Persulphate Oxidations. Part VIII.[1] Oxidation of Arylthio-, Arylsulphonyl-, and Arylamino-acetic Acids

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Persulphate oxidation of (biphenyl-2-ylthio)acetic acids gave $ArS\dot{C}R_2$ radicals which mainly cyclised to give monomeric and dimeric thiopyrans. The corresponding sulphonylacetic acid was less reactive giving a lower yield of cyclised product. Oxidation of (biphenyl-2-ylamino)acetic acids yielded only traces of cyclised products owing to the ease with which the intermediate $ArNR\dot{C}H_2$ radicals were oxidised further to cations.

In Part IV [2] we showed that oxidation of biphenyl-2-yloxyacetic acids with persulphate in boiling aqueous solution gave monomeric and dimeric pyrans formed by cyclisation of intermediate *o*-arylphenoxyalkyl radicals. With a view to comparing the relative ease of formation of $ArOCH_2^{\bullet}$, $ArSCH_2^{\bullet}$, and $ArNRCH_2^{\bullet}$ radicals (Ar = biphenyl-2-yl) and the facility with which they undergo intramolecular aromatic substitution we have now oxidised a number of biphenyl-2-ylthio- and biphenyl-2-ylamino-acetic acids with persulphate.

RESULTS

Oxidation of (biphenyl-2-ylthio)acetic acid (1; X = S, R = H) with persulphate gave a product mixture analogous to that obtained from biphenyl-2-yloxyacetic acid (1; X = O, R = H).[2] The main component was

[1] A. R. Forrester, A. S. Ingram, and R. H. Thomson, preceding paper.

[2] P. S. Dewar, A. R. Forrester, and R. H. Thomson, *J. Chem. Soc.* (*C*), 1971, 3950.

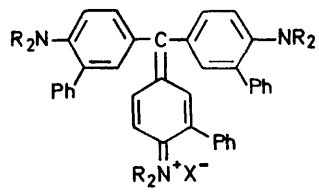
the thiopyran (5; X = S, R = H) (23%); this was accompanied by a little of the thiolactone (8; X = S) (ν_{CO} 1630 cm^{-1}) and dimeric material (*ca.* 13%) of molecular weight *ca.* 400 (osmometric) from which a crystalline product could not be obtained either by crystallisation or chromatography. This fraction we consider to be a mixture of the dimer (7; X = S, R = H) and its tetrahydro- and dihydro-precursors [*e.g.* (6)] since the n.m.r. spectrum showed signals from vinylic (τ 3·3—4·5) and methine and methylene (τ 6·0—7·4), as well as aromatic protons. The homologous acid (1; X = S, R = Me) gave a much higher yield of cyclised product (5; X = S, R = Me) (63%) and a dimeric fraction (*ca.* 23%) containing the disulphide (14; X = S) (*ca.* 4%). The latter could not be separated chromatographically until the dihydro- and tetrahydro-dimers, also present in this fraction, had been converted into the fully aromatised product (7; X = S, R = Me) by treatment with dichlorodicyanobenzoquinone (DDQ). We have assigned a symmetrical structure to compound (7; X = S, R = Me) [and, by analogy, to (7; X = S, R = H)] because the methyl protons resonate as a singlet (τ 8·34). Neither sulphoxides nor sulphones, which were important products in the persulphate oxidation of *o*-thiophenoxybenzoic acids,[3] were encountered in either of these oxidations.

Oxidative cyclisation of the sulphonylacetic acid (1; X = SO_2, R = H) was less efficient. Only 19% of the thiopyran dioxide (5; X = SO_2, R = H) was obtained and much unchanged acid was recovered. 2-Acetoxy- and 2-hydroxy-biphenyls were unexpected minor products, the latter arising from the former by hydrolysis. In contrast, oxidation of phenylsulphonylacetic acid gave neither phenyl acetate nor phenol. The route to 2-acetoxybiphenyl has yet to be explored.

