Persulphate Oxidations. Part VI.[1] Oxidation of Biphenyl-2-carboxamides

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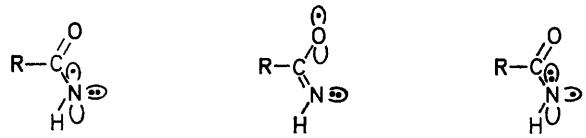
Persulphate oxidation of a series of *N*- and ring-substituted biphenyl-2-carboxamides gave the corresponding phenanthridones in yields ranging from 2 to 97%. Usually the phenanthridone was accompanied by small quantities of the appropriate dibenzo[*b*,*d*]pyran-6-one, both products arising *via* the same amidyl radical, which can cyclise on nitrogen or on oxygen. Oxidation of 2'-substituted biphenyl-2-carboxamides usually led to the elimination of the 2'-substituent and preferential cyclisation on oxygen: similar treatment of 2-acylaminobiphenyls gave low yields of *N*-acylcarbazoles.

AMIDYLS are among the least studied of organic radicals. Hitherto they have been generated mainly by photolysis of the corresponding *N*-halogeno-amides,[2] *N*-nitroso-amides,[3] or *NO*-diacylhydroxylamines[4] and have been shown to couple rapidly with other radicals,[4] abstract hydrogen inter- or intra-molecularly,[2,3] and to add to alkenes.[2,5] In these reactions the amidyls show a strong preference for reaction on nitrogen. Amidyls can



(1a) (1b) (1c)

be formulated as either mesomeric π-radicals [(1a) ⟷ (1b)] or as σ-radicals (1c), and simple molecular orbital calculations[6] have led to the conclusion that the σ-state (1c) is of lower energy. Unequivocal confirmation of this view by e.s.r. measurements is lacking, and there has been disagreement[7] about the interpretation of the spectra observed. However, in the most recent work[8] it was convincingly demonstrated that radicals generated by u.v. irradiation of *N*-nitroso-amides in toluene had the spectral parameters (a_N 7·0 G) expected of a π-type radical.

With a view to examining this and other facets of the chemistry of amidyls we have studied the behaviour of a series of *o*-arylphenylamidyls generated directly from the amides by oxidation with persulphate[9] in hot aqueous solution. In general, this has proved to be a useful method for producing aromatic amidyls (and phenanthridones) and one which is not compounded by a competing Hofmann degradation of the amides to amines.

RESULTS

Oxidation of biphenyl-2-carboxamide and a number of its *N*-substituted derivatives gave relatively high yields of the corresponding phenanthridones, accompanied by smaller quantities of dibenzo[*b*,*d*]pyran-6-ones (Table; experiments i—v). Since it is essential to keep the amide in solution as far as possible to obtain high yields of phenanthridones, these oxidations were effected in dilute solution. Aqueous organic solvents offered no advantage in this respect since their use led to more complex product mixtures. Formation of dealkylated products, mainly from *NN*-dimethylbiphenyl-2-carboxamide, was not unexpected, as dealkylations of aliphatic secondary and tertiary amides with persulphate have been observed[10] previously.

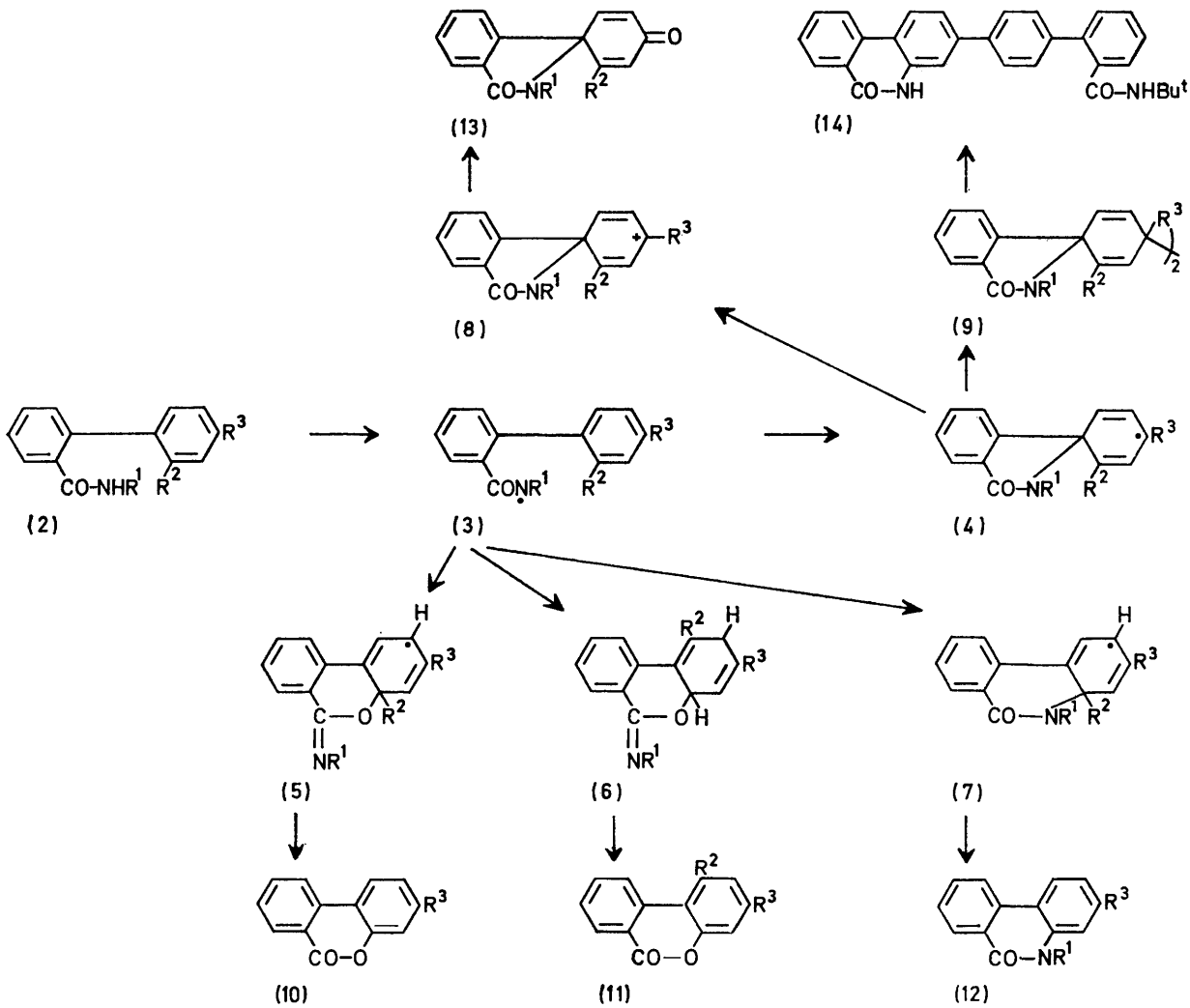
The small quantity of dimeric material (*M* 388) obtained from oxidation of biphenyl-2-carboxamide has been assigned the N–C coupled structure (15) since its spectra are generally similar to those of phenanthridone and it gave a monomethyl derivative which showed no i.r. absorption at wavenumbers higher than 3100 cm^{-1}. Consideration of steric factors suggests that it is linked *N* to '*para*'-*C* but this has not been confirmed. The same dimer was also formed, and in similar yield, by oxidation of phenanthridone with persulphate. Larger quantities of dimeric material were obtained from oxidations of the amide (2; R^1 = Bu^t, R^2 = R^3 = H). This showed n.m.r. signals attributable to olefinic (τ 3·8—4·38) and methine (τ 6·48—6·80), as well as t-butyl and aromatic protons. Because of its relatively high frequency carbonyl absorption (1680—1670 cm^{-1}) and its reluctance to react smoothly with dichlorodicyanobenzoquinone (DDQ) to give a dehydrogenated product, we consider that this compound is the spirodienyl dimer (9; R^1 = Bu^t, R^2 = R^3 = H) analogous to that (9; R^1 = Me, R^2 = R^3 = H) obtained previously by copper-catalysed decomposition of the diazonium salt derived from *N*-methyl-*N*-phenylanthranilamide.[11] The

