Addition of Nitrogen-, Oxygen-, and Sulphur-containing Nucleophiles to Aryl Ethynyl Ketones

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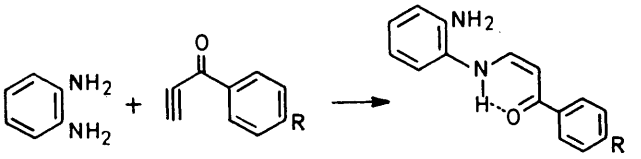
Addition of some nitrogen-, oxygen-, and sulphur-containing nucleophiles to the aryl ethynyl ketones (1)—(4) has been examined. Addition of *o*-phenylenediamine and *o*-aminophenol yielded the corresponding *cis*-β-aminovinyl ketones (5)—(7) and (10)—(12). Addition of secondary amines (morpholine and piperidine) yielded the *trans*-β-aminovinyl ketones (13)—(20). Catechol reacted with aryl ethynyl ketones to furnish 1,3-benzodioxole derivatives (21)—(23), salicylic acid and 2-hydroxy-3-naphthoic acid to give the oxalactones (24)—(30). However, 2-hydroxy-1-naphthoic acid yielded a mixture of the oxalactones (31)—(33) and 3-naphthoxy-1-arylprop-2-enones (35) and (36). Similarly thiosalicylic acid gave the corresponding thialactones (40) and (41) as addition products. Salicylaldehyde reacted with ethynyl phenyl ketone to give 3-benzoylchrom-3-en-2-ol (38).

THE cycloaddition [1,2] and nucleophilic addition [3-5] reactions of acetylenic esters have been extensively investigated and are well documented. Nucleophilic additions to acetylenic esters have been successfully employed in the synthesis of several interesting heterocyclic systems.[4,5] Acetylenic ketones, like the esters, are also vulnerable to attack at many sites and several examples of cycloadditions [6] and nucleophilic additions [7] have been reported. A recent review summarises the current status of ethynyl ketone chemistry.[8] In the present study, the addition of various nucleophiles to aryl ethynyl ketones has been investigated with the aim of delineating the stereochemistry of addition as well as the nature of the products formed. Furthermore it was anticipated that such nucleophilic additions to ethynyl ketones would either lead directly to interesting heterocyclic compounds or provide easy access to suitable precursors which can be transformed into heterocycles in subsequent steps. We report the results of addition of several mono- and bi-functional nucleophiles containing nitrogen, oxygen, and sulphur to aryl ethynyl ketones (1)—(4).

Nitrogen-containing Nucleophiles.—The reactions of some simple primary and secondary amines with aryl ethynyl ketones have been studied previously.[7a,b] McMullen and Stirling [7b] have shown with the aid of n.m.r. spectroscopy that primary amines on reaction with ethynyl phenyl ketone give an equilibrium mixture of *cis*- and *trans*-enamines, whose composition is solvent dependent.

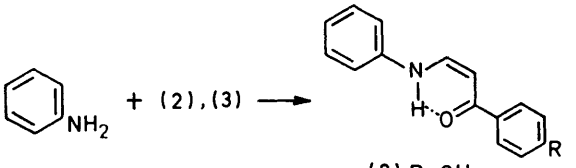
The addition of suitably *o*-substituted aromatic primary amines which could be elaborated in subsequent steps to heterocyclic compounds has not been explored very well. In the present case we have examined the addition of *o*-phenylenediamine and *o*-aminophenol to aryl ethynyl ketones (1)—(3). The structure of the crystalline 1 : 1 adducts (5)—(7) of *o*-phenylenediamine and aryl ethynyl ketones (1)—(3) follows from an examination of their i.r. and n.m.r. spectra. The *cis*-stereochemistry of the double bond in 3-*o*-aminophenylamino-1-arylprop-2-enones (5)—(7) follows from the coupling constant (J 8 Hz) of the olefinic protons at C-1 and -2. For comparison purposes, we also prepared the aniline adducts (8) and (9) of ethynyl ketones (2) and (3) and they too showed a coupling of 8 Hz between *cis*-olefinic protons. Further evidence for the presence of a primary amino group in compounds (5)—(7) was provided by a positive diazo coupling test. The formation of the *cis*-product can be ascribed to the stability imparted due to intramolecular hydrogen bonding in the enamine-ketones (5)—(7).



(1) R = H
(2) R = CH_3
(3) R = OCH_3
(4) R = Cl

(5) R = H
(6) R = CH_3
(7) R = OCH_3

SCHEME 1



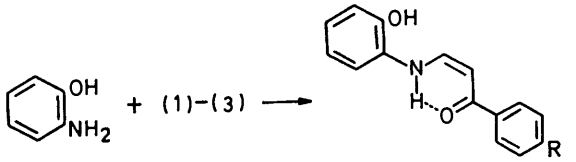
(8) R = CH_3
(9) R = OCH_3

SCHEME 2

While this work was in progress Ried and Konig [9] reported the formation of 1,5-benzodiazepines by the reaction of *o*-phenylenediamine with 1,3-diphenylprop-2-ynone. However, in our hands the enamine ketones (5)—(7) did not cyclise to give 1,5-benzodiazepine derivatives under a variety of conditions. The anomaly between the *o*-phenylenediamine adducts of terminal aryl ethynyl ketones and 1,3-diphenylprop-2-ynone cannot be explained satisfactorily.

