STUDIES IN SIGMATROPIC REARRANGEMENT OF 3-(4-ARYLOXY-BUT-2-YNYLOXY)-1-METHYLQUINOLIN-2-ONES: SYNTHESIS OF 3*H*-PYRANO[2,3-*c*]QUINOLIN-5(6*H*)-ONES AND FURO[2,3-*c*]QUINOLIN-4(5*H*)-ONES

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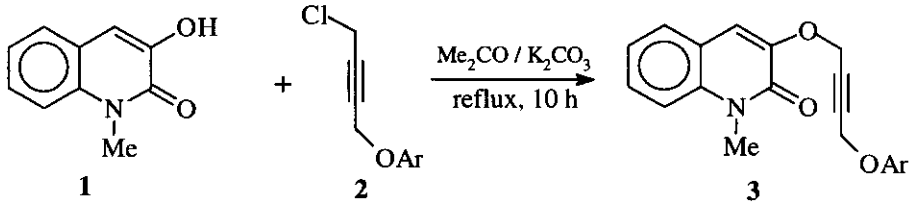
Abstract - 3-(4-Aryloxybut-2-ynyloxy)-1-methylquinolin-2-ones (**3**), in refluxing chlorobenzene, gave 1-aryloxymethyl-6-methyl-3*H*-pyrano[2,3-*c*] quinolin-5(6*H*)-ones (**4**) and / or, 1-aryloxymethyl-2,5-dimethylfuro[2,3-*c*]quinolin-4(5*H*)-ones (**5**). The base or the radical initiator (azoisobutyronitrile) does not seem to have any effect on the formation of the products. Substrates (**3**) provided only products (**5**) in the presence of toluene-4-sulphonic acid. All the substrates (**3**) studied so far underwent sigmatropic rearrangements at the 4-quinolin-3-ynyloxypropynyl function of compound (**3**) to give products (**4**) and/or (**5**).

INTRODUCTION.

Furo[3,2-*c*]quinolin-4(5*H*)-one and 2*H*-pyrano[3,2-*c*]quinolin-5(6*H*)-one derivatives are abundantly distributed in nature[1,2] and a number of syntheses[3,4] for these heterocycles have been reported which also include our own work[5,6]. 3*H*-Pyrano[2,3-*c*]quinolin-5(6*H*)-one system has not been reported in literature earlier. Although there are two methods for the synthesis of furo[2,3-*c*]quinolin-4(5*H*)-one system, based on the photochemical cyclization of furan-2-carboxanilide[7,8] and five step conversion of o-nitrotoluene,[9] both yields are low. From the lack of efficiency in the synthetic method for these titled heterocycles we became interested to a study on the development of an improved protocol for the synthesis of these heterocycles. Recently we have reported[12] the regioselective synthesis of furo[2,3-*c*]quinolin-4(5*H*)-ones and 3*H*-pyrano[2,3-*c*]quinolin-5(6*H*)-ones and here we report an efficient method for the synthesis of furo[2,3-*c*]quinolin-4(5*H*)-ones and 3*H*-pyrano[2,3-*c*]quinolin-5(6*H*)-ones *via* the thermal [3,3] sigmatropic rearrangement of 3-(4-aryloxybut-2-ynyloxy)-1-methylquinolin-5(6*H*)-ones (**3**).

RESULT AND DISCUSSION.

The starting 3-hydroxy-1-methylquinolin-2(1*H*)-one (**1**) was prepared from 1-methylisatin and diazomethane by a slight modification [12] of a published procedure.[13] The 3-(4-aryloxybut-2-ynyloxy)-1-methylquinolin-2-ones (**3a-h**) were synthesised by the nucleophilic substitution of 1-aryloxy-4-chlorobut-2-ynes (**2**) with (**1**) in the presence of anhydrous potassium carbonate and a small amount of sodium iodide (Finkelstein[14] conditions) in 78-85% yields (**Scheme 1**).

