Studies in [3.3] Sigmatropic Rearrangement:[1] Regioselective Synthesis of 1-Aryloxymethylpyrano[2,3-*c*][1]benzopyran-5(3*H*)-one and 1-Aryloxymethyl-2-methylfuro[2,3-*c*][1]benzopyran-4-one

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3-(4-Aryloxybut-2-ynyloxy)[1]benzopyran-2-one (**1**) in refluxing chlorobenzene gave exclusively 1-aryloxymethylpyrano[2,3-*c*][1]benzopyran-5(3*H*)-one (**6**) by a pericyclic path. Compound (**1**) when heated in nonpolar solvents or in the presence of acid or base, gave exclusively 1-aryloxymethyl-2-methylfuro[2,3-*c*][1]benzopyran-4-one (**10**). Additionally this reaction has been studied in the presence of a radical initiator, *viz.*, azoisobutyronitrile (AIBN), and induced to follow mainly the radical pathway to give the products (**10**). All the butynes (**1**) studied so far underwent sigmatropic rearrangements at the 4-coumarin-3-yloxypropynyl function of compound (**1**) to give product(s) (**6**) and/or (**10**).

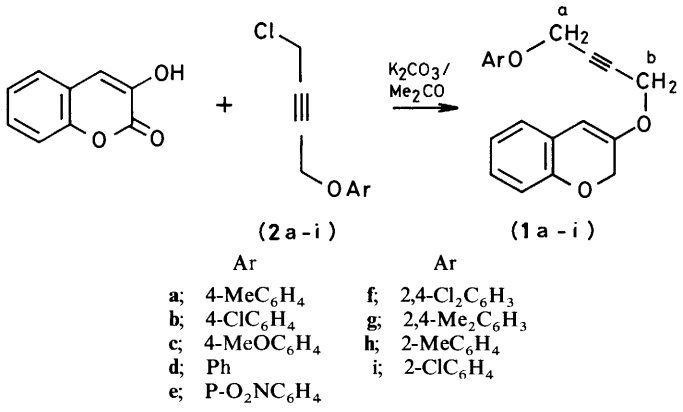
Coumarin[2] and its derivatives[3] are important because of their physiological activity whilst the biological activity[4,5] of 3-alkyl- and 4-alkyl coumarins[6] has made their synthesis of interest. Although the synthesis of dihydrofuranocoumarins had been reported earlier,[7] regioselective synthesis of simple 3,4-fused pyranocoumarins[8] by a [3.3] sigmatropic rearrangement of the coumarinyl propynyl ethers of 3- and 4-hydroxycoumarins was only recently reported. We have also recently demonstrated that 1-aryloxy-4-coumarin-4-yloxybut-2-ynes could serve as starting materials for the regioselective synthesis of pyranocoumarins[9] *via* a [3.3]sigmatropic rearrangement and subsequent ring closure by a pericyclic path.

Here, we describe our strategy for the regioselective synthesis of pyranocoumarins as well as furanocoumarins from the butyne derivatives, 1-aryloxy-4-coumarin-3-yloxybut-2-ynes (**1**) utilising a pericyclic pathway, an ionic pathway, and also a radical pathway for cyclisation of the initial [3.3] sigmatropic rearrangement intermediates (**3**) or (**4**).

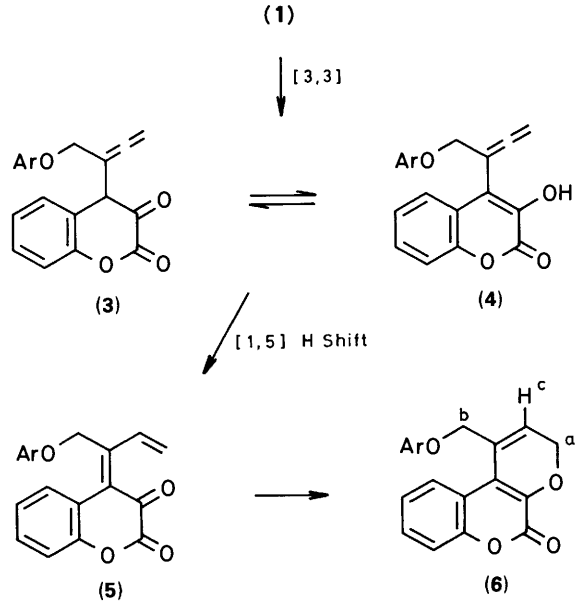
The starting materials, 1-aryloxy-4-coumarin-3-yloxybut-2-ynes (**1**) for this study were easily prepared by an S_N2 displacement of chlorine atom from 1-aryloxy-4-chlorobut-2-ynes (**2**) by a coumarin-3-yloxy anion. Different 1-aryloxy-4-chlorobutynes (**2**) were refluxed with 3-hydroxycoumarin in dry acetone in the presence of anhydrous potassium carbonate for 20 h. (See Scheme 1). The butynylcoumarins (**1a**—**i**), crystalline solids, were characterised from their elemental analyses and u.v., i.r., ^{1}H n.m.r. and mass spectral data; $\lambda_{max.}$ 222—225 and 280—292 nm; $\nu_{max.}$ 1 735—1 715, 1 635—1 600, 1 307—1 295, and 1 240—1 130 cm^{-1}; δ 4.70 (2 H, t, OCH_2^a) and 4.85 (2 H, t, OCH_2^b).

