Ring Closure to Ynone Systems: 5- and 6-*endo*- and -*exo*-*dig* Modes

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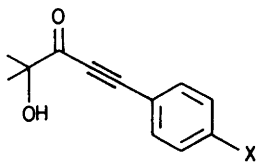
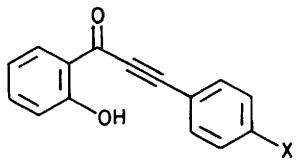
The rates of cyclisation of 2-hydroxy-2-methyl-5-arylpent-4-yn-3-ones in trifluoroacetic acid are reported. An approximate ρ value of −4.0 (using σ^+) and a kinetic isotope effect, K_{TFA}/K_{TFA-d}, of 4.2 are observed, which suggest that the reaction proceeds *via* rate-limiting triple-bond protonation and does not entail carbonyl protonation along the reaction co-ordinate. The base-catalysed ring closure occurs *via* the vinylic carbanion. A similar mechanistic picture appears to be involved in the cyclisation of 1-(2-hydroxyphenyl)-3-arylprop-2-yn-1-ones which yield a mixture of flavone and aurone in base, whilst in acid only the flavone is observed. In contrast with recent theoretical studies, the base-catalysed results appear to conform to Baldwin's original proposal of acute-angle approach of a nucleophile to a triple bond.

Publications [1,2] on ring closures by intramolecular nucleophilic attack on triple bonds encourage report of our work in this area, which systematically followed our previous studies [3–5] on *trig* modes of cyclisation. As before, we believed study of electron-demand variation, in this case by substituent change in the β-phenyl ring of compounds (**1a–c**) and (**2a–c**), might yield mechanistic information.



(**1**) **a**; X = H
b; X = Me
c; X = OMe



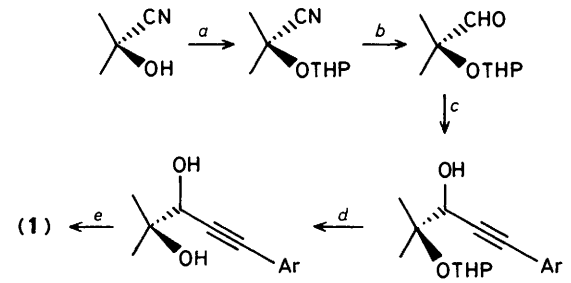
(**2**) **a**; X = H
b; X = Me
c; X = OMe

Questions of angle of approach of the nucleophile to the triple bond and the degree of involvement of the carbonyl group along the reaction pathway were of interest. According to stereoelectronic principles [6] the first intermediate generated in the base-catalysed addition to a conjugated acetylenic ketone (ynone) should be an allenic enolate, subsequent protonation producing the corresponding α,β-unsaturated ketone (enone). Similarly, the acid-catalysed Michael-addition mechanism would proceed through an allenic enol intermediate. Since the allene functionality cannot be accommodated without considerable strain in rings smaller than cyclo-octane [7,8] the intramolecular ynone conjugate addition to produce smaller rings is not expected to take place. Recent experimental reports, however, have indicated that small rings are readily formed;[1,2] thus a mechanistic study of such reactions appeared relevant.

Results and Discussion

2-Hydroxy-2-methyl-5-arylpent-4-yn-3-ones (**1a–c**) were prepared [9] as illustrated in Scheme 1. Ring closure rates of (**1a–c**) in trifluoroacetic acid (TFA) at 35 °C were measured by monitoring changes in the proton n.m.r. spectra following procedures previously described.[5]

The pseudo-first-order rate constants ($k/10^{-6}$ s^{-1}) were as follows: (**1a**) 6.85, (**1b**) 117, (**1c**) 9 630. Using σ^+ values, these indicate a ρ value of −4.0 (correlation coefficient 1.000). This is not of great significance with only three points, but these



