Cyclisation of Phenol- and Enol-acetylenes: Syntheses of 2,3-Dihydro-2-methylene-1,4-benzodioxins and -1,4-benzoxazines

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In the presence of yellow mercuric oxide, pyrocatecol mono(prop-2-ynyl) ether and its analogues were cyclised to afford 2,3-dihydro-2-methylene-1,4-benzodioxins. *o*-(*N*-Substituted-*N*-prop-2-ynyl)aminophenols were also cyclised to 2,3-dihydro-2-methylene-1,4-benzoxazines in good yield. In contrast, enol-acetylenes, such as 2-benzoyl-1-oxo-1-phenylpent-4-yne, gave 2,3,5-trisubstituted furans.

MERCURY-CATALYSED intermolecular condensation of an *o*-halogenophenol and an acetylide has been shown to give a benzofuran derivative.[1] On the other hand, many intramolecular cyclisation reactions catalysed by mercury(II) salts have appeared in the literature; the cyclisations were carried out between the double bond and hydroxy,[2,3] carbonyl,[4] and carboxy [3] groups in the molecule.

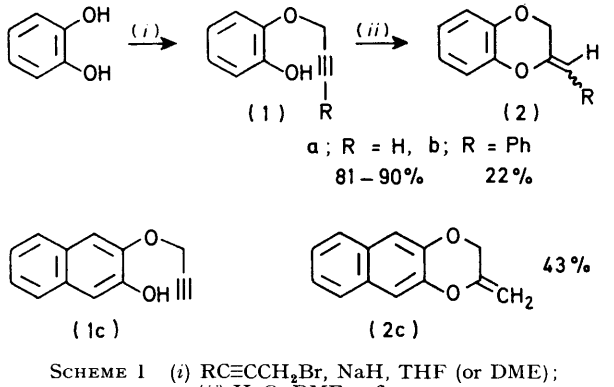
Recently I reported that acetylenecarboxylic acids cyclised in the presence of yellow mercuric oxide to give γ-methylenebutyrolactones.[5] This is a typical case of cyclisation between a triple bond and a carboxy group.

These results suggested that phenol-acetylenes in the presence of a mercury(II) salt would yield a heterocycle. I now report the syntheses of 2,3-dihydro-2-methylene-1,4-benzodioxins and -1,4-benzoxazines. Cyclisation of enol-acetylenes will also be discussed.

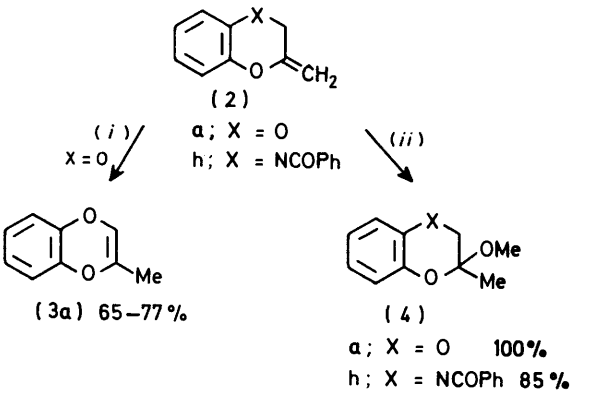
RESULTS AND DISCUSSION

Pyrocatecol mono(prop-2-ynyl) ether (1a), which was prepared from pyrocatecol and prop-2-ynyl bromide in the presence of sodium hydride in dry tetrahydrofuran (THF) or dimethoxyethane (DME), was treated with refluxing dimethylformamide (DMF) for 20 h in the presence of yellow mercuric oxide to give a colourless liquid, b.p. 90—94 °C at 20 mmHg, in 90% yield.

The i.r. spectrum showed that the phenolic hydroxy group and triple-bond absorption bands in the starting compound (1a) had disappeared, and had been replaced by vinylic double-bond bands at 1 665 and 890 cm^{-1}. The ^1H n.m.r. spectrum showed two doublets at δ 4.24 and 4.66 (*J* 2 Hz). The mass spectrum showed a molecular peak at *m/e* 148. These results indicate that this liquid is 2,3-dihydro-2-methylene-1,4-benzodioxin (2a).[6]



SCHEME 1 (*i*) $RC{\equiv}CCH_2Br$, NaH, THF (or DME); (*ii*) HgO, DMF, reflux



SCHEME 2 (*i*) Bu^{t}OK in DMSO, or *p*-$MeC_6H_4SO_2OH$ in benzene, reflux; (*ii*) *p*-$MeC_6H_4SO_2OH$ in MeOH, reflux

The structure of (2a) was also supported by the following chemical evidence; the *exo*-methylene compound (2a) was isomerised to the *endo*-methylene (3a) by treatment with potassium t-butoxide in dimethyl sulphoxide (DMSO),[6] or toluene-*p*-sulphonic acid [7] in dry benzene.

