Intramolecular Cyclisations of Biphenyl-2-carboxyl Radicals: Evidence for a Π-State Aroyloxyl Radical

By **Stephen A. Glover,* Stephen L. Golding, André Goosen,** and **Cedric W. McCleland,** Organic Chemistry Research Laboratories, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth 6000, South Africa

Biphenyl-2-carboxyl radicals generated by homolysis of acyl hypoiodites cyclise intramolecularly giving mainly δ-lactones through Ar_2-6 cyclisation. 2'-Alkoxybiphenyl-2-carboxyl radicals do not give the expected Ar_1-5 cyclisation product but undergo a homolytic *ipso*-substitution of the 2'-substituent. The phenanthrene-4-carboxyl radical gives 5*H*-phenanthro[4,5-*bcd*]pyran-5-one. Consideration of the molecular orbitals involved suggests that the biphenyl-2-carboxyl radicals are in the π-ground state and have a higher energy, and, therefore, a less thermally accessible Σ-state than the corresponding amido-radicals. It is suggested that acyloxyl radicals which readily decarboxylate have either a Σ-ground state or a thermally accessible excited Σ-state.

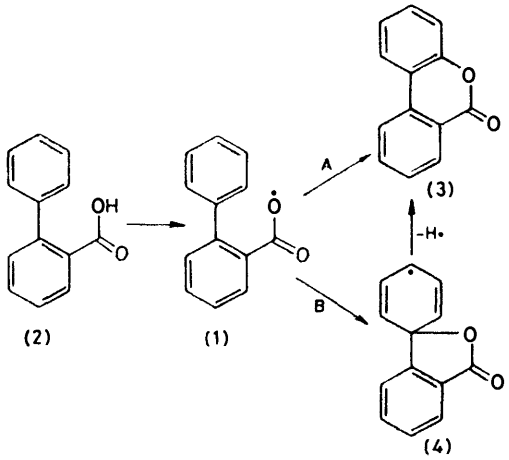
RECENTLY we reported that amido-radicals, generated by the photolysis of the corresponding *N*-iodoamides, react intramolecularly with aromatic rings.[1-4] In this way, biphenyl-2-carboxamides gave good yields of both Ar_2-6 and Ar_1-5 cyclised products when photolysed in the presence of t-butyl hypoiodite in t-butyl alcohol, a medium which not only generated the *N*-iodoamides, but also promoted efficient scavenging of the spirodienyl radicals (from Ar_1-5 cyclisation) to give the spirolactams.[2] Substituted biphenyl-2-carboxamides [4] also cyclised, the products being determined by both the electronic and steric effect of the substituent.[4] Phenanthrene-4-carboxamide gave Ar_2-6 products.[3]

From symmetry considerations in the transition states for these reactions, we concluded that amido-radicals probably participate through their Σ-state in the formation of spiro-γ-lactams (Ar_1-5 cyclisation) and through their Π-states where planar (Ar_2-6) products are formed.[3] Similar orbital overlap arguments indicate that Σ-state amidyls should add intramolecularly to olefins [5] while according to Chow and his co-workers, π-state amidyls are implicated in intramolecular hydrogen abstraction reactions.[6]

Skell has ascribed the different selectivities of succinimidyl radicals in hydrogen-abstraction reactions under different conditions to the Π and Σ_N states of the radical. Only the Σ_N state added to unsaturated systems.[7]

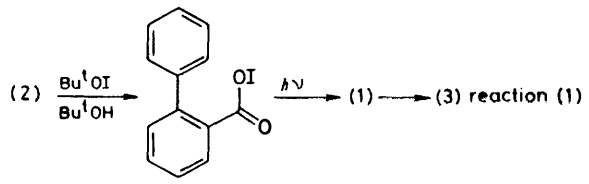
Since acyl hypoiodites can be generated from the reaction of carboxylic acids with t-butyl hypoiodite and these are a potential source of acyloxyl radicals,[8] we have investigated the behaviour of related aroyloxyl radicals in the t-butyl alcohol–t-butyl hypoiodite trapping medium.

Aroyloxyl radicals have a lower tendency to decarboxylate than aliphatic radicals [9] and consequently biphenyl-2-carboxyl radicals (1) have been trapped intramolecularly as dibenzo[*bd*]pyranone (3) upon electrolysis of the sodium salt of the acid,[10] pyrolysis of the corresponding diaroylperoxides,[10,11] cobalt-catalysed oxidations with oxygen and di-t-butyl peroxide,[12] copper-catalysed decomposition of the corresponding diacyl peroxides,[13] and oxidation with lead tetra-acetate [14] and persulphate.[15] Notably, no γ-lactones were isolated from these reactions, although Thomson and his co-workers have suggested that in the persulphate oxidation, no distinction could be made between direct cyclisation at the C-2' position (pathway A) or formation



and rearrangement of spirodienyl radical (4) [15] (pathway B).

We likewise have found that photolysis of the acyl hypoiodite of biphenyl-2-carboxylic acid (2), generated in t-butyl alcohol with t-butyl hypoiodite, gives only the dibenzopyranone (3). The free-radical nature of the reaction was indicated by the low yields for the dark reactions (Table 1) and the acyloxyl radical is postulated



as a likely intermediate in the reaction (1). Dilatometry indicated that decarboxylation was not a significant reaction pathway at room temperature.

The formation of (3) most probably occurs by direct cyclisation of the acyloxyl radical at the 2'-position of (1)

since the amido-radical cyclisations showed that spirodienyl radicals are efficiently converted into spirodienyl t-butyl ethers and spirodienones under these conditions [2,3] and the radical (4) would be expected to behave likewise.