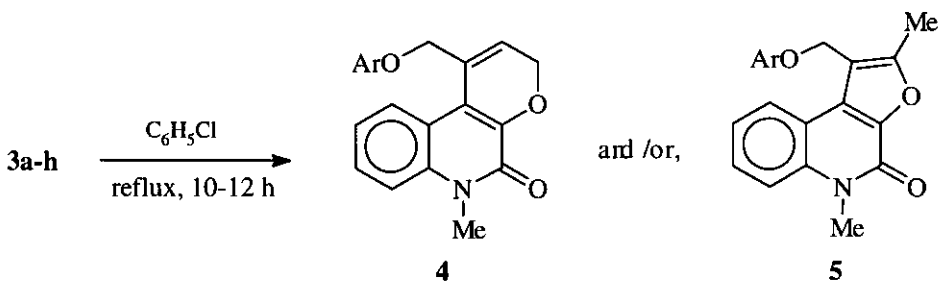


1 **2** **3**

a	C_6H_5	e	4-ClC_6H_4
b	2-MeC_6H_4	f	2,4-$Cl_2C_6H_3$
c	4-$MeOC_6H_4$	g	2,4-$Me_2C_6H_3$
d	3,5-$Me_2C_6H_3$	h	4-MeC_6H_4

Scheme 1

Thermal [3,3] sigmatropic rearrangement of **3** was utilized for the synthesis of furo- (**4**) and 2*H*-pyrano-quinolones (**5**). Substrate (**3a**) was heated in refluxing chlorobenzene [11] for 10 h to give 1-aryloxymethyl-5-methyl-3*H*-pyrano[2,3-*c*]quinolin-5(6*H*)-one (**4a**) in 90% yield. Similar treatment of substrates (**3b**) and (**3c**) also furnished products (**4b**) and (**4c**), respectively. However, the thermal reaction of **3d,e** gave **4d,e** in 85% and 90% yields together with 1-aryloxymethyl-2,5-dimethylfuro[2,3-*c*]quinolin-4(5*H*)-ones (**5d**, 10%) and (**5e**, 7%), respectively (**Scheme 2**). In contrast, **3f-h** furnished only furoquinolones (**5f-h**) in 90-95% yields.



4 **5**

Scheme 2

Addition of azoisobutyronitrile or hydroquinone as a radical initiator in the reaction mixture has no effect on the formation of products. Similarly substrate (**3a**) was refluxed in pyridine to give product (**4a**) in 5% yield and the reaction was incomplete even after 20 h. The same reaction {substrate (**3a**)} was carried out in refluxing dimethylaniline to give only the product (**4a**) in 75% yield. The reactions of **3a,b.d.e** in chlorobenzene in the presence of toluene-4-sulphonic acid gave the products (**5a,b,d,e**) in 75-92% yields