In refluxing chlorobenzene (132 °C) compounds (**1**) underwent an initial [3.3] sigmatropic rearrangement to give the allenylenol (**4**). In absence of any other agents normally the pericyclic pathway is followed to give 1-aryloxymethylpyrano[2,3-*c*]benzopyran-5(3*H*)-one. (**6**) (Scheme 2). All these products, crystalline solids, were characterised on the basis of their elemental analyses and spectral data: $\lambda_{max.}$ 242—249, 278—292, and 344—345 nm; $\nu_{max.}$ 1 725—1 710, 1 645—1 638, 1 610—1 580, and 1 255—1 148 cm^{-1}; δ 6.22—6.50 (1 H, t, J 5 Hz, H^c); *m/z* 213 (−ArO), 212 (213 − H), and 115 (3 × −CO and − CH_2).

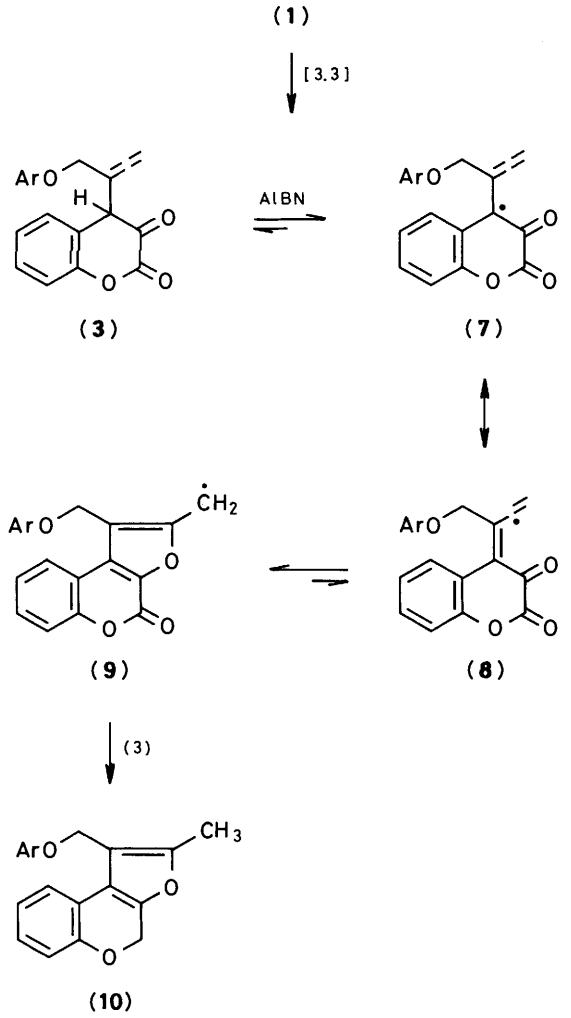
The reaction has also been successfully studied in carefully purified solvents *viz.*, ethylbenzene and xylene. The formation of (**6**) from (**1**) is explicable by a [3.3] sigmatropic rearrangement, enolisation, [1,5] H shift, and an electrocyclic ring closure[11] (see Scheme 2).



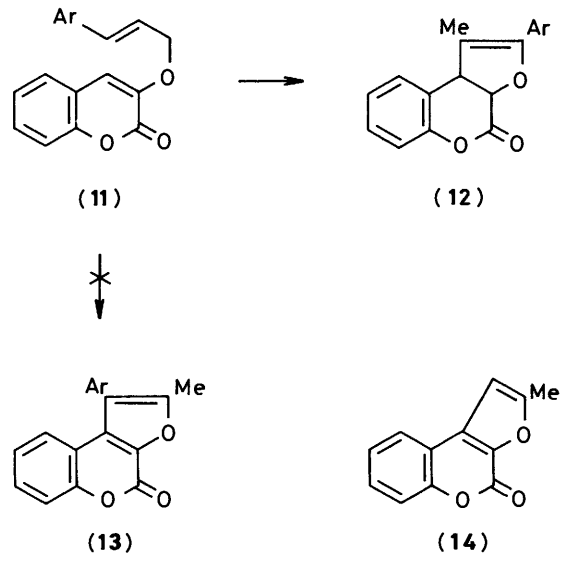
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

We next studied the [3.3] sigmatropic rearrangement in the presence of a radical initiator, *viz.*, azoisobutyronitrile (AIBN) or benzoyl peroxide in order to generate a radical from the initially formed allene intermediate (**3**). We expected to generate a radical of type (**7**), since such a radical, being benzylic and α to keto and allylic groups, would be a likely intermediate. With this end in view compounds (**1**) were refluxed in purified chlorobenzene in the presence of a small amount of azoisobutyronitrile (AIBN) for 2.5—4 h to give the furanocoumarin (**10**) (70—80%) and the pyranocoumarin (**6**) (10—15%) (See Scheme 3). These new products were characterised as 1-aryloxymethyl-2-methylfuro[2,3-*c*][1]benzopyran-4-ones (**10**) from their elemental analyses and spectral data: $\lambda_{max.}$ 225—228 and 275—285 nm; $\nu_{max.}$ 1 735—1 725, 1 610—1 575, and 1 240—1 098 cm^{-1}; δ 2.54—2.64 (3 H, s).