γ-Lactone spirodienones were isolated from 2′-octyloxy- and 2′-isopropoxy-biphenyl-2-carboxylic acids (see later). Furthermore, planar phenanthrene-4-carboxylic acid

TABLE 1

Yields of dibenzopyranone (3) from biphenyl-2-carboxylic acid (2) and t-butyl hypoiodite in t-butyl alcohol

	t/h	% yield
hν	3	25
Heat and dark (83 °C)	52	8
Dark (26 °C)	6	0.6

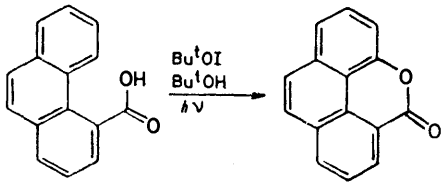
(5) gave the Ar_2-6 cyclised product 5*H*-phenanthro[4,5-*bcd*]pyran-5-one (6) in 20% yield.

The predominance of Ar_2-6 cyclisation proved to be a general feature of cyclisations of other substituted biphenyl-2-carboxyl radicals.

Unlike its *N*-methyl amide analogue, which gave mainly the Ar_1-5 product,[4] 4′-methoxybiphenyl-2-carboxylic acid (7) underwent Ar_2-6 cyclisation in low yield to give 3-methoxy-6*H*-dibenzo[5,6-*bd*]pyran-6-one (8) (*ca.* 17%) and a minor, unidentified species which was also formed in a dark reaction and therefore probably not derived from the acyloxyl radical.

Similarly, while 2′-methoxybiphenyl-2-carboxamido-radicals cyclised exclusively at the 1′-position,[4] 2′-alkoxybiphenyl-2-carboxyl-radicals (9)—(12) gave mainly dibenzopyranone (3) even when bulky isopropoxy- and octyloxy-groups were present on the 2′-position (Table 2). However, here at least, low yields of 2′-isopropoxy- and 2′-octyloxy-1,3-dihydroisobenzofuran-1-spiro-1′-cyclohexa-2′,5′-diene-3,4′-diones (13) and (14) were obtained (presumably by an analogous sequence to the formation of spirodienones from biphenyl-2-carboxamides [2,4]).

The amido-radical cyclisations clearly indicated that a 2′-methoxy-substituent favoured a twisted conformation



(5) (6)

of the rings and hence Ar_1-5 cyclisation.[4] This effect would be enhanced in substrates (10), (11), and (12) since the spatial requirements of alkyl substituents increase with branching.[16] The preponderance of Ar_2-6 cyclisation in biphenyl-2-acyloxyl systems cannot therefore be accounted for on steric grounds.

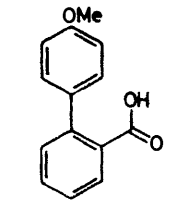
The loss of 2′-substituents in these reactions has been noted by other authors.[14,15] Similar relative yields of

TABLE 2

Substrate	t/h	Dibenzopyranone (3) (%)	Other products (%)
2′-Methoxy (9)	3	76	
2′-Ethoxy (10)	4.3	13	*a*
2′-Isopropoxy (11)	3	57	(13) *ca.* 10
2′-Octyloxy (12)	7	56	(14) *ca.* 5; $C_8H_{17}OH$ 58 and $C_7H_{15}CHO$ 6
2′-Nitro (15)	3.5	0	

[a] A trace of γ-lactone was detected in the i.r. spectrum of the crude reaction mixture at 1 770 cm^{-1}.

dibenzopyranone (3) were found from the lead tetra-acetate oxidations of (2), (9), and (15) thus suggesting a common cyclisation mechanism presumably involving the acyloxyl radical (Table 3).[14] The relative yields from the analogous persulphate oxidations differed markedly from both the hypoiodite and lead tetra-acetate re-



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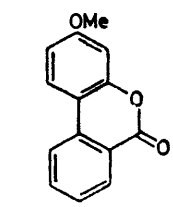

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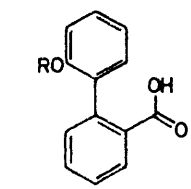
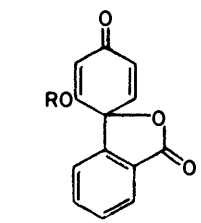
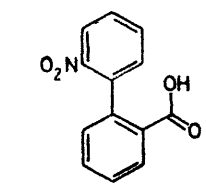


(9) R = Me
(10) R = Et
(11) R = Pr^i
(12) R = Octyl



(13) R = Pr^i
(14) R = Octyl



(15)

actions, confirming the proposals by Thomson and his co-workers [15] that formation of dibenzopyranone from the persulphate oxidation of 2′-methoxy- and 2′-nitro-biphenyl-2-carboxylic acids occur, at least in part, by alternative mechanisms.