Table 1

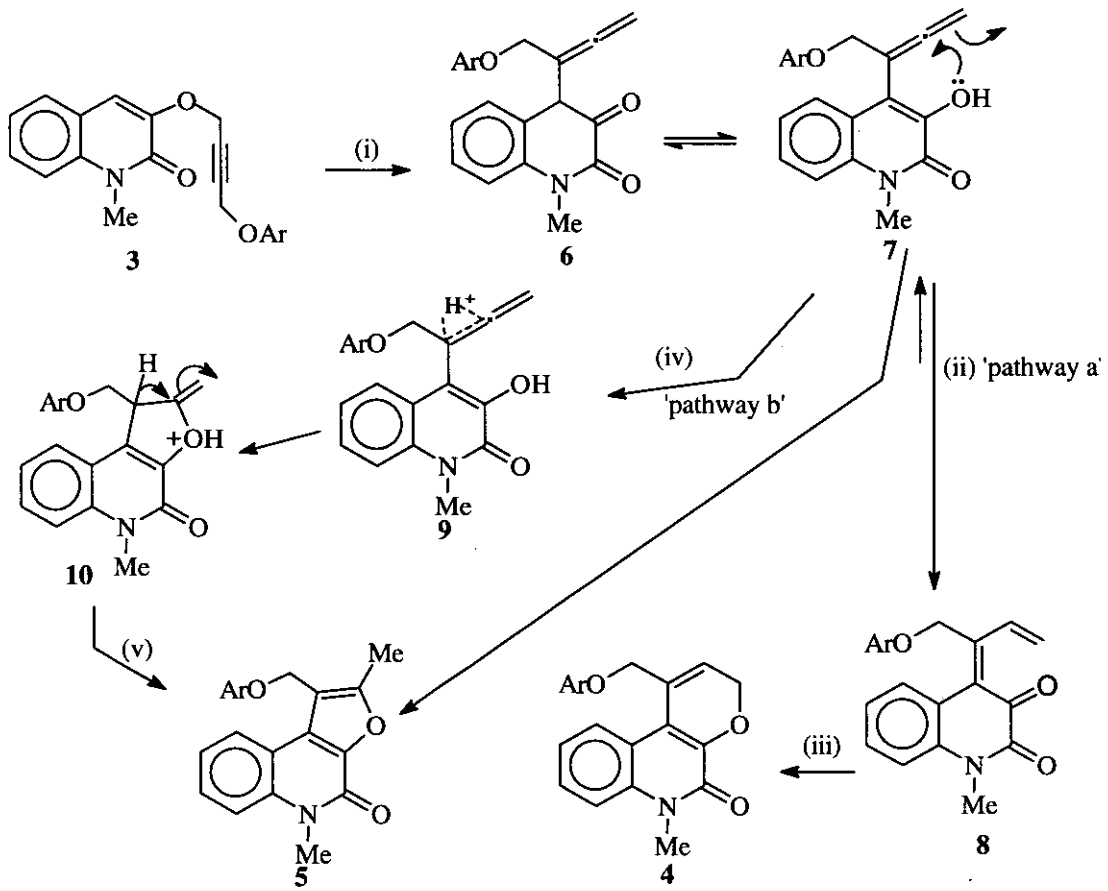
3	Solvent(additive)	Yield (%) of 4	5
a	Chlorobenzene	90	_
b	,,	90	_
c	,,	92	_
d	,,	85	10
e	,,	90	7
f	,,	_	95
g	,,	_	94
h	,,	_	90
a	Pyridine †	5	_
a	Dimethylaniline	75	_
a	Chlorobenzene(TsOH)	_	80
b	,,	_	75
d	,,	_	90
e	,,	_	92
d	Chlorobenzene ‡	88	5
f	,,	_	75
d	Dimethylaniline	75	_
f	,,	_	70

† incomplete reaction

‡ purified solvent.

It seems that chlorobenzene used in the reactions of **3d-h** perhaps contained acidic contamination, which might have partly influenced the formation of furoquinolones (**5**). Thus, the ethers (**3d**) and (**3f**) were similarly treated under refluxing purified chlorobenzene or dimethylaniline to afford the corresponding pyrano product (**4d**) and furano product (**5f**), respectively. Substrate (**3f**) seems to behave differently.

The formation of products (**4**) and/or (**5**) from the substrates (**3**) is explicable by the initial [3,3] sigmatropic rearrangement of the ether (**3**) to give **6** followed by enolisation to **7**, subsequent [1,5]-hydrogen shift and electrocyclic ring closure[15] giving products (**4**) (pathway "a"). On the other hand, the reaction in presence of acid takes place through protonation of the allenyl group of intermediate (**7**) and cyclization to products (**5**) (pathway "b") (**Scheme 3**)



Scheme 3 Reactions: (i) [3s,3s] shift (ii) [1s,5s]H shift (iii) eletrocyclic ring closure (iv) H^+ (v) $-H^+$

In conclution, the rearrangement of **3** followed by cyclization provides an efficient method for selective synthesis of furo- (**4**) and pyranoquinolinones (**5**).

EXPERIMENTAL

Melting points were determined in a sulphuric acid bath and uncorrected. UV absorption spectra were recorded on a Hitachi 200-20 spectrophotometer for ethanol. IR spectra were run for KBr discs on a Perkin-Elmer 1330 apparatus. ^{1}H-NMR spectra were determined for solutions in deuteriochloroform with

$SiMe_4$ as internal standard on Zeol FX-100 (100 MHz) at IICB Calcutta, Bruker 250 MHz at the University of Konstanz, Germany and Bruker 200 MHz at IIT Kharagpur. Elemental analysis and recording of mass apectra were carried out by RSIC (CDRI), Luclnow and also by the University of Konstanz, Germany. Silica gel (60-120 mesh) was obtained from Qualigen. 1-Aryloxy-4-chlorobut-2-ynes (**2a-h**) were prepared according to earlier published procedure.[16]