Likewise *o*-aminophenol also yielded only open chain 1 : 1 adducts (10—(12) with ethynyl ketones (1)—(3). The *cis*-stereochemistry of the double bond in the propenones (10)—(12) follows from the coupling constant

(J 8 Hz) of olefinic protons at C-1 and -2. This also is in contrast with the reported formation of 1,5-benzothiazepine derivatives in the reaction of 1,3-diphenylprop-2-ynones with *o*-aminothiophenol.[9]

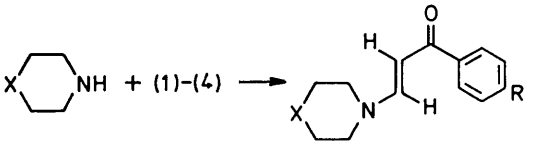


(10) R = H
(11) R = CH_3
(12) R = OCH_3

SCHEME 3

In contrast to the addition of primary amines, the addition of secondary amines to activated acetylenes favours the formation of *trans*-isomers due to the opposing dipoles of the activating group and the C–N bond and also by the absence of non-bonded interactions between the activating groups and the dialkylamino groups. We have now prepared a number of secondary amine (piperidine and morpholine) adducts of ketones (1)—(4) with a view to studying their photochemistry at a later stage. *trans*-Stereochemistry of the double bond is indicated in the products (13)—(20) (Table) by examination of the coupling constant (J 13 Hz) of the olefinic protons at C-1 and -2. A change of solvent from benzene to methanol does not affect the stereochemistry of the products, although such solvent dependence had earlier been reported to influence the stereochemistry of addition of secondary amines to a triple bond.[7b]

Oxygen- and Sulphur-containing Nucleophiles.—In an earlier communication,[7e] the stereospecific formation of disubstituted enol ethers by the addition of phenol to ketones (1)—(3) was reported. The addition of phenol containing an *ortho*-functionality capable of participating subsequently in an intramolecular fashion with the initially formed intermediate can be expected to provide cyclic oxygenated derivatives. To explore the possibility of such additions providing synthetic routes to oxygenated heterocyclics, we have now examined the reaction of *o*-hydroxyphenol (catechol) and a few *o*-hydroxy-acids such as salicylic, 2-hydroxy-3-naphthoic,



(13) X = O, R = H (17) X = CH_2, R = H
(14) X = O, R = CH_3 (18) X = CH_2, R = CH_3
(15) X = O, R = OCH_3 (19) X = CH_2, R = OCH_3
(16) X = O, R = Cl (20) X = CH_2, R = Cl

SCHEME 4

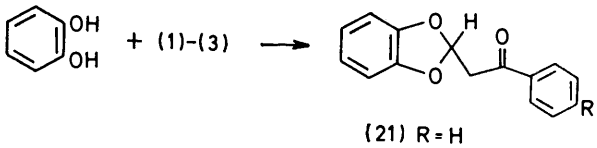
and 2-hydroxy-1-naphthoic acid, and an *o*-hydroxyaldehyde (salicylaldehyde) with aryl ethynyl ketones.

Products from addition of morpholine and piperidine to aryl ethynyl ketones

Product	Yield * (%)	M.p.† (°C)	δ([$^2H_6$]DMSO)	$\nu_{max.}$(KBr)/cm^{-1}	Formula	Calc. (found) (%)
(13)	88	95—97	3.3 (4 H, t, J 4 Hz, NCH_2), 3.6 (4 H, t, J 4 Hz, OCH_2), 5.85 (1 H, d, J 13 Hz, olefinic), 7.2—8.0 (6 H, m, olefinic and Ar)	1 640 (C=O)	$C_{13}H_{15}NO_2$	C, 71.9 (71.4) H, 6.9 (6.4) N, 6.45 (6.4)
(14)	99	79—81	2.3 (3 H, s, $ArCH_3$), 3.3 (4 H, t, J 4 Hz, NCH_2), 3.6 (4 H, t, J 4 Hz OCH_2), 5.9 (1 H, d, J 13 Hz, olefinic), 7.2—7.9 (5 H, m, olefinic and Ar)	1 620 (C=O)	$C_{14}H_{17}NO_2$	C, 72.7 (72.95) H, 7.3 (6.95) N, 6.05 (6.15)
(15)	89	85—87	3.35 (4 H, t, J 4 Hz, NCH_2), 3.7 (4 H, t, J 4 Hz, OCH_2), 3.85 (3 H, s, $ArOCH_3$), 5.9 (1 H, d, J 13 Hz, olefinic), 6.9—7.95 (5 H, m, olefinic and Ar)	1 640 (C=O)	$C_{14}H_{17}NO_3$	C, 68.0 (67.55) H, 6.9 (6.5) N, 5.65 (6.15)
(16)	84	110—112	3.4 (4 H, t, J 4 Hz, NCH_2), 3.7 (4 H, t, J 4 Hz, OCH_2), 5.82 (1 H, d, J 13 Hz olefinic), 7.3—7.95 (5 H, m, olefinic and Ar)	1 640 (C=O)	$C_{13}H_{14}ClNO_2$	C, 62.0 (61.65) H, 5.5 (5.25) N, 5.5 (5.15)
(17)	93	92—94	1.5 (6 H, s, CH_2), 3.2br (4 H, s, N–CH_2), 5.8 (1 H, d, J 13 Hz, olefinic), 7.3—8.0 (6 H, olefinic and Ar)	1 640 (C=O)	$C_{14}H_{17}NO$	C, 78.15 (78.6) H, 7.9 (8.1) N, 6.5 (6.8)
(18)	70	88—90	1.5 (6 H, s, CH_2), 2.3 (3 H, s, $ArCH_3$), 3.3br (4 H, s, NCH_2), 5.8 (1 H, d, J 13 Hz, olefinic), 7.1—7.9 (5 H, m, olefinic and Ar)	1 640 (C=O)	$C_{15}H_{19}NO$	C, 78.6 (78.2) H, 8.3 (8.55) N, 6.1 (6.1)
(19)	74	100—103	1.5 (6 H, s, CH_2), 3.2 (4 H, s, NCH_2), 3.7 (3 H, s, $ArOCH_3$), 5.8 (1 H, d, J 13 Hz, olefinic), 6.9—7.9 (5 H, m, olefinic and Ar)	1 640 (C=O)	$C_{15}H_{19}NO_2$	C, 73.45 (72.9) H, 7.75 (8.05) N, 5.7 (5.5)
(20)	60	128—130	1.55 (6 H, s, CH_2), 3.3 (4 H, s, NCH_2), 5.8 (1 H, d, J 13 Hz, olefinic), 7.35—7.9 (5 H, m, olefinic and Ar)	1 640 (C=O)	$C_{14}H_{16}ClON$	C, 67.45 (67.8) H, 6.4 (6.65) N, 5.6 (5.95)