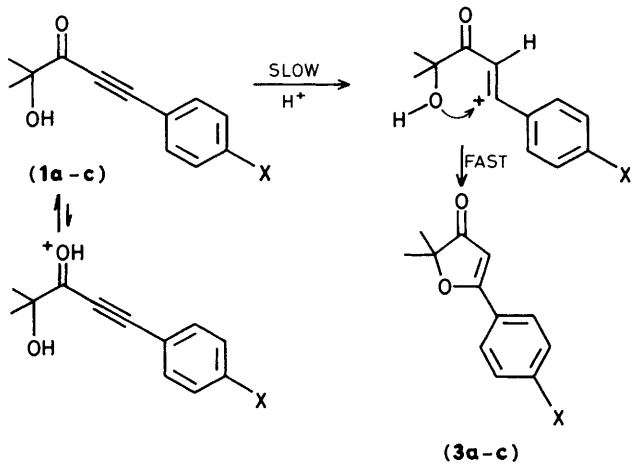
Scheme 1. Preparative pathway for 2-hydroxy-2-methyl-5-arylpent-4-yn-3-ones (**1a–c**). *Reagents:* (*a*) DHP–H^+; (*b*) (*i*) $LiAlH(OEt)_3$ (*ii*) H^+; (*c*) (*i*) ArC≡CLi (*ii*) H^+; (*d*) DOWEX 50W–MeOH; (*e*) MnO_2–CH_2Cl_2.

compounds require quite lengthy and expensive synthesis. The result, however, may be of sufficient accuracy to be used in subsequent arguments.

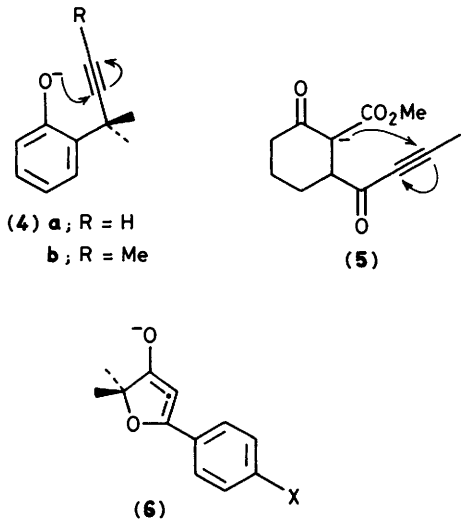
By following the reaction in [^{2}H]TFA, a solvent kinetic isotope effect (KIE) of 4.19 was found for (**1c**). Similar ρ and KIE values have been observed [10–17] in acid-catalysed hydrations, which proceed *via* rate-limiting proton transfers to give a vinyl carbenium ion, which then rapidly undergoes nucleophilic attack. Thus, phenylbenzoylacetylene has a pseudo-first-order rate constant for hydration in aqueous sulphuric acid of $H_0 = -3$ of 1.76×10^{-6} at 35 °C.† This H_0 value corresponds to the effective H_0 value of pure TFA,[18] for which there will be no appreciable protonation of the carbonyl-group oxygen atom.[15,19] ρ and KIE values for the substituted series are −4.2 and 2.0 to 3.9, respectively.[15] A KIE of 4.33 has been reported for the rate of addition of neat TFA/[^{2}H]TFA to (*E*)but-2-ene.[20] These comparisons suggest the cyclisation of (**1a–c**) proceeds by rate-limiting protonation of the triple bond. Bending of the vinyl carbenium ion to which there is only a low energy barrier [21–23] allows overlap of the oxygen lone pair of the nucleophile and vacant sp^2 orbital in the second step. The carbonyl group is thus not involved in conjugative interaction with the reacting centre at any point along the reaction co-ordinate (Scheme 2).

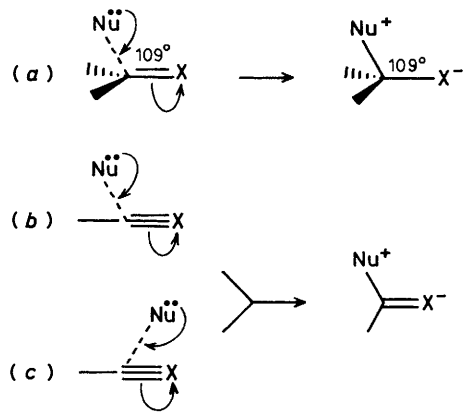
Previous workers [2,24] have demonstrated the facile ring closure in base of related systems (**4**) and (**5**). This strongly suggests that the ring closure of (**1a**) in base to yield bullatenone [9] is also best described as proceeding through an intermediate carbanion, for which carbonyl-group conjugate

† Derived from calculated rates at 25 and 44.6 °C from reference 15.