Very little cyclisation was achieved by oxidation of the amino-acids (1; X = NH or NMe, R = H). A complex mixture of products was obtained from compound (1; X = NH, R = H); only the amines (12; X = NH and NMe) (11 and 3%, respectively) could be separated and identified. The homologous acid (1; X = NMe, R = H) similarly gave the amines (12; X = NMe) (20%) and (11; X = NMe, R = H) (19%) in addition to a small quantity of the cyclised products (13; X = NMe) (5%) and (8; X = NMe) (1%). The expected dihydrophenanthridine (5; X = NMe, R = H)

[3] P. M. Brown, P. S. Dewar, A. R. Forrester, and R. H. Thomson, *J.C.S. Perkin I*, 1972, 2842.

was found to autoxidise rapidly to the phenanthridone (8; X = NMe), and the carbazole (13; X = NMe) was obtained in a separate experiment from the amine (12; X = NMe) by oxidation with persulphate under the usual conditions. Other products were formaldehyde and the triphenylmethane dyes (15). These showed n.m.r. signals attributable to *N*-methyl (τ 6·7—8·2), amino- (τ 5·38), and vinylic and aromatic (τ 3·4—4·7) protons, and were formed by condensation of formaldehyde with the amines (12; X = NMe) and (11; X = NMe, R = H) and further oxidation (*cf.* ref. 4). In the mass spectrometer the dyes volatilised as their leuco-compounds, forming ions at *m/e* 587 (1·1%), 573 (3·9), 559 (100), and 545 (13·8). The main peak corresponds to the dye (15) with three methyl groups.



(15)

The mixture (15) in ethanol showed $\lambda_{max.}$ 237, 306, 550sh, and 595 nm, which is similar to the absorption spectrum of Methyl Violet. The colour was discharged on addition of 0·1M-alkali and restored with intensification of the absorption at 595 nm on acidification, indicating that some of the dye was present initially in its leuco-form.

DISCUSSION

The key intermediates in the oxidation of the thioacetic acids (1; X = S, R = H or Me) are the thioalkyl radicals (3; X = S, R = H or Me) which arise from the anions of the acids by electron transfer [*i.e. via* (2a or b)] to sulphate radical anions followed by decarboxylation. Once formed these radicals may cyclise to cyclohexadienyl radicals (4; X = S, R = H or Me) which are then either aromatised (probably by further reaction with persulphate or sulphate radical anions) or dimerise to give the thiopyrans (5; X = S, R = H or Me) and related dimers, respectively. This scheme is similar to one that we have proposed [2] for the conversion of *o*-phenylphenoxyacetic acids into monomeric and dimeric pyrans. Similarity in the combined yields of monomeric and dimeric cyclised products from the phenoxyacetic (1; X = O, R = Me) and thiophenoxyacetic (1; X = S, R = Me) acids (both *ca.* 86%) implies that the *ortho*-phenyl group is an equally effective trap for both $ArO\dot{C}Me_2$ and $ArS\dot{C}Me_2$ radicals. Although the radicals $ArO\dot{C}H_2$ and $ArS\dot{C}H_2$ appear to behave differently, the former giving about twice as much cyclised product as the latter, it is not known whether the substantial amount of intractable material produced from (1; X = S, R = H) is due to the formation of non-cyclised products or to further oxidation of cyclised products. It has been suggested [5] that disulphides may be formed from arylthioalkyl radicals by carbene elimination followed by dimerisation as shown, but the

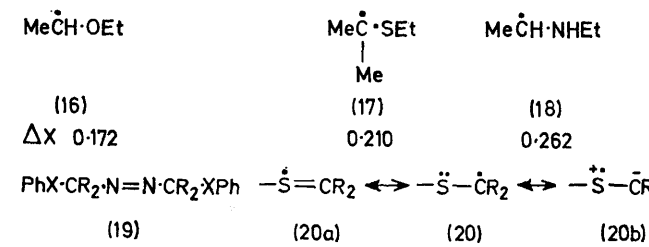
$$ArSCR_2^{\bullet} \longrightarrow ArS^{\bullet} + R_2C: \longrightarrow ArSSAr$$

supporting evidence is not compelling. Formation of the disulphide (14) from the acid (1; X = S, R = Me) under our conditions can be explained most simply in terms of oxidation of the radical (3; X = S, R = Me) to the cation (9; X = S, R = Me) followed by solvolysis and hydrolysis to give the thiol (12; X = S), which is then oxidised.