The possibility of side-chain oxidation resulting in the

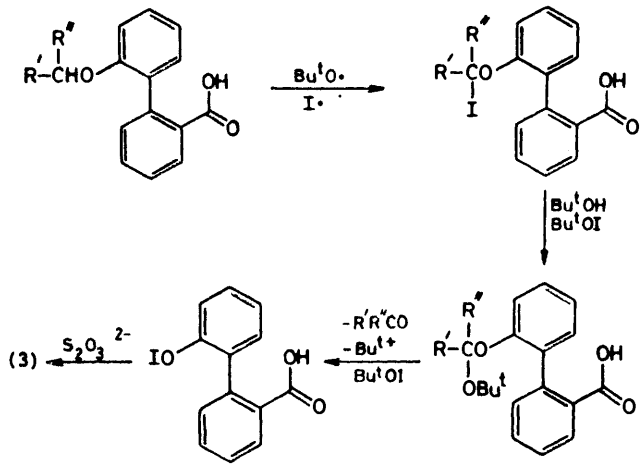
TABLE 3

	Yields of dibenzopyranone (3)		
	2′-OMe (9)	2′-H (2)	2′-NO_2 (15)
Bu^{t}OI/hν/Bu^{t}OH [a]	76	25	0
$Pb(OAc)_4$ [14]	68	22	3.6
Persulphate [15]	30	26	23

[a] Reaction time 3 h.

formation of 2′-hydroxybiphenyl-2-carboxylic acid which could cyclise to (3) upon work-up (Scheme 1) was discounted.

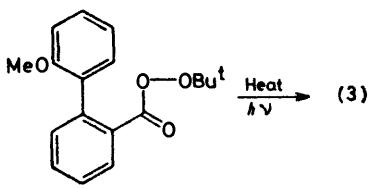
Evidence that de-alkoxylation occurred as a result of cyclisation of the acyloxylradical was obtained from two experiments.



SCHEME 1

Firstly, the thermal decomposition of the t-butyl perester of the 2′-methoxy-acid (16)* in refluxing toluene gave only dibenzopyranone (3) (52%) and 1,2-diphenylethane (by hydrogen abstraction from toluene). Photochemical cleavage at room temperature (< 300 nm) also gave a low yield of (3).

Secondly, when 2′-octyloxybiphenyl-2-carboxylic acid was irradiated in t-butyl alcohol in the presence of t-butyl hypoiodite, dibenzopyranone (56%) and the spirodienone (14) as well as n-octanol (58%) and octanal (6%) were obtained. Although octanal could be formed by



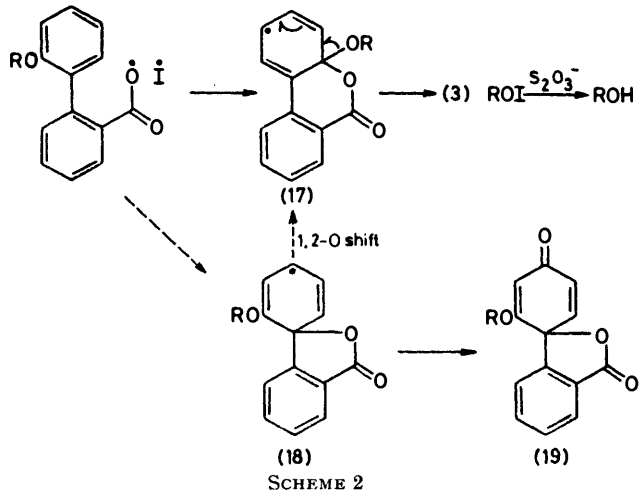
(16)

side-chain oxidation (Scheme 1), the oxidation of alcohols to aldehydes with t-butyl hypoiodite is known [17] and in a control reaction octanol was converted into octanal in 19% yield under the reaction conditions.

We therefore conclude that the alkoxy-substituent is lost in the fast rearomatisation of (17) (Scheme 2). Radical (17) could be formed from the γ-lactone spirodienyl radical (18) which undergoes a 1,2-oxygen migration in competition with the trapping process [2,4]

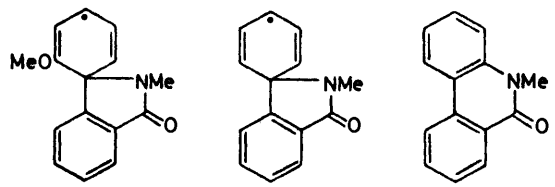
* Previously it was reported [14] that the corresponding diacyl peroxide could not be prepared since its precursor, the acyl chloride, cyclised spontaneously to dibenzopyranone by cleavage of the O–Me bond. We have found that the acid chloride can be prepared by briefly digesting the parent acid in thionyl chloride at 4 °C, followed by removal of the excess of reagent under reduced pressure.

which leads to (19). However, the near quantitative scavenging of the corresponding γ-lactam spirodienyl radicals under identical reaction conditions [4] militates against this pathway. Furthermore, Hey *et al.* have

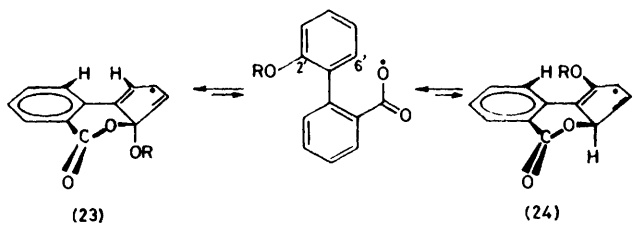


SCHEME 2

shown that the 2′-methoxy-*N*-methyl-3-oxoisoindoline-1-spiro-1′-cyclohexa-2′,5′-dienyl radical (20) does not rearrange readily, for purely steric reasons, under conditions in which the unsubstituted radical (21) rearranged efficiently to the *N*-methylphenanthridone (22).[18]



We consider therefore that (17) is formed by a direct reversible attack of the acyloxyl radical at the 2′-position. This position, although less prone to electrophilic radical [19] attack than the 6′-position,† leads to the thermodynamically more stable dienyl radical intermediate (23) in which the alkoxy-substituent is turned

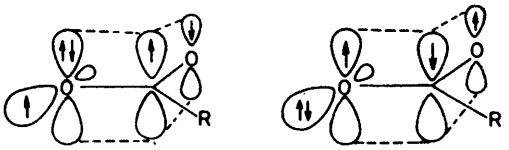


away from the plane of the rings, as opposed to the intermediate (24). The reversible addition of acyloxyl radicals to aromatics has been established [11a,13,20]

The failure of biphenyl-2-carboxylic acid (2) and its

† Hückel Free Valence values for the 2′ and 6′ positions are 0.3 and 0.44 respectively. For comparison the F_r values for the α and β positions of naphthalene are 0.453 and 0.404 respectively.