Scheme 2. Ring-closure reaction pathway for 2-hydroxy-2-methyl-5-arylpent-4-yn-3-ones.



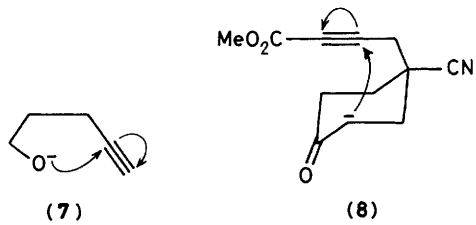


Scheme 3. Angles of approach of a nucleophile to (*a*) the double bond (109°); (*b*) the triple bond (obtuse angle); (*c*) the triple bond (acute angle).

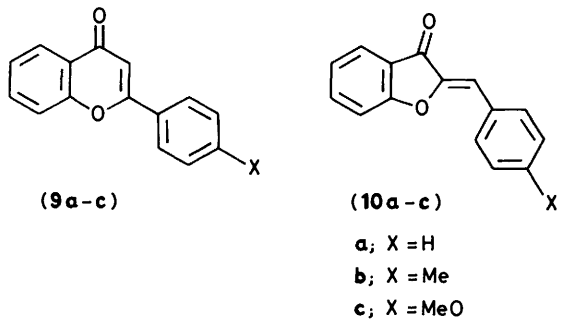
stabilisation is not required nor available, since it would require the impossibly strained allenic-enolate intermediate (**6**). Alternatively, attack on the π-bond orthogonal to the carbonyl group is sterically feasible, the increasing electron density residing in the p-orbital orthogonal to the carbonyl π-system.[2]

These base-catalysed reactions illustrate the controversy over the question of optimum approach to a triple bond by a nucleophile (Scheme 3).

It was originally stated[25] that ring closures to triple bonds occur preferentially in the *endo* mode and through an acute approach trajectory of about 60°. However, it has since been observed that both *endo* and *exo* pathways are common with a predominance for the latter,[26] while several theoretical studies indicate that the favoured path of approach of a nucleophile to a triple bond is at an obtuse angle of 120–127°.[27–32] Most intriguingly, Trost[33] has questioned the acute approach to the triple bond on the basis of the observation of the reactions shown in structures (**7**) and (**8**), although these 5-*exo-dig* routes do appear to involve an acute angle approach. Similarly, models reveal that base-catalysed ring closures of (**1**), (**4**), and (**5**) are described by an acute-angle trajectory.



With this point in mind, we turned our attention to ring closures of 1-(2-hydroxyphenyl)-3-arylprop-2-yn-1-ones (**2a–c**) to yield flavones (**9a–c**) and aurones (**10a–c**). Cyclisation of ynone systems of type (**2**) (but with methyl groups substituted in the benzoyl ring and no β-ring substituents) is reported to give



varying amounts of the corresponding flavones and aurones, depending on conditions,[1] indicating competition between 5-*exo-dig* and 6-*endo-dig* modes. Cyclisation was stated not to occur in acid media[1] (hydrogen chloride in EtOH), although it was later noted that a chromone was produced in toluene-*p*-sulphonic acid.[34] These conclusions conflict to some extent with previous reports: Okajiima[35] reported that such ring closures in H_3PO_4–AcOH gave exclusively the flavones whilst in ethanolic sodium hydroxide (8% NaOH in 95% EtOH) they yielded the appropriate aurones. However, it has been independently observed that the base-catalysed cyclisation of (**2a**) affords the flavone only.[36]

