

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

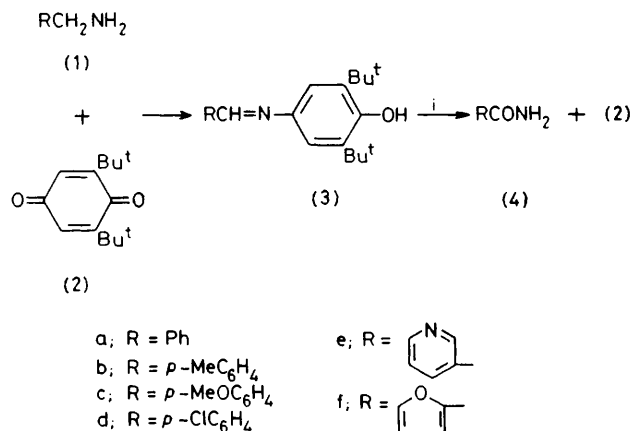
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Summary Condensation of the arylmethylamines (1) and 2,6-di-*t*-butyl-*p*-benzoquinone gives the 4-(*N*-arylmethyleneamino)-2,6-di-*t*-butylphenols (3) in good yield, base-catalysed oxygenation of which leads to selective formation of the amides (4).

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 RuCl₃ 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



i; O₂, Bu^tOK—Bu^tOH or KOH—EtOH

TABLE. Base-catalysed oxygenation of compounds (3)

Compound ^a	M.p./°C	Yield ^b /%	Reaction time/h ^c		Product yield/% ^{b,e}			
			Method A ^d	Method B ^d	(4) Method A	Method B	Method A (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 O₂ 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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¹ R. Tang, S. E. Diamond, N. Neary, and F. Mares, *J.C.S. Chem. Comm.*, 1978, 562.

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

³ A. Nishinaga, T. Itahara, T. Shimizu, and T. Matsuura, *J. Amer. Chem. Soc.*, 1978, **100**, 1820.

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