[1] Part V, P. M. Brown, P. S. Dewar, A. R. Forrester, and R. H. Thomson, preceding paper.
[2] R. S. Neale, *Synthesis*, 1971, **1**, 1 and references cited therein.
[3] Y. L. Chow, N. S. Tam, and A. C. H. Lee, *Canad. J. Chem.*, 1969, **47**, 2441; Y. L. Chow and J. N. S. Tam, *J. Chem. Soc.* (*C*), 1970, 1138.
[4] B. Danieli, P. Manitto, and G. Russo, *Chem. and Ind.*, 1969, 329; 1971, 203.
[5] D. Touchard and J. Lessard, *Tetrahedron Letters*, 1971, 4425.
[6] E. Hedaya, R. L. Hinman, V. Schomaker, S. Theodoropulos, and L. M. Kyle, *J. Amer. Chem. Soc.*, 1967, **89**, 4875.
[7] M. C. R. Symons, *J. Chem. Phys.*, 1971, **55**, 1493; *J. Chem. Soc.* (*A*), 1971, 3205; H. Bower, J. McRae, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2400; P. W. Lau and W. C. Lin, *J. Chem. Phys.*, 1969, **51**, 5139; N. Cyr and W. C. Lin, *ibid.*, p. 3701.
[8] P. Tordo, E. Flesia, G. Labrot, and J.-M. Surzur, *Tetrahedron Letters*, 1972, 1413; P. Tordo, E. Flesia, and J.-M. Surzur, *ibid.*, p. 183; T. Koenig, J. A. Hoobler, and W. R. Mabey, *J. Amer. Chem. Soc.*, 1972, **94**, 2514.
[9] (*a*) P. M. Brown, J. Russell, R. H. Thomson, and A. G. Wylie, *J. Chem. Soc.* (*C*), 1968, 842; (*b*) P. S. Dewar, A. R. Forrester, and R. H. Thomson, *ibid.*, 1971, 3950.
[10] H. L. Needles and R. E. Whitfield, *J. Org. Chem.*, 1964, **29**, 3632.
[11] D. Collington, D. H. Hey, and C. W. Rees, *J. Chem. Soc.* (*C*), 1968, 1017, 1026; D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 105.

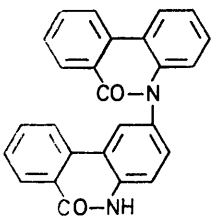
Yields [a] (%) of products obtained on oxidation of biphenyl-2-carboxamides with persulphate

	Biphenyl-2-carboxamide (2)			Corresponding phenanthridone (12)	Corresponding dibenzopyranone (11)	Dibenzo[*b*,*d*]-pyran-6-one	Other products
	R^1	R^2	R^3				
i	H	H	H	38		6	<1·0 (15)
ii	Me	H	H	62		11	2 (12; $R^1 = R^3 = H$) + (13; R^1 = Me, $R^2 = H$) [c]
iii	Me_2 [b]	H	H	18·5		3·5	+ (12; $R^1 = R^3 = H$)
iv	Bu^t	H	H	51·5		13	+ (12; $R^1 = R^3 = H$); 6·5 (13; $R^1 = Bu^t$, $R^2 = H$); 21 (9; $R^1 = Bu^t$, $R^2 = R^3 = H$)
v	Ph	H	H	97		+	
vi	H	H	NO_2	32	5	<1·0	
vii	Me	H	NO_2	6	+	+	
viii	H	H	OMe	2	+	+	
ix	Me	H	OMe	4·5	+	+	5 (13; R^1 = Me, $R^2 = H$)
x	H	H	Br	14		+	
xi	H	NO_2	H		<1	27	4 (12; $R^1 = R^3 = H$)
xii	Me	NO_2	H		+	15	
xiii	H	CO_2H	H			74	1·5 (12; $R^1 = R^3 = H$)
xiv	Ph	CO_2H	H			1	7 (16); 7 (12; R^1 = Ph, $R^3 = H$)
xv	H	$CO{\cdot}NH_2$	H			12	4 (17)
xvi	Ph	CO·NHPh	H				25 (12; R^1 = Ph, $R^3 = H$)

