MeC_6H_4, R^2 = H) (2·5 g.), lead tetra-acetate (3·65 g.), and acetic acid (15 ml.) was stirred at room temperature for 10 min. The mixture darkened and a yellow precipitate was deposited. The precipitate was collected, washed with a little acetic acid and then ether, and dissolved in hot benzene (50 ml.). The solution was boiled with charcoal, filtered, and diluted with light petroleum. As it cooled, the *di-imine* (1·5 g.) crystallised and had m.p. 144—145° (Found: C, 56·0; H, 3·5; N, 9·0. $C_{14}H_{10}N_2O_4S$ requires C, 55·7; H, 3·3; N, 9·3%); $\lambda_{max.}$ ($CHCl_3$) 318 nm. (log ε 4·35); $\nu_{max.}$ 1817, 1673, and 1600 $cm.^{-1}$; τ ($CDCl_3$) 7·52 (s, CH_3), 3·02 (dd, *J* 10 and 2 c./sec., 5-*H*), 2·56 (d, *J* 10 c./sec., 4-H), 2·40 (d, *J* 2 c./sec., 7-H), 2·62 and 2·10 (AA′BB′, *J* 8 c./sec., tosyl). There was also a small doublet (*J* 2 c./sec.) at τ 3·65 with an area corresponding to only a fraction of a proton which presumably arises from 7-H in the other geometrical isomer.[3]

6-*Benzenesulphonimidobenzoxazol*-2(3H)-*one* (II; R^1 = Ph, R^2 = H).—This was prepared as described above from the benzoxazolone (I; R^1 = Ph, R^2 = H) (1·45 g.), lead tetra-acetate (2·25 g.), and acetic acid (10 ml.). The *di-imine* (1·0 g.) had m.p. 134—136° (benzene–light petroleum) (Found: C, 54·6; H, 2·8; N, 9·8. $C_{13}H_8N_2O_4S$ requires C, 54·2; H, 2·8; N, 9·7%); $\lambda_{max.}$ ($CHCl_3$) 322 nm. (log ε 4·39); $\nu_{max.}$ (Nujol) 1815, 1670, and 1600 $cm.^{-1}$; τ ($CDCl_3$) 2·99 (dd, *J* 10 and 2 c./sec., 5-H), 2·53 (d, *J* 10 c./sec., 4-H), 2·45—1·95 (m, ArH and 7-H). There was also a weak signal at τ 3·63 (*J* 2 c./sec.) assigned to 7-H in the other geometrical isomer.

6-*Toluene*-p-*sulphonamido*-5-*chlorobenzoxazol*-2(3H)-*one* (I; R^1 = *p*-MeC_6H_4, R^2 = Cl).—Dry hydrogen chloride was passed through a solution of the di-imine (II; R^1 = *p*-MeC_6H_4, R^2 = H) (0·10 g.) in benzene (20 ml.) for 20 min. The resulting colourless solution was evaporated to dryness and the residue was crystallised from aqueous ethanol to give the *chlorobenzoxazol*-2-*one*, m.p. 265—267° (Found: C, 49·9; H, 3·0; N, 7·9. $C_{14}H_{11}ClN_2O_4S$ requires C, 49·6; H, 3·3; N, 8·3%); $\nu_{max.}$ 3250, 3070, 1760, and 1620 $cm.^{-1}$; τ 7·62 (s, CH_3), 2·74 and 2·40 (2s, 4-H and 7-H), 2·72 and 2·35 (AA′BB′, *J* 8 c./sec., tosyl).

5-Chlorobenzoxazol-2(3*H*)-one [4] (20 g.) was added slowly in portions to nitric acid (100 ml.; 67%) at 50°. After completion of addition the mixture was kept for 20 min., and then poured into water. The product was recrystallised from 50% aqueous ethanol to give 5-*chloro*-6-*nitrobenzoxazol*-2(3H)-*one*, m.p. 207—209° (lit.,[4] 207°) (Found: C,

[6] V. Kalcheva and D. Simov, *Compt. Rend. Acad. Bulgare Sci.*, 1965, **18**, 449, (*Chem. Abs.*, 1965, **63**, 8336h).