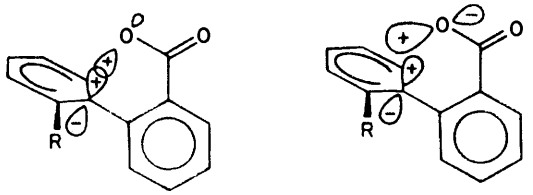
alkoxylated derivatives (7) and (9)—(12) to give significant amounts of Ar_1-5 products, is surprising. The entropy of activation for Ar_1-5 cyclisation of the *N*-methylbiphenyl-2-carboxamido-radical was in the range 67—100 J K^{-1} mol^{-1} more favourable than the activation entropy for the Ar_2-6 process.[3] Furthermore 2'-alkoxy-substituents should favour Ar_1-5 cyclisation through their electronic as well as their steric effect, since in a twisted conformation of the biphenyl nucleus, the 2'-alkoxylated ring would have similar properties to anisole in which the *ortho*-position is activated towards attack by the electrophilic acyloxyl radical. A similar electronic effect was



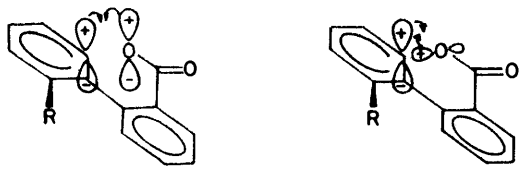
Σ (25) Π (26)

evident from the relative rates of Ar_1-5 and Ar_2-6 cyclisations of the *N*-methylbiphenyl-2-carboxamido-radical and its 4'-methoxy-derivative. The ratio $^kAr_1$-5/$^kAr_2$-6 increased from 2 to 6 upon methoxylation at the 4'-position.[4]

The difference in reactivity between acyloxyl and amido-radicals cannot, it seems, be rationalised on the basis of different electronic and steric effects in the recipient aromatic rings. An explanation might lie in an analysis of the radical entities themselves. Like the amido-radical,[3] the acyloxyl radical can exist in either a Σ or a Π electronic configuration (25) and (26).



(27) (28)



(29) (30)

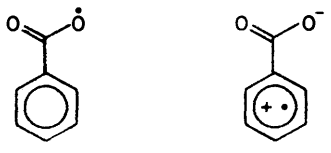
R = H, alkoxy

In the twisted conformation of the aromatic rings which favours Ar_1-5 cyclisation,[3,4] the best overlap between the acyloxy-group and a Π-molecular orbital at the 1'-position would be attained by a Σ-state acyloxyl radical (27). The Π-state acyloxyl radical would result in an orthogonal overlap between the interacting orbitals (28).

A Π-state (29) or a Σ-state (30) could react at the 2'-position to give Ar_2-6 products.*

The nature of the ground state electronic configuration of the acyloxyl radical is still under dispute.

G-Tensors from e.s.r. spectra of benzoyloxyl as well as other acyloxyl radicals, generated in single crystals, suggest that these radicals are in the Σ-state.[21]



Σ (31) Π (32)

INDO calculations predict a Π-ground state for the benzoyloxyl and formyloxyl radicals,[22] but *ab initio* calculations indicate that an unsymmetrical Σ-ground state would be the lowest in energy for the formyloxyl radical.[23] The same conclusions were drawn from NDDO calculations on formyloxyl and acetoxyl radicals.[24] Norman and his co-workers [25] have recently proposed a Σ-ground state for the aroyloxyl radical since Ti^{III} reduction of the peracid produces an acyloxyl radical (31)

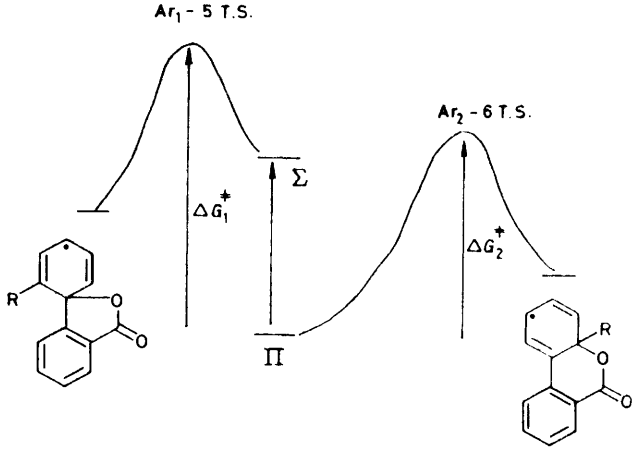


FIGURE 1

which reacts differently to the Π-state radical zwitterion (32) formed upon persulphate oxidation of the aromatic ring. They conclude that the radical (31) can, therefore, not be a canonical form of (32) and is probably in a Σ orbital.