* Based on crude product. † Recrystallised from ethyl acetate–ether mixture.

Base catalysed addition of catechol to ketones (1)—(3) in benzene gave crystalline 1 : 1 adducts (21)—(23) in

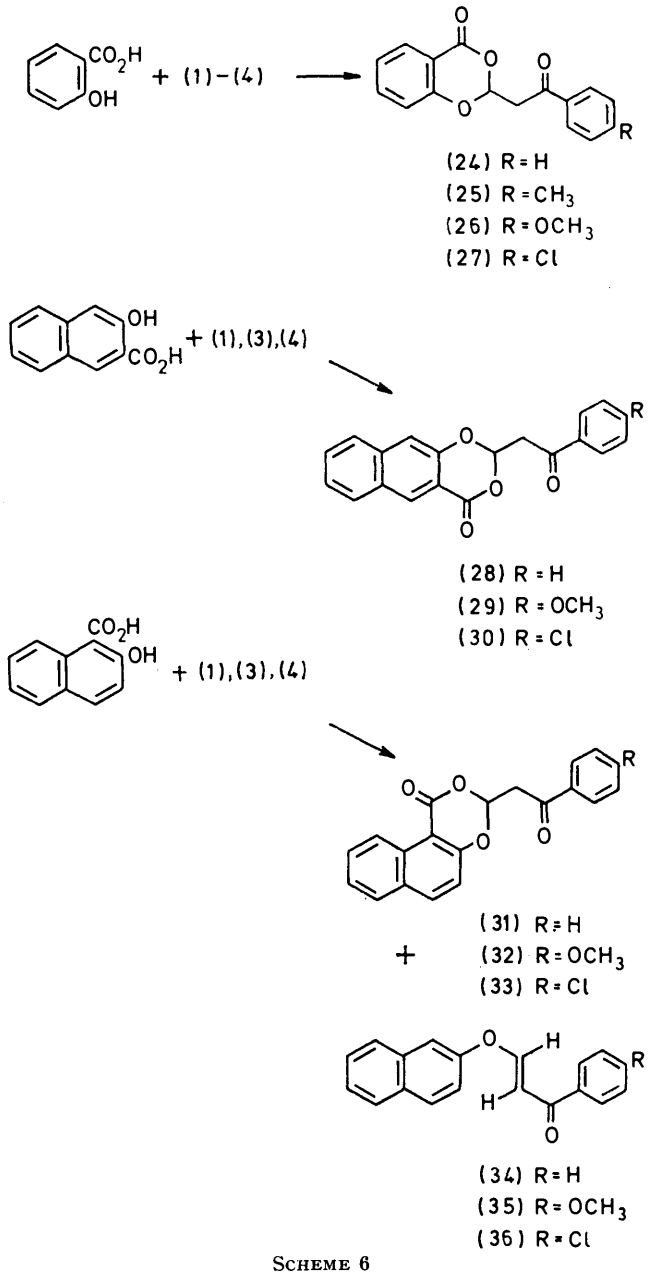


(21) R = H
(22) R = CH_3
(23) R = OCH_3

SCHEME 5

excellent yields (Scheme 5). A cyclic 1,3-benzodioxole structure is proposed on the strength of the n.m.r. spectral data (see Experimental section).

