

UNUSUAL RING CONTRACTION OF 3*H*-PYRANO[2,3-*c*]QUINOLIN-5(6*H*)-ONES TO FURO[2,3-*c*]QUINOLIN-4(5*H*)-ONES

Krishna C. Majumdar,* Anup K. Kundu, and Paritosh Biswas

Department of Chemistry, University of Kalyani,
Kalyani - 741 235, W. B., India

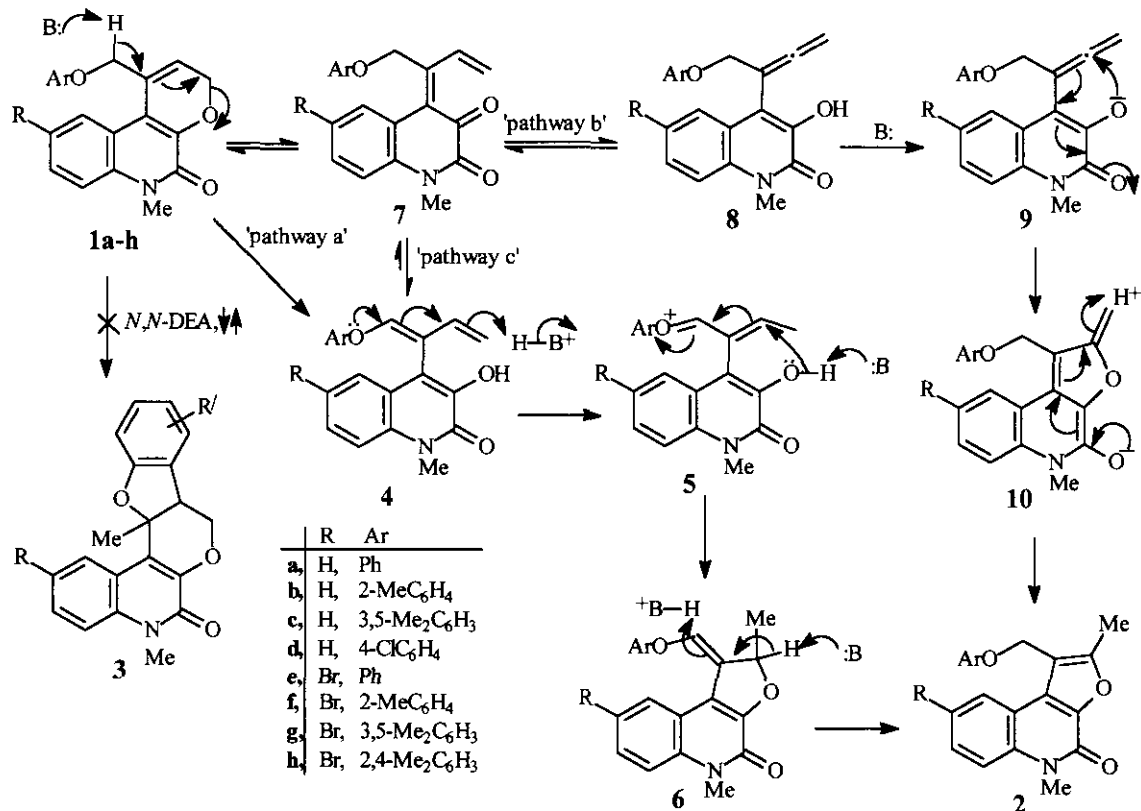
Abstract - A number of 1-aryloxymethyl-3*H*-pyrano[2,3-*c*]quinolin-5(6*H*)-ones (**1a-h**) on heating in *N,N*-diethylaniline for 8 h afforded 1-aryloxymethyl-2-methyl-furo[2,3-*c*]quinolin-4(5*H*)-ones (**2a-h**) in 66-79 % yields.

Furo[3,2-*c*]quinolin-4(5*H*)-one and 2*H*-pyrano[3,2-*c*]quinolin-5(6*H*)-one derivatives are abundant in nature^{1,2} and their synthesis has been reported in literature.³⁻⁶ Synthesis of the corresponding furo[2,3-*c*]quinolones has earlier been reported in low yields.⁷⁻⁹ To our knowledge pyrano[2,3-*c*]quinolones have not been reported earlier. We have recently reported a simple synthesis for these heterocyclic ring systems.¹⁰ Since the aryloxybutynyl ethers of 3-hydroxycoumarin are found to behave differently,^{11,12} we have studied the thermal rearrangement of 3-(4-aryloxybut-2-ynyloxy)-1-methylquinolin-2-ones¹³ to give 3*H*-pyrano[2,3-*c*]quinolones (**1**) and furo[2,3-*c*]quinolones (**2**). These 3*H*-pyrano[2,3-*c*]quinolones (**1**) contain allyl phenyl ether moiety, a potential site for further [3,3] sigmatropic rearrangement (Claisen). This prompted us to undertake a study on the thermal rearrangement of 3*H*-pyrano[2,3-*c*]quinolones (**1**) with a view to synthesise polyheterocycles (**3**). Here we report the results of this investigation.