General Procedure for the Preparation of 3-Hydroxy-1-methylquinolin-2-(1*H*)-one (1):

1-Methylisatin (1.5 g, 9.3 mmol) was taken in dry acetone (50 mL) in a round bottom flask at rt and the ice-cold ethereal solution of diazomethane was added dropwise to it. Nitrogen gas was evolved and after the completion of addition the initial red solution become yellow. The reaction mixture was kept at 0°C for 20 h and stripped off the solvent. The solid product obtained was washed with ethanol and then recrystallised from chloroform to give colourless needles (0.9 g, 55%).

Compound (1), mp 186°C; IR (ν, cm^{-1}): 3254 and 1618; NMR (δ, ppm) (100 MHz): 3.83 (s, 3H), 7.12 (s, 1H) and 7.16-7.80 (m, 5H).

General Procedure for the Preparation of 3-(4-Aryloxybut-2-ynyloxy)-1-methylquinolin-2-ones (3a-h):

A mixture of 3-hydroxy-1-methylquinolin-2(1*H*)-one (**1**) (0.175 g, 1 mmol), an appropriate 1-aryloxy-4-chlorobut-2-yne (**2**) (0.33 g, 1 mmol), anhydrous potassium carbonate (3 g, 21.74 mmol) and sodium iodide (0.05 g) in dry acetone (50 mL) was refluxed for 8-10 h. The reaction mixture was then cooled, fillered and the solvent was removed. The residue was extacted with chloroform (3x25 mL). The chloroform extract was washed with water (3x25 mL) and dried (Na_2SO_4). After removal of chloroform, the crude mass was chromatographed over silica gel. The product (**3a-h**) was obtained when the column was eluted with benzene.

Compound (3a), mp 106°C (85%); UV (λ, nm): 223 (log ε 4.51), 276 (log ε 3.88) and 320 (log ε 3.86); IR (ν, cm^{-1}): 1715, 1585, and 1490; NMR (δ, ppm) (100 MHz): 3.76 (s, 3H), 4.72 (t, J=1.5 Hz, 2H), 4.88 (t, J=1.5 Hz, 2H), 6.76-7.20 (m, 5H) and 7.24-7.60 (m, 5H); MS (m/z) 319 (M^+). Anal. Calcd for $C_{20}H_{17}NO_3$: C, 75.24; H, 5.33; N, 4.39. Found C, 75.12; H, 5.45; N, 4.46.

Compound (3b), mp 108°C (84%); UV (λ, nm): 222 (log ε 4.39), 276 (log ε 3.73) and 319 (log ε 3.70); IR (ν, cm^{-1}): 1700, 1600, and 1450; NMR (δ, ppm) (100 MHz): 2.16 (s, 3H), 3.76 (s, 3H), 4.72 (t, J=1.5 Hz, 2H), 4.88 (t, J=1.5 Hz, 2H), 6.78-7.20 (m, 5H) and 7.25-7.60 (m, 4H); MS (m/z) 333 (M^+). Anal. Calcd for $C_{21}H_{19}NO_3$: C, 75.68; H, 5.71; N, 4.20. Found C, 75.41; H, 5.66; N, 4.10.

Compound (3c), gummy mass (80%); UV (λ, nm): 223 (log ε 4.70), 276 (log ε 4.02) and 319 (log ε 4.03); IR (ν, cm^{-1}): 1655, 1610, 1515, and 1420; NMR (δ, ppm) (250 MHz): 3.70 (s, 3H), 3.76 (s, 3H),

4.66 (t, J=1.5 Hz, 2H), 4.88 (t, J=1.5 Hz, 2H), 6.68-6.85 (m, 4H), 7.02 (s, 1H) and 7.19-7.46 (m, 4H); MS (m/z) 349 (M^+). Anal. Calcd for $C_{21}H_{19}NO_4$: C, 72.21; H, 5.44; N, 4.01. Found C, 72.06; H, 5.74; N, 4.29.