Base catalysed addition of salicylic, 2-hydroxy-3-naphthoic, and 2-hydroxy-1-naphthoic acid to aryl ethynyl ketones gave crystalline 1 : 1 adducts in high yields. The i.r. and n.m.r. spectra were found to be in agreement with the oxalactone (2-phenacyl-1,3-benzodioxan-4-one) structures (24)—(33) for the adducts (Scheme 6). Thus absorptions at 1 740—1 760 and



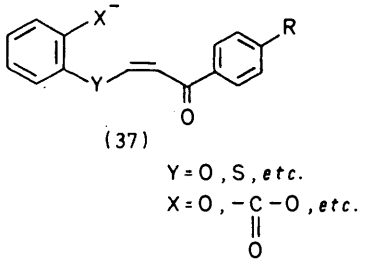
SCHEME 6

1 680—1 700 cm^{-1} clearly show the presence of a lactone and a benzoyl group respectively. This is further supported by the presence of a doublet at δ *ca.* 3.7 and a triplet at δ *ca.* 6.4 for the methylene and methine protons adjacent to two oxygens, respectively.

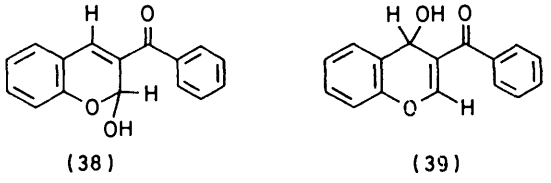
In the reaction of 2-hydroxy-1-naphthoic acid with ketones (1), (3), and (4) equal amounts of *trans*-3-β-naphthoxy-1-arylprop-2-enones (34)—(36) were also isolated in addition to the lactone products (31)—(33), apparently formed by the initial decarboxylation of 2-hydroxy-1-naphthoic acid followed by addition. 2-Hydroxy-1-naphthoic acid is known to undergo thermal decarboxylation to give β-naphthol.[10] The adducts (31)—(33) were found to be stable when refluxed with triethylamine in benzene for a prolonged period, the conditions under which the above addition was effected.

The formation of various cyclic compounds can be readily explained in terms of initial nucleophilic addition to form the enol ether (37) followed by favourable 5-*Exo-Trig* and 6-*Exo-Trig* types of ring closure.[11]

Unlike salicylic and hydroxynaphthoic acids, the triethylamine catalysed reaction of salicylaldehyde with ethynyl phenyl ketone in benzene was very complex and



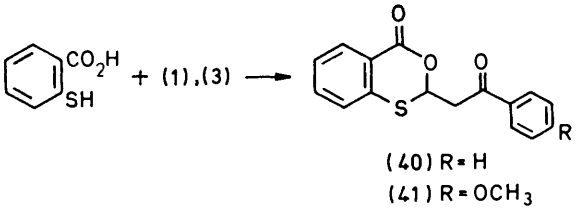
yielded an inseparable mixture of several components. However, when the reaction was conducted in aqueous ethanol containing a catalytic amount of sodium hydroxide under nitrogen at room temperature, a 32% yield of a crystalline material (38) was obtained. The compound had a molecular ion peak at 252 in the mass spectrum and showed absorptions at 3 400 and 1 640 cm^{-1} indicating the presence of an hydroxy and benzoyl group respectively. *A priori* two possible structures (38) or (39) can be expected for the addition product.



However further evidence in favour of structure (38) was provided by the n.m.r. spectrum of the compound which showed a broad doublet (*J* 5 Hz) at δ 4.0 due to a free hydroxy proton and another broad doublet (*J* 5 Hz) at δ 6.6 indicative of a proton flanked by two oxygens and a multiplet at δ 7.0—8.0 integrating for ten protons assignable to 4-H and the aromatic protons. The n.m.r. spectrum of (38), after D_2O exchange showed a singlet at δ 6.6 due to 2-H, whereas the signal at δ 4.0 completely disappeared as expected.

Reaction of thiosalicyclic acid with aryl ethynyl ketones was also investigated with a view to isolating sulphur-containing cyclic derivatives. Triethylamine catalysed addition of thiosalicyclic acid to aryl ethynyl ketones (1) and (3) in benzene gave crystalline adducts in

good yields. I.r. and n.m.r. data strongly supported the thialactone structures (40) and (41).



SCHEME 7

EXPERIMENTAL

M.p.s are uncorrected and were determined on a Fisher–Johns apparatus. N.m.r. spectra were recorded on Varian A-60 D or T-60 spectrometers, with tetramethylsilane as internal standard. Nucleophiles employed for the preparation of various compounds were obtained from commercial sources and used without further purification. Aryl ethynyl ketones (1)—(4) were prepared according to literature procedures.[7e] The yields reported here are those of crude products. No effort was directed towards the optimisation of yields. Analytical samples were prepared by recrystallisation from a suitable solvent as mentioned in each case.

General Procedure for Reaction with Nitrogen-containing Nucleophiles.—A mixture of the appropriate nitrogen-containing nucleophile (0.01 mol) and the aryl ethynyl ketone (0.01 mol) in dry benzene (25 ml) was boiled under reflux for 1 h. On cooling the product precipitated and was collected by filtration. The crude product was then recrystallised. The following compounds were prepared.