The starting materials (**1a-h**) for this study were prepared according to our earlier published procedure¹³ from the corresponding 3-(4-aryloxybut-2-ynyloxy)-1-methylquinolin-2-ones.

N,N-Diethylaniline is known as a versatile solvent for conducting thermal Claisen rearrangement of allyl phenyl and phenyl propargyl ethers. Therefore, we subjected substrate (**1a**) to further rearrangement by refluxing in *N,N*-diethylaniline for 8 h. A white crystalline solid, mp 180 °C was obtained in 79 % yield. This was characterised as 1-aryloxymethyl-2-methylfuro[2,3-*c*]quinolin-4(5*H*)-one (**2a**) from its elemental analysis and spectral data. This is also evidenced from its mixed mp and superimposable IR spectrum with an authentic sample.¹³ Formation of product (**2a**) excluded any occurrence of further Claisen rearrangement. Encouraged by this unusual result we similarly treated substrates (**1b-h**) in

refluxing *N,N*-diethylaniline. All the substrates furnished the 1-aryloxymethyl-2-methylfuro[2,3-*c*]quinolin-4(5*H*)-ones, (**2b-h**) in 66-79 % yields (Scheme).

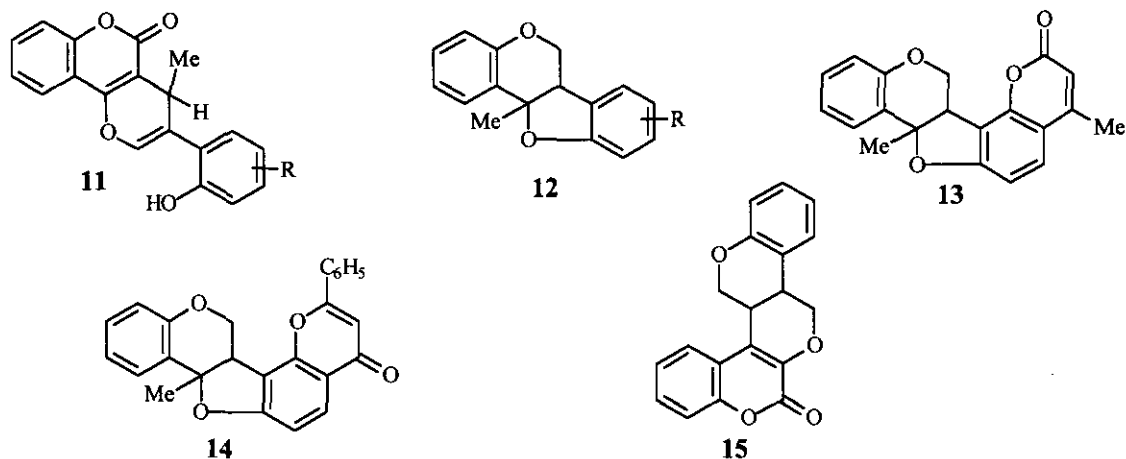


Scheme

This unusual ring contraction *i.e.* conversion of pyran ring to 2-methylfuran ring may be explained by base-catalyzed elimination-addition to provide **5** followed by its cyclization to give **2** (pathway a). A second mechanism may involve the reversal of the electrocyclic ring closure (**1** $\rightleftharpoons$ **7**) and [1, 5] H shift (**7** $\rightleftharpoons$ **8**) at elevated temperature to give intermediate allenyl enols (**8**) which then undergo an unusual intramolecular hetero-Michael reaction leading to the formation of a highly delocalized anion (**10**) (formally a lactam trienolate) which is protonated at the least hindered terminus to give **2** (pathway b). A third mechanism would involve tautomerism of **7** into its enol (**4**) followed by base-catalyzed addition and cyclization to give **2** (pathway c).

It is relevant to mention here that widely different results were obtained earlier from similar substrates *e.g.* 4-aryloxymethylpyrano[3,2-*c*][1]benzopyran-5(2*H*)-ones when refluxed in *N,N*-diethylaniline gave product (**11**) arising out of the Claisen rearrangement,¹⁴ whereas 4-aryloxymethyl- Δ^3 -chromene¹⁵ gave furopyran (**12**). 7-(4-Chromenylmethoxy)coumarin¹⁶ and 7-(4-chromenylmethoxy)flavone¹⁷ under similar treatment in refluxing diethylaniline afforded the furopyrans (**13**) and (**14**) respectively. 1-Aryloxy-

methylpyrano[2,3-*c*]coumarins gave [6,6] pyranopyrans¹⁸ (15).



From this study it is concluded that the pyran derivatives (1) undergo an unusual ring contraction to form furan derivatives (2) in refluxing *N,N*-diethylaniline by the opening of the pyran ring followed by base-catalysed cyclization. The reaction is shown to be a general one by the successful conversion of eight pyran derivatives to their corresponding furan derivatives. To our knowledge this is the first example of such a ring contraction.

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