In the present studies acid-catalysed cyclisation was achieved in TFA to give the corresponding flavones (**9a–c**). Formation of (**9c**) in TFA at 20 °C over 18 h occurs readily and in high yield (89%) whilst no formation of (**9a**) or (**9b**) is observed under the same conditions. Reflux in TFA over 48 h does yield exclusively (**9b**) and for the unsubstituted derivative under the same conditions, (**9a**) is observed with a small percentage of starting material (21%). It hence seems likely that the cyclisation is more rapid with electron-donating substituents and that the ρ value is large and negative, although, the close similarity of the proton n.m.r. spectra of (**2**) and (**9**) in TFA prevented rate-constant

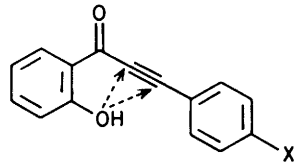
Table. Ring closure of ynones (**2a–c**) in base.

Compd.	Conditions[a]	Yield (%)	Flavone (%)	Aurone (%)
(**2a**)	1.1 equiv. NaOMe MeOH, 2 h, r.t.	89.6	59.9	40.1
(**2a**)	10 equiv. NaOMe MeOH, 2 h, r.t.	86.3	59.0	41.0
(**2b**)	1.1 equiv. NaOMe MeOH, 2 h, r.t.	91.3	70.0	30.0
(**2b**)	1.1 equiv. NaOMe MeOH, 12 h, r.t.	87.6	70.8	29.2
(**2c**)	1.1 equiv. NaOMe MeOH, 2 h, r.t.	95.1	73.9	26.1

[a] 1.5 mmol of (**2a–c**) were allowed to react in 10 cm^3 of solvent.

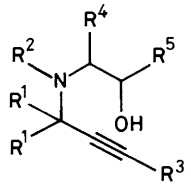
determination. This is consistent with the rate-determining protonation of carbon mechanism shown for the ynones (**1a–c**).

For base-catalysed ring closures of (**2a–c**) the results in the Table again show the propensity for a nucleophile poised centrally, above a carbon–carbon triple bond, to attack at either end, in both forms (*5-exo-dig*, *6-endo-dig*) by an acute angle of attack (**11**), as indicated by molecular models. The production of the aurone (**10**), as well as flavone (**9**), again indicates that activation of the triple bond by resonance withdrawal by the carbonyl group is not required. This is also the case with reaction (**4**).[24] Cyclisation of (**4**) and (**12**)[37] indicates the influence of the inductive effect of substituents adjacent to the triple bond. Ring closure of the unsubstituted compound (**4a**) in base probably proceeds *via* rate-determining ring closure to give

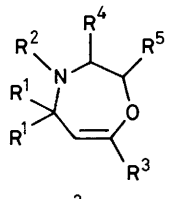


(**11**)

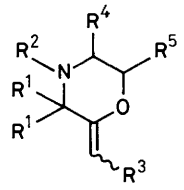
a vinyl carbanion which rapidly acquires a proton, whilst the methyl derivative (**4b**) shows general acid acatalysis and exhibits a small solvent deuterium isotope effect.[24] Similarly, the base-catalysed cyclisation of 3-alkyl-*N*-(β-hydroxyethyl)-1,1-dialkylprop-2-ynylamines (**12**) yields either the seven-membered 2,3,4,5-tetrahydro-1,4-oxazepines (**13**) or the six-membered 2-methylenemorpholines (**14**), the controlling factor



(**12**)



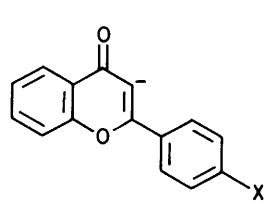
(**13**) R^3 = alkyl



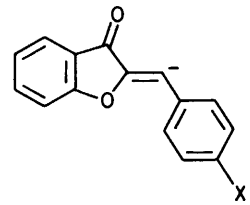
(**14**) R^3 = Ph, Cl, SMe

being the nature of the alkyne substituent R^3. Inductively electron-donating groups lead to seven-membered rings while electron-withdrawing substituents give the six-membered rings.[37]