Compound (3d), mp 116^{0}C (79%); UV (λ, nm): 223 (log ε 4.44), 276 (log ε 3.75) and 319 (log ε 3.79); IR (ν, cm^{-1}): 1710, 1630, 1595, and 1450; NMR (δ, ppm) (250 MHz): 2.17 (s, 6H), 3.76 (s, 3H), 4.67 (t, J=1.5 Hz, 2H), 4.88 (t, J=1.5 Hz, 2H), 6.51 (s, 3H), 7.00 (s, 1H) and 7.19-7.46 (m, 4H); MS (m/z) 347 (M^+). Anal. Calcd for $C_{22}H_{21}NO_3$: C, 76.08; H, 6.05; N, 4.03. Found C, 76.32; H, 6.16; N, 4.24.

Compound (3e), mp 122^{0}C (81%); UV (λ, nm): 223 (log ε 4.30), 276 (log ε 3.63) and 320 (log ε 3.63); IR (ν, cm^{-1}): 1775, 1750, 1720, 1595, and 1415; NMR (δ, ppm) (100 MHz): 3.77 (s, 3H), 4.69 (t, J=1.5 Hz, 2H), 4.89 (t, J=1.5 Hz, 2H), 6.72-7.26 (m, 5H) and 7.30-7.60 (m, 4H). Anal. Calcd for $C_{20}H_{16}NO_3Cl$: C, 67.89; H, 4.53; N, 3.96. Found C, 67.96; H, 4.75; N, 4.20.

Compound (3f), mp 136^{0}C (80%); UV (λ, nm): 222 (log ε 4.42), and 319 (log ε 3.78); IR (ν, cm^{-1}): 1775, 1720, 1590, and 1415; NMR (δ, ppm) (100 MHz): 3.80 (s, 3H), 4.80 (t, J=1.5 Hz, 2H), 4.90 (t, J=1.5 Hz, 2H), 6.82-7.10 (m, 3H) and 7.18-7.66 (m, 5H); Anal. Calcd for $C_{20}H_{15}NO_3Cl_2$: C, 61.86; H, 3.87; N, 3.61. Found C, 62.10; H, 3.67; N, 3.85.

Compound (3g), mp 102^{0}C (82%); UV (λ, nm): 223 (log ε 4.60), 276 (log ε 3.94) and 319 (log ε 3.96); IR (ν, cm^{-1}): 1640, 1630, 1590, and 1490; NMR (δ, ppm) (250 MHz): 2.16 (s, 3H), 2.18 (s, 3H), 3.74 (s, 3H), 4.67 (t, J=1.5 Hz, 2H), 4.85 (t, J=1.5 Hz, 2H), 6.72-6.88 (m, 3H), 7.00 (s, 1H) and 7.16-7.48 (m, 4H); MS (m/z) 347 (M^+). Anal. Calcd for $C_{22}H_{21}NO_3$: C, 76.08; H, 6.03; N, 4.03. Found C, 76.28; H, 6.28; N, 4.25.

Compound (3h), mp 80^{0}C (78%); UV (λ, nm): 223 (log ε 4.25), 276 (log ε 3.58) and 319 (log ε 3.59); IR (ν, cm^{-1}): 1770, 1715, 1605, 1560 and 1490; NMR (δ, ppm) (100 MHz): 2.21 (s, 3H), 3.76 (s, 3H), 4.68 (t, J=1.5 Hz, 2H), 4.88 (t, J=1.5 Hz, 2H), 6.72-7.08 (m, 5H) and 7.30-7.58 (m, 4H); MS (m/z) 333 (M^+). Anal. Calcd for $C_{21}H_{19}NO_3$: C, 75.68; H, 5.71; N, 4.20. Found C, 75.56; H, 5.82; N, 4.12.

General Procedure for the Synthesis of Compounds (4) and (5):

Compound **(3a-h)** (0.1 g.) was heated in refluxing chlorobenzene (2 mL) for 10-12 h. The reaction was monitored by TLC. Chlorobenzene was removed by elution of the column (silica gel) with petrolium ether (bp 60-80^{0}C). Elution of the column with chloroform and benzene furnished products **(4a-e)** and **(5d-e, f-h)** respectively.

