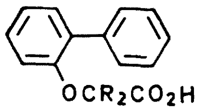
New Reactions with Persulphate: Oxidation of *o*-Phenylphenoxyacetic Acids

By P. S. DEWAR, A. R. FORRESTER, and R. H. THOMSON*

(*Department of Chemistry, University of Aberdeen, Old Aberdeen* AB9 2UE, *Scotland*)

Summary Intramolecular cyclisation of *o*-phenylphenoxymethyl radicals, formed by persulphate oxidation of *o*-phenylphenoxyacetic acid, yields cyclohexadienyl radicals which are either oxidised to dibenzopyran and a related bis-acetal, or dimerise.

THE preceding Communication[1] outlines the wide variety of products which can be obtained by oxidising carboxylic acids with persulphate. We now describe a further reaction in which radicals of type $ArOCH_2\cdot$ cyclise efficiently on to a neighbouring benzene ring.



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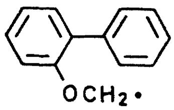

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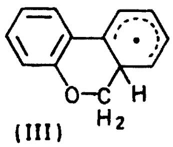

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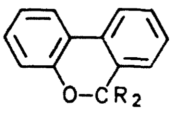

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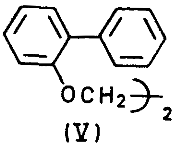

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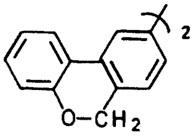

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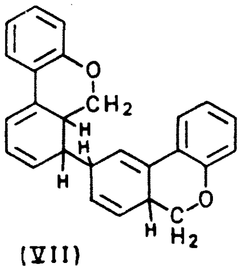

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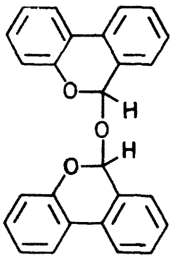

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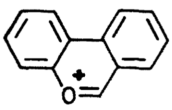
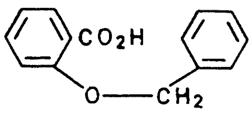
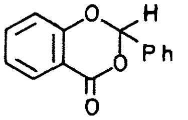


(IX)



(X)



(XI)

Persulphate oxidation of (I; R = H and Me) gave the pyrans (IV; R = H and Me)† (60% and 82%, respectively) (*cf.* ref. 2) and oily mixtures of dimers (5—10%). The oil from (I; R = H) eventually yielded crystalline material which we regard as the unsymmetrical dimer (VII). The n.m.r. spectrum shows, in addition to multiplets for 8 aromatic and 6 olefinic protons, two quartets (each 2H) centred at τ 5·67 and 6·28, assigned to the methylene protons and a multiplet (4H) centred at τ 6·77 attributed to the methine protons. Spin decoupling confirmed that one proton in each methylene group (*J* 10 Hz) was coupled to an adjacent methine proton (*J* 4 Hz) (a model shows that the other is virtually at right angles and hence *J* 0 Hz). Pyrolysis at 140° converts (VII) into the monomer (IV; R = H), and the dimers (V) (also obtained from 2-hydroxybiphenyl and 1,2-dibromoethane) and (VI) [λ_{max} 258, 313 nm (log ϵ 4·69, 4·44), τ 2·10—3·20 (14H, m, Ar*H*), 4·83 (4H, s, $-CH_2-$); *cf.* (IV), λ_{max} 262(sh), 270, 310 nm (log ϵ 4·02, 4·04, 3·81), τ 2·30—3·30 (8H, m, Ar*H*), 5·07 (2H, s, $-CH_2-$)]. In the pyrolysis, (VII) most probably dissociates to (III) which partially reverts to (II) and then dimerises to give (V), but (VI) may be formed either by dehydrogenation of (VII) or by way of (II) in which case the position of the internuclear linkage in (VI) may be different from that in (VII), and is not yet established. The formation of (VII) provides evidence for the intermediacy of (II) while not excluding the possibility that (II) may be oxidised, in part, to the corresponding cation before cyclisation to the pyran.

Another dimeric product derived from (I; R = H), isolated most easily when the reaction was terminated after 15 min, is the bis-acetal (VIII). On electron bombardment it fragments to give major peaks in the mass spectrum at *m/e* 182 and 196 assigned to the radical ions of (IV; R = H) and benzocoumarin, respectively. The pyran (IV; R = H) is easily autoxidised (ordinary samples are usually contaminated with benzocoumarin), and (VIII) clearly arises by oxidation of (IV; R = H) to (IV; R = H and OH) followed by dehydration. Treatment of the perchlorate of (IX) with water readily formed (IV; R = H and OH) in solution but all attempts to isolate this gave (VIII). Treatment with ethanol, however, afforded the stable acetal (IV; R = H and OEt).

In another approach to the pyran (IV; R = H) we oxidised *o*-benzyloxybenzoic acid (X) but the products were benzaldehyde and the lactone (XI) [ν_{CO} 1745 cm^{-1}, τ 3·52 (1H, s)]. Similarly, *o*-benzylbenzoic acid gives 3-phenylphthalide.[3]

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

(*Received, May* 18*th*, 1970; *Com.* 761.)

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

[1] P. M. Brown, P. S. Dewar, A. R. Forrester, A. S. Ingram, and R. H. Thomson, preceding Communication.
[2] P. M. Brown, J. Russell, R. H. Thomson, and A. G. Wylie, *J. Chem. Soc.* (*C*), 1968, 842.
[3] J. Russell and R. H. Thomson, *J. Chem. Soc.*, 1962, 3379.