[a] Yields allow for recovered starting material; + indicates trace quantities. [b] *NN*-Dimethylbiphenyl-2-carboxamide. [c] Detected by n.m.r. but not isolated.



presence of a number of 'nearly equivalent' t-butyl signals in the n.m.r. spectrum of this crystalline product suggests that it is a mixture of stereoisomers, but attempts to separate these by fractional crystallisation were unavailing. Pyrolysis of the dimer (9; $R^1 = Bu^t$, $R^2 = R^3 = H$) in 1,2,4-trichlorobenzene at 214° gave a complex mixture, the principal component of which was the quaterphenyl derivative (14) (*M* 446) (*cf.* refs. 11 and 12). Its i.r. spectrum showed absorption at 3340 and 3080 (NH), and at 1665 (δ-lactam) and 1650 cm^{-1} (amide), and in its n.m.r. spectrum there was only one t-butyl resonance and signals from neither olefinic nor methine protons were evident.



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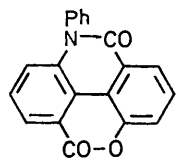

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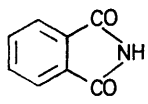

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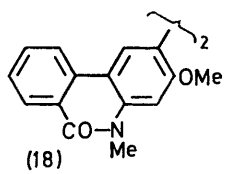

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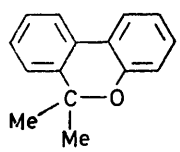

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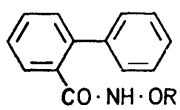

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Another minor product from the oxidation of the *N*-t-butylamide was identified as the spirodienone (13; $R^1 = Bu^t$, $R^2 = H$) after comparison of its spectra with those of the known *N*-methyl analogue.[11] The presence in its n.m.r. spectrum of a quartet centred at τ 3·37 (*J* 6 Hz) due to the cyclohexadienone protons and i.r. absorption at 1690 and 1660 cm^{-1} characterised this product. Careful examination of the n.m.r. spectra of the crude reaction mixtures obtained from the parent and other *N*-substituted amides (Table; experiments i—v) revealed that substantial quantities of spiro-compounds were formed only from the t-butylamide.

The effect which the introduction of a 4′-substituent has on the course of these persulphate oxidations of biphenyl-2-carboxamides is indicated in the Table (experiments vi—x). In general, much lower yields of phenanthridones were obtained, and usually traces of both substituted and unsubstituted dibenzopyranones were detected. The lower yields of phenanthridones can be accounted for in part by the relative insolubilities of these amides in the aqueous medium. Use of an excess of persulphate in such cases resulted in preferential consumption of the products rather than of the substrate and much larger quantities of intractable material were obtained. Isolation of a small amount of the dienone (13; $R^1 = Me$, $R^2 = H$) from the methoxy-amide (2; $R^1 = Me$, $R^2 = H$, $R^3 = OMe$) was significant.

The presence of a substituent in the 2′-position had a major effect on the product distribution (Table; experiments xi—xvi). Except with one amide (experiment xiv) little or none of the corresponding phenanthridone was obtained; dibenzopyranone, accompanied in some instances by traces of the corresponding substituted dibenzopyranone (11; $R^3 = H$), was the main product. Elimination of aromatic substituents has been encountered previously during oxidative cyclisation of a series of 2′-substituted biphenyl-2-carboxylic acids with persulphate.[9a] However, we have excluded the possibility that dibenzopyranones arise (in these and in other examples given in the Table) by cyclisation of the acids formed by hydrolysis of these amides in the weakly acidic medium. In control experiments the amides were refluxed in an acidic solution obtained by prior hydrolysis of the appropriate amount of persulphate.

Isolation of a small amount of the doubly cyclised product (16), identified mainly from its mass and i.r. spectra [1745 (δ-lactone) and 1665 cm^{-1} (δ-lactam)] is unique in this work. Formation of phthalimide from the diamide (experiment xv) could only occur by extensive degradation of an intermediate product, and because of the low yield obtained we did not pursue this unexpected result.

Attempts to extend the scope of these amide oxidations by cyclising 2-acylaminobiphenyls to *N*-acylcarbazoles by treatment with hot persulphate were only partly successful. 2-Acetylaminobiphenyl gave a 7% yield of *N*-acetylcarbazole and much intractable material; 2-benzoylaminobiphenyl gave a higher yield of *N*-benzoylcarbazole together with much unchanged starting material. Because of the sensitivity of these *N*-acylcarbazoles to persulphate in boiling aqueous solution these yields could not be improved by increasing the ratio of persulphate to substrate. Several oxidations of *N*-*p*-tolylsulphonylaminobiphenyl in neutral and alkaline solution failed to yield any of the corresponding carbazole, although the sulphonamide was completely consumed and the expected product was resistant to persulphate.

DISCUSSION

Formation of Phenanthridones.—Thermolysis of persulphate gives sulphate radical anions whose hydrolysis to hydroxyl radicals only becomes important in alkaline solution.[13] Hence, we consider that phenanthridones

[12] D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 113.

[13] R. O. C. Norman, P. M. Storey, and P. R. West, *J. Chem. Soc.* (*B*), 1970, 1087; R. O. C. Norman and P. M. Storey, *ibid.*, p. 1099.