[7] R. L. Clark and A. A. Passolano, *J. Amer. Chem. Soc.*, 1958, **80**, 1662.

39·2; H, 1·7; N, 13·4. $C_7H_3ClN_2O_4$ requires C, 39·1; H, 1·4; N, 13·0%); $\lambda_{max.}$ 243 and 317 nm. (log ε 4·06 and 3·61); $\nu_{max.}$ 3280br, 3135, 1780, and 1637 cm.$^{-1}$; τ ([$^2H_6$]acetone) 2·62 and 2·07 (2s, 4-H and 7-H). The foregoing nitro-compound (10 g.) was hydrogenated at 50 lb./sq. in. over Adams catalyst in ethanol for 48 hr. to give the amine (8 g.), which was dissolved in pyridine (125 ml.) and treated with toluene-*p*-sulphonyl chloride (8 g.) for 2 hr. The product isolated was chlorotoluenesulphonamidobenzoxazolone, m.p. 265—267° (aqueous ethanol) identical in all respects with that obtained above.

6-*Benzenesulphonamido*-5-*chlorobenzoxazol*-2(3H)-*one* (I; R^1 = Ph, R^2 = Cl).—This was prepared as described above from the di-imine (II; R^1 = Ph, R^2 = H) (0·42 g.) in benzene. The *chloro-compound* (0·34 g.) had m.p. 257—258° (methanol) and was identical with a sample prepared by benzenesulphonation of 6-amino-5-chlorobenzoxazol-2(3*H*)-one (Found: C, 48·1; H, 2·9; N, 8·4. $C_{13}H_9ClN_2O_4S$ requires C, 48·1; H, 2·8; N, 8·6%); $\lambda_{max.}$ 245, 268, 275, and 293 nm. (log ε 3·98, 3·62, 3·62, and 3·78), $\nu_{max.}$ 3300br, 1778, and 1755 cm.$^{-1}$.

5-*Chloro*-6-*toluene*-p-*sulphonimidobenzoxazol*-2(3H)-*one* (II; R^1 = *p*-MeC_6H_4, R^2 = Cl).—A mixture of the chloro-compound (I; R^1 = *p*-MeC_6H_4, R^2 = Cl) (1·0 g.) and lead tetra-acetate (1·35 g.) in acetic acid (10 ml.) was stirred at room temperature for 30 min. The yellow precipitate so formed was recrystallised from benzene–light petroleum to give the *di-imine*, m.p. 188—189° (Found: C, 49·7; H, 2·5; N, 8·3. $C_{14}H_9ClN_2O_4S$ requires C, 49·9; H, 2·7; N, 8·3%); $\lambda_{max.}$ 329 nm. (log ε 4·34); $\nu_{max.}$ 2935, 1837, and 1671 cm.$^{-1}$; τ ($CDCl_3$) 7·50 (s, CH_3), 2·42 and 2·40 (2s, 4-H and 7-H) and 2·55 and 2·00 (AA′BB′, *J* 8 c./sec., tosyl).

When hydrogen chloride was passed into a solution of this di-imine (0·05 g.) in benzene (10 ml.) a white solid was formed which crystallised from aqueous ethanol to give 5,(4 or 7)-*dichloro*-p-*toluene*-6-*sulphonamidobenzoxazol*-2(3H)-*one*, m.p. 341° (decomp.) (Found: C, 45·4; H, 2·3; N, 8·0. $C_{14}H_{10}Cl_2N_2O_4S$ requires C, 45·0; H, 2·7; N, 7·6%); $\lambda_{max.}$ 246 and 294 nm. (log ε 4·02 and 3·76); $\nu_{max.}$ 3360, 3280, 1770, and 1615 cm.$^{-1}$; τ 7·59 (s, CH_3), 2·69 (s, 4- or 7-H), 2·67 and 2·30 (AA′BB′, *J* 8 c./sec., tosyl).

