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

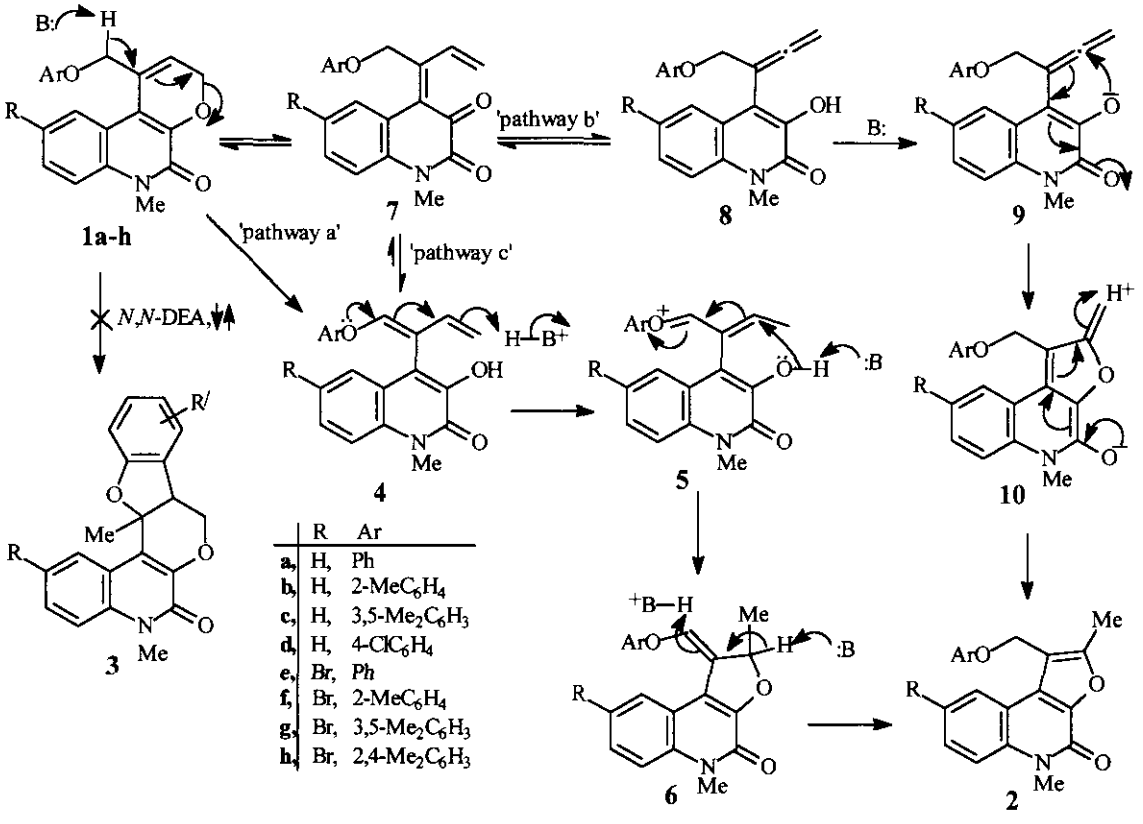
Abstract - A number of 1-aryloxymethyl-3*H*-pyrano[2,3-*c*]quinolin-5(6*H*)-ones (**1a-h**) on heating in *N*,*N*-diethylaniline for 8 h afforded 1-aryloxymethyl-2-methyl-furo[2,3-*c*]quinolin-4(5*H*)-ones (**2a-h**) in 66-79 % yields.

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-ones[13] 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 procedure[13] 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 ^{0}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 Clasien 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).

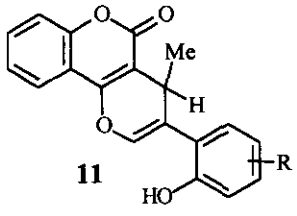


Scheme

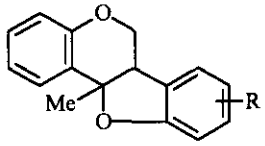
This unusual ring contraction *i.e.* conversion of pyran ring to 2-methylfuran ring may be explained by base-catalyzed elimination-addition to provide **5** followed by its cyclization to give **2** (pathway a). A second mechanism may involve the reversal of the electrocyclic ring closure (**1** ⇌ **7**) and [1, 5] H shift (**7** ⇌ **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-chromene[15] gave furopyran (**12**). 7-(4-Chromenylmethyloxy)coumarin[16] and 7-(4-chromenylmethyloxy)flavone[17] under similar treatment in refluxing diethylaniline afforded the furopyrans (**13**) and (**14**) respectively. 1-Aryloxy-

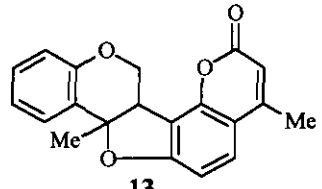
methylpyrano[2,3-*c*]coumarins gave [6,6] pyranopyrans[18] (**15**).