The enol-ether (2a) adds methanol in the presence of a catalytic amount of toluene-*p*-sulphonic acid to give 2,3-dihydro-2-methoxy-2-methyl-1,4-benzodioxin (4a) in quantitative yield.

This cyclisation reaction, from (1a) to (2a), did not proceed in refluxing benzene or dioxan even in the presence of mercuric oxide, and most of the starting material (1a) was recovered. When (1a) was treated in refluxing DMF without mercuric oxide, cyclisation again did not occur. On heating at 150—160 °C in DMSO, (1a) gave only decomposition products. In hexamethylphosphoric triamide (HMPA) at 150—160 °C, (1a) cyclised to (2a) in low yield. Mercuric acetate was also used as catalysed, and the results are summarised in Table 1.

Pyrocatecol mono-(3-phenylprop-2-ynyl) ether (1b) was treated in the same way, but this phenol-acetylene was cyclised with difficulty; only 22% of the *syn,anti* mixture (2b) was obtained after 60 h in refluxing DMF.[5]

Naphthalene-2,3-diol mono(prop-2-ynyl)ether (1c) was cyclised by a similar treatment to afford 2,3-dihydro-2-methylene-1,4-naphtho[2,3-*b*]dioxin (2c) in 43% yield.

TABLE 1

Selection of optimum condition for the formation of (2a)

Catalyst	Solvent	Reaction time/h	Yield of (2a) (%)
None	DMF	24	0
HgO	None [a]	24	0
	Benzene	24	0
	Dioxan	24	0
	DMF	20	81—90
	HMPA [b]	22	23 [c]
	DMSO [b]	24	0 [c]
$Hg(OAc)_2$	Chloroform (room temperature)	24	Trace
	Chloroform	24	13
	Dioxan	24	Trace

[a] The mixture was heated at 100 °C. [b] The solution was heated at 150—160 °C. [c] The starting material (1a) was not recovered.

o-(*N*-Prop-2-ynyl)aminophenol (1d) was prepared from *o*-aminophenol and prop-2-ynyl bromide by the usual method. The phenol-acetylene (1d) was treated as above, but it was unstable under the cyclisation conditions, and only a trace amount of the oxazine (2d) was detected.

On the other hand, *o*-(*NN*-diprop-2-ynyl)aminophenol (1e) gave a 75% yield of 2,3-dihydro-2-methylene-(*N*-prop-2-ynyl)-1,4-benzoxazine (2e). The structure of (2e) was assigned on the basis of spectroscopic data (Table 3).

The phenol-acetylenes (1f—h) were synthesised from mono(prop-2-ynyl)aminophenol (1d) and benzyl bromide, acetic anhydride, and benzoyl chloride. The spectral data of these phenol-acetylenes are listed in Table 2. The cyclisation of (1f—h) was carried out by a similar procedure to give the 1,4-benzoxazines (2f—h) in 66, 75, and 78% yield, respectively.

2-Methylene-1,4-benzoxazines also added methanol in good yield; *e.g.*, (2h), when treated with a catalytic amount of toluene-*p*-sulphonic acid in refluxing methanol, afforded *N*-benzoyl-2,3-dihydro-2-methoxy-2-methyl-1,4-benzoxazine (4h) in 85% yield.

β-Diketones, such as dibenzoylmethane, can easily enolise. α-Prop-2-ynyl-β-diketones, which are equivalent to enol-acetylenes [type (5)], were expected to cyclise to afford the *exo*-enol-ether (6) or the *endo*-enol-ether (7).