Compound (4a), gummy mass (90%); UV (λ, nm): 223 (log ε 4.07), and 320 (log ε 3.40); IR (ν, cm^{-1}): 1655, 1635, 1595, and 1470; NMR (δ, ppm) (100 MHz): 3.79 (s, 3H), 4.77 (d, J=4 Hz, 2H), 4.93 (s, 2H); 6.28 (t, J=4 Hz, 1H), 6.87-7.11 (m, 5H), 7.39-7.51 (m, 3H) and 7.83 (d, J=8 Hz, 1H); MS (m/z) 319

(M^+). Anal. Calcd for $C_{20}H_{17}NO_3$: C, 75.24; H, 5.33; N, 4.39. Found C, 75.44; H, 5.63; N, 4.25.**Compound (4b),** mp 118°C (90%); UV (λ, nm): 225 (log ε 4.10), and 330 (log ε 3.36); IR (ν, cm^{-1}): 1660, 1625, 1605 and 1460; NMR (δ, ppm) (100 MHz): 2.16 (s, 3H), 3.80 (s, 3H), 4.78 (d, J=4 Hz, 2H), 4.94 (s, 2H), 6.28 (t, J=4 Hz, 1H), 6.72-7.24 (m, 5H) 7.39-7.56 (m, 2H) and 7.84 (d, J=8 Hz, 1H); MS (m/z) 333 (M^+). Anal. Calcd for $C_{21}H_{19}NO_3$: C, 75.68; H, 5.71; N, 4.20. Found C, 75.62; H, 5.54; N, 4.15.

Compound (4c), gummy mass (92%); UV (λ, nm): 226 (log ε 4.66), and 327 (log ε 3.87); IR (ν, cm^{-1}): 1658, 1628, 1600 and 1455; NMR (δ, ppm) (250 MHz): 3.78 (s, 3H), 3.80 (s, 3H), 4.78 (d, J=4.7 Hz, 2H), 4.87 (s, 2H), 6.29 (t, J=4.6 Hz, 1H), 6.80-6.98 (m, 4H), 7.15-7.25 (m, 1H), 7.38-7.53 (m, 2H) and 7.82 (d, J=8Hz, 1H); MS (m/z) 349 (M^+). Anal. Calcd for $C_{21}H_{19}NO_4$: C, 72.21; H, 5.44; N, 4.01. Found C, 72.42; H, 5.61; N, 4.21.

Compound (4d), mp 204°C (85%); UV (λ, nm): 225 (log ε 4.50), and 427 (log ε 3.78); IR (ν, cm^{-1}): 1770, 1720, 1695, 1610, 1560, and 1430; NMR (δ, ppm) (100 MHz): 2.28 (s, 6H), 3.80 (s, 3H), 4.79 (d, J=4 Hz, 2H), 4.88 (s, 2H), 6.28 (t, J=4 Hz, 1H), 6.54-6.72 (m, 3H), 7.26-7.56 (m, 3H) and 7.88 (d, J=8 Hz, 1H); MS (m/z) 347 (M^+). Anal. Calcd for $C_{22}H_{21}NO_3$: C, 76.08; H, 6.05; N, 4.03. Found C, 76.24; H, 5.86; N, 4.18.

Compound (5d), mp 200°C (10%); UV (λ, nm): 224 (log ε 4.55), 276 (log ε 3.75) and 313 (log ε 3.68); IR (ν, cm^{-1}): 1680, 1615, 1485 and 1390; NMR (δ, ppm) (100 MHz): 2.28 (s, 6H), 2.56 (s, 3H), 3.83 (s, 3H), 5.21 (s, 2H), 6.68 (s, 3H), 7.32-7.64 (m, 3H) and 8.04 (d, J=8 Hz, 1H); MS (m/z) 347 (M^+). Anal. Calcd for $C_{22}H_{21}NO_3$: C, 76.08; H, 6.05; N, 4.03. Found C, 76.18; H, 6.17; N, 4.18.