3-o-*Aminophenylamino*-1-*phenylprop*-2-*enone* (5). This was obtained from *o*-phenylenediamine and ethynyl phenyl ketone (84%). Recrystallisation from ethyl acetate–ethanol furnished orange-yellow needles, m.p. 163—164° (Found: C, 75.75; H, 5.95; N, 11.85. $C_{15}H_{14}N_2O$ requires C, 75.6; H, 5.9; N, 11.75%), $\nu_{max.}$ (KBr) 1 645 (C=O), 3 450, and 3 500 cm^{-1} (NH), $\delta(CDCl_3)$ 3.7—4.1 (NH_2), 6.2 (1 H, d, *J* 8 Hz, olefinic), 7.0—8.3 (10 H, m, olefinic and ArH), and 9.0—9.5 (NH).

3-o-*Aminophenylamino*-1-p-*tolylprop*-2-*enone* (6). This was obtained from *o*-phenylenediamine and ethynyl *p*-tolyl ketone (79%). Recrystallisation from ethyl acetate–ethanol gave orange crystals, m.p. 155—156° (Found: C, 76.3; H, 6.45; N, 11.0. $C_{16}H_{16}N_2O$ requires C, 76.2; H, 6.35; N, 11.1%), $\nu_{max.}$ (KBr) 1 650 (C=O), 3 350, and 3 500 cm^{-1} (NH), $\delta(CDCl_3)$ 2.4 (3 H, s, $ArCH_3$), 3.5—3.9 (2 H, NH_2), 6.0 (1 H, d, *J* 8 Hz, olefinic), and 6.7—7.95 (9 H, m, olefinic and Ar).

3-o-*Aminophenylamino*-1-p-*methoxyphenylprop*-2-*enone* (7). This was prepared from *o*-phenylenediamine and ethynyl *p*-methoxyphenyl ketone (64%). Recrystallisation from ethyl acetate–ethanol yielded orange crystals, m.p. 176° (Found: C, 71.4; H, 6.15; N, 10.55. $C_{16}H_{16}N_2O_2$ requires C, 71.65; H, 5.95; N, 10.45%), $\nu_{max.}$ (KBr) 1 645 (C=O), 3 400, and 3 500 cm^{-1} (NH), $\delta(CDCl_3)$ 3.5—3.95 (2 H, NH_2), 3.9 (3 H, s, $ArOCH_3$), 6.05 (1 H, d, *J* 8 Hz, olefinic), and 6.7—8.05 (9 H, m, olefinic and Ar).

3-*Anilino*-1-p-*tolylprop*-2-*enone* (8). This was prepared from aniline and ethynyl *p*-tolyl ketone (46%). Recrystallisation from pentane–benzene yielded light lemon-yellow microcrystals, m.p. 165—166° (Found: C, 81.4; H, 6.5; N, 6.1. $C_{16}H_{15}NO$ requires C, 81.0; H, 6.3; N, 5.9%), $\nu_{max.}$ (KBr) 1 630 (C=O) and 3 300 cm^{-1} (NH), $\delta(CDCl_3)$ 2.4 (3 H, s, $ArCH_3$), 6.05 (1 H, d, *J* 8 Hz, olefinic), 7.1—8.0 (9 H, m, olefinic and Ar).

3-*Anilino*-1-p-*methoxyphenylprop*-2-*enone* (9). This was prepared from aniline and ethynyl *p*-methoxyphenyl ketone (75%). Recrystallisation from pentane–benzene gave lemon-yellow, silky crystals, m.p. 133—134° (Found: C, 75.6; H, 6.01; N, 5.65. $C_{16}H_{15}NO_2$ requires C, 75.9; H, 5.9; N, 5.5%), $\nu_{max.}$ (KBr) 1 640 (C=O) and 3 300 cm^{-1} (NH), $\delta(CDCl_3)$ 3.9 (3 H, s, $ArOCH_3$), 6.00 (1 H, d, *J* 8 Hz, olefinic), and 6.9—8.1 (9 H, m, olefinic and Ar).

Preparation of 3-o-*Hydroxyphenylamino*-1-*arylprop*-2-*enone* (10)—(12).—3-(o-*Hydroxyphenylamino*)-1-*phenylprop*-2-*enone* (10) was prepared from *o*-aminophenol and ethynyl phenyl ketone (83%). Recrystallisation from ethyl acetate–methanol yielded bright yellow crystals, m.p. 206—208° (Found: C, 75.5; H, 5.6; N, 5.75. $C_{15}H_{13}NO_2$ requires C, 75.3; H, 5.4; N, 5.8%), $\nu_{max.}$ (KBr) 1 635 (C=O), 3 150, and 3 350 cm^{-1} (OH and NH), $\delta(CDCl_3$–[$^2H_6$]DMSO) 3.35br (1 H, ArOH), 3.95 (1 H, d, *J* 8 Hz, olefinic), 6.85—8.0 (9 H, m, olefinic and Ar), and 9.73br (1 H, NH). The 1-p-*tolyl analogue* (11) was prepared from *o*-aminophenol and ethynyl *p*-tolyl ketone (79%). Recrystallisation from ethyl acetate–methanol yielded deep yellow crystals, m.p. 221—222° (Found: C, 75.95; H, 6.1; N, 5.45. $C_{16}H_{15}NO_2$ requires C, 75.8; H, 5.9; N, 5.5%), $\nu_{max.}$ (KBr) 1 625 (C=O), 3 150, and 3 650 cm^{-1} (OH and NH), δ([$^2H_6$]DMSO) 2.4 (3 H, s, $ArCH_3$), 3.25br (1 H, ArOH), 6.05 (1 H, d, *J* 8 Hz, olefinic), 7.0—8.0 (8 H, m, olefinic and Ar), and 9.78br (1 H, NH). The 1-p-*methoxyphenyl analogue* (12) was obtained from *o*-aminophenol and ethynyl *p*-methoxyphenyl ketone (59%). Recrystallisation from ethyl acetate–methanol furnished yellow crystals, m.p. 217° (Found: C, 71.25; H, 5.7; N, 5.3. $C_{16}H_{15}NO_3$ requires C, 71.3; H, 5.55; N, 5.2%), $\nu_{max.}$ (KBr) 1 640 (C=O), 3 350, and 3 450 cm^{-1} (OH and NH). Due to its poor solubility, a well resolved n.m.r. spectrum could not be obtained.