These results[24,37] accord well with ours, and suggest that cyclisation occurs *via* the respective vinylic carbanion precursors (**15**) and (**16**) (although a concerted mechanism is not completely ruled out). The more inductively electron-donating the nature of the β-phenyl ring, the less stable is the carbanion (**16**) and hence less aurone is seen in the product mixture. The possibility of equilibrium formation of aurone is discounted by the observation firstly of the same product ratios over varying times of reactions and secondly of the stability of the aurone (**10a**) to the same basic conditions as employed in the ring closure. Flavones have been observed not to ring-open under various basic conditions.[38,39]



(**15**)



(**16**)

It has been thought that in electronically unbiased cyclisations the *exo-dig* closure is preferred.[24,40] In this particular case the inductive effect of the carbonyl group should work in favour of flavone production. Variation of the nature of the β-phenyl ring tends to suggest that there is indeed a competitive balance, although the effect of substituents is only small. A recent theoretical study[41] has shown that acetylenes undergo nucleophilic attack far more readily when bent than when linear. The queries over the preferential mode of attack may thus be a consequence of a greater degree of flexibility than previously thought.

Experimental

General.—I.r. spectra were recorded using Perkin–Elmer 297 and 298 spectrophotometers. ^{1}H N.m.r. spectra were recorded at 60 MHz using a JEOL PMX 60 SI instrument and at 400 MHz using a JEOL GX 400. Unless otherwise stated, all n.m.r. spectra were recorded as solutions in deuteriochloroform at 60 MHz. Chemical shifts are quoted in ppm downfield from internal tetramethylsilane. Melting points were determined on a Reichert model Kofler hot-stage apparatus and are uncorrected. Yields are not optimised.

Kinetics.—The kinetics of cyclisation of 2-hydroxy-2-methyl-5-arylpent-4-yn-3-ones (**1a–c**) were made at 35 °C in TFA using 10% w/v solutions. The reaction was monitored by changes in the proton n.m.r. spectrum at 60 MHz with time: the *gem*-dimethyl groups in the ring-closed compound resonate at lower field than in the hydroxy-ynone and the vinylic proton of the product appears as a singlet *ca.* δ 6. The ring-closed products were isolated from the reaction mixture by quenching and chromatography.

Product Determination.—The acid and base solutions of 1-(2-hydroxyphenyl)-3-arylprop-2-yn-1-ones (**2a–c**) were quenched with Na_2CO_3(aq)–ice and $HCl_{(aq)}$–ice, respectively. Extraction with ether, drying ($MgSO_4$), and evaporation afforded a pale yellow solid which was subjected to high-field ^{1}H n.m.r. spectroscopy ($CDCl_3$). Integration at 400 MHz of the resonances due to the vinylic protons of the products which

appear upfield of the aromatic signals allows the determination of the ratio of flavone (**9**) to aurone (**10**). Assignment of the vinylic peaks to the appropriate isomer, flavone, or aurone, was established by comparison with the spectra of the respective compounds prepared separately. These were shown to be identical with the products separated from the reaction mixture by column or thin-layer chromatography. Reaction of aurone (**10a**) (0.170 g, 0.77 mmol) with sodium methoxide (0.46 g, 0.85 mmol) in methanol (5 cm^3) was worked up in an analogous manner. Neutral aliquots taken at 10 min, 2 h, and 48 h were subjected to t.l.c. and high-field n.m.r. spectroscopy and indicated no ynone (**2a**) or flavone (**9a**) formation.

Physical and spectroscopic properties of the key compounds are given below.

Substituted Phenylacetylenes.—The required substituted phenylacetylenes were prepared following literature procedures.[42,43] Commercial phenylacetylene was used as required without further purification.

2-*Hydroxy*-2-*methyl*-5-*arylpent*-4-*yn*-3-*ones* (**1a–c**).—Compounds (**1a–c**) were prepared following the method of Baldwin *et al.*[9] with only slight modifications.

2-*Hydroxy*-2-*methyl*-5-*phenylpent*-4-*yn*-3-*one* (**1a**): (74%) $\nu_{max.}$(film) 3 450 (OH), 2 220 (C≡C), and 1 668 cm^{-1} (CO); δ 1.56 (6 H, s, CH_3), 3.56 (1 H, br, OH), 3.82 (3 H, s, OCH_3), and 6.70–7.68 (4 H, m, ArH).