2-Benzoyl-1-oxo-1-phenylpent-4-yne (5a) was synthesised from dibenzoylmethane and prop-2-ynyl bromide by the usual method, and cyclisation was attempted

TABLE 2

Spectral data of phenol-acetylenes (1a—h)

Compound	$\nu_{max.}$ [a]/cm^{-1} OH	$\nu_{max.}$ [a]/cm^{-1} C≡C	δ [b]/p.p.m. (*J* in Hz) *OH*	δ [b]/p.p.m. (*J* in Hz) C≡C*H*	δ [b]/p.p.m. (*J* in Hz) $-XCH_2C\equiv$ [c]	*m/e* (relative intensity in parentheses)
(1a)	3 480 3 260	2 120	5.70s	244t (2.5)	456d (2.5)	148 (M^+) (68), 109 (100), 91 (12), 81 (74), 53 (22)
(1b)	3 480	2 230 [d]	5.62s		4.82s	224 (M^+) (42), 197 (30), 147 (17), 115 (100), 105 (21), 89 (21) 77 (30)
(1c)	3 480 3 280	2 120	6.02s	2.50t (2.0)	4.66d (2.0)	198 (M^+) (66), 159 (30), 142 (26), 131 (100), 102 (23), 77 (34)
(1d)	3 310 3 255	2 130 [d]	4.66s	2.08t (2.0)	3.83d (2.0)	147 (M^+) (73), 108 (100), 80 (98), 53 (20)
(1e)	3 350 3 260	2 100 [d]	6.76s	2.26t (2.0)	3.78d (2.0)	185 (M) (46), 146 (100), 118 (26), 91 (30), 65 (25)
(1f)	3 350 3 260	2 100 [d]	4.28s [e]	2.18t (2.5)	3.46d (2.5)	237 (M^+) (48), 146 (100), 118 (17), 91 (86), 65 (35)
(1g)	3 270	2 110 [d]	9.92s [b]	3.04t (3.0)	3.92q (3.0, 17) 4.83q (3.0, 17)	189 (M^+) (39), 147 (100), 108 (97), 80 (36), 52 (16)
(1h)	3 260	2 110	9.91s [f]	3.02t (2.5)	4.08q (2.5, 16) 4.92q (2.5, 16)	251 (M^+) (16), 105 (100), 91 (7), 77 (65), 51 (26)

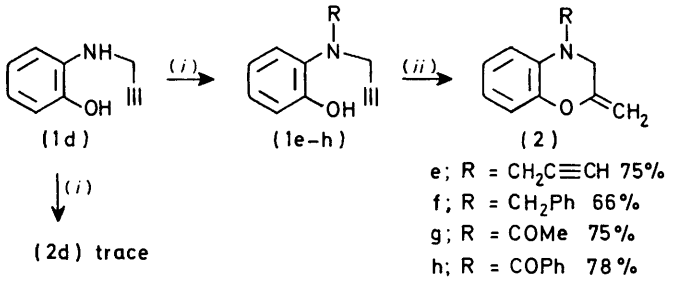
[a] KBr. [b] In CCl_4. [c] (1a—c), X = O, (1d—h), X = N. [d] Liquid film (NaCl cell). [e] In $CDCl_3$. [f] In $(CD_3)_2SO$.

TABLE 3

Spectral data of benzodioxins and benzoxazines

Compound	$\nu_{max.}$ [a]/cm^{-1} C=C		δ [b]/p.p.m. C=CH_2		(*J* in Hz) $-XCH_2C=$ [c]	*m/e* (relative intensity in parentheses)
2(a)	1 665	890	4.24d (2.0)	4.66d (2.0)	4.40m	148 (M^+) (69), 135 (34), 121 (22), 90 (20), 80 (44), 63 (25), 52 (100)
(2c)	1 665	890 [d]	4.30d (2.0)	4.72d (2.0)	4.50s	198 (M^+) (66), 159 (30), 142 (26), 131 (100), 102 (23), 77 (34)
(2e)	1 665	890	4.08d (1.5)	4.54d (1.5)	3.58s	185 (M^+) (100), 160 (96), 146 (82), 120 (36), 91 (48), 77 (30), 65 (54), 51 (38)
(2f)	1 665	890	3.97d (2.0)	4.48d (2.0)	4.25s	237 (M^+) (45), 146 (32), 91 (100), 65 (17)
2(g)	1 660	885	4.24d (1.5)	4.54d (1.5)	4.23s	189 (M^+) (91), 147 (100), 146 (68), 120 (48), 118 (23), 91 (17), 65 (18), 51 (18), 43 (71)
(2h)	1 660	890 [d]	4.24d (2.0)	4.62d (2.0)	4.31s	251 (M^+) (30), 105 (100), 77 (50), 51 (17)

[a] Liquid film (NaCl cell). [b] In CCl_4. [c] (1a and c), X = O: (1e—h), X = N. [d] KBr.