Preparation of 1-*Aryl*-3-*morpholinoprop*-2-*enones* (13)—(16) *and* 1-*Aryl*-3-*piperidinoprop*-2-*enones* (17)—(20).—These compounds were prepared from the reaction of aryl ethynyl ketones (1)—(4) with morpholine and piperidine, respectively according to the general procedure given above. Details of the products are given in the Table.

General Procedure for Reactions with Oxygen- and Sulphur-containing Nucleophiles.—A mixture of oxygen- or sulphur-containing nucleophile (0.01 mol) and aryl ethynyl ketone (0.01 mol) was refluxed for 5 h in dry benzene (25 ml) in the presence of a few drops of triethylamine. The mixture was cooled and the solid which separated was collected by filtration. Recrystallisation from a suitable solvent furnished the analytical sample. In this manner, the following compounds were prepared and characterised.

2-*Phenacyl*-1,3-*benzodioxoles* (21)—(23). Reaction of catechol with ethynyl phenyl ketone furnished 2-*phenacyl*-1,3-*benzodioxole* (21) in near quantitative yield. Recrystallisation from methanol gave buff coloured, shining plates, m.p. 85° (Found: C, 75.1; H, 5.6. $C_{15}H_{12}O_3$ requires C, 75.0; H, 5.0%), $\nu_{max.}$ (KBr) 1 690 cm^{-1} (C=O), $\delta(CDCl_3)$ 3.65 (2 H, d, *J* 5 Hz, CH_2), 6.78 (1 H, t, *J* 5 Hz, $\begin{matrix}O\\O\end{matrix}\!>\!CH$), and 6.94—8.25 (9 H, m, Ar). Reaction of catechol with ethynyl *p*-tolyl ketone yielded 2-(p-*methylphenacyl*)-1,3-*benzodioxole* (22) in near quantitative yield. Recrystallisation from methanol furnished off-white, shiny plates, m.p. 106° (Found: C, 75.3; H, 5.0. $C_{16}H_{14}O_3$ requires C,

75.6; H, 5.5%), $\nu_{max.}$ (KBr) 1 700 cm^{-1} (C=O), δ($CDCl_3$) 2.4 (3 H, s, $ArCH_3$), 3.55 (2 H, d, *J* 5 Hz, CH_2), and 6.72 (1 H, t, *J* 5 Hz, O>CH<O), and 6.81—7.92 (8 H, m, Ar). Likewise, addition of catechol to ethynyl *p*-methoxyphenyl ketone furnished 2-(p-*methoxyphenacyl*)-1,3-*benzodioxole* (23) in 74% yield. Recrystallisation from methanol yielded crystals, m.p. 88° (Found: C, 71.35; H, 5.25. $C_{16}H_{14}O_4$ requires C, 71.1; H, 5.2%), $\nu_{max.}$ (KBr) 1 690 cm^{-1} (C=O), δ($CDCl_3$) 3.4 (2 H, d, *J* 5 Hz, CH_2), 3.7 (3 H, s, $ArOCH_3$), 6.43 (1 H, t, *J* 5 Hz, O>CH<O), and 6.58—7.69 (8 H, m, Ar).