The comparative reluctance of the sulphonyl acid (1; X = SO_2, R = H) to react with sulphate radical anions, as measured by the acid recovered (45%) and low yield of cyclised product (5; X = SO_2, R = H) (19%), was not unexpected in view of previous oxidations of sulphone acids.[3] Replacement of sulphur (+*M*) by sulphonyl (−*M*) in (1; R = H) thus effects electron removal from the corresponding anions in a predictable way.

In contrast, we attribute the low yield of cyclised products obtained from the amino-acids (1; X = NH or NMe, R = H) not to any difficulty in forming the aminoalkyl radicals (3; X = NH or NMe, R = H) but rather to the relatively high rate at which they are consumed in other reactions, further oxidation to the corresponding cation (9) by reaction with persulphate, and disproportionation to (9) and (10) being dominant. The former process leads, after solvolysis and hydrolysis, to a dealkylated amine (12), and the latter to a mixture of (11) and (12). Oxidation by peroxides [6] and disproportionation, especially in acid solution,[7] are both known reactions of aminoalkyl radicals.

The differences observed in the behaviour of the radicals (3; X = O, S, or NR) may be accounted for in terms of their relative thermodynamic and kinetic stabilities. Although e.s.r. data are not available for these radicals it is possible to estimate their relative stabilities by analogy with the radicals (16)—(18). The



ability (ΔX) of the groups OEt, SEt, and NHEt to remove unpaired spin density from the adjacent tervalent

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carbon atoms in the radicals (16)—(18) can be derived by use of Fischer's equation [8] (with $Q_H^{\beta\text{-}CH_3} = 29{\cdot}3$) and known values [8-10] for $a_H^{\beta\text{-}CH_3}$ (unfortunately, measured under different conditions). This suggests the following order of thermodynamic stabilities for the radicals (3): (3; X = O) < (3; X = S) < (3; X = NR). The same order may also be obtained by comparing the relative ease of abstraction of hydrogen atoms by phenyl [11] or t-butoxyl [12] radicals from anisole, thioanisole, and *NN*-dimethylaniline, but this comparison is probably less valid because the transition states in such exothermic processes are thought [13] to have little free radical character. Relative rates of decomposition give more reliable information about the stability of the radicals that they produce,[13] and it has been shown [14] that the rate of decomposition of compound (19; X = S) is greater than that of (19; X = O), but the absence of data on (19; X = NR) makes this comparison incomplete. It is significant that the relative stabilities of α-oxyalkyl and α-thioalkyl radicals seem to be opposite to those of the cations derived from them (α-oxyalkyl halides are hydrolysed much more rapidly than α-thioalkyl halides [15]). This implies that electron-sharing conjugation (20a) involving sulphur *d*-orbitals as well as electron transfer conjugation (20b) plays a significant part in stabilising radicals of this type (20). Since there will be little difference in the stabilities of the cyclohexadienyl radicals (4; X = O, S, or NR) the activation energy for intramolecular substitution will be smallest for the thermodynamically least stable member of the group (3; X = O, S, or NR) and most cyclisation would be expected to occur with that member, *i.e.* the aryloxyalkyl radicals. Such was the case. However, the situation is complicated by competing reactions, principal among which is the oxidation of the radicals by persulphate to carbonium ions which yield non-cyclised products. Ionisation or oxidation potentials for the radicals being compared have not been measured but our results give a clear indication that arylaminoalkyl radicals (3; X = NR) are significantly more easily oxidised than their oxygen and sulphur counterparts.

Thus, of the acids examined, the amino-acids undergo oxidative decarboxylation most readily ($E_{\frac{1}{2}}$ values for anisole, thioanisole, and dimethylaniline are 1·76, 1·565, and 0·53 V, respectively) [16] to radicals which, because of their relatively high thermodynamic stability, react intermolecularly with themselves (disproportionation) or with persulphate (oxidation) in preference to cyclising on to the adjacent aromatic ring. Differences in the relative stabilities of the aryloxyalkyl and arylthioalkyl radicals are apparently much smaller.