Ahluwalia *et al.*,[12] while reporting the Claisen rearrangement of 3-cinnamyloxycoumarin (**11**) claimed to have obtained (**12**) instead of (**13**) from mechanistic considerations (see Scheme 4). This report prompted us to confirm rigorously the structure of product (**10a**) by homodecoupling, ^{13}C n.m.r., and HETCOR experiments.[1] In addition, we have synthesized[13] compound (**14**) from 2-methyldihydrofuro[2,3-*c*][1]benzopyran-4-one: this compound has a signal at δ 2.56 (d, $J \approx 1$ Hz, 2-CH_3) whereas Ahluwalia's compound (**12**) is reported to have the corresponding signal at δ 2.38 (s). In spite of this we believe that the structural assignment (**10**) for the product from the cyclisation of (**3**) in the presence of a radical initiator is correct. This cyclisation also gives 10—15% of (**6**) which is probably formed following the pericyclic pathway in the competing reactions (see Scheme 3).

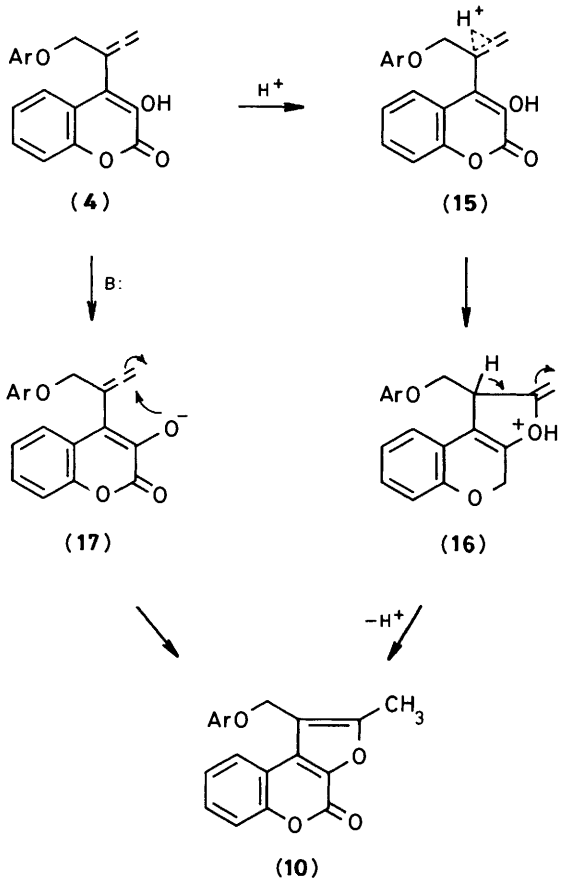
We were also interested in studying the cyclization of the intermediate allenyl enol derivative (**4**) following an ionic pathway. To this end the rearrangement of compounds (**1**) were studied at 140 °C in solvents such as PEG-600, in basic solvents *N*,*N*-dimethylaniline (DMA), or in ethylbenzene in the presence of toluene-*p*-sulphonic acid. In each case the furanocoumarins (**10**) were obtained in excellent yield. Product (**10**) was also obtained when the reaction was carried out in refluxing pyridine for 20 h, although the reaction was not complete and some unchanged starting material was recovered along with (**10**). The formation of (**10**) from (**4**) may be explained as shown in Scheme 5.

While studying this reaction we encountered difficulties in using commercial chlorobenzene, ethylbenzene, and xylene. In most cases a mixture of products (**6**) and (**10**) was obtained. Although we were unable to separate and characterise the impurity present in the commercial solvents which was responsible for the formation of product (**10**), we were able to ascertain that some radical initiator might be present in the commercial solvents by the following experiment. In the case of 1-coumarin-3-yloxy-4-(*p*-tolyloxy)butyne (**1a**) only product (**10a**) was obtained when the reaction was performed in commercial solvents, whereas addition of hydroquinone to the reaction mixture gave product (**6a**) alongwith (**10a**). The effect of impurity on the course of the cyclisation of (**3**) is evident from the results in the Table.

To test the generality of the regioselectivity, nine butynes have been studied and in each case the regioselectivity has been achieved. The method, therefore, provides a regioselective ring closure for the synthesis of this type of substituted pyranocoumarins (**6a**—**i**) and furanocoumarins (**10a**—**i**) in a simple manner. The advantages of this method rests on the predetermined direction of ring closure and the variety of substituents that can be incorporated into the starting materials (**1**) and thus in the newly formed pyranocoumarins (**6**) and furanocoumarins (**10**).

Experimental

M.p.s were determined in a sulphuric acid bath and are uncorrected. U.v. absorption spectra were recorded on a



Scheme 5.

Hitachi 200-20 spectrometer for solutions in ethanol. I.r. spectra were run for KBr discs on a Perkin-Elmer 1330 apparatus. ^{1}H N.m.r. spectra were determined for solutions in deuteriochloroform with $SiMe_4$ as internal standard on Hitachi R-600 (60 MHz), Zeol Fx-100 (100 MHz) at the Indian Institute of Chemical Biology, Calcutta and Bruker AM-300L (270 MHz). Elemental analyses and recording of mass spectra were carried out by RSIC (CDRI), Lucknow. Silica gel (60—120 mesh) was obtained from B.D.H. Extracts were dried over anhydrous sodium sulphate. Ether refers to diethyl ether. Light petroleum and petroleum refer to the fractions b.p. 40—60 °C and 60—80 °C respectively. The solvents chlorobenzene, ethylbenzene, and xylene were purified by successively washing with freshly prepared aqueous iron(II) sulphate, dried (Na_2SO_4), refluxed with solid iron(II) sulphate, distilled, and then refluxed with hydroquinone and distilled twice before use.