We contend that since the biphenyl-2-carboxyl radicals do not readily undergo Ar_1-5 cyclisation, they must exist mainly in a Π-ground state (26). The Σ-state configuration (25) which can cyclise at the 1'-position through a low-energy transition state must be sufficiently

* In a previous paper [3] we suggested that only the Π-state amidyl could be involved in Ar_2-6 cyclisation. We now accede that a Σ-state amidyl could also participate in phenanthridone formation but since amidyls have a Π-ground state, the arguments used in the aforementioned paper remain essentially the same.

higher in energy to make the Ar_1-5 mode of cyclisation non-competitive with the Ar_2-6 process (Figure 1, $\Delta G_1^{\ddagger} > \Delta G_2^{\ddagger}$). It is conceivable that $\Delta G_2^{\ddagger}$ would be raised and $\Delta G_1^{\ddagger}$ lowered through their respective $\Delta S^{\ddagger}$ terms by increasing bulkiness of the substituent R resulting in the formation of both products with substrates (11) and (12).

On the basis of the above postulate, the difference in reactivity between the biphenyl-2-carboxyl and -amido-radicals could be in the difference between the energies of their respective Σ and Π-doublet states, this difference being smaller in the case of the biphenyl-2-carboxamido-radicals thus making Ar_1-5 cyclisation the predominant process. Interestingly the INDO energy differences for the formamido- and the formyloxyl radicals are 100 [26] and 155 [22a] K J mol^{-1} respectively.

The thermal attainment of a higher electronic state should be possible where energy differences between the states are small and the reaction pathways of the respective species have appropriate free energies of activation. An analogy can be found in the observed singlet and triplet state reactions of carbenes.[27]

Finally the postulate is compatible with the observation that decarboxylation, like Ar_1-5 cyclisation, is also a non-competitive process. Consideration of the symmetries of the orbitals in the Σ and Π acyloxyl radical states indicates that decarboxylation should, like Ar_1-5 cyclisations, proceed through the Σ-state radical (Figure 2).

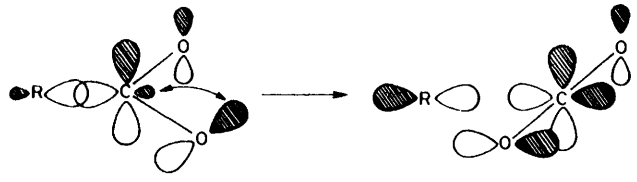


FIGURE 2

Koenig has shown that the Σ-state of the formyloxyl radical correlates with the ground state of carbon dioxide whereas the lower energy Π-state correlates with an excited state.[22a] Similarly, Skell has recently attributed the ring opening reaction of succinimidoyl radicals to the excited Σ-state.[7]

We tentatively propose that a contributing factor to the greater general stability of aroyloxyl as opposed to alkoyloxyl radicals might be due to the fact that alkoyloxyl radicals have either a Σ-ground state or a low energy and therefore a thermally accessible excited Σ-state. On the other hand aroyloxyl radicals could have a greater preference for a Π-ground state which is inert to decarboxylation. Inter-[20] or intra-molecular trapping of Π-state aroyloxyl radicals, as exemplified by the cyclisations described above, thus compete more favourably with the decarboxylation process.

This postulate would account for the recent results observed by Norman and his co-workers [25] if it is assumed that persulphate oxidation of carboxylates generates radical zwitterions which transform into Π-state aroyloxylspecies and Ti^{III} reduction of the hydroperoxides produces Σ-state aroyloxyl radicals.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were recorded on a Perkin–Elmer 297 spectrophotometer. ^1H N.m.r. spectra (60 MHz) were recorded with a Perkin-Elmer R12A spectrometer, with tetramethylsilane as internal standard, and mass spectra (A.E.I. MS9 instrument) were recorded at the N.C.R.L./C.S.I.R. laboratories in Pretoria.

Irradiations were carried out with a 1 000 W tungsten lamp unless otherwise specified. Silica gel for preparative t.l.c. was Merck HF 254—366 type 60 (nach Stahl).

G.l.c. analysis for octanol and octanal were performed on a Packard–Becker 420 gas chromatograph with F.I.D. Column A was packed with 15% di-isodecyl phthalate on Chromosorb P80-100.

Preparation of Carboxylic Acids and Derivatives.—Biphenyl-2-carboxylic acid (2),[28] 2′-methoxybiphenyl-2-carboxylic acid (9),[4] m.p. 160—162 °C, (lit.,[14] 152—153 °C), and phenanthrene-4-carboxylic acid (5) [3] were synthesised by known procedures.

2′-Isopropoxybiphenyl-2-carboxylic acid (11). 6*H*-Dibenzo[5,6-*bd*]pyran-6-one [10] (3 g) was refluxed in ethanolic aqueous potassium hydroxide (5%; 50 ml) for 3.5 h. The solution was washed with chloroform and evaporated to give the dipotassium salt of 2′-hydroxybiphenyl-2-carboxylic acid (2 g) which was refluxed for 24 h with 18-crown-6 (0.3 g, 0.001 mol) and isopropyl iodide (1.86 g, 0.011 mol) in acetonitrile (50 ml).[29] The acetonitrile was removed *in vacuo* and after dilution with chloroform, the mixture was washed with water (10 ml), dried, and concentrated to give a mixture of 18-crown-6 and isopropyl 2′-isopropoxybiphenyl-2-carboxylate δ($CDCl_3$) 0.85—1.3 (12 H, 2 × d), 4.05—4.6, 4.7—5.25 (1 H, m), and 6.7—7.99 (8 H, m). The mixture (1.3 g) was saponified with ethanolic aqueous potassium hydroxide (10%, 40 ml), washed with chloroform (to remove 18-crown-6), and acidified (dilute HCl). The chloroform extract was dried and concentrated to give an oil (0.56 g, 0.002 mol) which crystallised from carbon tetrachloride–light petroleum (b.p. 40—60 °C) as needles of 2′-isopropoxybiphenyl-2-carboxylic acid, m.p. 126—128 °C, M^+ 256; δ($CDCl_3$) 1.06—1.3 (6 H, d), 4.05—4.6 (1 H, septet), and 6.7—8.3 (8 H, m); $\nu_{max.}$ ($CHCl_3$) 2 950br, 1 670, and 1 465 cm^{-1} (Found: C, 74.6; H, 6.3. $C_{16}H_{16}O_3$ requires C, 74.98; H, 6.29%).

