New Reactions with Persulphate: Oxidation of Diphenyl Sulphide-2-carboxylic Acids and Aromatic Amides

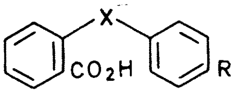
By P. MARGARET BROWN, P. S. DEWAR, A. R. FORRESTER, A. S. INGRAM, and R. H. THOMSON*
(*Department of Chemistry, University of Aberdeen, Old Aberdeen* AB9 2UE, *Scotland*)

Summary Diphenyl sulphide-2-carboxylic acids rearrange to aryl esters of diphenyl disulphide-2,2′-dicarboxylic acids, biphenyl-2-carboxamides cyclise to phenanthridones, and 2-acylaminobiphenyls to carbazoles, on oxidation with persulphate.

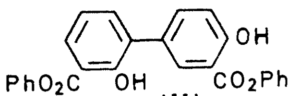
PERSULPHATE oxidation of aromatic carboxylic acids frequently leads to oxidative cyclisation *via* the intermediate radicals ArCO$_2$· and Ar·, *e.g.*, biphenyl-2-carboxylic acid yields 3,4-benzocoumarin[1] and *o*-benzoylbenzoic acid gives fluorenone.[2] Exceptionally, *o*-phenoxybenzoic acid (I; X = O, R = H) afforded the rearranged product (II),[3] and no cyclised compounds could be detected.

We now report some new reactions effected by this reagent. Persulphate oxidation of the sulphur analogue (I; X = S, R = Me) gave principally the sulphoxide (I; X = SO, R = Me), together with starting material and the diester (III; R = Me),† m.p. 162—163° (15%). Structure (III; R = Me) was deduced from analytical and spectroscopic data, and hydrolysis to *p*-cresol and diphenyl disulphide-2,2′-dicarboxylic acid, and was confirmed by synthesis from the two latter compounds. Similarly (I; X = S, R = H and MeO) gave (III; R = H and MeO) in low yield, most of the methoxylated ester being oxidised to the –SO$_2$–S– level. By analogy with the formation of (II), (III) probably arises by cyclisation of the initial carboxyl radical to give (IV), and hence (V) which dimerises. The overall result is the oxidative migration of an aryl group from sulphur to oxygen.

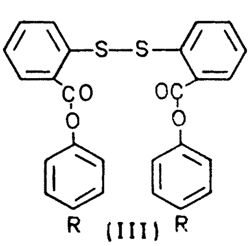
Very little has been published on the oxidation of the amides of aromatic carboxylic acids.[4] We find that persulphate oxidation of the amides (VI; R^1 = R^2 = R^3 = H, R^1 = R^3 = H, R^2 = Me, Bu^t, and Ph) gives good yields (45—97%) of the corresponding phenanthridones (VII). Best results were obtained at amide concentrations sufficiently low to ensure a homogeneous reaction. [In a two-phase system, oxidation of benzamide, in benzene, with aqueous persulphate, gave benzanilide (12%).] The dimethylamide (VI; R^1 = R^2 = Me, R^3 = H) gave (VII; R = Me), one methyl group being eliminated, and formaldehyde was detected. These cyclisations are much cleaner and more efficient than other persulphate oxidations, in our experience. In most reactions 3,4-benzocoumarin was formed in small amount (*ca.* 3%) but the amide (VI; R^1 = R^2 = H, R^3 = NO$_2$) gave (VII; R = H) (3%) and 3,4-benzocoumarin (22%), and (VI; R^1 = R^2 = H, R^3 = CO$_2$H) afforded only 3,4-benzocoumarin (60%). Similar group eliminations were noted previously.[2] As separate experiments showed that both (VI) and (VII) were resistant to hydrolysis under the experimental conditions, we conclude that phenanthridones and 3,4-benzocoumarin are formed from the same mesomeric amido-radical, $\mathrm{ArC({=}O)\dot{N}H \longleftrightarrow ArC({-}\dot{O}){=}NH}$ which cyclises on both nitrogen and oxygen.



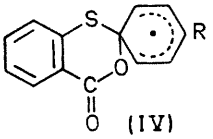
(I)



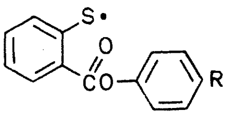
(II)



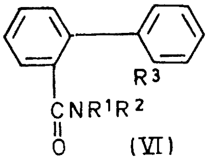
(III)



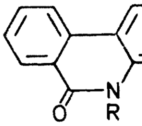
(IV)



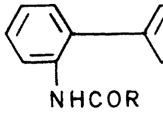
(V)



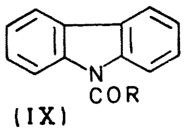
(VI)



(VII)



(VIII)



(IX)

In the oxidation of the 2-acylaminobiphenyls (VIII; R = Me and Ph) cyclisation on nitrogen only was observed which gave the carbazoles (IX; R = Me and Ph) (12 and 18%, respectively), the other products being mainly polymeric (*cf.* ref. 5).

This work was supported by the United States Army through its European Research Office.

(*Received, May* 18*th*, 1970; *Com.* 760.)

---

† Satisfactory analytical and spectroscopic data have been obtained for all new compounds reported.

[1] P. M. Brown, J. Russell, R. H. Thomson, and A. G. Wylie, *J. Chem. Soc.* (*C*), 1968, 842.
[2] J. Russell and R. H. Thomson, *J. Chem. Soc.*, 1962, 3379.
[3] R. H. Thomson and A. G. Wylie, *J. Chem. Soc.* (*C*), 1966, 321.
[4] D. H. R. Barton, A. L. J. Beckwith, and A. Goosen, *J. Chem. Soc.*, 1965, 181.
[5] W. A. Waters and J. E. White, *J. Chem. Soc.* (*C*), 1968, 740.