General Procedure for the Preparation of 1-*Aryloxy*-4-*chlorobut*-2-*ynes* (**2a**—**i**).—These compounds were prepared according to published procedure.[10]

1-Chloro-4-(4-nitrophenoxy)but-2-yne (**2e**) (55%), m.p. 98 °C; $\lambda_{max.}$ (EtOH) 225 and 300 nm; $\lambda_{max.}$(KBr) 2 928, 2 120, 2 010. 1 600, 1 385, and 710 cm^{-1}; ($CDCl_3$; 270 MHz) 4.20 (s, 2 H), 4.90 (s, 2 H), 7.05 (d, 2 H), and 8.25 (d, 2 H).

1-Chloro-4-(2,4-dimethylphenoxy)but-2-yne (**2g**) (60%), b.p. 120 °C/0.3 mmHg; $\lambda_{max.}$(EtOH) 238 and 278 nm; $\lambda_{max.}$(liquid film) 2 930, 1 620, 1 385, and 720 cm^{-1}; δ ($CDCl_3$; 270 MHz) 2.22 (s, 3 H), 2.30 (s, 3 H), 4.20 (s, 2 H), 4.72 (s, 2 H), and 6.50—7.35 (m, 3 H).

Preparation of 3-(4-*Aryloxybut*-2-*ynyloxy*)[1]*benzopyran*-2-*one* (**1a**—**i**).—A mixture of 3-hydroxycoumarin (1.62 g, 0.01 mol), an appropriate 1-aryloxy-4-chlorobut-2-yne (0.015 mol), and anhydrous potassium carbonate (3 g) in dry acetone (75 ml) was refluxed for 20—25 h. The reaction mixture was then cooled, filtered, and evaporated and the residue extracted with chloroform. The extract was washed with 10% aqueous sodium carbonate, brine, and, water, and dried (Na_2SO_4). Evaporation then gave the crude product which was then chromatographed over silica gel (60—120 mesh).

Compound (**1a**) (80%), m.p. 155 °C; $\lambda_{max.}$ 225, 285, and 308 nm; $\nu_{max.}$ 1 735, 1 635, 1 610, 1 512, 1 300, 1 225, and 1 140 cm^{-1}; δ 2.20 (s, 3 H, CH_3), 4.68 (t, 2 H, *J* 1.5 Hz, CH_2^a), 4.85 (t, 2 H, *J* 1.5 Hz, CH_2^b), and 6.70—7.28 (m, 9 H, 4-H and ArH); *m*/*z* 320 (M^+) (Found: C, 74.7; H 5.2; $C_{20}H_{16}O_4$ requires C, 75.0; H, 5.0%).

Compound (**1b**) (82%), m.p. 155 °C, $\lambda_{max.}$ 228, 288, and 308 nm; $\nu_{max.}$ 1 725, 1 615, 1 600, 1 495, 1 307, 1 240, and 1 170 cm^{-1}; δ 4.68 (t, 2 H, *J* 1.5 Hz, CH_2^a), 4.82 (t, 2 H, *J* 1.5 Hz, CH_2^b), 6.72—7.52 (m, 9 H, 4-H and ArH); *m*/*z* 342 and 340 (M^+) (Found: C, 67.3; H, 4.11; $C_{19}H_{13}ClO_4$ requires C, 66.96; H, 3.82%).

Compound (**1c**) (70%), m.p. 135 °C; $\lambda_{max.}$ 225, 290, and 308 nm; $\nu_{max.}$ 1 725, 1 630, 1 608, 1 505, 1 300, 1 220, and 1 140 cm^{-1}; δ 3.72 (s, 3 H, OCH_3), 4.72 (t, 2 H, *J* 1.5 Hz, CH_2^a), 4.9 (t, 2 H, *J* 1.5 Hz, CH_2^b), and 6.70—7.55 (m, 9 H, 4-H and ArH); *m*/*z* 336 (M^+) (Found: C, 71.2; H, 4.95; $C_{20}H_{16}O_5$ requires C, 71.43; H, 4.76%).

Compound (**1d**) (80%), m.p. 138 °C; $\lambda_{max.}$ 228, 290, and 308 nm; $\nu_{max.}$ 1 715, 1 600, 1 490, 1 300, 1 220, and 1 130 cm^{-1}; δ 4.78 (t, 2 H, *J* 1.5 Hz, CH_2^a), 4.90 (t, 2 H, *J* 1.5 Hz, CH_2^b), 6.85—7.70 (m, 10 H, 4-H and ArH); *m*/*z* 306 (M^+) (Found: C, 74.35; H, 4.3; $C_{19}H_{14}O_4$ requires C, 74.51; H, 4.58%).