EXPERIMENTAL

For general methods see Part V.[3]

Preparation of Arylthio-, Arylsulphonyl-, and Arylamino-acetic Acids.—Biphenyl-2-ylthio-,[17] phenylsulphonyl-,[18] and biphenyl-2-ylsulphonyl-[17] acetic acids were prepared by literature methods. The following are new.

2-(*Biphenyl-2-ylthio*)-2-*methylpropanoic acid* (1; X = S, R = Me) (cf. *ref*, 19). Powdered sodium hydroxide (22 g) was added in portions during 2 h to a stirred solution of biphenyl-2-thiol [17] (12·4 g) and chloretone dihydrate [20] (2-trichloromethylpropan-2-ol dihydrate) (28·6 g) in acetone (100 ml) at 0°. Stirring was continued at room temperature for 12 h; the solution was then evaporated and the residue was dissolved in water. The aqueous solution was washed with ether and then acidified. The oil which separated was extracted into ether and the ethereal solution was washed (H_2O), dried ($MgSO_4$), and evaporated. Crystallisation of the residual oil gave 2-(*biphenyl-2-ylthio*)-2-*methylpropanoic acid* as prisms, m.p. 125·5—126·5° (from petroleum) (17·8 g, 97%) (Found: C, 70·8; H, 6·1; S, 11·6. $C_{16}H_{16}O_2S$ requires C, 70·6; H, 5·9; S, 11·75%), $\nu_{max.}$ 3300—2500 and 1700 cm^{-1}, $\lambda_{max.}$ 250sh and 285sh nm (log ε 3·99 and 3·35), τ 2·2—2·9 (9H, m, ArH) and 8·74 (6H, s, 2Me).

(*Biphenyl-2-ylamino*)*acetic acid* (1; X = NH, R = H). A solution of 2-aminobiphenyl (16·9 g, 0·1 mol) and ethyl bromoacetate (16·7 g, 0·1 mol) in dry toluene (100 ml) under reflux was stirred with potassium carbonate (40 g) for 65 h. The potassium salts were collected and the toluene and unchanged ester were distilled off *in vacuo*. The residual oil was dissolved in ether and the solution was washed with 2M-hydrochloric acid and water, dried ($MgSO_4$), and evaporated. The residue was distilled to give *ethyl* (*biphenyl-2-ylamino*)*acetate*, b.p. 175—178° at 2 mmHg, m.p. 45—46° (from petroleum) (13·5 g, 53%) (Found: C, 75·6; H, 6·9; N, 5·5. $C_{16}H_{17}NO_2$ requires C, 75·3; H, 6·7; N, 5·5%), $\nu_{max.}$ 3420 and 1745 cm^{-1}, $\lambda_{max.}$ 238, 260sh, and 309 nm (log ε 4·35, 3·74, and 3·60), τ 2·4—2·76 (9H, m, ArH), 5·84 (2H, q, *J* 7 Hz, $CH_2{\cdot}CH_3$), 6·15 (2H, s, $N{\cdot}CH_2$), and 8·77 (3H, t, *J* 7 Hz, Me).

A solution of this ester (5·1 g) and potassium hydroxide (10 g) in aqueous ethanol (1 : 1; 200 ml) was heated under reflux for 2 h. The ethanol was removed *in vacuo* and the remaining aqueous solution was acidified and extracted with chloroform. The extract was washed (H_2O), dried ($MgSO_4$), and evaporated to give (*biphenyl-2-ylamino*)*acetic acid* as yellow prisms, m.p. 122—124° (from benzene–petroleum) (4·55 g, 100%) (Found: C, 74·3; H, 5·7; N, 6·3. $C_{14}H_{13}NO_2$ requires C, 74·0; H, 5·8; N, 6·2%),

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$\nu_{max.}$ 3420 (NH) and 3300—2300 (OH) cm^{-1}, $\lambda_{max.}$ 229, 265sh, and 310 nm (log ε 4·32, 3·63, and 3·54), τ [$(CD_3)_2SO$] 2·5—3·6 (9H, m, ArH) and 6·2 (2H, s, CH_2).