2′-Ethoxybiphenyl-2-carboxylic acid (10). This compound, prepared from 6*H*-dibenzo[5,6-*bd*]pyran-6-one and ethyl iodide by a procedure similar to the preceding one, crystallised from benzene–light petroleum (b.p. 40—60 °C), m.p. 69—72 °C, M^+ 242; δ($CDCl_3$) 1.0—1.3 (3 H, t), 3.62—4.1 (2 H, q), and 6.6—7.0 (8 H, m); $\nu_{max.}$ ($CHCl_3$) 2 990br and 1 700 cm^{-1} (Found: C, 74.5; H, 5.8. $C_{15}H_{14}O_3$ requires C, 74.36; H, 5.82%).

2′-Octyloxybiphenyl-2-carboxylic acid (12). This compound was synthesised from n-octyl iodide and 6*H*-dibenzo-[5,6-*bd*]pyran-6-one according to the above procedure. The acid was separated from the non-volatile octyl iodide by column chromatography on silica gel (chloroform elution) and was a yellow oil, M^+ 326; δ($CDCl_3$) 0.55—1.9 (15 H, m), 3.5—4.05 (2 H, t), and 6.65—8.1 (8 H, m); $\nu_{max.}$ ($CHCl_3$) 2 940br, 1 700, and 1 248 cm^{-1} (Found: C, 76.9; H, 8.14. $C_{21}H_{26}O_3$ requires C, 77.27; H, 8.03%).

2′- and 4′-Nitrobiphenyl-2-carboxylic acids. These compounds were obtained by nitration of finely powdered 6*H*-dibenzo[5,6-*bd*]pyran-6-one with 50% nitric acid at 70 °C for 2 h. Filtration afforded a pale yellow powder which was

separated by fractional crystallisation from ethanol into 4'-nitrobiphenyl-2-carboxylic acid, m.p. 228—229 °C (lit.,[30] m.p. 226—227 °C) and the more soluble 2'-nitrobiphenyl-2-carboxylic acid, m.p. 163—166 °C (lit.,[31] m.p. 168 °C).

4'-Methoxybiphenyl-2-carboxylic acid (7). 4'-Nitrobiphenyl-2-carboxylic acid (1 g) was hydrogenated over PtO_2 in ethyl acetate. The crude 4'-aminobiphenyl-2-carboxylic acid was diazotised in 10% H_2SO_4 and converted into 4'-hydroxybiphenyl-2-carboxylic acid by standard procedures. The hydroxy-acid crystallised from ethanol–water as needles (0.61 g), m.p. 208—211 °C (lit.,[32] m.p. 205.5 °C). Methylation (with methyl iodide and sodium hydride in methanol) and alkaline hydrolysis afforded 4'-methoxybiphenyl-2-carboxylic acid which crystallised from benzene–light petroleum (b.p. 40—60 °C) as needles, m.p. 138—140 °C (lit.,[33] m.p. 139—141 °C) and was identical (i.r. and n.m.r.) to an authentic sample.[4]

t-Butyl perester of 2'-methoxybiphenyl-2-carboxylic acid * (16). 2'-Methoxybiphenyl-2-carboxylic acid (0.5 g, 0.002 mol) was stirred at 4 °C in thionyl chloride (3.3 g, 0.028 mol) for 25 min. The excess of thionyl chloride was removed under reduced pressure at room temperature. N.m.r. and i.r. analysis of the residue showed that it contained 6*H*-dibenzo[5,6-*bd*]pyran-6-one (33%; $\nu_{max.}$ 1 735 cm^{-1}) and 2'-methoxybiphenyl-2-carbonyl chloride (66%; $\nu_{max.}$ 1 786 cm^{-1}). A solution of the mixture (0.3 g) in dichloromethane (20 ml) was added dropwise to sodium t-butyl peroxide [prepared by stirring together t-butyl hydroperoxide (0.79 g, 0.009 mol) and sodium hydride (0.233 g, 0.01 mol) in dichloromethane (20 ml) at 4 °C for 0.5 h] and allowed to stir for 2.5 h at 4 °C. The mixture was diluted with cold dichloromethane (25 ml) and washed with cold dilute sodium hydroxide (3 × 25 ml), dried, and concentrated to an oil (0.891 g). Preparative plate chromatography on silica gel (chloroform–benzene elution) gave the t-butyl perester of 2'-methoxybiphenyl-2-carboxylic acid (0.35 g) as an oil, δ($CDCl_3$) 1.06 (9 H, s), 3.28 (3 H, s), and 6.7—7.95 (8 H, m); $\nu_{max.}$ ($CHCl_3$) 2 995, 1 760, 1 370, and 905 cm^{-1} (Found: C, 71.6; H, 6.9. $C_{18}H_{20}O_4$ requires C, 71.98; H, 6.71%).