6-*Benzenesulphonimido*-5-*chlorobenzoxazol*-2(3H)-*one* (II; R^1 = Ph, R^2 = Cl).—This was prepared as described above from the chloro-compound (I; R^1 = Ph, R^2 = Cl) (0·32 g.), lead tetra-acetate (0·45 g.), and glacial acetic acid (2 ml.). Recrystallisation from benzene–light petroleum gave the *di-imine* (0·21 g.), m.p. 183—184° (Found: C, 48·8; H, 2·3; N, 8·3. $C_{13}H_7ClN_2O_4S$ requires C, 48·4; H, 2·2; N, 8·7%), $\lambda_{max.}$ ($CHCl_3$) 269 and 330 nm. (log ε 3·64 and 4·37); $\nu_{max.}$ 1825 cm.$^{-1}$; τ ($CDCl_3$) 2·3—2·4 (m, ArH and 4-H and 7-H) and 1·9 (m, ArH).

5-*Azido*-6-*toluene*-p-*sulphonamidobenzoxazol*-2(3H)-*one* (I; R^1 = *p*-MeC_6H_4, R^2 = N_3).—(*a*) To a solution of the compound (II; R^1 = *p*-MeC_6H_4, R^2 = H) (0·25 g.) in acetic acid (10 ml.) was added, with stirring, sodium azide (0·10 g.). The solution turned brown-red and on the addition of water a solid separated. Recrystallisation from aqueous ethanol gave the *azide* (0·21 g.), m.p. 168—170° (decomp.) (Found: C, 49·0; H, 2·8; N, 19·9. $C_{13}H_{11}N_5O_4S$ requires C, 48·7; H, 3·2; N, 20·3%); $\lambda_{max.}$ 224 nm. (log ε 4·35), $\lambda_{infl.}$ 288 and 380 nm. (log ε 3·82 and 3·12); $\nu_{max.}$ 3280, 3060, 2125, 1770, and 1629 cm.$^{-1}$, τ 7·59 (s, CH_3), 2·91 (s, 4-H or 7-H), 2·47 (s, 4-H or 7-H) and 2·67 and 2·34 (AA′BB′, *J* 7 c./sec., tosyl).

(*b*) To a solution of the compound (II; R^1 = *p*-MeC_6H_4, R^2 = Cl) (0·05 g.) in acetic acid (10 ml.) was added a solution of sodium azide (0·015 g.) in water (5 ml.). After 15 min., the solution was diluted with water and the precipitate was collected. Recrystallisation from aqueous ethanol gave the azide, m.p. 168—170° (decomp.). The i.r. and n.m.r. spectra of both samples were identical.

5-*Amino*-6-*toluene*-p-*sulphonamidobenzoxazol*-2(3H)-*one* (I; R^1 = *p*-MeC_6H_4, R^2 = NH_2).—To a solution of the foregoing azide (0·06 g.) in 5% sodium hydroxide solution (5 ml.) was added a solution of sodium dithionite (0·50 g.) in water (10 ml.). The mixture was boiled for 15 min., cooled, and neutralised with 3N-hydrochloric acid. The precipitate was crystallised from aqueous ethanol to give the *amine* (0·05 g.), m.p. 214—216° (Found: C, 53·0; H, 4·3; N, 12·8. $C_{14}H_{13}N_3O_4S$ requires C, 52·6; H, 4·1; N, 13·2%); $\nu_{max.}$ 3470, 3385, 3270, 3235, 1758, and 1680 cm.$^{-1}$; τ 7·50 (s, CH_3), 3·32 and 2·22 (2s, 4-H and 7-H) and 2·57 and 2·35 (AA′BB′, *J* 8 c./sec., tosyl).