Compound (**1e**) (75%), m.p. 195 °C; $\lambda_{max.}$ 225, 292, and 308 nm; $\nu_{max.}$ 1 703, 1 627, 1 605, 1 593, 1 490, 1 295, 1 230, and 1 150 cm^{-1}; δ 4.78 (t, 2 H, *J* 1.5 Hz, CH_2^a), 4.95 (t, 2 H, *J* 1.5 Hz, CH_2^b), and 6.90—7.50 (m, 9 H, 4-H and ArH); *m*/*z* 351 (M^+) (Found: C, 64.7; H, 3.6. $C_{19}H_{13}NO_6$ requires C, 64.96; H, 3.70%).

Compound (**1f**) (82%), m.p. 150 °C; $\lambda_{max.}$ 228, 288, and 308 nm; $\nu_{max.}$ 1 730, 1 630, 1 610, 1 480, 1 300, 1 235, 1 225, and 1 140 cm^{-1}; δ 4.78 (t, 2 H, *J* 1.5 Hz, CH_2^a), 4.85 (t, 2 H, *J* 1.5 Hz, CH_2^b), 6.90—7.50 (m, 8 H, 4-H and ArH); *m*/*z* 374 (M^+) and 376 (Found: C, 60.55; H, 3.1; $C_{19}H_{12}Cl_2O_4$ requires C, 60.80; H, 3.20%).

Compound (**1g**) (85%), m.p. 127 °C; $\lambda_{max.}$ 222, 280, 285, and 308 nm; $\nu_{max.}$ 1 738, 1 628, 1 610, 1 495, 1 300, 1 220, and 1 140 cm^{-1}; δ 2.18 (s, 3 H, $ArCH_3$), 2.22 (s, 3 H, $ArCH_3$), 4.75 (t, 2 H, *J* 1.5 Hz, CH_2^a), 4.88 (t, 2 H, *J* 1.5 Hz, CH_2^b), and 6.75—7.50 (m, 8 H, 4-H and ArH); *m*/*z* 334 (M^+) (Found: C, 75.6; H, 5.45; $C_{21}H_{18}O_4$ requires C, 75.45; H, 5.38%).

Compound (**1h**) (72%), m.p. 118 °C; $\lambda_{max.}$ 225, 280, 292, and 308 nm; $\nu_{max.}$ 1 725, 1 630, 1 605, 1 495, 1 300, 1 240, and 1 115 cm^{-1}; δ 2.15 (s, 3 H, $ArCH_3$), 4.75 (t, 2 H, *J* 1.5 Hz, CH_2^a), 4.90 (t, 2 H, *J* 1.5 Hz, CH_2^b), and 6.95—7.50 (m, 9 H, 4-H and ArH); *m*/*z* 320 (M^+) (Found: C, 75.25; H, 4.85. $C_{20}H_{16}O_4$ requires C, 75.0; H, 5.0%).

Compound (**1i**) (70%), m.p. 120 °C; $\lambda_{max.}$ 225, 282, 290, and 308 nm; $\nu_{max.}$ 1 725, 1 630, 1 605, 1 485, 1 300, 1 240, and 1 155 cm^{-1}; δ 4.78 (t, 2 H, *J* 1.5 Hz, CH_2^a), 4.85 (t, 2 H, *J* 1.5 Hz, CH_2^b), and 6.95—7.50 (m, 9 H, 4-H and ArH); *m*/*z* 342 and 340 (M^+) (Found: C, 67.2; H, 4.05. $C_{19}H_{13}ClO_4$ requires C, 66.96; H, 3.82%).

General Procedure for the Synthesis of 1-*Aryloxymethylpyrano*[2,3-c][1]*benzopyran*-5(3H)-*ones* (**6a**).—Compound (**1**) (0.2 g) was refluxed in chlorobenzene (5 ml) for 4 h. T.l.c. indicated the quantitative conversion of (**1**). Chlorobenzene was removed under pressure and the crude product was subjected to column chromatography over silica gel. Elution of the column with benzene–petroleum (1:1) gave the pyranocoumarin (**6**) (80—92%).

Compound (**6a**) (92%), m.p. 135 °C; $\lambda_{max.}$ 242s, 278w, 285w, and 345m nm; $\nu_{max.}$ 1 725, 1 238, and 1 148 cm^{-1}; δ 2.40 (s, 3 H,

Table. Rearrangement of (**1a**—i) in commercial chlorobenzene

Starting Material	Yield (%) of pyranocoumarin (**6**)	Yield (%) of furanocoumarin (**10**)
(**1a**)	—	90
(**1b**)	60	25
(**1c**)	70	10
(**1d**)	20	65
(**1e**)	75	10
(**1f**)	58	25
(**1g**)	20	60
(**1h**)	65	12
(**1i**)	60	15

$ArCH_3$), 4.70—4.84 (d, 2 H, *J* 5Hz, CH_2^a), 4.95 (s, 2 H, OCH_2^b), 6.26—6.42 (t, 1 H, *J* 5Hz, H^c), and 6.80—7.85 (m, 8 H, ArH); *m/z* 320 (M^+) (Found: C, 75.2; H, 4.9. $C_{20}H_{16}O_4$ requires C, 75.0; H, 5.0%).