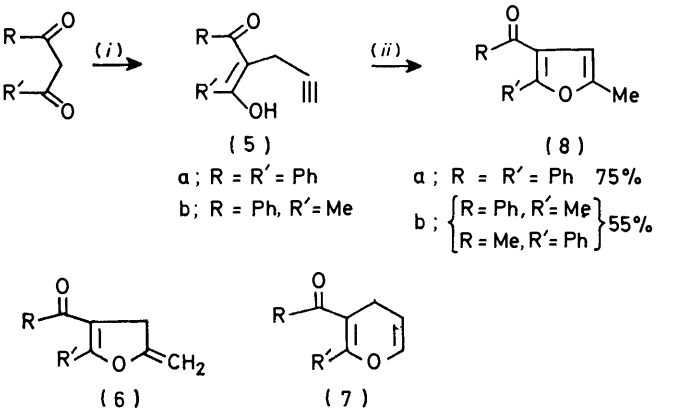


SCHEME 3 (*i*) RX, dry solvent, set aside at room temperature in the dark; (*ii*) HgO, DMF, reflux

by a similar procedure to that described above. Although a longer reaction time was necessary, after purification by column chromatography on silica gel, a 75% yield of a yellow viscous oil was obtained. From the spectral data this was neither the desired *exo*-methylene compound (6a) (R = R′ = Ph) nor the *endo*-methylene one (7a) (R = R′ = Ph), and it was assigned structure (8a).[8]

The mechanism of the formation of the furan (8) is considered to be *via* the initially formed *exo*-methylene compound (6) [from (5)] which then thermally isomerises by a 4-hydrogen shift to give (8).

A similar furan synthesis has been reported by Schulte and his co-workers,[9] the only difference being the use of zinc carbonate as catalyst. It probably proceeds by a similar mechanism.



SCHEME 4 (*i*) $HC{\equiv}CCH_2Br$, NaH, THF; (*ii*) HgO, DMF, reflux

EXPERIMENTAL

M.p.s and b.p.s are uncorrected. N.m.r. spectra were recorded with a JEOL JNM-MH-100 spectrometer using $SiMe_4$ as internal standard. I.r. spectra were obtained on a Hitachi EPI-G2 spectrometer. Mass spectra were measured with a JEOL JMS-D300 spectrometer. Thin layer and column chromatography used Merck Kieselgel G (type 60) and 70—230 mesh silica gel, respectively. THF and DME were distilled from $LiAlH_4$, DMSO, and HMPA were distilled from calcium hydride. DMF was distilled, and then all solvents were dried over molecular sieves (4A 1/16).

Pyrocatecol Mono(prop-2-ynyl) Ether (1a). *General Procedure A*.—In a 200-ml two-necked round-bottomed flask with a septum cap and a calcium chloride tube, 2.52 g (52.5 mmol) of sodium hydride (50% in oil) and a stirring bar were placed. After washing the sodium hydride with n-hexane (3 × 10 ml) and flushing with nitrogen, dry THF (80 ml) was added to the vessel. To this mixture pyrocatecol (5.5 g, 50 mmol) in THF (20 ml) was added dropwise during 90 min under a nitrogen atmosphere. After stirring for 5 h at room temperature prop-2-ynyl bromide (5.36 g, 45 mmol) in THF (5 ml) was added to the blue mixture, and stirring was continued for an additional 17 h at room temperature. The reaction mixture was poured into ice–water, acidified with diluted hydrochloric acid, and the aqueous mixture was extracted with ether (3 × 50 ml). The ether layer was washed with brine, dried over anhydrous sodium sulphate, and concentrated. The residue showed three spots on t.l.c., with R_F values of 0.54 (component A), 0.44 (component B), and 0.15 (pyrocatecol) [eluant benzene–ethyl acetate (9 : 1)]. It was separated by silica gel column chromatography with benzene as eluant. Component A is dialkylated pyrocatecol; $\delta(CCl_4)$ 2.38 (t, 2 H, *J* 2 Hz), 4.60 (d, 4 H, *J* 2 Hz), and 6.80—7.04 (m, 4 H). Component B is pyrocatecol mono(prop-2-ynyl) ether (1a), b.p. 125—133 °C at 17 mmHg (lit.,[10] b.p. 120—130 °C at 14 mmHg) which was crystallised from n-hexane to give colourless needles, m.p. 47—48 °C, yield 1.59 g (23.8%) (Found: C, 72.8; H, 5.41%. $C_9H_7O_2$ requires C, 73.0; H, 5.44%). The reaction was also carried out in DME. In both solvents the yield of (1a) was 22—27%.

