# Novel Synthetic Route to Amides from Arylmethylamines *via* Schiff Bases derived from Amines and 2,6-Di-t-butyl-*p*-benzoquinone

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*Summary* Condensation of the arylmethylamines (**1**) and 2,6-di-t-butyl-*p*-benzoquinone gives the 4-(*N*-arylmethyleneamino)-2,6-di-t-butylphenols (**3**) in good yield, base-catalysed oxygenation of which leads to selective formation of the amides (**4**).

IN general, it is difficult to oxidise selectively the α-methylene group of an amine to the corresponding amide. Recently, Tang *et al.*[1] have reported that the oxygenation of amines catalysed by $RuCl_3$ gives nitriles accompanied by the formation of small amounts of amides. We report here a new, efficient method for the preparation of amides from arylmethylamines. When solutions of equimolar amounts of the arylmethylamines (**1**) and 2,6-di-t-butyl-*p*-benzoquinone (**2**) in ethanol were refluxed under nitrogen, the 4-(*N*-arylmethyleneamino)-2,6-di-t-butylphenols (**3**) were obtained as crystals in good yields when the mixtures were cooled. Compounds (**3**) apparently result from isomerization *in situ* of the quinone imines formed first. The formation of (**3**) is of particular interest when compared with results obtained from the reaction of amines and 3,5-di-t-butyl-*o*-benzoquinone where benzoxazole derivatives are mainly formed.[2]

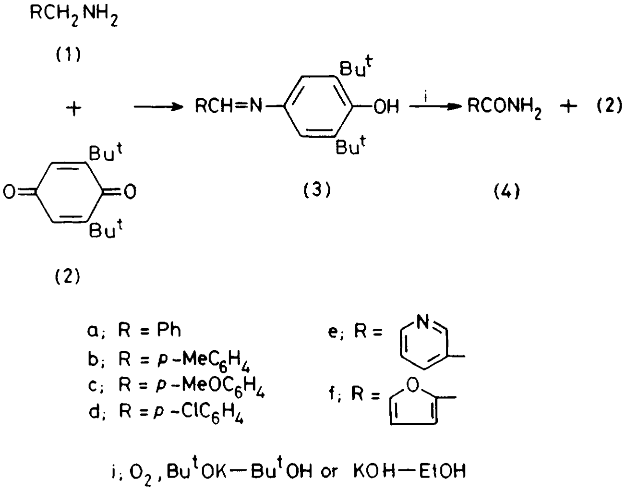

TABLE. Base-catalysed oxygenation of compounds (**3**)

| Compound[a] | M.p./°C | Yield[b]/% | Reaction time/h[c] Method A[d] | Reaction time/h[c] Method B[d] | Product yield/%[b,e] (4) Method A | Product yield/%[b,e] (4) Method B | Product yield/%[b,e] (2) Method A | Product yield/%[b,e] (2) Method B |
|---|---|---|---|---|---|---|---|---|
| (**3a**) | 147—148 | 82 | 6 | 1 | 66 | 62 | 10 | 70 |
| (**3b**) | 151—152 | 61 | 5 | 1 | 70 | 38 | 10 | 70 |
| (**3c**) | 136—137 | 72 | 3·5 | 1 | 73 | 15 | 10 | 70 |
| (**3d**) | 140—141 | 49 | 2 | 0·5 | 85 | 79 | 10 | 70 |
| (**3e**) | 133—134 | 62 | 2 | 1·5 | 69 | 50 | 10 | 70 |
| (**3f**) | 158—159 | 42 | 2·5 | 1 | 36 | 59 | 10 | 70 |

[a] Compounds (**3a**), (**3c**), and (**3d**) are known: E. Manda, *Bull. Chem. Soc. Japan*, 1974, **47**, 2727. The others are new and analytical and spectral data are in good agreement with the structures. [b] Isolated yield. N.m.r. spectroscopic determination shows nearly quantitative formation of (**3**). [c] Time required for completion of reaction. [d] Method A: compound (**3**) (1 mmol) in $Bu^tOH$ (20 ml) containing $Bu^tOK$ (3 mmol) at 25 °C. Method B: (**3**) (1 mmol) in EtOH (30 ml) containing KOH (3 mmol) at 0 °C. [e] Products were identical with authentic samples (i.r. and m.p. data).

Interestingly, when dioxygen is bubbled through a solution of (**3**) in $Bu^tOH$–$Bu^tOK$ or EtOH–KOH the corresponding amides (**4**) and benzoquinone (**2**) are formed, which are readily isolated from the mixture. The results are given in the Table. The overall reaction provides a selective oxidation of the methylene group of the amines (**1**) to give the amides (**4**). The low yield of benzoquinone (**2**) in $Bu^tOH$ solution is due to the instability of (**2**) under these conditions: (**2**) is fairly stable in an oxygenated KOH–EtOH solution but when $O_2$ is bubbled through a solution of (**2**) in $Bu^tOH$–$Bu^tOK$ a complex mixture is obtained.

The present amide formation can be rationalized by assuming decomposition of a hydroperoxidic intermediate resulting from selective dioxygen incorporation into the *para* position and the imino carbon in (**3**), taking into account the results obtained in regioselective dioxygen incorporation into phenolate anions.[3,4]

Attempts to form (**4**) directly from (**1**) in the presence of catalytic amounts of (**2**) were not successful. In aprotic solvents such as tetrahydrofuran (THF) and dimethylformamide (DMF), the oxygenation of (**3**) was not selective and gave a complex mixture.

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[2] E. J. Corey and K. Achiwa, *J. Amer. Chem. Soc.*, 1969, **91**, 1429.

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[4] A. Nishinaga, T. Itahara, T. Matsuura, A. Rieker, D. Koch, K. Albert, and P. B. Hitchcock, *J. Amer. Chem. Soc.*, 1978, **100**, 1826.