Compound (**6b**) (85%), m.p. 184 °C; $\lambda_{max.}$ 249s, 282w, 288w, and 344m nm; $\nu_{max.}$ 1 710, 1 638, 1 595, 1 225, and 1 150 cm^{-1}; δ 4.72—4.84 (d, 2 H, *J* 5.0 Hz, CH_2^a), 4.88 (s, 2 H, OCH_2^b), 6.22—6.43 (t, 1 H, *J* 5.0 Hz, H^c), and 6.76—7.80 (m, 8 H, ArH); *m/z* 342, 340 (M^+) 213 (base peak, *M* −4′-chlorophenoxy), 187, 185, and 157 *etc.* (Found: C, 66.8; H, 3.7. $C_{19}H_{13}ClO_4$ requires C, 66.96; H, 3.82%).

Compound (**6c**) (85%), m.p. 154 °C; $\lambda_{max.}$ 244, 292, 300, and 345 nm; $\nu_{max.}$ 1 715, 1 640, 1 235, and 1 150 cm^{-1}; δ 3.8 (s, 3 H, OCH_3), 4.72—4.84 (d, 2 H, *J* 5 Hz, CH_2^a), 4.88 (s, 2 H, OCH_2^b), 6.25—6.50 (t, 1 H, *J* 5 Hz, H^c), and 6.88—7.95 (m, 8 H, ArH); *m/z* 336 (M^+) (Found: C, 71.55; H, 4.6. $C_{20}H_{16}O_5$ requires C, 71.43; H, 4.76%).

Compound (**6d**) (80%), m.p. 124 °C; $\lambda_{max.}$ 242, 266, 275, and 345 nm; $\nu_{max.}$ 1 720, 1 638, 1 600, 1 235, and 1 115 cm^{-1}; δ 4.78—4.90 (d, 2 H, *J* 5 Hz, CH_2^a), 4.92 (s, 2 H, CH_2^b), 6.28—6.40 (t, 1 H, *J* 5 Hz, H^c), and 6.88—7.80 (m, 9 H, ArH); *m/z* 306 (M^+) (Found: C, 74.25; H, 4.75. $C_{19}H_{14}O_4$ requires C, 74.51; H, 4.58%).

Compound (**6e**) (85%), m.p. 190 °C; $\lambda_{max.}$ 242, 266, 275, and 345 nm; $\nu_{max.}$ 1 720, 1 595, 1 255, and 1 150 cm^{-1}; δ 4.80—4.92 (d, 2 H, *J* 5 Hz, CH_2^a), 5.08 (s, 2 H, CH_2^b), 6.28—6.44 (t, 1 H, *J* 5 Hz, H^c), and 6.96—8.32 (m, 8 H, ArH); *m/z* 351 (M^+) (Found: C, 65.15; H, 3.9. $C_{19}H_{13}NO_6$ requires C, 64.96; H, 3.70%).

Compound (**6f**) (88%), m.p. 140 °C; $\lambda_{max.}$ 235, 285, 294, and 345 nm; $\nu_{max.}$ 1 710, 1 640, 1 250, 1 200, and 1 155 cm^{-1}; δ 4.78—4.90 (d, 2 H, *J* 5 Hz, CH_2^a), 4.98 (s, 2 H, CH_2^b), 6.28—6.44 (t, 1 H, *J* 5 Hz, H^c), and 6.82—7.78 (m, 7 H, ArH); *m/z* 374 (M^+) and 376 (Found: C, 60.95, H, 3.0. $C_{19}H_{12}Cl_2O_4$ requires C, 60.80; H, 3.20%).

Compound (**6g**) (85%), m.p. 135 °C; $\lambda_{max.}$ 242, 278, 284, and 345 nm; $\nu_{max.}$ 1 720, 1 645, 1 230, and 1 160 cm^{-1}; δ 2.12 (s, 3 H, $ArCH_3$), 2.30 (s, 3 H, $ArCH_3$), 4.80—4.90 (d, 2 H, *J* 5 Hz, CH_2^a), 4.92 (s, 2 H, CH_2^b), 6.26—6.40 (t, 1 H, *J* 5 Hz, H^c), and 6.68—7.84 (m, 7 H, ArH); *m/z* 334 (M^+) (Found: C, 75.7; H, 5.6. $C_{21}H_{18}O_4$ requires C, 75.48; H, 5.38%).

Compound (**6h**) (80%), m.p. 125 °C; $\lambda_{max.}$ 242, 272, 280, and 345 nm; $\nu_{max.}$ 1 712, 1 600, 1 240, and 1 155 cm^{-1}; δ 2.10 (s, 3 H, $ArCH_3$), 4.78—4.90 (d, 2 H, *J* 5 Hz, CH_2^a), 4.92 (s, 2 H, CH_2^b), 6.26—6.40 (t, 1 H, *J* 5 Hz, H^c), and 6.76—7.80 (m, 8 H, ArH); *m/z* 320 (M^+) (Found: C, 75.2; H, 5.2. $C_{20}H_{16}O_4$ requires C, 75.0; H, 5.0%).

Compound (**6i**) (82%), m.p. 135 °C; $\lambda_{max.}$ 242, 275, 285, and 345 nm; $\nu_{max.}$ 1 710, 1 600, 1 235, and 1 142 cm^{-1}; δ 4.80—4.92 (d, 2 H, *J* 5 Hz, CH_2^a), 5.00 (s, 2 H, CH_2^b), 6.32—6.46 (t, 1 H, *J* 5 Hz, H^c), and 6.90—7.86 (m, 8 H, ArH); *m/z* 342 and 340 (M^+) (Found: C, 67.2; H, 4.1. $C_{19}H_{13}ClO_4$ requires C, 66.96; 3.82%).