arise in our system by cyclisation on nitrogen of amidyl radicals (3) formed from the corresponding amides by hydrogen abstraction by sulphate radical anions. Aromatisation of the intermediate cyclohexadienyl radicals (7) is then effected by further reaction with sulphate radical ions and/or persulphate anions, since the rate of decomposition of persulphate in hot aqueous solution (normally a pseudo-first-order process, $k = 2{\cdot}35 \times 10^5\ s^{-1}$) is enhanced by the presence of biphenyl-2-carboxamide and the decomposition is then no longer a first-order process (*cf.* ref. 9*b*). Addition of an excess of copper(II) ions to an oxidation of the amide (2; $R^1 = Me$, $R^2 = R^3 = H$) increased the yield of the phenanthridone from 62 to 80%. Presumably copper(II) ions assist the aromatisation step [14] rather than oxidise amidyls to amidyl cations, as these would undergo solvolysis or Hofmann rearrangement. In support of this, heating the hydroxamic acid (20; R = H) in dilute aqueous acid gave only the Hofmann product, 2-aminobiphenyl. Isolation of the spirodienyl dimer (9; $R^1 = Bu^t$, $R^2 = R^3 = H$) and the dienone (13; $R^1 = Bu^t$, $R^2 = H$) indicates that, in certain cases at least, the amidyl has an alternative mode of cyclisation on to C-1′. Indeed it is possible [11] that the cyclohexadienyl radicals (4) and (7) may exist in equilibrium with the amidyl radical (3), and that for steric reasons the radical (4; $R^1 = Bu^t$, $R^2 = R^3 = H$) reacts more easily at C-4′ than (7; $R^1 = Bu^t$, $R^2 = R^3 = H$) does at C-2′. Hence, some of the product arises from (4; $R^1 = Bu^t$, $R^2 = R^3 = H$) as a consequence of the size of the t-butyl group. The dienone (13; $R^1 = Bu^t$, $R^2 = H$) is probably formed by oxidation of the cyclohexadienyl radical (4; $R^1 = Bu^t$, $R^2 = R^3 = H$) with either persulphate or persulphate radical anions followed by solvolysis of the carbonium ion so formed and further oxidation.[15] The increase in the yield of spirodienone (6·5 ⟶ 13%) at the expense of spirodienyl dimer when the t-butylamide was oxidised in the presence of a five-fold excess of copper(II) supports this view. Formation of the dienone (13; $R^1 = Me$, $R^2 = H$) from the methoxy-amide (2; $R^1 = Me$, $R^2 = H$, $R^3 = OMe$) presumably follows a similar course. Significantly, under our oxidising conditions the C–C coupled dimeric phenanthridone (18), reported [15] recently, was not obtained from the methoxy-amide (2; $R^1 = Me$, $R^2 = H$, $R^3 = OMe$).

It has been suggested [15] that cyclohexadienyl radicals (7) may be formed in these oxidations (from the methoxy-amides at least) by initial radical cation formation followed by intramolecular nucleophilic capture by the amide function, rather than by cyclisation of the amidyl (3). In view of the high yields obtained from the methoxy-amides this seems improbable, as the radical cation would surely be solvolysed before it could react with the amide group.

[14] J. K. Kochi, A. Bemis, and C. L. Jenkins, *J. Amer. Chem. Soc.*, 1968, **90**, 4616 and earlier papers; D. L. Struble, A. L. J. Beckwith, and G. E. Gream, *Tetrahedron Letters*, 1970, 4795.

Dibenzopyranone Formation.—Formation of dibenzopyranone from biphenyl-2-carboxamide and its *N*-substituted derivatives may be accounted for most simply by cyclisation of the amidyl on oxygen followed by aromatisation and hydrolysis [(3) ⟶ (5) ⟶ (10)]. To test this hypothesis we prepared biphenyl-2-carboxamide with the carbonyl function labelled (8·4%) with ^{18}O. According to the foregoing sequence, oxidation should give the lactam (12) labelled on the carbonyl oxygen atom and the lactone (10) labelled on the ether oxygen atom. This proved to be the case. In the mass spectrum of the phenanthridone the *m/e* 169 ($M - C^{18}O$) peak was not enhanced with respect to *m/e* 167 ($M - C^{16}O$), showing that all of the label was lost in the elimination of carbon monoxide from the molecular ion. However, in the mass spectrum of the dibenzopyranone the peak at *m/e* 170 ($M - C^{18}O$) was enhanced (4·2%) relative to that at *m/e* 168 ($M - C^{16}O$) although not to the extent of the ^{18}O incorporated in the parent amide. To confirm that the label was entirely on the ether oxygen atom the dibenzopyranone was converted into the pyran (19) by reaction with methylmagnesium iodide. The mass spectrum of this product showed complete retention of the label (8·4%). Hence the proposed scheme is confirmed, but in the fragmentation of the dibenzopyranone molecular ion into the dibenzofuran cation and carbon monoxide, oxygen scrambling occurs.

The formation of dibenzopyranone from amides with a 2′-substituent (experiments xi—xvi) could occur in a similar way, or by indirect displacement of the substituent by hydroxyl (*via* initial $SO_4^{-\cdot}$ attack) followed by spontaneous lactonisation. In order to distinguish between these possibilities the amides (2; $R^1 = R^3 = H$, $R^2 = NO_2$) and (2; $R^1 = R^3 = H$, $R^2 = CO_2H$) were oxidised in $H_2{}^{18}O$ (20% enrichment). The mass spectrum of the dibenzopyranone derived from the nitro-amide showed complete incorporation of the label (20%). If the dibenzopyranone is formed by direct displacement then the label would be on the carbonyl oxygen atom and the ratio of the $M - C^{18}O$ and $M - C^{16}O$ peak intensities should be the same as in the spectrum of the unlabelled dibenzopyranone (0·06). However, if indirect displacement occurs then the ether oxygen atom would be labelled and the ratio should equal the $(M + 2) : M$ ratio in the spectrum of the labelled dibenzopyranone (0·2). In fact, the measured $(M - C^{18}O) : (M - C^{16}O)$ ratio was 0·1, again suggesting oxygen scrambling in the elimination of CO from the molecular ion. By conversion into the pyran (19) as before it was shown (mass spectrometry) that the label was completely lost and hence that the nitro-group had been displaced by a direct cyclisation of the amide group on oxygen.

When the carbamoyl acid (2; $R^1 = R^3 = H$, $R^2 = CO_2H$) was oxidised in labelled water there was no incorporation of ^{18}O into the dibenzopyranone produced.

[15] D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 118.

This indicates that oxidative cyclisation of the carboxylic acid with intramolecular displacement of the amide group prevails over the alternative displacement of the carboxy-group by the amide. However, this order of reactivity is reversed when there is a phenyl substituent on the nitrogen atom (Table; experiment xiv). Preferential attack of the amidyl group at the substituted 2′-position leading to dibenzopyranone rather than at the 6′-position leading to a substituted dibenzopyranone (Table: experiments xi—xvi) presumably arises because of non-bonding interaction between the 2′-substituent and the 6-hydrogen atom. This would make conformations in which the amidyl group closely approaches the unsubstituted 6′-position unfavourable. The large difference (13—97%) in the yields of cyclised products from 2-benzoylaminobiphenyl and *N*-phenylbiphenyl-2-carboxamide underlines the importance of geometrical factors for efficient cyclisation in this series.