2-*Hydroxy*-2-*methyl*-5-(4-*methylphenyl*)*pent*-4-*yn*-3-*one* (**1b**): (90%) $\nu_{max.}$(film) 3 470 (OH), 2 200 (C≡C), and 1 668 cm^{-1} (CO); δ 1.52 (6 H, s, CH_3), 2.36 (3 H, s, $ArCH_3$), *ca.* 3.68 (1 H, br, OH), and 7.04–7.60 (4 H, m, ArH).

2-*Hydroxy*-5-(4-*methoxyphenyl*)-2-*methylpent*-4-*yn*-3-*one* (**1c**): (68%) $\nu_{max.}$(film) 3 460 (OH), 2 198 (C≡C), and 1 660 cm^{-1} (CO); δ 1.52 (6 H, s, CH_3), 3.68 (1 H, br, OH), 3.82 (3 H, s, OCH_3), and 6.70–7.68 (4 H, m, ArH).

2,2-*Dimethyl*-5-*phenylfuran*-3(2H)-*one* (bullatenone) (**3a**).—(73%) m.p. 67–68 °C (from hexane) (lit.,[9] 67.5–68.5 °C); ν_{CO} 1 708 cm^{-1}; δ 1.50 (6 H, s, CH_3), 5.96 (1 H, s, COCH), and 7.40–7.90 (5 H, m, ArH).

2,2-*Dimethyl*-5-(p-*tolyl*)*furan*-3(2H)-*one* (**3b**): (76%) m.p. 64–65 °C (from hexane) (Found: C, 77.0; H, 6.9. $C_{13}H_{14}O_2$ requires C, 77.19; H, 6.99%); ν_{CO} 1 708 cm^{-1}; δ 1.48 (6 H, s, CH_3), 2.40 (3 H, s, $ArCH_3$), 5.88 (1 H, s, COCH), and 7.08–7.80 (4 H, m, ArH).

5-*Methoxyphenyl*-2,2-*dimethylfuran*-3(2H)-*one* (**3c**): (93%) m.p. 96–97.5 °C (from hexane) (Found: C, 71.35; H, 6.45. $C_{13}H_{14}O_3$ requires C, 71.53; H, 6.41%); ν_{CO} 1 688 cm^{-1}; δ 1.48 (6 H, s, CH_3), 3.86 (3 H, s, OCH_3), 5.82 (1 H, s, COCH), and 6.84–7.88 (4 H, m, ArH).

1-(2-*Hydroxyphenyl*)-3-*arylprop*-2-*yn*-1-*ones* (**2a–c**).—Compounds (**2a–c**) were prepared by a modification of the method of Okajiima.[35]

1-(2-*Hydroxyphenyl*)-3-*phenylprop*-2-*yn*-1-*ol*: (79%) m.p. 85 °C [from ether–light petroleum (40–60 °C)] (lit.,[35] 86 °C); $\nu_{max.}$ 3 500br, 3 365 (OH), and 2 250 cm^{-1} (C≡C); δ *ca.* 3.0 (1 H, br, CHO*H*), 5.82 (1 H, s, C*H*OH), and 6.66–7.70 (10 H, m, ArH, and ArOH).

1-(2-*Hydroxyphenyl*)-3-(p-*tolyl*)*prop*-2-*yn*-1-*ol*: (75%) m.p. 100–102 °C (from ethyl acetate–hexane); $\nu_{max.}$ 3 560, 3 340 (OH), and 2 240 cm^{-1} (C≡C); δ 2.32 (3 H, s, CH_3), 3.04 (1 H, br, CHOH), 5.84 (1 H, s, CHOH), and 6.68–7.60 (9 H, m, ArH and ArOH).

1-(2-*Hydroxyphenyl*)-3-(4-*methoxyphenyl*)*prop*-2-*yn*-1-*ol*: (82%) m.p. 90 °C (from hexane) (lit.,[35] 90 °C); $\nu_{max.}$ 3 558, 3 400 (OH), and 2 256 and 2 225 cm^{-1} (C≡C); δ 3.5 (1 H, br, CHOH), 3.69 (3 H, s, OCH_3), 5.84 (1 H, s, CHOH), and 6.58–7.72 (9 H, m, ArH and ArOH).