5-*Azido*-6-*benzenesulphonamidobenzoxazol*-2(3H)-*one* (I; R^1 = Ph, R^2 = N_3).—Prepared by both methods described immediately above from the di-imines (II; R^1 = Ph, R^2 = H) and (II; R^1 = Ph, R^2 = Cl). The *azide* had m.p. 178—180° (decomp.) (methanol) (Found: C, 46·9; H, 2·8; N, 21·4. $C_{13}H_9N_5O_4S$ requires C, 47·1; H, 2·8; N, 21·2%); $\nu_{max.}$ 3250, 3000, 2118, 1778br and 1630 cm.$^{-1}$.

5-*Benzenesulphonyl*-6-*toluene*-p-*sulphonamidobenzoxazol* 2(3H)-*one* (I; R^1 = MeC_6H_4, R^2 = SO_2Ph).—To a stirred solution of compound (II; R^1 = *p*-MeC_6H_4, R^2 = H) (0·20 g.) in acetic acid (10 ml.) was added sodium benzenesulphinate (0·20 g.). After 5 min., the colourless solution was diluted with water and the precipitate so formed was recrystallised from ethyl acetate. The *sulphone* (0·20 g.) had m.p. 216—218° (Found: C, 54·3; H, 3·6; N, 6·6. $C_{20}H_{16}N_2O_6S_2$ requires C, 54·1; H, 3·6; N, 6·4%); $\lambda_{max.}$ 231 and 312 nm. (log ε 4·52 and 3·76); $\lambda_{infl.}$ 265 and 274 nm. (log ε 3·97 and 3·89); $\nu_{max.}$ 3280, 1779, and 1620 cm.$^{-1}$; τ 7·58 (s, CH_3), 2·40 (m, phenyl), 2·76 and 2·10 (AA′BB′, *J* 8 c./sec., tosyl), 1·93 (s, 4-H or 7-H) and 0·72 and 0·18 (2s, NH).

6-*Benzenesulphonamido*-5-*benzenesulphonylbenzoxazol*-2(3H)-*one* (I; R^1 = Ph, R^2 = SO_2Ph).—This was prepared as described above from the di-imine (II; R^1 = Ph, R^2 = H) (0·09 g.) and sodium benzenesulphinate (0·09 g.). The *sulphone* (0·06 g.) had m.p. 200° (ethyl acetate) (Found: C, 52·5; H, 3·5; N, 6·6. $C_{19}H_{14}N_2O_6S_2$ requires C, 53·0; H, 3·3; N, 6·5%); τ 2·55 (s, 7-H), 2·6—2·1 (m, ArH) and 1·98 (s, 4-H).

5-(*Diacetylmethyl*)-6-*toluene*-p-*sulphonamidobenzoxazol*-2(3H)-*one* (I; R^1 = *p*-MeC_6H_4, R^2 = $CHAc_2$).—To a solution of acetylacetone (0·10 g.) and sodium methoxide (0·054 g.) in methanol (40 ml.) was added the di-imine (II; R^1 = *p*-MeC_6H_4, R^2 = H) (0·30 g.); the mixture was stirred overnight at room temperature. The mixture was poured into water and the precipitate was collected. The precipitate was dissolved in chloroform and the solution was filtered and evaporated to dryness. Recrystallisation of the residue gave the *product* (0·08 g.), m.p. 269—270° (aqueous ethanol) (Found: C, 56·4; H, 5·3; N, 7·4. $C_{19}H_{18}N_2O_6S$ requires C, 56·8; H, 4·9; N, 7·0%); $\lambda_{max.}$ 223 nm. (log ε 4·52); $\nu_{max.}$ 3150, 2890, 1765, and 1622 cm.$^{-1}$; τ 7·55 (s, CH_3), 7·16 and 6·95 (2s, aliphatic CH_3), 5·88 (s, methine), 2·54 and 2·19 (AA′BB′, *J* 8 c./sec., tosyl), 1·79 and 1·50 (2s, ArH).