Our general conclusion that *o*-arylphenylamidyls participate in intramolecular homolytic substitution by reacting mainly on nitrogen, unless certain 2′-substituents are present, has been confirmed by observing the behaviour of the amidyl (3; $R^1 = R^2 = R^3 = H$) generated in an alternative way. Thus, photolysis [4] of the *O*-acylhydroxamic acid (20; R = Bz) gave mainly phenanthridone (38%) accompanied by only a trace of dibenzopyranone. Although the reluctance of amidyls to react on oxygen has been adduced as evidence for their existence in a σ-ground state (1c) such evidence is not compelling. Our results are best accommodated by a mesomeric π-structure for the amidyl and so support the most recent e.s.r. results.[8] However, the structural and other features which determine the form in which this ambident radical reacts are not yet clear.

EXPERIMENTAL

For general methods see preceding paper.[1]

Synthesis of Starting Amides.—Biphenyl-2-carboxamide,[16] *N*-methyl-,[17] *NN*-dimethyl-,[18] *N*-phenyl-,[17] *N*-t-butyl-,[19] 4′-nitro-,[20] 4′-bromo-,[21,22] 4′-methoxy-,[23] 4′-methoxy-*N*-methyl-,[15] and 2′-nitro-[24] biphenyl-2-carboxamides, *NN*′-diphenylbiphenyl-2,2′-dicarboxamide,[25] biphenyl-2,2′-dicarboxamide,[26] and 2′-carbamoylbiphenyl-2-carboxylic acid,[26] and its *N*-phenyl derivative [27] were prepared by treatment of the corresponding acid chlorides with the appropriate amine. The following are new: N-*methyl*-4′-*nitrobiphenyl*-2-*carboxamide*, pale yellow needles, m.p. 209—211° (from aqueous ethanol) (Found: C, 65·8; H, 5·0; N, 10·9. $C_{14}H_{12}N_2O_3$ requires C, 65·6; H, 4·7; N, 10·9%); N-*methyl*-2′-*nitrobiphenyl*-2-*carboxamide*, pale yellow needles, m.p. 136·5—137° (from aqueous ethanol) (Found: C, 65·7; H, 4·7; N, 11·0. $C_{14}H_{12}N_2O_3$ requires C, 65·6; H, 4·7; N, 10·9%).

Oxidation of Biphenyl-2-carboxamides.—General Procedure. A solution of potassium persulphate (0·01 mol) in water (100 ml) was added, dropwise, with stirring during 30 min to a solution (or suspension) of the amide (0·01 mol) in water (100 ml) at 100°. The mixture was stirred for a further 1·5 h at 100°, cooled, and extracted with ether; the extracts were dried ($MgSO_4$) and evaporated. Products were isolated from the crude residue by t.l.c.

(i) Biphenyl-2-carboxamide (2; $R^1 = R^2 = R^3 = H$) gave phenanthridone,[26] m.p. 291—292° (from chloroform) (714 mg, 38%), dibenzo[*b*,*d*]pyran-6-one,[28] m.p. 92—93° (107 mg, 6%), starting amide (106 mg), and 5-(5,6-*dihydro*-6-*oxophenanthridin*-2-*yl*)*phenanthridone* (15) as prisms, m.p. >350° (from aqueous ethanol) (12 mg, <1%) (Found: C, 80·1; H, 4·4; N, 7·5%; *M*, 388·1206. $C_{26}H_{16}N_2O_2$ requires C, 80·4; H, 4·2; N, 7·2%; *M*, 388·1212), $\lambda_{max.}$ 242, 260, 275sh, 327, and 342 nm (log ε 4·86, 3·68, 3·43, 3·21, and 3·13), $\nu_{max.}$ 3180, 1680, and 1655 cm^{-1}.

(ii) *N*-Methylbiphenyl-2-carboxamide (2; $R^1 = Me$, $R^2 = R^3 = H$) gave *N*-methylphenanthridone,[29] m.p. 105—105·5° (from chloroform–petroleum) (1·16 g, 62%), phenanthridone (38 mg, 2%), dibenzo[*b*,*d*]pyran-6-one (190 mg, 11%), and unchanged amide (232 mg).

(iii) *NN*-Dimethylbiphenyl-2-carboxamide gave *N*-methylphenanthridone (420 mg, 18·5%), phenanthridone (trace), dibenzo[*b*,*d*]pyran-6-one (68 mg, 3·5%), and unchanged amide (84 mg).

(iv) *N*-t-Butylbiphenyl-2-carboxamide (2; $R^1 = Bu^t$, $R^2 = R^3 = H$) gave N-*t-butylphenanthridone*, pale yellow needles, m.p. 230—233° (from aqueous ethanol) (1·03 g, 51·5%) (Found: C, 81·0; H, 7·1; N, 5·9. $C_{17}H_{17}NO$ requires C, 81·2; H, 6·8; N, 5·6%), $\lambda_{max.}$ 226sh, 240, 260, 278, 327, and 341 nm (log ε 4·47, 4·54, 3·19, 2·99, 2·94, and 2·94), $\nu_{max.}$ 1666 cm^{-1}, τ 1·35—2·8 (8H, m, ArH) and 8·74 (9H, s, Bu^t); 2-*t-butylisoindoline*-1-*spiro*-1′-*cyclohexa*-2′,5′-*diene*-3,4′-*dione* (13; $R^1 = Bu^t$, $R^2 = H$), needles, m.p. 210—212° (from aqueous ethanol) (143 mg, 6·5%) (Found: C, 76·3; H, 6·4; N, 5·1%; *M*, 267·1264. $C_{17}H_{17}NO_2$ requires C, 76·4; H, 6·4; N, 5·2%; *M*, 267·1259), $\lambda_{max.}$ (hexane) 230 nm (log ε 4·59), $\nu_{max.}$ 1690 and 1660 cm^{-1}, τ 2·15—2·92 (4H, m, ArH), 3·17 (2H, d, *J* 6 Hz, C=CH), 3·58 (2H, d, *J* 6 Hz, C=CH), and 8·39 (9H, s, Bu^t); 2,2″-*di-t-butyl*-4,4″-*bi*-(*isoindoline*-1-*spiro*-1′-*cyclohexa*-2′,4′-*diene*)-3,3″-*dione* (9; $R^1 = Bu^t$, $R^2 = R^3 = H$), prisms, m.p. 224—225° (from aqueous ethanol) (410 mg, 21%) (Found: C, 80·6; H, 7·1; N, 5·3%; *M*, 504·2770. $C_{34}H_{36}N_2O_2$ requires C, 80·9; H, 7·2; N, 5·5%; *M*, 504·2777), $\lambda_{max.}$ (hexane) 230 nm (log ε 4·75), $\nu_{max.}$ 1685 cm^{-1}, τ 2·13—3·19 (8H, m, ArH), 3·80—4·39 (8H, m, C=CH), 6·48—6·80 (2H, m, CH), and 8·35 and 8·37 (18H, 2 s each 9H, 2 Bu^t); dibenzo[*b*,*d*]pyran-6-one (205 mg, 13%); and unchanged amide (510 mg).