N-*Biphenyl-2-yl*-N-*methylaminoacetic acid* (1; X = NMe, R = H). A solution of ethyl (biphenyl-2-ylamino)acetate (5·1 g) and dimethyl sulphate (8 g) in dry acetone (50 ml) under reflux was stirred with potassium carbonate (14 g) for 100 h. The salts were collected and the excess of dimethyl sulphate was distilled off *in vacuo*. Distillation of the residual oil gave *ethyl* N-*biphenyl-2-yl*-N-*methylaminoacetate*, b.p. 150—153° at 1 mmHg (5·2 g, 97%) (Found: C, 75·5; H, 7·3; N, 5·5. $C_{17}H_{19}NO_2$ requires C, 75·8; H, 7·1; N, 5·2%), $\nu_{max.}$ 1750 cm^{-1}, $\lambda_{max.}$ 237, 273, and 309 nm (log ε 4·28, 3·73, and 3·46), τ 2·3—3·2 (9H, m, ArH), 6·0 (2H, q, *J* 7 Hz, $CH_3{\cdot}CH_2$), 6·52 (2H, s, $N{\cdot}CH_2$), 7·21 (3H, s, NMe), and 8·87 (3H, t, *J* 7 Hz, $CH_2{\cdot}CH_3$).

The foregoing ester (3 g) was hydrolysed as before to give N-*biphenyl-2-yl*-N-*methylaminoacetic acid*, m.p. 198—199·5° (from ethanol) (2·8 g, 100%) (Found: *M*, 241·1100. $C_{15}H_{15}NO_2$ requires *M*, 241·1103), $\nu_{max.}$ 3160—2160 and 1735 cm^{-1}, $\lambda_{max.}$ 250, 270, and 307 nm, τ ($CF_3{\cdot}CO_2D$) 2·1—2·8 (9H, m, ArH), 5·22 (2H, s, CH_2), and 6·48 (3H, s, Me). This product autoxidised rapidly on exposure to air and a satisfactory elemental analysis could not be obtained.

Oxidations with Persulphate.—The acids (0·0025 mol) were oxidised with potassium persulphate (0·0025 mol) as described previously.[2] Products were obtained from the crude reaction mixtures by chromatographic (t.l.c. or p.l.c.) separation on silica gel (GF254) in petroleum–ether (19 : 1) unless otherwise stated. Yields are based on acid consumed.

(i) Biphenyl-2-ylthioacetic acid gave 6*H*-dibenzo[*b*,*d*]-thiopyran (5; X = S, R = H), m.p. 73·5—74° (lit.,[21] 75·5°) (115 mg, 24%); dimeric material (65 mg, *ca.* 13%) [Found: *M*, 400 (osmometric in acetone). $C_{26}H_{18}S_2$ requires *M*, 394], τ 1·9—3·3 (m, ArH), 3·3—4·5 (m, C=CH), 5·1 (s, CH_2), and 6·0—7·4 (m, CH_2 and CH); dibenzo[*b*,*d*]-thiopyran-6-one (8; X = S), m.p. 124—126·5° (lit.,[22] 131—133°) (5 mg, 1%), $\nu_{max.}$ 1630 cm^{-1}, $\lambda_{max.}$ 239, 245, 265, 273, 315sh, 339, 354sh nm (log ε 4·61, 4·65, 4·00, 3·98, 3·53, 3·70, and 3·61), τ 1·46—1·83 (2H, m, ArH) and 2·03—3·0 (6H, m, ArH); unchanged acid (26 mg); and intractable material (*ca.* 200 mg). Formaldehyde was detected by the chromotropic acid test [23] on the aqueous solution after oxidation was complete.

(ii) 2-(Biphenyl-2-ylthio)-2-methylpropanoic acid gave 6,6-*dimethyldibenzo*[b,d]*thiopyran* (5; X = S, R = Me) as an oil, b.p. 142—144° at 0·8 mmHg (357 mg, 63·4%) (Found: C, 79·7; H, 6·1; S, 13·8. $C_{15}H_{14}S$ requires C, 79·6; H, 6·2; S, 14·1%), $\lambda_{max.}$ 244, 257, 279, and 322 nm (log ε 4·20, 4·27, 3·85, and 3·36), τ 2·1—3·0 (8H, m, ArH) and 8·4 (6H, s, Me), and a mixture of dimeric products (131 mg, *ca.* 23%).

