New Rearrangement in the Quinoline Series

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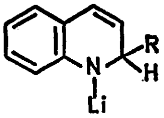
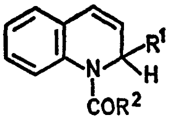
Summary *N*-Lithio-1,2-dihydroquinolines (I) react with acid chlorides or esters to give the corresponding *N*-acylated derivatives (II), certain of which undergo rearrangement to the tertiary carbinols (III), in the presence of organolithium compounds.

PREVIOUS assumptions that reactions between quinolines and organolithium reagents proceed through the *N*-lithio-1,2-dihydroquinoline intermediates (I) have recently[1] been given substantial support. Thus with ethyl chloroformate the 1,2-dihydroquinolines (II; R^2 = OEt) are formed.

When the intermediate from the reaction between quinoline and phenyl-lithium, presumably (Ia), was treated with 1 equiv. of methyl benzoate or benzoyl chloride at 0° [2] the major product was (IIa) (75%)† together with a by-product (5%). This by-product was the sole product (100% based on the ester) when 0·5 equiv. of methyl benzoate is added at refluxing ether temperatures. Analysis and spectral data indicate the structure (III; R = Ph)[3] for this compound.

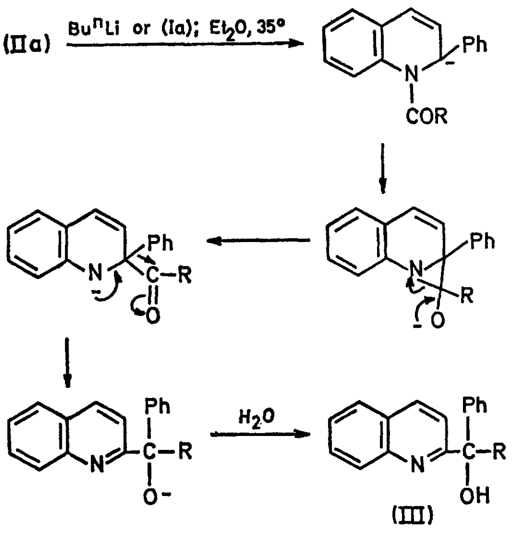


(I)	R
a;	Ph
b;	Bu



(II)	R^1	R^2
a;	Ph	Ph
b;	Bu	Ph
c;	Ph	Me
d;	Bu	Me

Subsequent reactions between (II) and n-butyl-lithium, or (Ia) in boiling ether solvent gave the carbinol (III) (60—80%) together with n-butane or 2-phenyl-1,2-dihydroquinoline respectively. Structural analogies between (IIa) and 'Reissert' compounds (II; R^1 = CN, R^2 = aryl), sub-



Scheme

stantiated by similarities in their spectra,[4] led us to believe that this reaction was analogous to the base-catalysed rearrangement[4b] of such Reissert compounds to 2-aroylquinolines (Scheme). The interaction of methyl *p*-toluate and (Ia) gave the carbinol (III; R = *p*-tolyl) confirming that one aryl group came from the ester and the other from the aryl-lithium.

The acetyl derivatives (IIc and d),† and also (IIb)† [prepared from the adducts (I) and the corresponding methyl ester or acid chloride at 0°] failed to undergo rearrangement; instead attack at the amide grouping occurred to give amongst other products 2-phenyl- or 2-n-butyl-quinoline. The acetyl Reissert analogues behave in a similar manner.[4e] It is probable that in (IIb) the α-hydrogen is not sufficiently acidic to be removed by the organolithium base. Hence for successful rearrangement of the (II) to the tertiary carbinols (III), it appears that both R^1 and R^2 in (II) must be aryl.

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† Satisfactory spectra and analytical data were obtained for these compounds.

[1] C. E. Crawforth, O. Meth-Cohn, and C. A. Russell, *J.C.S. Chem. Comm.*, 1972, 259.

[2] For the pyridine analogues, see C. S. Giam and E. E. Knaus, *Tetrahedron Letters*, 1971, 4961.

[3] M. R. F. Ashworth, R. P. Daffen, and D. Ll. Hammick, *J. Chem. Soc.*, 1939, 809.

[4] (*a*) R. Bramley and M. D. Johnson, *J. Chem. Soc.*, 1965, 1372; (*b*) V. Boekelheide and J. Weinstock, *J. Amer. Chem. Soc.*, 1952, **74**, 660; (*c*) W. E. McEwan, R. H. Terss, and I. W. Elliot, *ibid.*, p. 3605; (*d*) R. F. Collins and T. Henshall, *ibid.*, 1958, **80**, 159; (*e*) A. P. Wolf, W. E. McEwan, and R. H. Glazier, *ibid.*, 1956, **78**, 861.