[16] C. Graebe and A. Sc. Rateanu, *Annalen*, 1894, **279**, 257.
[17] T. Mukai, *Bull. Chem. Soc. Japan*, 1959, **32**, 272.
[18] H. O. House and W. M. Bryant, *J. Org. Chem.*, 1966, **31**, 3482.
[19] G. W. Kenner, M. J. T. Robinson, C. M. B. Taylor, and B. R. Webster, *J. Chem. Soc.*, 1962, 1756.
[20] D. H. Hey, J. A. Leonard, and C. W. Rees, *J. Chem. Soc.*, 1963, 5251.
[21] W. S. Waring, B.P. 859,342/1961 (*Chem. Abs.*, 1960, **55**, 14,389).
[22] J. R. E. Hoover, A. W. Chow, R. J. Stedman, N. M. Hall, H. S. Greenberg, M. M. Dolan, and R. J. Ferlauto, *J. Medicin. Chem.*, 1964, **7**, 245.
[23] T. Muroi, *Nippon Kagaku Zasshi*, 1956, **77**, 1084 (*Chem. Abs.*, 1959, **53**, 5250).
[24] C. Angelini, *Ann. Chim.* (*Italy*), 1957, **47**, 879.
[25] R. B. Hill, R. L. Sublett, and H. G. Ashburn, *J. Chem. and Eng. Data*, 1963, **8**, 233.
[26] H. W. Underwood and E. L. Kochmann, *J. Amer. Chem. Soc.*, 1924, **46**, 2075.
[27] F. Bell and F. Briggs, *J. Chem. Soc.*, 1941, 282.
[28] D. H. Hey, J. A. Leonard, and C. W. Rees, *J. Chem. Soc.*, 1962, 4579.
[29] C. Graebe and C. A. Wander, *Annalen*, 1893, **276**, 252.

(v) *N*-Phenylbiphenyl-2-carboxamide (2; R^1 = Ph, R^2 = R^3 = H) gave *N*-phenylphenanthridone,[30] m.p. 222—224° (from aqueous ethanol) (1·4 g, 97%), dibenzo[*b*,*d*]pyran-6-one (trace), and unchanged amide (1·28 g).

(vi) 4′-Nitrobiphenyl-2-carboxamide (2; R^1 = R^2 = H, R^3 = NO_2) gave 3-nitrophenanthridone,[31] pale yellow needles, m.p. 343—347° (from acetic acid) (707 mg, 32%); 3-nitrodibenzopyran-6-one,[32] needles, m.p. 203—205° (from aqueous acetone) (104 mg, 5%); dibenzo[*b*,*d*]pyran-6-one (10 mg, 0·5%); and unchanged amide (220 mg). The residual aqueous solution, after removal of organic material, gave a positive test for nitrite ions.

(vii) *N*-Methyl-4′-nitrobiphenyl-2-carboxamide (2; R^1 = Me, R^2 = H, R^3 = NO_2) (1·05 g, 0·004 mol) gave *N-methyl-3-nitrophenanthridone*, pale yellow needles, m.p. 220° (from aqueous ethanol) (50 mg, 6%) (Found: C, 65·8; H, 4·0; N, 11·1. $C_{14}H_{10}N_2O_3$ requires C, 66·1; H, 4·0; N, 11·0%), $\lambda_{max.}$ 225, 230, 255, 262, 272sh, 301, 312, and 365 nm (log ε 5·33, 5·32, 5·29, 5·28, 5·18, 5·01, 5·05, and 4·87), $\nu_{max.}$ 1665, 1535, and 1345 cm^{-1}, τ 1·50—2·84 (7H, m, ArH) and 6·26 (3H, s, Me); 3-nitrodibenzo[*b*,*d*]pyran-6-one (trace); dibenzo[*b*,*d*]pyran-6-one (trace); and unchanged amide (170 mg).

(viii) 4′-Methoxybiphenyl-2-carboxamide (2; R^1 = R^2 = H, R^3 = MeO) (1·04 g, 0·0045 mol) gave 3-methoxyphenanthridone,[33] needles, m.p. 241—242° (22 mg, 2%); 3-methoxydibenzo[*b*,*d*]pyran-6-one,[34] needles, m.p. 143·5—144·5° (trace); dibenzo[*b*,*d*]pyran-6-one (trace); and intractable material (891 mg). The residual aqueous solution, after extraction, gave a positive test for formaldehyde.

(ix) *N*-Methyl-4′-methoxybiphenyl-2-carboxamide (2; R^1 = Me, R^2 = H, R^3 = NO_2) (0·15 g, 0·0006 mol) gave *N*-methyl-3-methoxyphenanthridone (7 mg, 4·5%), 3-methoxydibenzo[*b*,*d*]pyran-6-one (trace), dibenzo[*b*,*d*]pyran-6-one (trace), and the spirodienone (13; R^1 = Me, R^2 = H) (7 mg, 5%).