Preparation of Oxalactones (24)—(30).—Reaction of salicylic acid with aryl ethynyl ketones (1)—(4) in the presence of triethylamine, as described above, yielded the following compounds: 2-(*phenacyl*)-1,3-*benzodioxan*-4-*one* (24) (75%), crystals (from benzene), m.p. 85—86° (Found: C, 71.25; H, 4.2. $C_{16}H_{12}O_4$ requires C, 71.6; H, 4.4%), $\nu_{max.}$ (KBr) 1 700 (C=O) and 1 750 cm^{-1} (lactone), δ($CDCl_3$) 3.7 (2 H, d, *J* 5 Hz, CH_2), 6.25 (1 H, t, *J* 5 Hz, O>CH<O), and 6.8—8.0 (9 H, m, Ar); 2-(p-*methylphenacyl*)-1,3-*benzodioxan*-4-*one* (25) (57%), microcrystals (from benzene), m.p. 158—160° (Found: C, 72.9; H, 4.65. $C_{17}H_{14}O_4$ requires C, 72.3; H, 4.9%), $\nu_{max.}$ (KBr) 1 700 (C=O) and 1 760 cm^{-1} (lactone), δ($CDCl_3$–[$^2H_6$]DMSO) 2.45 (s, $ArCH_3$), 3.7 (2 H, d, *J* 5 Hz, CH_2), 6.3 (1 H, t, *J* 5 Hz, O>CH<O), and 7.0—8.0 (8 H, m, Ar); 2-(p-*methoxyphenacyl*)-1,3-*benzodioxan*-4-*one* (26) (92%), crystals (from benzene), m.p. 141—143° (Found: C, 68.4; H, 5.1. $C_{17}H_{14}O_5$ requires C, 68.4; H, 4.7%), $\nu_{max.}$ (KBr) 1 680 (C=O) and 1 740 cm^{-1} (lactone), δ($CDCl_3$) 3.65 (2 H, d, *J* 5 Hz, CH_2), 3.85 (3 H, s, $ArOCH_3$), 6.2 (1 H, t, *J* 5 Hz, O>CH<O), and 6.8—8.0 (8 H, m, Ar); 2-(p-*chlorophenacyl*)-1,3-*benzodioxan*-4-*one* (27) (76%), microcrystals (from benzene), m.p. 174—176° (Found: C, 63.2; H, 3.9. $C_{16}H_{11}ClO_4$ requires C, 63.45; H, 3.6%), $\nu_{max.}$ (KBr) 1 680 (C=O) and 1 740 cm^{-1} (lactone), δ($CDCl_3$) 3.7 (2 H, d, *J* 5 Hz, CH_2), 6.35 (1 H, t, *J* 5 Hz O>CH<O), and 7—8.15 (8 H, m, Ar).

Reaction of 2-hydroxy-3-naphthoic acid with aryl ethynyl ketones (1), (3), and (4) in the presence of triethylamine yielded the following compounds: 2-*phenacyl*-4H-*naphtho*[2,3-d]-m-*dioxin*-4-*one* (28), (79%), recrystallised from benzene–chloroform, m.p. 179—181° (Found: C, 75.65; H, 4.1. $C_{20}H_{14}O_4$ requires C, 75.45; H, 4.4%), $\nu_{max.}$ (KBr) 1 680 (C=O) and 1 740 cm^{-1} (lactone), δ($CDCl_3$) 3.75 (2 H, d, *J* 5 Hz, CH_2), 6.4 (1 H, t, *J* 5 Hz, O>CH<O), 7.3—8.1 (10 H, m, Ar), 8.64 (1 H, s, 5-H); 2-(p-*methoxyphenacyl*)-4H-*naphtho*-[2,3-d]-m-*dioxin*-4-*one* (29) (42%), recrystallised from benzene–chloroform, m.p. 193—195° (Found: C, 72.35; H, 4.75. $C_{21}H_{16}O_5$ requires C, 72.4; H, 4.6%), $\nu_{max.}$ (KBr) 1 680 (C=O) and 1 740 cm^{-1} (lactone), δ($CDCl_3$) 3.7 (2 H, d, *J* 5 Hz, CH_2), 3.9 (3 H, s, $ArOCH_3$), 6.4 (1 H, t, *J* 5 Hz, O>CH<O), 6.9—8.1 (9 H, m, Ar), and 8.64 (1 H, s, 5-H); 2-(p-*chlorophenacyl*)-4H-*naphtho*[2,3-d]-m-*dioxin*-4-*one* (30) (54%), recrystallised from benzene–chloroform, m.p. 201—203° (Found: C, 67.7; H, 4.2. $C_{20}H_{13}ClO_4$ requires C, 68.1; H, 3.7%), $\nu_{max.}$ (KBr) 1 680 (C=O) and 1 740 cm^{-1} (lactone), δ($CDCl_3$) 3.7 (2 H, d, *J* 5 Hz, CH_2), 6.35 (1 H, *J* 5 Hz, O>CH<O), 7.3—8.1 (9 H, m, Ar), and 8.69 (1 H, s, 5-H).