Rearrangement of 3-(4-*Aryloxybut*-2-*ynyloxy*)[1]*benzopyran*-2-*one* (**1**) *in the Presence of a Radical Initiator*.—Compound (**1**) (0.2 g) in chlorobenzene (5 ml) was refluxed in the presence of azoisobutyronitrile (AIBN) (5 mg). The reaction was monitored by t.l.c. Complete conversion of starting material took place in 2.5 h. Chlorobenzene was removed under reduced pressure and the crude product was subjected to column chromatography over silica gel. Elution of the column with benzene–light petroleum (1:1) furnished the furanocoumarin (**10**) (70—80%) and the pyranocoumarin (**6**) (10—15%).

Compound (**10a**) [80%; along with *ca.* 10% of (**6a**)], m.p. 194 °C; $\lambda_{max.}$ 228s and 285s nm; $\nu_{max.}$ 1 735, 1 610, 1 576, 1 215, and 1 100 cm^{-1}; δ 2.33 (s, 3 H, $ArCH_3$), 2.56 (s, 3 H, 2-CH_3 furan ring), 5.15 (s, 2 H, OCH_2), 6.19 (AA′BB″, 2 H, *J* 8.3 Hz, 2′- and 6′-H), 7.15 (AA′BB″, 2 H, *J* 8.3 Hz, 3′- and 5′-H), 7.27 (ddd, 1 H, *J* 8.3, 7.8, and 1.9 Hz, 8-H), 7.42 (dd, 1 H, *J* 8.5, 1.9 Hz, 6-H), 7.45 (ddd, *J* 8.3, 8.3, 1.4 Hz, 7-H), and 7.85 (dd, 1 H, *J* 7.8, 1.4 Hz, 9-H). These ^{1}H n.m.r. assignments were established by homo-decoupling experiments; δ_C 12.4 (2-CH_3), 20.4 ($ArCH_3$), 60.5 (OCH_2), 113.9 (C-1), 114.9 (*ortho* C-2′, 6′), 117.4 (C-6), 124.6 (C-8), 124.8 (C-9), 129.5 (C-7), 130.1 (*meta* C-3′, 5′) 131.1 (*para* C-4′), 133.1 (C-3b), 136.5 (C-3e), 152.4 (C-5a), 155.7 (*ipso* C-1′), 160.0 (C-2 and C-4); *m/z* 320 (M^+), 213 (base peak, *M* −4′-cresyloxy), 185, 157 *etc.* (Found C, 75.3; H, 5.1. $C_{20}H_{16}O_4$ requires C, 75.0; H, 5.0%).

Compound (**10b**) (75%) [along with 12% of (**6b**)], m.p. 174 °C; $\lambda_{max.}$ 228s and 285s nm; $\nu_{max.}$ 1 725, 1 615, 1 570, 1 210, and 1 098 cm^{-1}; δ 2.54 (s, 3 H, 2-CH_3), 5.16 (s, 2 H, OCH_2), and 6.88—7.86 (m, 8 H, ArH); *m/z* 342, 340 (M^+), 213 (base peak), 185, and 157 *etc.* (Found C, 66.75; H, 3.6. $C_{19}H_{13}ClO_4$ requires C, 66.96; H, 3.82%).

Compound (**10c**) (70%) [along with 15% of (**6c**)], m.p. 160 °C; $\lambda_{max.}$ 226 and 288 nm; $\nu_{max.}$ 1 725, 1 215, and 1 110 cm^{-1}; δ 2.54 (s, 3 H, 2-CH_3), 3.80 (s, 3 H, OCH_3), 5.16 (s, 2 H, OCH_2), and 6.90—7.96 (m, 8 H, ArH); *m/z* 336 (M^+) (Found: C, 71.6; H, 4.9. $C_{20}H_{16}O_5$ requires C, 71.43; H, 4.76%).

Compound (**10d**) (72%) [along with 10% of (**6d**)], m.p. 162 °C; $\lambda_{max.}$ 225 and 275 nm; $\nu_{max.}$ 1 730, 1 215, and 1 100 cm^{-1}; δ 2.58 (s, 3 H, 2-CH_3), 5.21 (s, 2 H, OCH_2), and 6.98—7.94 (m, 9 H, ArH); *m/z* 306 (M^+) (Found: C, 74.2; H, 4.75. $C_{19}H_{14}O_4$ requires C, 74.51; H, 4.58%).

Compound (**10e**) (74%) [along with 12% of (**6e**)], m.p. 230 °C; $\lambda_{max.}$ 226 and 300 nm; $\nu_{max.}$ 1 725, 1 235, and 1 112 cm^{-1}; δ 2.64 (s, 3 H, 2-CH_3), 5.32 (s, 2 H, OCH_2), and 7.04—8.36 (m, 8 H, ArH); *m/z* 351 (M^+) (Found: C, 65.25; H, 3.9. $C_{19}H_{13}NO_6$ requires C, 64.96; H, 3.70%).