Pyrocatecol mono-(3-phenylprop-2-ynyl) ether (1b). By general procedure (A) pyrocatechol (40 mmol) and 3-phenylprop-2-ynyl bromide (30 mmol) (b.p. 130—135 °C at 20 mmHg) (lit.,[11] b.p. 110—120 °C at 8 mmHg) yielded 1.73 g (25.7%) of (1b) as a yellow viscous oil, which was crystallised from n-hexane to give colourless needles, m.p. 77—79 °C (Found: C, 80.7; H, 5.50. $C_{15}H_{12}O_2$ requires C, 80.3; H, 5.39%).

2-Hydroxy-3-(prop-2-ynyloxy)naphthalene (1c). According to the general procedure (A), 1.46 g (37%) of (1c) was obtained from 2,3-dihydroxynaphthalene (22 mmol) and prop-2-ynyl bromide (20 mmol) as a yellow solid, which was recrystallised from benzene to give colourless needles, m.p. 95—96 °C. This compound is very easily air-oxidised, and so an elemental analysis could not be obtained.

o-(N-Prop-2-ynyl)aminophenol (1d). *General Procedure* B.—A mixture of *o*-aminophenol (1.09 g, 10 mmol) in ethyl acetate (5 ml) and prop-2-ynyl bromide (1.10 g, 9.2 mmol) in ether (5 ml) was set aside at room temperature for 48 h. The resulting dark red solution and precipitates were poured into water and adjusted to pH 7—8 with dilute sodium bicarbonate solution. The aqueous solution was extracted with ethyl acetate (3 × 20 ml), washed with brine, dried over anhydrous sodium sulphate, and concentrated. The residue was separated by silica gel column chromatography [benzene–ethyl acetate (9 : 1)]. The earlier fractions were collected and concentrated to give a red viscous oil, which was *o-(NN*-diprop-2-ynyl)aminophenol (1e) (122 mg, 7.2%); the later fractions were collected and concentrated to afford 888 mg (65.8%) of (1d) as a red viscous oil, which was crystallised from toluene as light yellow plates, m.p. 95—97 °C (lit.,[12] m.p. 97—98 °C). The spectral data are listed in Table 2.

o-(NN-Diprop-2-ynyl)aminophenol (1e). According to the general procedure (B), both reactants were dissolved in acetone and set aside at room temperature for 24 h; (1d)

(44.9%) and (1e) (28.3%) were obtained. When the reaction time was extended to 4 d, the products were (1d) (11%) and (1e) (82%). The alkylation was also carried out without solvent for 7 d by procedure (B); only 10.5% of (1d) and 24.3% of (1e) were obtained. Compound (1e) is an unstable red viscous oil.

o-(N-*Benzyl*-N-*prop*-2-*ynyl*)*aminophenol* (1f). According to the general procedure (B), from 6.5 mmol of (1d) and 7.8 mmol of benzyl bromide, 1.20 g (84.5%) of (1f) was obtained as an unstable red viscous oil.

o-(N-*acetyl*-N-*prop*-2-*ynyl*)*aminophenol* (1g). According to the general procedure (B), 1.05 g (55.8%) of (1g) was obtained from 10 mmol of (1d) and an equimolar amount of acetic anhydride for 4 d. Compound (1g) was crystallised from chloroform–acetone (2 : 1) to give colourless plates, m.p. 158—160 °C (Found: C, 69.7; H, 5.8; N, 7.3. $C_{11}H_{11}NO_2$ requires C, 69.8; H, 5.86; N, 7.40%).

Column chromatography (silica gel) of the mother-liquors using benzene–ethyl acetate (4 : 1) as eluant gave 278 mg (24.1%) of *o*-(*N*-acetyl-*N*-prop-2-ynyl)aminophenol acetate [contaminated with (1g)]; $\delta(CCl_4)$ 1.74 (s, 3 H), 2.20 (s, 3 H), 3.84 (ABX quartet, 1 H, J_{AB} 17, J_{AX} 3 Hz), 4.72 (ABX quartet, 1 H, J_{AB} 17, J_{BX} 3 Hz), and 7.04—7.48 (m, 4 H). This acetate was hydrolysed with 5%-sodium hydroxide solution (4 ml) for 24 h at room temperature, then worked up as usual to give pure (1g) almost quantitatively.

o-(N-*Benzoyl*-N-*prop*-2-*ynyl*)*aminophenol* (1h). By procedure (B), (1d) (10 mmol) and an equimolar amount of benzoyl chloride in methylene chloride (5 ml) were allowed to react for 48 h, to give a mixture of the desired (1h) and *o*-(*N*-benzoyl-*N*-prop-2-ynyl)aminophenol benzoate. This mixture was then hydrolysed with 5% sodium hydroxide solution (20 ml) as described above, to yield 74.1% of (1h) as a yellow solid. This solid was recrystallised from ethyl acetate to give light yellow cubes, m.p. 156—157 °C (Found: C, 76.4; H, 5.15; N, 5.5. $C_{16}H_{13}NO_2$ requires C, 76.5; H, 5.22; N, 5.57%).