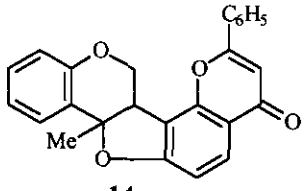
11



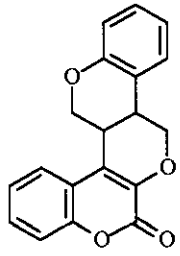
12



13



14



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.

ACKNOWLEDGEMENT

We thank the CSIR (New Delhi) for financial assistance.

REFERENCES

1. L. Jurd and M. Benson, *J. Chem. Soc.*, 1983, 92.
2. R. F. C. Brown, J. J. Hobbs, G. K. Hughes, and E. Ritchie, *Austral. J. Chem.*, 1954, **7**, 348; R. Brown, G. K. Hughes, and E. Ritchie, *Chem. and Ind. (London)*, 1955, 1385; D. Lavie, N. Danieli, R. Weitman, and E. Glotter, *Tetrahedron*, 1968, **24**, 3011; D. L. Dreyer and A. Lee, *Phytochemistry*, 1972, **11**, 763; D. R. Taylor and J. M. Warner, *Phytochemistry*, 1973, **12**, 1359; J. Reisch, J. Korosi, K. Szendrei, I. Novak, and E. Minker, *Phytochemistry*, 1975, **14**, 1678.
3. J. Reisch, *Arch. Pharm. Ber. Dtsch., Pharm. Ges.*, 1967, **300**, 533 (*Chem. Abstr.*, 1968, **68**, 39866); M. F. Grundon, R. J. Green, and J. C. Caston, *J. Chem. Res.(S)*, 1985, 135; *(M)*, 1985, 1877; Th. Kappe, P. F. Fritz, and E. Ziegler, *Chem. Ber.*, 1973, **106**, 1927; V. S. Rao and M. Darbarwar, *Synth. Commun.*, 1989, **19**, 2713.
4. J. W. Huffman and T. M. Hsu, *Tetrahedron Lett.*, 1972, 141; F. Piozzi, P. Venturella, and A. Bellino, *Gazz. Chim. Ital.*, 1969, **99**, 711; A. Groot and B. J. M. Jansen, *Tetrahedron Lett.*, 1975, 3407; R. M. Bowman, M. F. Grundon, and K. J. James, *J. Chem. Soc., Perkin Trans. 1*, 1973, 1055; M. Ramesh, P. S. Mohan, and P. Shanumgam, *Tetrahedron*, 1984, **40**, 4041; M. F. Grundon, D. M.

Harrison, M. G. Magee, M. J. Rutherford, and S. A. Surgenor, *Proc. R. Ir. Acad., Sect. B.*, 1983, **83**, 103; J. Reisch, A. Bathe, B. H. W. Rosenthal, A. Salehi, and A. Reza, *J. Heterocycl. Chem.*, 1987, **24**, 869.

5. K. C. Majumdar and P. K. Choudhury, *Heterocycles*, 1991, **32**, 73.
6. K. C. Majumdar and P. K. Choudhury, *Synth. Commun.*, 1993, **23**, 1087.
7. Y. Kanaoka and K. Itoh, *Synthesis*, 1972, 36.
8. R. B. Bates, V. V. Kane, A. R. Martin, R. B. Majumdar, R. Ortega, Y. Hatanaka, K. San-nohe, and Y. Kanaoka, *J. Org. Chem.*, 1987, **52**, 3178.
9. T. Usui, Y. Tsubone, and A. Tanaka, *J. Heterocycl. Chem.*, 1985, **22**, 849.
10. K. C. Majumdar, A. K. Kundu, and P. Chatterjee, *J. Chem. Res.(S)*, 1995, 387; *(M)*, 1995, 2301.
11. K. C. Majumdar, R. N. De, A. T. Khan, S. K. Chattapadhyay, K. Dey, and A. Patra, *J. Chem. Soc., Chem. Commun.*, 1988, 777; K. C. Majumdar and R. N. De, *J. Chem. Soc., Perkin.Trans. 1*, 1989, 1901.
12. K. C. Majumdar, D. P. Das, G. H. Jana, and A. T. Khan, *Indian J. Chem.*, 1994, **33B**, 120.
13. K. C. Majumdar and A. K. Kundu, *Heterocycles*, 1997, **45**, 1467.
14. K. C. Majumdar, D. P. Das, and G. H. Jana, *Synth. Commun.*, 1993, **23**, 2171.
15. K. C. Majumdar, K. K. Balasubramanion, and B. S. Thyagarajan, *J. Heterocycl. Chem.*, 1973, **10**, 159; B. S. Thyagarajan, K. K. Balasubramanion, and R. BhimaRao, *Tetrahedron*, 1967, **23**, 1893.
16. K. C. Majumdar and A. K. Gupta, *Indian J. Chem.*, 1990, **29B**, 752.
17. K. C. Majumdar and S. K. Ghosh, *J. Chem. Res.(S)*, 1994, 461; *(M)*, 1994, 2301.
18. K. C. Majumdar, P. Chatterjee, and S. Saha, *Tetrahedron Lett.*, 1998, **39**, 7147.

Received, 26th October, 1998