General Procedure for the Photolytic Reaction of Carboxylic Acids with t-Butyl Hypoiodite.—A solution of potassium t-butoxide (12 equiv.) in t-butyl alcohol (100 ml), contained in a 250 ml, 3-necked Pyrex flask fitted with a mercury-sealed stirrer and covered with aluminium foil, was allowed to attain thermal equilibrium by immersion in a constant-temperature bath (25 °C) while being irradiated with a 1 000 W tungsten bulb. Iodine monochloride (10 equiv.) was added dropwise and the mixture stirred for a further 15 min. The appropriate carboxylic acid was added and the flask connected to a dilatometric apparatus filled with benzene which had been saturated with carbon dioxide. The aluminium foil was removed and the temperature and any volume changes were monitored during the irradiation period. No significant volume changes were registered while the temperature was maintained within 1 °C of ambient.

The reaction mixture was poured into an excess of aqueous sodium thiosulphate solution and the neutral components extracted into chloroform which was then dried and concentrated.

Biphenyl-2-carboxylic Acid (2).—(a) *Irradiated reaction.* After irradiation for 3 h and work-up, biphenyl-2-carboxylic acid (0.989 g; 0.005 mol) afforded a gum (0.445 g). The aqueous phase was extracted continuously with chloroform and the extract was dried (Na_2SO_4) and concentrated to give unchanged biphenyl-2-carboxylic acid (41%) which was identical to an authentic specimen (i.r., n.m.r., and t.l.c.). The gum was chromatographed (preparative t.l.c.) to afford 6*H*-dibenzo[5,6-*bd*]pyran-6-one (25%) and biphenyl-2-carboxylic acid (6.5%) both identical (i.r., n.m.r., and t.l.c.) to authentic samples.

(b) *Dark reaction.* The above reaction was repeated in the dark at room temperature for 6 h. Work-up of the reaction mixture in the usual manner and chromatography afforded the unchanged starting material (83%) and 6*H*-dibenzo[5,6-*bd*]pyran-6-one (0.6%).

(c) *Thermal reaction.* The above dark reaction was repeated under reflux for 52 h. Work-up in the usual manner produced an oil which upon chromatography (preparative t.l.c.) afforded 6*H*-dibenzo[5,6-*bd*]pyran-6-one (8%) which was identical (i.r., n.m.r., and t.l.c.) with an authentic sample, and a solid (1.18 g) from which biphenyl-2-carboxylic acid (64%) was isolated as the only base-soluble component.

Irradiation of 2'-Methoxybiphenyl-2-carboxylic Acid (9).—2'-Methoxybiphenyl-2-carboxylic acid (1 g, 0.004 mol) was irradiated for 3 h and after work-up gave a gum (0.829 g). Continuous extraction of the aqueous phase with chloroform afforded unchanged 2'-methoxybiphenyl-2-carboxylic acid (29%). The gum was chromatographed (preparative t.l.c.) to give 6*H*-dibenzo[5,6-*bd*]pyran-6-one (76%). A minor band with a lower R_F-value gave an unidentified solid (43 mg)whose n.m.r. spectrum revealed aromatic protons, but no methoxy-substituent.

Irradiation of 2'-Isopropoxybiphenyl-2-carboxylic Acid (11).—2'-Isopropoxybiphenyl-2-carboxylic acid (0.935 g, 0.004 mol) was irradiated for 3 h and after work-up gave a gum (1.137 g). Continuous extraction of the aqueous phase with chloroform failed to recover the unchanged starting acid.

The gum was chromatographed (preparative t.l.c.) to yield 6*H*-dibenzo[5,6-*bd*]pyran-6-one (57%) and a mixture (0.48 g) containing γ-lactone species [$\nu_{max.}$ ($CHCl_3$) 1 785 cm^{-1}]. The mixture was resolved by repetitive preparative t.l.c. to give, as the only pure component, 2'-isopropoxy-1,3-dihydroisobenzofuran-1-spiro-1'-cyclohexa-2',5'-diene-3,4'-dione (0.094 g) which was crystallised from benzene–light petroleum (b.p. 40—60 °C) as needles, m.p. 139—141 °C, M^+ 270, *m/e* 228 and 212; δ($CDCl_3$) 0.94 (3 H, d), 1.2 (3 H, d), 4.38 (1 H, septet), 5.68 (1 H, d, $J_{AX} < 1$ Hz), 6.31 (1 H, dd, J_{XA} 1 Hz, J_{AB} 10 Hz), 6.51 (1 H, d, J_{BA} 10 Hz), and 7.17—8.1 (4 H, m); $\nu_{max.}$ ($CHCl_3$) 1 786, 1 673, and 1 608 cm^{-1} (Found: C, 70.3; H, 5.3. Calc. for $C_{16}H_{14}O_4$: C, 71.1; H, 5.2%).

Irradiation of 2'-Ethoxybiphenyl-2-carboxylic Acid (10).—Irradiation of 2'-ethoxybiphenyl-2-carboxylic acid (1 g, 0.004 mol) for 4.3 h afforded a gum (0.552 g). Continuous extraction of the aqueous phase in chloroform gave a solid (0.398 g) which was combined with the gum and chromatographed (preparative t.l.c.). Benzocoumarin (13%) and the unchanged 2'-ethoxybiphenyl-2-carboxylic acid (60%), both identical (i.r., n.m.r., and t.l.c.) to authentic specimens, were obtained as the only major components. A minor impure component (<17 mg) displayed a γ-lactone carbonyl in the i.r. spectrum at $\nu_{max.}$ 1 768 cm^{-1} but was discarded.