A solution of this mixture of dimeric products (131 mg) and DDQ (136 mg) in dioxan (5 ml) was left at room temperature for 20 h, and then heated under reflux for 1 h. After removal of the solvent the residue was eluted from a short alumina column with chloroform. The eluate was evaporated and the residual oil chromatographed (p.l.c.) on silica to give biphenyl-2-yl disulphide (14; X = S), m.p. 117—118° (lit.,[24] 115·5—116°) (17 mg, 3·5%) and 6,6,6′,6′-*tetramethyl*-9,9′-*bi*(*dibenzo*[b,d]*thiopyranyl*) (7; X = S, R = Me), m.p. 202—204° (from chloroform–petroleum) (56 mg, 9·7%) (Found: C, 79·7; H, 6·0; S, 13·9%; *M*, 450·1444. $C_{30}H_{26}S_2$ requires C, 80·0; H, 5·8; S, 14·2%; *M*, 450·1476), $\lambda_{max.}$ 248sh, 257, and 325 nm (log ε 4·77, 4·81, and 3·85), τ 1·8—2·9 (14H, m, ArH) and 8·34 (12H, s, 4 Me).

(iii) Biphenyl-2-ylsulphonylacetic acid gave 6H-*dibenzo*-[b,d]*thiopyran* 5,5-*dioxide* (5; X = SO_2, R = H), m.p. 143—143·5° (from chloroform–petroleum) (59 mg, 20%) (Found: C, 67·9; H, 4·4; S, 13·9. $C_{13}H_{10}O_2S$ requires C, 67·8; H, 4·4; S, 13·9%), $\lambda_{max.}$ 246sh, 262sh, 270, 290sh, and 302sh nm (log ε 3·89, 4·12, 4·14, 3·86, and 3·69), τ 1·8—3·0 (8H, m, ArH) and 5·63 (2H, s, CH_2); 2-acetoxybiphenyl, m.p. 62·5—63° (15 mg); 2-hydroxybiphenyl, m.p. 56—58° (6 mg); and unchanged acid (314 mg).

(iv) *N*-Biphenyl-2-yl-*N*-methylaminoacetic acid gave 2-dimethylaminobiphenyl,[25] b.p. 94° at 0·5 mmHg (92 mg, 19%); *N*-methylcarbazole,[26] m.p. 87—87·5° (19 mg, 4·2%); 2-methylaminobiphenyl,[27] m.p. 33—34° (93 mg, 20%); *N*-methylphenanthridone,[28] m.p. 108—108·5° (4 mg, 1·0%); and a purple fraction of low R_F. This was rechromatographed on silica in chloroform–methanol (9 : 1) to give the purple dyes (15) (23 mg, *ca.* 5%) (Found: *M* + 2, 559·2975. Calc. for $C_{40}H_{35}N_3$: *M* + 2, 559·2988), $\nu_{max.}$ 3440—3100 cm^{-1}, $\lambda_{max.}$ 237, 306, 550, and 595 nm, τ 3·4—4·7 (m, ArH and C=CH), 5·38br (s, NH), and 6·7—8·2 (m, methyls), *m/e* 587 (1·2%), 573 (3·9), 559 (100), 545 (13·8), and 367 (75). Formaldehyde was detected by the chromotropic acid [23] test in the aqueous solution after oxidation.

(v) (Biphenyl-2-ylamino)acetic acid gave 2-aminobiphenyl (45 mg, 11%); 2-methylaminobiphenyl (14 mg, 3%); and unchanged acid (33 mg). Formaldehyde was detected in the solution after oxidation.

(vi) 2-Methylaminobiphenyl (92 mg) after oxidation with persulphate (135 mg) in water (10 ml) gave *N*-methylcarbazole (11 mg, 16%) and unchanged amine (22 mg, 24%).

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