(x) 4′-Bromobiphenyl-2-carboxamide (2; R^1 = R^2 = H, R^3 = Br) (0·495 g, 0·0018 mol) gave 3-*bromophenanthridone*, needles, m.p. 280—280·5° (sublim.) (48 mg, 14%) (Found: C, 57·1; H, 3·1; Br, 29·7; N, 5·4%; *M*, 272·9795. $C_{13}H_8{}^{79}BrNO$ requires C, 57·0; H, 2·9; Br, 29·2; N, 5·1%; *M*, 272·9790), $\lambda_{max.}$ 226sh, 235, 240, 260, 278, 326, and 341 nm (log ε 5·47, 5·54, 5·54, 4·19, 3·99, 3·94, and 3·94), $\nu_{max.}$ 3150 and 1665 cm^{-1}; dibenzo[*b*,*d*]pyran-6-one (trace); and unchanged amide (162 mg).

(xi) 2′-Nitrobiphenyl-2-carboxamide (2; R^1 = R^3 = H, R^2 = NO_2) (7·75 g, 0·032 mol) gave phenanthridone (130 mg, 4%); 1-*nitrodibenzo*[b,d]*pyran-6-one*, yellow needles, m.p. 199—200° (sublim.) (<1%) (Found: C, 64·9; H, 2·9; N, 5·9. $C_{13}H_7NO_4$ requires C, 64·7; H, 2·9; N, 5·8%), $\lambda_{max.}$ 235, 250sh, 260sh, and 320 nm (log ε 4·55, 4·40, 4·30, and 4·30), $\nu_{max.}$ 1745, 1545, and 1350 cm^{-1}; dibenzo[*b*,*d*]pyran-6-one (940 mg, 27%); and unchanged amide (3·5 g).

(xii) *N*-Methyl-2′-nitrobiphenyl-2-carboxamide (2; R^1 = Me, R^2 = NO_2, R^3 = H) (3·07 g, 0·012 mol) gave dibenzo[*b*,*d*]pyran-6-one (230 mg, 15%), 1-nitrodibenzo[*b*,*d*]pyran-6-one (trace), and unchanged amide (0·97 g).

(xiii) 2′-Carbamoylbiphenyl-2-carboxylic acid (2; R^1 = R^3 = H, R^2 = CO_2H) (8·2 g, 0·034 mol) in 0·01M-sodium hydroxide solution (340 ml) after treatment with potassium persulphate (9·52 g, 0·034 mol) in water (100 ml) in the usual way gave phenanthridone (104 mg, 1·5%), dibenzo[*b*,*d*]pyran-6-one (4·9 g, 74%), intractable material (1·17 g), and unchanged amide (trace).

(xiv) 2′-Phenylcarbamoylbiphenyl-2-carboxylic acid (2; R^1 = Ph, R^2 = CO_2H, R^3 = H) (6·05 g, 0·019 mol) in 0·01M-sodium hydroxide (190 ml), after treatment with potassium persulphate (5·13 g, 0·019 mol) in water (100 ml) in the usual way, gave *N*-phenylphenanthridone [28] (190 mg, 7%), unchanged amide (2·8 g), dibenzo[*b*,*d*]pyran-6-one (28 mg, 1%), and 9-*phenyl*[1]*benzopyrano*[5,4,3-cde]*quinoline*-5,10(9H)-*dione* (16) (220 mg, 7%) (Found: *M*, 313·0739. $C_{20}H_{11}NO_3$ requires *M*, 313·0739), $\lambda_{max.}$ 220, 232, 240, 258sh, 265sh, 325sh, 347, and 365 nm (log ε 4·73, 4·77, 4·73, 4·50, 4·08, 4·35, 4·52, and 4·56), $\nu_{max.}$ 1745 and 1665 cm^{-1}. Elemental analyses and m.p. determinations for this product were unsatisfactory because it was extremely electrostatic.

(xv) Biphenyl-2,2′-dicarboxamide (3·51 g, 0·013 mol) in water (100 ml), after treatment with potassium persulphate (10·5 g, 0·039 mol) in water (400 ml) in the usual way, gave dibenzo[*b*,*d*]pyran-6-one (100 mg, 12%), phthalimide, m.p. 227° (from aqueous ethanol) (35 mg, 4%), and unchanged amide (2·1 g).

(xvi) *NN*′-Diphenylbiphenyl-2,2′-dicarboxamide (0·98 g, 0·0025 mol) gave *N*-phenylphenanthridone (36 mg, 25%) and unchanged amide (0·77 g).

(xvii) Phenanthridone (0·97 g, 0·005 mol) in water (100 ml), after treatment with potassium persulphate (5·40 g, 0·02 mol) in water (100 ml) at 100°, gave 5-(5,6-dihydro-6-oxophenanthridin-2-yl)phenanthridone (7 mg, 6%) and unchanged amide (0·85 g).

(xviii) *N*-t-Butylbiphenyl-2-carboxamide (2; R^1 = Bu^t, R^2 = R^3 = H) (1·26 g, 0·005 mol) and copper(II) sulphate pentahydrate (6·25 g, 0·025 mol) in water (50 ml), after treatment with potassium persulphate (1·35 g, 0·005 mol) in water (50 ml), gave *N*-t-butylphenanthridone (330 mg, 44%), the dienone (13; R^1 = Bu^t, R^2 = H) (106 mg, 13%), and unchanged amide (504 mg).

(xix) *N*-Methylbiphenyl-2-carboxamide (1·05 g, 0·005 mol) on oxidation with persulphate as described in (xviii) gave *N*-methylphenanthridone (520 mg, 86%), dibenzo[*b*,*d*]pyran-6-one (46 mg, 8%), and unchanged amide (400 mg).

Oxidation of Acylaminobiphenyls.—2-Acetamidobiphenyl (3 g, 0·014 mol) on oxidation with potassium persulphate (3·85 g, 0·014 mol) in the usual way gave *N*-acetylcarbazole,[35] m.p. 67—68° (from chloroform) (200 mg, 7%), and unchanged amide (1·03 g).