Irradiation of 2'-Nitrobiphenyl-2-carboxylic Acid (15).—2'-Nitrobiphenyl-2-carboxylic acid (0.712 g, 0.003 mol), after irradiation for 3.5 h, afforded the unchanged starting material (75%).

Irradiation of 2'-Octyloxybiphenyl-2-carboxylic Acid (12).—After irradiation for 7 h, 2'-octyloxybiphenyl-2-carboxylic

* See footnote * on p. 844.

acid (1 g, 0.003 mol) gave, on work-up, an oil (0.958 g) which was subjected to g.l.c. analysis (column A; 120—150 °C) and shown to contain octanol (58%) and octanal (6%).

The reaction mixture was chromatographed (preparative t.l.c.) to give benzocoumarin (0.34 g, 0.002 mol, 57%) identical (i.r., n.m.r., and t.l.c.) to an authentic specimen and a gum, 2'-octyloxy-1,3-dihydroisobenzofuran-1-spiro-1'-cyclohexa-2',5'-diene-3,4'-dione (5%), M^+ 340, *m/e* 228 and 212; δ($CDCl_3$) 0.5—1.7 (15 H, m) 3.5—4.0 (2 H, m) 5.68br (1 H, s) 6.32 and 6.53 (2 H, distorted AB system J_{AB} 9 ≃ Hz), and 7.2—8.1 (4 H, m); $\nu_{max.}$ ($CHCl_3$) 1 784, 1 670, and 1 608 cm^{-1} (Found: C, 73.3; H, 7.7. Calc. for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11%). The base line gave a mixture (0.22 g) shown to consist mainly of the unchanged starting material (t.l.c.).

Irradiation of Octanol (Blank Reaction).—A mixture of octanol (0.199 g, 0.002 mol) and t-butyl hypoiodite was irradiated for 6.5 h and worked-up to give an oil (0.170 g) which was analysed by g.l.c. (column A) to reveal octanal and unchanged octanol in the ratio 0.23 : 1.00.

Thermal Decomposition of the t-Butyl Biphenylperoxycarboxylate (16).—A solution of t-butyl 2'-methoxybiphenyl-2-peroxycarboxylate (0.08 g, 3×10^{-4} mol) in toluene (25 ml) was refluxed for 21.5 h. The toluene was distilled off under reduced pressure to give an oil which was chromatographed (preparative t.l.c.) to yield benzocoumarin (52%) and 1,2-diphenylethane (0.012 g), δ($CDCl_3$) 2.91 (4 H, s) and 7.23 (10 H, s), identical with an authentic specimen (n.m.r. and t.l.c.).

Irradiation Reaction of (16).—A solution of t-butyl 2'-methoxybiphenyl-2-peroxycarboxylate (0.109 g, 4×10^{-4} mol) in toluene (8 ml) was irradiated, through quartz, for 1.5 h under nitrogen atmosphere. The toluene was removed *in vacuo* to give an oil (0.130 g) which was chromatographed (preparative t.l.c.) to give benzocoumarin (6%).

Phenanthrene-4-carboxylic Acid (5).—(a) *Irradiation reaction.* Phenanthrene-4-carboxylic acid (1 g, 0.005 mol) was irradiated in the presence of t-butyl hypoiodite for 6.25 h and then worked up to give a solid (0.403 g). The aqueous layer was acidified and extracted continuously with chloroform to give the unchanged starting material (1.188 g) contaminated with some sulphur. The solid was chromatographed (preparative t.l.c.) to give 5*H*-phenanthro[4,5-*bcd*]pyran-5-one (20%), m.p. 181—183 °C, needles from acetone (lit.,[34] 183 °C); δ($CDCl_3$) 7.4—7.95 (6 H, m), 8.23 (1 H, dd, *J* 8 and 2 Hz), and 8.53 (1 H, dd, *J* 7.5 and 2 Hz); $\nu_{max.}$ ($CHCl_3$) 1 734, 1 597, 839, and 824 cm^{-1}.

(b) *Dark reaction.* Phenanthrene-4-carboxylic acid, reacted as above in the dark for 7 h, afforded starting material on work-up.

4'-Methoxybiphenyl-2-carboxylic Acid (7).—The acid (0.5 g, 0.002 mol) in t-butyl alcohol (50 ml) was irradiated for 5 h in the presence of t-butyl hypoiodite (12 equiv.). The oil from work-up (1.1 g) was separated by plate chromatography into the starting acid (80%), 3-methoxydibenzo[5,6-*bd*]pyran-6-one (17%), which crystallised from benzene–light petroleum (b.p. 40—60 °C) as needles [m.p. 142—144 °C (lit.,[35] 141 °C); δ($CDCl_3$) 7.87 (s, 3 H), 6.8—7.03 (m, 2 H), and 7.2—8.45 (m, 5 H); $\nu_{max.}$ ($CHCl_3$) 1 728 and 1 621 cm^{-1}] and a minor unidentified solid which crystallised from benzene–light petroleum (b.p. 40—60 °C) but melted over a range (250—260 °C); $\nu_{max.}$ ($CHCl_3$) 1 790 and 1 682 cm^{-1}. This compound was different (i.r., n.m.r., and m.p.) from 1,3-dihydroisobenzofuran-1-spiro-1'-cyclohexa-2',5'-diene-3,4'-dione and was formed in similar yield from an identical dark reaction which gave 3-methoxydibenzo[5,6-*bd*]pyran-6-one (1%) and starting material.

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