Compound (4e), gummy mass (90%); UV (λ, nm): 225 (log ε 4.21), and 277 (log ε 3.57); IR (ν, cm^{-1}): 1640, 1610, 1500, and 1470; NMR (δ, ppm) (100 MHz): 3.97 (s, 3H), 4.77 (d, J=4 Hz, 2H), 4.92 (s, 2H), 6.27 (t, J=4 Hz, 1H), 6.60-7.04 (m, 4H), 7.40-7.52 (m, 3H) and 7.76 (d, J=8 Hz, 1H). Anal. Calcd for $C_{20}H_{16}NO_3Cl$: C, 67.89; H, 4.53; N, 3.96. Found C, 67.66; H, 4.75; N, 4.16.

Compound (5e), mp 174°C (7%); UV (λ, nm): 224 (log ε 4.23), 277 (log ε 3.58) and 319 (log ε 3.64); IR (ν, cm^{-1}): 1680, 1600, 1450, and 1350; NMR (δ, ppm) (100 MHz): 2.56 (s, 3H), 3.83 (s, 3H), 5.21 (s, 2H), 6.84-7.08 (m, 2H) and 7.30-7.68 (m, 5H), 7.96 (d, J=8 Hz, 1H). Anal. Calcd for $C_{20}H_{16}NO_3Cl$: C, 67.89; H, 4.53; N, 3.96. Found C,6 7.62; H, 4.45; N, 4.12.

Compound (5f), mp 231°C (95%); UV (λ, nm): 224 (log ε 4.41), and 319 (log ε 3.55); IR (ν, cm^{-1}): 1650, 1570, 1480 and 1400; NMR (δ, ppm) (100 MHz): 2.56 (s, 3H), 3.84 (s, 3H), 5.32 (s, 2H), 6.89-7.28 (m, 3H), 7.36-7.56 (m, 3H) and 8.09 (d, J=8Hz, 1H). Anal. Calcd for $C_{20}H_{15}NO_3Cl_2$: C, 61.86; H, 3.87; N, 3.61. Found C, 61.66; H, 3.95; N, 3.52.

Compound (5g), mp 154°C (94%); UV (λ, nm): 224 (log ε 4.60), 276 (log ε 3.84) and 313 (log ε 3.74); IR (ν, cm^{-1}): 1675, 1600, 1440 and 1380; NMR (δ, ppm) (250 MHz): 2.05 (s, 3H), 2.28 (s, 3H), 2.54 (s,

3H), 3.82 (s, 3H), 5.18 (s, 2H), 6.90-7.05 (m, 3H), 7.28-7.51 (m, 3H) and 8.02 (d, J=8 Hz, 1H); MS (m/z) 347 (M^+). Anal. Calcd for $C_{22}H_{21}NO_3$: C, 76.08; H, 6.05; N, 4.03. Found C, 76.18; H, 6.18; N, 4.21. **Compound (5h),** mp 156^{0}C (90%); UV (λ, nm): 223 (log ε 4.14), 277 (log ε 3.38) and 318 (log ε 3.24); IR (ν, cm^{-1}): 1795, 1685, 1615, 1540, and 1400; NMR (δ, ppm) (100 MHz): 2.31 (s, 3H), 2.54 (s, 3H), 3.83 (s, 3H), 5.20 (s, 2H), 6.82-7.20 (m, 4H), 7.29-7.60 (m, 3H) and 8.03 (d, J=8 Hz, 1H); MS (m/z) 333 (M^+). Anal. Calcd for $C_{21}H_{19}NO_3$: C, 75.68; H, 5.71; N, 4.20. Found C, 75.45; H, 5.62; N, 4.12.

Rearrangement of Compound (3a-b, d-e) in Chlorobenzene in the Presence of Toluene-4-sulphonic Acid:

Compound **(3a-b, d-e)** (0.03 g.) was heated in refluxing chlorobenzene (1.5 mL) with toluene-4-sulphonic acid (0.01 g, 0.05 mmol) for 8 h. TLC indicated complete convertion of starting material to products. Usual work-up of the reaction mixture and subsequent column chromatography over silica gel, using benzene as eluant, gave pure products **(5a-b, d-e)** in 75-92% yields, respectively, which were characterised as furo derivatives by comparison of their mp, mixed melting point, superimposable IR spectra with those of authentic samples.

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