2-Benzamidobiphenyl (1·87 g, 0·0068 mol) with potassium persulphate gave *N*-benzoylcarbazole,[36] m.p. 96—98° (from ethanol) (162 mg, 13%), and unchanged amide (600 mg).

2-(*p*-Tolylsulphonylamino)biphenyl (500 mg, 0·0015 mol) with potassium persulphate gave a complex mixture of products which did not include *N*-(*p*-tolylsulphonylamino)-carbazole [37] (t.l.c.).

Hydrolyses of Amides.—The resistance of the biphenyl-2-carboxamides to hydrolysis was tested by heating the amides (0·0025 mol) at 100° for 2 h in aqueous ethanolic (1 : 1) solution rendered acidic by the prior decomposition

[30] T. M. Moynehan and D. H. Hey, *Proc. Chem. Soc.*, 1957, 209.
[31] F. J. Moore and E. H. Huntress, *J. Amer. Chem. Soc.*, 1927, **49**, 1324.
[32] H.-L. Pan and T. L. Fletcher, *J. Org. Chem.*, 1960, **25**, 1106.
[33] C. L. Arcus, M. M. Coombs, and J. V. Evans, *J. Chem. Soc.*, 1956, 1498.
[34] W. R. H. Hurtley, *J. Chem. Soc.*, 1929, 1870.
[35] C. Graebe and C. Glaser, *Annalen*, 1872, **163**, 343.
[36] T. S. Stevens and S. H. Tucker, *J. Chem. Soc.*, 1923, 2140.
[37] S. H. Tucker, *J. Chem. Soc.*, 1926, 546.

of potassium persulphate (0·0025 mol). In each case the amide was recovered quantitatively and negligible quantities of acidic organic material were detected.

Pyrolysis of the Dimer (9; $R^1 = Bu^t$, $R^2 = R^3 = H$).—A solution of the dimer (50 mg) in 1,2,4-trichlorobenzene (500 mg) was heated under reflux for 20 min, cooled, treated with chloroform (2 ml), and chromatographed (column) on basic alumina (petroleum and then dichloromethane as eluant). Further chromatography (t.l.c.) of the solid obtained from the dichloromethane fraction, on silica (chloroform as eluant), gave 4′-(5,6-*dihydro*-6-*oxophenanthridin*-3-*yl*)-N-*t*-*butylbiphenyl*-2-*carboxamide* (14), needles, m.p. 320° (from aqueous ethanol) (11 mg) (Found: *M*, 446·1977. $C_{30}H_{26}H_2O_2$ requires *M*, 446·1994), $\lambda_{max.}$ 335 and 352 (log ε 4·93 and 4·94), $\nu_{max.}$ 3340, 3080—3000, 1680, and 1650 cm^{-1}, τ 1·43—1·65 (3H, m, ArH), 2·1—2·65 (12H, m, ArH), 3·80br (2H, s, NH), and 8·79 (9H, s, Bu^t).

Conversion of Dibenzo[b,d]*pyran*-6-*one into* 6,6-*Dimethyldibenzo*[b,d]*pyran*.—The ketone was treated with methylmagnesium iodide as described by Cahn [38] to give the pyran, b.p. 127—130° at 0·8 mmHg, in high yield.

o-*Phenylbenzohydroxamic Acid*.—To hydroxylamine hydrochloride (13·9 g, 0·2 mol) in methanol (50 ml) at 30—40° a solution of potassium hydroxide (16·8 g, 0·3 mol) in methanol (50 ml) was added slowly, with stirring, the temperature being moderated by cooling in an ice-bath. Ethyl *o*-phenylbenzoate (22·6 g, 0·1 mol) was then added, dropwise, and the precipitate was collected. Evaporation of the filtrate gave an oil which was treated with water, and the resultant solution was washed with ether. Acidification of the aqueous solution with hydrochloric acid gave o-*phenylbenzohydroxamic acid* as needles, m.p. 142·5—143·5° (from chloroform–petroleum) (16·5 g, 77%) (Found: C, 73·0; H, 5·5; N, 6·9. $C_{13}H_{11}NO_2$ requires C, 73·2; H, 5·2; N, 6·6%), $\lambda_{max.}$ (hexane) 213 and 237 nm (log ε 4·44 and 4·25), $\nu_{max.}$ 3160br and 1630 cm^{-1}, τ 0·90br (1H, s, NH or OH) and 1·1—1·45 (10H, m, ArH and NH or OH).

A solution of the foregoing acid (213 mg) in ethanol (10 ml) and 2M-hydrochloric acid (10 ml) was heated under reflux for 2 h. The alcohol was distilled off *in vacuo* and the aqueous solution was neutralised with potassium hydrogen carbonate and then extracted with ether. The extracts were dried and evaporated, and the residue was chromatographed (t.l.c.) with benzene to give 2-aminobiphenyl (18 mg, 11%).

O-*Benzoyl*-o-*phenylbenzohydroxamic Acid*.—o-Phenylbenzohydroxamic acid (2·13 g, 0·01 mol) was dissolved in 0·1M-sodium hydroxide (100 ml) and the solution was evaporated to dryness. The dried salt was suspended in dioxan (20 ml) and benzoyl chloride (1·41 g, 0·01 mol) was added slowly with stirring. The mixture was then treated with water and the precipitate which separated was collected, dried, and crystallised from chloroform–petroleum to give the *product* as plates, m.p. 137° (600 mg, 19%) (Found: C, 75·4; H, 4·9; N, 4·4. $C_{20}H_{15}NO_3$ requires C, 75·7; H, 4·8; N, 4·4%), $\lambda_{max.}$ (hexane) 218sh, 235, 263, and 283sh nm (log ε 4·53, 4·59, 4·23, and 3·63), $\nu_{max.}$ 3280 and 1645 cm^{-1}.

The foregoing ester (650 mg) in dried benzene was photolysed for 12 h with a medium-pressure mercury vapour Hanovia lamp. Evaporation of the solvent and chromatography (t.l.c.) of the residue gave phenanthridone (120 mg, 33%) and dibenzo[*b*,*d*]pyran-6-one (trace).

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[38] R. S. Cahn, *J. Chem. Soc.*, 1933, 1400.