Persulphate Oxidation of Some *N*-Methylbiphenyl-2-carboxamides

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Summary Oxidations of some *N*-methylbiphenyl-2-carboxamides by aqueous potassium persulphate give γ-lactam derivatives as well as the expected phenanthridones, especially in alkaline solution.

OXIDATION of *N*-methylbiphenyl-2-carboxamide (**1**) by persulphate[1] or by lead tetra-acetate–iodine[2] gives *N*-methylphenanthridone (**5**), and mechanisms involving cyclisation of biphenyl-2-carboxamido-radicals (**4**) have been inferred. We now report (i) that in the presence of oxygen and potassium carbonate an additional product from the aqueous persulphate oxidation of (**1**) is the dienone (**8**); (ii) that the product of persulphate oxidation of the methoxy-derivatives (**2**) and (**3**) show a pronounced pH-dependence, and (iii) that the methoxyphenanthridone (**7**) formed from (**3**) may be further oxidised, in the absence of added base, to give the dimer (**9**) in good yield. The principal results are summarised in the Table.

TABLE

Products of persulphate oxidation of N-*methylbiphenyl-2-carboxamides*

Amide	Conditions[a]	Products[b] Phenanthridone (%)	Other (%)
(**1**)	80°; K_2CO_3; O_2[c]	(**5**) (40)	(**8**) (10)
(**2**)	100°; K_2CO_3 absent	(**5**) (10); **6** (n.d.)	(**10**) (45)
(**2**)	100°; K_2CO_3	(n.d.)	(**11**) (25); (**12**) (20)[d]
(**3**)	100°; K_2CO_3 absent[e]	(**7**) (47)	(**8**) (14)
(**3**)	100°; K_2CO_3	(**7**) (9)	(**8**) (70)

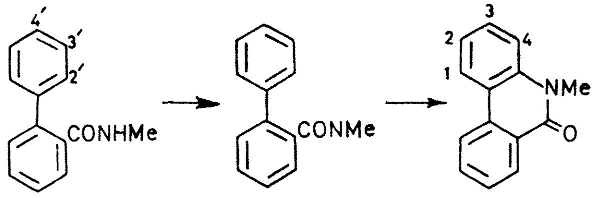
[a] Experiments were normally[c] carried out in boiling aqueous solution in the absence of oxygen, using excess of potassium persulphate. Heating was discontinued when *ca.* 90% of the amide was consumed. In experiments with potassium carbonate, sufficient was added to maintain an alkaline solution throughout the reaction.

[b] Yields are in percentages based on amide consumed (n.d. = not detected).

[c] The temperature of this reaction was maintained at 80°. In the absence of oxygen or carbonate, the only product was (**5**) (*ca.* 80%).

[d] Dienol (**12**) is oxidised to (**11**) by persulphate.

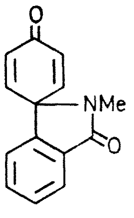
[e] Reaction taken only to *ca.* 20% conversion. Prolonged oxidation gave a good yield of (**9**) which is also formed by oxidation of (**7**) alone.



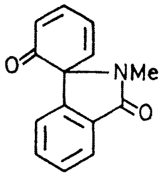
(**1**) unsubstituted
(**2**) 2'-OMe
(**3**) 4'-OMe

(**4**)

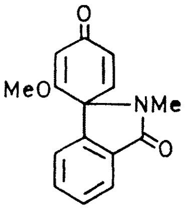
(**5**) unsubstituted
(**6**) 1-OMe
(**7**) 3-OMe



(**8**)



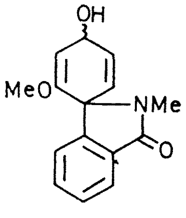
(**10**)



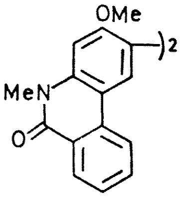
(**11**)

Evidently, under conditions where the reaction mixture is prevented from becoming acidic by the addition of carbonate, products of cyclisation to a spiro-γ-lactam structure are important. The effect of pH in this system is not yet fully understood, though acid-catalysis of persulphate oxidation has been discussed recently.[3] This aspect of the work will be further discussed in the full paper.

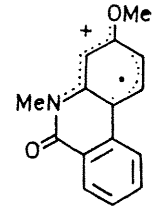
The oxidation of anisole by persulphate has been suggested to proceed *via* the initial removal of one electron.[4] By analogy with preferred mechanisms for anodic substitution reactions,[5] we suggest that carboxamido-radicals are not intermediates in the oxidations of the methoxy-amides, but that instead cyclisation occurs by intramolecular nucleophilic capture of an aromatic radical cation [*e.g.* as (**13**)].



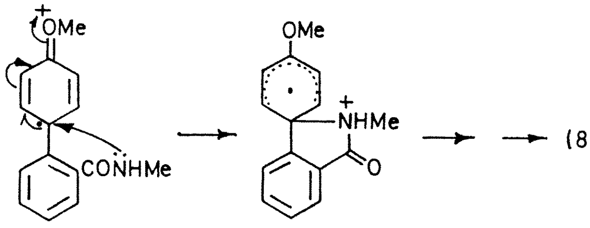
(**12**)



(**9**)



(**14**)



(**13**)

This behaviour may prove to have some generality in oxidation reactions.[6]

The dimer (**9**) is most easily rationalised as a product of radical cation (**14**) dimerisation followed by proton loss.

Demethylation leading from (**2**) and (**3**) to the dienones (**10**) and (**8**), respectively, is considered to proceed *via* a cyclohexadienyl cation.[7]

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