1-(2-*Hydroxyphenyl*)-3-*phenylprop*-2-*yn*-1-*one* (**2a**): (95%) m.p. 64–65 °C [from light petroleum (60–80 °C)] (lit.,[35] 65–66 °C); $\nu_{max.}$ 2 210 (C≡C) and 1 630 cm^{-1} (CO); δ 6.76–8.20 (9 H, m, ArH), and 11.75 (1 H, s, ArOH).

1-(2-*Hydroxyphenyl*)-3-(4-*methylphenyl*)*prop*-2-*yn*-1-*one* (**2b**): (89%) m.p. 94–96 °C (from hexane) (Found: C, 81.30; H, 5.10. $C_{16}H_{12}O_2$ requires C, 81.33; H, 5.13%); $\nu_{max.}$ 2 200 (C≡C) and 1 628 cm^{-1} (CO); δ 2.36 (3 H, s, CH_3), 6.78–8.20 (8 H, m, ArH), and 11.82 (1 H, s, ArOH).

1-(2-*Hydroxyphenyl*)-3-(4-*methoxyphenyl*)*prop*-2-*yn*-1-*one* (**2c**), (62%) m.p. 79–80 °C (from hexane) (lit.,[35] 80 °C); $\nu_{max.}$ 2 198, 2 183 (C≡C) and 1 618 cm^{-1} (CO); δ 3.76 (3 H, s, OCH_3), 6.72–8.26 (8 H, m, ArH), and 11.83 (1 H, s, ArOH).

Flavones (**9a–c**) *and Aurones* (**10a–c**).—Compounds (**9a–c**) and (**10a–c**) were prepared by the reported procedure[44] and a modification of the Wheeler aurone synthesis,[45] respectively.

Flavone (**9a**);* (63%) m.p. 99 °C (lit.,[44] 96–97 °C); ν_{CO} 1 648 cm^{-1}; δ(400 MHz) 6.75 (1 H, s, COCH) and 6.90–8.24 (9 H, m, ArH).

4′-*Methylflavone* (**9b**), (57%), m.p. 116–117.5 °C (Found: C, 81.20; H, 5.10. $C_{16}H_{12}O_2$ requires: C, 81.33; H, 5.13%); ν_{CO} 1 640 cm^{-1}; δ(400 MHz) 2.39 (3 H, s, CH_3), 6.75 (1 H, s, COCH), and 7.26–8.28 (8 H, m, ArH).

4′-*Methoxyflavone* (**9c**), (53%), m.p. 160–161 °C (lit.,[46] 157–158 °C); ν_{CO} 1 650 cm^{-1}; δ(400 MHz) 3.89 (3 H, s, OCH_3), 6.75 (1 H, s, COCH), and 7.01–8.24 (9 H, m, ArH).

Aurone (**10a**):† (71%) m.p. 110 °C (lit.,[47] 110 °C); ν_{CO} 1 710 cm^{-1}; δ(400 MHz) 6.87 (1 H, s, C=CH), and 7.15–7.91 (9 H, m, ArH).

4′-*Methylaurone* (**10b**): (20%), m.p. 94 °C (Found: C, 81.30; H, 5.15. $C_{16}H_{12}O_2$ requires C, 81.33; H, 5.13%); ν_{CO} 1 710 cm^{-1}; δ(400 MHz) 2.40 (3 H, s, CH_3), 6.84 (1 H, s, C=CH) and 7.06–7.92 (8 H, m, ArH).

4′-*Methoxyaurone* (**10c**): (64%) m.p. 134–135 °C (lit.,[45] 135–136 °C); ν_{CO} 1 708 cm^{-1}; δ(400 MHz) 3.86 (3 H, s, OCH_3), 6.88 (1 H, s, C=CH), and 6.96–8.23 (8 H, m, ArH).

* 2-Phenylchromen-4-one.

† 2-Benzylidenebenzo[*b*]furan-3(2*H*)-one.

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