Compound (**10f**) (70%) [along with 10% of (**6f**)], m.p. 198 °C; $\lambda_{max.}$ 228, 234, and 285 nm; $\nu_{max.}$ 1 724, 1 575, 1 240, and 1 115 cm^{-1}; δ 2.56 (s, 3 H, 2-CH_3), 5.28 (s, 2 H, OCH_2), and 6.92—8.00 (m, 7 H, ArH); *m/z* 374 (M^+), 376 (Found: C, 61.05; H, 3.05. $C_{19}H_{12}Cl_2O_4$ requires C, 60.80; H, 3.20%).

Compound (**10g**) (78%) [along with 10% of (**6g**)], m.p. 180 °C; $\lambda_{max.}$ 225 and 285 nm; $\nu_{max.}$ 1 735, 1 615, 1 580 1 225, and 1 100 cm^{-1}; δ 2.10 (s, 3 H, $ArCH_3$), 2.32 (s, 3 H, $ArCH_3$), 2.58 (s, 3 H, 2-CH_3), 5.16 (s, 2 H, OCH_2), and 6.82—7.96 (m, 7 H, ArH); *m/z* 334 (M^+) (Found: C, 75.3; H, 5.15. $C_{21}H_{18}O_4$ requires C, 75.45; H, 5.38%).

Compound (**10h**) (75%) [also 12% of (**6h**)], m.p. 188 °C; $\lambda_{max.}$ 228 and 275 nm; $\nu_{max.}$ 1 735, 1 210, and 1 100 cm^{-1}; δ 2.12 (s, 3 H, $ArCH_3$), 2.56 (s, 3 H, 2-CH_3), 5.20 (s, 2 H, OCH_2), and 6.96—7.96 (m, 8 H, ArH); *m/z* 320 (M^+) (Found: C, 74.8; H, 5.15. $C_{20}H_{16}O_4$ requires C, 75.0; H, 5.0%).

Compound (**10i**) (70%) [also 15% of (**6i**)], $\lambda_{max.}$ 226 and 280 nm; $\nu_{max.}$ 1 725, 1 210, and 1 098 cm^{-1}; δ 2.56 (s, 3 H, 2-CH_3), 5.30 (s, 2 H, OCH_2), and 7.00—8.08 (m, 8 H, ArH); *m/z* 342 and 340 (M^+) (Found: C, 67.1; H, 3.55. $C_{19}H_{13}ClO_4$ requires C, 66.96; H, 3.82%).

Rearrangement of Compound (**1**) *in* N,N-*Diethylaniline: General Procedure for the Synthesis of* 1-*Aryloxymethyl*-2-*methylfurano*[2,3-c][1]*benzopyran*-4-*one*.—Compound (**1**) (0.2 g) in *N*,*N*-diethylaniline (5 ml) was heated in an oil-bath at 140 °C. T.l.c. indicated the complete conversion of starting material (**1**) in 4 h. The reaction mixture was cooled and poured into ice-cold 6M hydrochloric acid. Crude solid separated and this was extracted with chloroform. The extract was washed with dilute hydrochloric acid, brine, and water, and dried (Na_2SO_4). Evaporation gave the crude product which was chromatographed over silica gel. Elution of the column with benzene–petroleum (1:1) gave compound (**10a**—**i**); (**10a**) (90%), m.p. 194 °C; (**10b**) (85%), m.p. 174 °C; (**10c**) (80%), m.p. 160 °C; (**10d**) (85%), m.p. 162 °C; (**10e**) (80%), m.p. 230 °C; (**10f**) (82%), m.p. 198 °C; (**10g**) (88%), m.p. 180 °C; (**10h**) (85%), m.p. 188 °C; (**10i**) (80%), m.p. 190 °C.

Rearrangement of Compound (**1a**) *in Polyethylene Glycol*.—Compound (**1a**) (0.2 g) in polyethylene glycol-600 (5 ml) was heated at 140 °C for 4 h. The reaction mixture was cooled and poured into water (50 ml) and the solid which separated was extracted with chloroform. The organic layer was washed with water, dried (Na_2SO_4), and evaporated and the residue recrystallised from chloroform–light petroleum to give exclusively (**10a**) (0.18 g, 90%), m.p. 194 °C.

Rearrangement of Compound (**1a**) *in Pyridine*.—Compound (**1a**) (0.2 g) was refluxed in pyridine (5 ml) at 116 °C for 20 h. The reaction mixture was cooled and poured into ice-cold 6M hydrochloric acid. The crude product which separated was extracted with chloroform, and the extract washed successively with dilute HCl, brine, and water and then dried (Na_2SO_4). Removal of chloroform and chromatography of the residue over silica gel furnished compound (**10a**) (80%) along with unchanged starting material (20%).

Rearrangement of Compound (**1a**) *in Ethylbenzene in the Presence of Toluene*-p-*sulphonic Acid*.—Compound (**1a**) (0.2 g) was refluxed in ethylbenzene (5 ml) with toluene-*p*-sulphonic acid (0.02 g) for 4 h. T.l.c. indicated complete conversion of starting material and quantitative formation of product (**10a**). The reaction mixture was cooled, chloroform added, and the solution washed with aqueous sodium carbonate, brine, and water and then dried (Na_2SO_4). Removal of solvent *in vacuo* and column chromatography over silica gel furnished product (**10a**) (0.18 g, 90%), m.p. 194 °C.

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