Addition of 2-Hydroxy-1-naphthoic Acid to Aryl Ethynyl Ketones. General Procedure.—A solution of aryl ethynyl ketone (0.01 mol) and 2-hydroxy-1-naphthoic acid (0.01 mol) in benzene (30 ml) containing triethylamine (3 drops) was refluxed for 6 h. The solvent was removed under vacuum and the solid residue showed two spots on t.l.c. (silica gel). The residue was carefully crystallised from benzene to give lactones (31)—(33). The mother liquor was set aside. Further recrystallisations from benzene furnished analytically pure lactones. In this manner 2-*phenacyl*-1H-*naphtho*[2,1-d]-m-*dioxin*-1-*one* (31) (34%), m.p. 199—202° (Found: C, 75.9; H, 4.25. $C_{20}H_{14}O_4$ requires C, 75.5; H, 4.4%), $\nu_{max.}$ (KBr) 1 690 (C=O) and 1 750 cm^{-1} (lactone), δ($CDCl_3$) 3.8 (2 H, d, *J* 5 Hz, CH_2), 6.4 (1 H, t, *J* 5 Hz, O>CH<O), and 7.01—8.2 (11 H, m, Ar); the 2-p-*methoxyphenacyl analogue* (32) (42%), m.p. 179—181° (Found: C, 72.45; H, 4.35. $C_{21}H_{16}O_5$ requires C, 72.4; H, 4.6%), $\nu_{max.}$ (KBr) 1 700 (C=O) and 1 750 cm^{-1} (lactone), δ($CDCl_3$) 3.8 (2 H, d, *J* 5 Hz, CH_2), 3.9 (3 H, s, $ArOCH_3$), 6.4 (1 H, t, *J* 5 Hz, O>CH<O), and 7.0—8.2 (10 H, m, Ar); and the 2-p-*chlorophenacyl analogue* (33) (41%), m.p. 212—214° (Found: C, 68.3; H, 4.1. $C_{20}H_{13}ClO_4$ requires C, 68.1; H, 3.7%), $\nu_{max.}$ (KBr) 1 680 (C=O) and 1 740 cm^{-1} (lactone), δ($CDCl_3$) 3.8 (2 H, d, *J* 5 Hz, CH_2), 6.3 (1 H, t, *J* 5 Hz, O>CH<O), and 7.1—8.2 (10 H, m, Ar), were prepared.

The mother liquor after the separation of lactones (31)—(33), in each case, was concentrated, cooled, and triturated with a little pentane, when the *trans*-1-aryl-3-β-naphthoxyprop-2-enones (34)—(36) precipitated out. Further recrystallisation from benzene–pentane gave analytically pure naphthol adducts (34)—(36), and were characterised as follows: trans-3-β-*naphthoxy*-1-*phenylprop*-2-*enone* (34) (47%), m.p. 91—92° (Found: C, 83.35; H, 5.1. $C_{19}H_{14}O_2$ requires C, 83.2; H, 5.1%), $\nu_{max.}$ (KBr) 1 680 cm^{-1} (C=O), δ($CDCl_3$) 7.0 (1 H, d, *J* 12 Hz, olefinic) and 7.3—8.3 (14 H, m, olefinic and ArH); trans-3-β-*naphthoxy*-1-p-*methoxyphenylprop*-2-*enone* (35) (49%), m.p. 110—111° (Found: C, 79.25; H, 5.2. $C_{20}H_{16}O_3$ requires C, 78.95; H, 5.25%), $\nu_{max.}$ (KBr) 1 680 cm^{-1} (C=O), δ($CDCl_3$) 3.7 (3 H, s, $ArOCH_3$), 6.9 (1 H, d, *J* 12 Hz, olefinic), and 7.3—8.3 (13 H, m, olefinic and ArH); and trans-3-β-*naphthoxy*-1-p-*chlorophenylprop*-2-*enone* (36) (45%), m.p. 87—90° (Found: C, 73.9; H, 4.4. $C_{19}H_{13}ClO_2$ requires C, 73.9; H, 4.2%), $\nu_{max.}$ (KBr) 1 680 cm^{-1} (C=O), δ($CDCl_3$) 6.9 (1 H, d, *J* 12 Hz, olefinic), and 7.3—8.3 (13 H, m, olefinic and ArH).

Addition of Salicylaldehyde to Ethynyl Phenyl Ketone.—To a solution of salicylaldehyde (0.01 mol) and ethynyl phenyl ketone (0.01 mol) in ethanol (10 ml) was added aqueous sodium hydroxide [0.08 g in water (5 ml)] and the mixture was stirred at room temperature for 5 h under nitrogen. The solvent was removed under vacuum and the residue was diluted with water (10 ml). Extraction with ether (2 × 20 ml), washing with brine, and removal of solvent gave crude 2-*hydroxy*-3-*benzoylchrom*-3-*ene* (38) in 32% yield. Further recrystallisation from ether gave m.p. 127—129° (Found: C, 76.0; H, 4.76%, $C_{16}H_{12}O_3$ requires C, 76.18; H, 4.76%) (see Discussion section for spectral data).

Addition of Thiosalicylic Acid to Aryl Ethynyl Ketones.—

The addition of thiosalicylic acid to aryl ethynyl ketones (1) and (3) was carried out as described for salicylic acid to furnish *2-phenacyl-3,1-benzoxathiin-4-one* (40) (53%), m.p. 128—129° (Found: C, 67.5; H, 4.65. $C_{16}H_{12}O_3S$ requires C, 67.6; H, 4.2%), $\nu_{max.}$ (KBr) 1 690 (C=O) and 1 720 cm^{-1} (lactone), δ([$^2H_6$]DMSO) 4.0 (2 H, d, *J* 6 Hz, CH_2), 6.35 (1 H, t, *J* 6 Hz, ), 7.4—8.2 (9 H, m, Ar) and the *2-p-methoxyphenacyl analogue* (41) (51%), m.p. 153—155° (Found: C. 65.35; H, 4.65. $C_{17}H_{14}O_4S$ requires C, 64.95; H, 4.45%), $\nu_{max.}$ (KBr) 1 675 (C=O) and 1 730 cm^{-1} (lactone), respectively. A well resolved n.m.r. spectrum for (41) could not be obtained due to its poor solubility.

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