Aromatic Annelation by Reaction of Arylimidoyl Radicals with Alkynes: a New Synthesis of Quinolines

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An easily effected aromatic annelation is described, involving the reaction of arylimidoyl radicals with alkynes to give quinolines.

Imidoyl radicals have been investigated by e.s.r. spectroscopy by several workers and the spectroscopic results have been rationalized on the assumption that they possess a σ-electronic configuration.[1] However, the chemical reactivity of these radicals and their use as intermediates for organic syntheses have so far received little attention. The only reported reactions are hydrogen abstraction and β-scission,[2] the latter only occurring when the imidoyl nitrogen is linked to an alkyl or benzylic group.

We now report a useful aromatic annelation reaction leading to good yields of substituted quinolines, effected by arylimidoyls when allowed to react with alkynes.

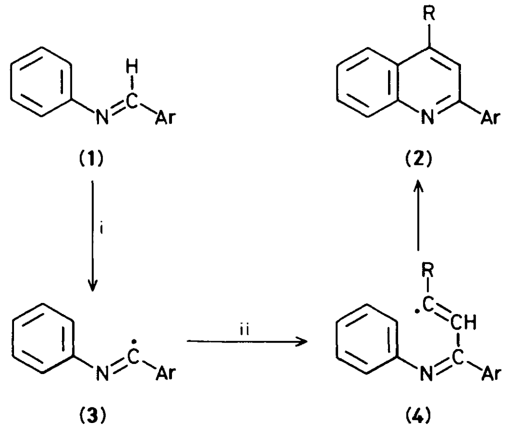
In a typical experiment the *N*-benzylideneaniline (**1**) (5 mmol) and di-isopropyl peroxydicarbonate (DPDC) (10 mmol) were kept at 60 °C in benzene (35 ml) with an appropriate alkyne (15 mmol) until decomposition of DPDC was complete. From the reaction mixture the substituted quinoline (**2**) could be separated, with, in a few cases, small amounts of isopropyl *N*-arylcarbamate and unchanged imine (Scheme 1 and Table 1).

These results are consistent with the intermediacy of the imidoyl radical (**3**) which adds to the unsubstituted carbon atom of the alkyne with formation of the vinyl radical (**4**). The subsequent intramolecular homolytic substitution on the aryl

Table 1. Substituted quinolines (**2**).

Product	R	Ar	% Yield[a]	M.p. or [b.p.] (t/°C)	Ref.
(**2a**)	Ph	Ph	75	112—113	4
(**2b**)	,,	m-$NO_2C_6H_4$	65	153—155	[c]
(**2c**)	,,	p-$NO_2C_6H_4$	15	159—161	4
(**2d**)	,,	p-ClC_6H_4	65	105—106	4
(**2e**)	,,	p-$MeOC_6H_4$	75	83—84	[c]
(**2f**)	COMe	Ph	70	75—76	5
(**2g**)	,,	m-$NO_2C_6H_4$	30	141—143	[c]
(**2h**)	,,	p-$NO_2C_6H_4$	13	194—195	[c]
(**2i**)	,,	p-ClC_6H_4	65	101—102	6
(**2j**)	,,	p-$MeOC_6H_4$	85	[205—208 (0.1 Torr)]	[c]
(**2k**)	CO_2Et	Ph	75	56—57	7
(**2l**)	,,	m-$NO_2C_6H_4$	35	110—111	8[b]
(**2m**)	,,	p-$NO_2C_6H_4$	18	135—137	8[b]
(**2n**)	,,	p-ClC_6H_4	75	72—73	9
(**2o**)	,,	p-$MeOC_6H_4$	80	78—79	[c]

[a] Yields were calculated for pure product based on starting imine. [b] Lit. m.p. 95—98 °C for a mixture of *m*- and *p*-nitro isomer. [c] New compound; satisfactory ^1H n.m.r. and mass spectra and elemental analyses were obtained.



Scheme 1. *Reagents:* i, DPDC, benzene, 60 °C; ii, $R-C\equiv CH$.

ring directly linked to the nitrogen atom leads to (**2**) (Scheme 1). Analogous aromatic annelation, *via* addition of aryl radicals to dimethyl acetylendicarboxylate has also been reported by Cadogan and co-workers.[3]

The present quinoline synthesis seems to have greater applicability than that employing analogous imidoyl cations.[4] For instance, no reaction between $PhN=CClPh$ and ethyl propiolate in the presence of tin(IV) chloride is observed, while $PhN=CHPh$ in the presence of DPDC reacts with the same alkyne affording high yields of 2-phenyl-4-ethoxycarbonylquinoline (**2k**).

This novel annelation of arylimidoyl radicals with alkynes appears to be capable of considerable extension *via* the use of other imidoyl radicals and/or other acetylenic derivatives.

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