The Reaction between Piperidine and 6-*Benzenesulphonimidobenzoxazol*-2(3H)-*one*.—To a solution of piperidine

(1·5 g.) in benzene (30 ml.) was added a solution of the di-imine (0·58 g.) in benzene (60 ml.) during 15 min. The mixture was kept overnight, evaporated to dryness, and the residue was swirled with chloroform (15 ml.). The insoluble material crystallised from pyridine to give NN-*pentamethylene*-N′-(4-*benzenesulphonamido*-2-*hydroxy*-5-*piperidino*)*phenylurea* (III) (0·19 g.), m.p. 203—204° (Found: C, 59·8; H, 6·5; N, 11·9. $C_{23}H_{30}N_4O_4S$ requires C, 60·2; H, 6·6; N, 12·2%); M^+ at *m/e* 458; $\nu_{max.}$ (Nujol) 3350, 3150, 1635, 1330, and 1155 cm.$^{-1}$; τ 8·17 and 7·75 (m, piperidino CH_2), 6·33 and 6·15 (m, piperidino CH_2N), 3·76 and 1·59 (2s, 3-H and 6-H of the phenol ring) and 2·3 (m, ArH).

The chloroform-soluble material was chromatographed on silica. Elution with chloroform–methanol (25 : 2) gave a yellow solid which after recrystallisation from benzene and acetone gave 2-*benzenesulphonamido*-5-*piperidinecarboxamido*-1,4-*benzoquinone* (IV; R^1 = Ph, R^2 = N·[CH_2]$_4$·CH_2) (0·065 g.), m.p. 188° (Found: C, 55·3; H, 4·9; N, 11·2. $C_{18}H_{19}N_3O_5S$ requires C, 55·5; H, 4·9; N, 10·8%; M^+ at *m/e* 389); $\lambda_{max.}$ 315 nm. (log ε 4·10); $\nu_{max.}$ 3340, 3140, 1675, 1650, 1640, 1605, 1340, and 1140 cm.$^{-1}$; τ ($CDCl_3$) 8·38 (m, piperidino CH_2), 6·58 (m, piperidino CH_2–N), 3·54 and 2·81 (2s, quinonoid), 2·5—2·35 (m, ArH), 2·2—2·0 (m, ArH and NH) and 1·94 (s, NH). On addition of deuterium oxide the peak at 1·94 disappeared and the signal at 2·2—2·0 was simplified and then possessed an area equivalent to two protons.

The Reaction between Methanol and 6-*Toluene*-p-*sulphonimidobenzoxazol*-2(3H)-*one*.—To a suspension of the di-imine (0·15 g.) in methanol (10 ml.) was added two drops of boron trifluoride–ether. The solid slowly dissolved to give a red solution. After 1·5 hr., water was added and the precipitate so formed was collected and recrystallised from aqueous ethanol to give 2-*toluene*-p-*sulphonamido*-5-*methoxycarbamido*-1,4-*benzoquinone* (IV; R^1 = *p*-MeC_6H_4, R^2 = OMe) (0·04 g.), m.p. 213—215° (Found: C, 51·4; H, 4·0; N, 7·7. $C_{15}H_{14}N_2O_6S$ requires C, 51·4; H, 4·0; N, 8·0%), M^+ at *m/e* 350; $\lambda_{max.}$ 221 and 311 nm. (log ε 4·36 and 4·18); $\nu_{max.}$ 3360, 3250, 1752, 1664, and 1609 cm.$^{-1}$; τ 7·57 (s, CH_3), 6·09 (s, OCH_3), 3·37 and 2·75 (2s, quinonoid H), 2·56 and 2·09 (AA′BB′, *J* 8 c./sec., tosyl) and 1·79 and 1·32 (2s, NH).

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