2,3-*Dihydro*-2-*methylene*-1,4-*benzodioxin* (2a). *General Procedure C.*—In a 50-ml round-bottomed flask (1a) (500 mg), yellow mercuric oxide (30 mg), and DMF (8 ml) were mixed, and then refluxed for 20 h under a nitrogen atmosphere. The solution turned from colourless to dark brown. DMF was carefully removed under reduced pressure (20—25 mmHg) at below 60 °C. The dark brown residue was purified by silica gel column chromatography (eluant benzene) to give a colourless liquid (451 mg, 90%), b.p. 90—94 °C at 20 mmHg (lit.,[6] b.p. 89—90 °C at 18 mmHg). The spectral data of this liquid were identical with those of an authentic sample.

The Selection of Optimum Conditions for the Formation of (2a).—A mixture of (1a) (250 mg), mercuric oxide or mercuric acetate (15—20 mg; 6—8%), and solvent (4 ml) was refluxed for the appropriate time (see Table 1) under a nitrogen atmosphere. Solvent was removed under reduced pressure and the resulting residue was purified by silica gel column chromatography (eluant benzene). Table 1 shows the isolated yield of (2a). The pure product was identified by n.m.r. spectral and t.l.c. comparison with an authentic sample.

2-*Methyl*-1,4-*benzodioxin* (3a). Compound (2a) (200 mg) was treated with potassium t-butoxide in dry DMSO by known method,[6] to give (3a). This isomerisation was also performed by heating (2a) (382 mg) and toluene-*p*-sulphonic acid (8 mg) in refluxing dry benzene (10 ml) for 3 h. The product was purified by silica gel column chromatography with n-hexane to give pure (3a); δ (in CCl_4) 1.64 (d, 3 H, *J* 1.0 Hz), 5.58 (m, 1 H), and 6.44—6.74 (m, 4 H); i.r. (liquid film): 1 715, 1 600, and 1 265 cm^{-1}.

2,3-*Dihydro*-2-*methoxy*-2-*methyl*-1,4-*benzodioxin* (4a). Compound (2a) (147 mg) was treated with toluene-*p*-sulphonic acid (5 mg) in refluxing methanol (10 ml) for 3 h. After concentration the residue was passed through silica gel (to remove toluene-*p*-sulphonic acid) to give a colourless oil, b.p. 102—105 °C at 8—10 mmHg; i.r. (liquid film): 1 600, 1 395, and 750 cm^{-1}; $\delta(CCl_4)$ 1.40 (s, 3 H), 3.24 (s, 3 H), 3.70 (d, 1 H, *J* 10 Hz), 3.98 (d, 1 H, *J* 10 Hz), and 6.76 (s, 4 H); *m/e* 180 (M^+) (21%), 166 (18), 149 (100), 148 (54), 109 (27), 72 (40), and 53 (18) (Found: C, 66.3; H, 6.7. $C_{10}H_{12}O_3$ requires C, 66.6; H, 6.71%).

2,3-*Dihydro*-2-*benzylidene*-1,4-*benzodioxin* (2b). By the general procedure C, heating (1b) (3.5 mmol) for 60 h gave (2b) (176 mg, 22%) as a yellow viscous oil; i.r. (liquid film): 1 680, 1 670, 1 600, and 1 495 cm^{-1}; *m/e* 224 (M^+), 197, 146, 116, 115, 105, and 77. In the n.m.r. spectrum (in CCl_4) of (2b) two methylene proton signals appeared at δ 4.50 and 4.70 as narrow multiplets with a ratio of *ca.* 2 : 1, and two olefinic proton signals appeared at δ 5.44 and 6.36 with a ratio of *ca.* 2 : 1. The *syn*-proton (adjacent to the oxygen) signal should appear at lower field than the *anti*-proton,[5,13] so the pair of the signals at δ 4.50 and 5.44 is assigned to the *anti*-(2b) isomer, and the other pair of signals to the *syn*-(2b) isomer; the molar ratio of *syn* : *anti* is *ca.* 1 : 2.

2,3-*Dihydro*-2-*methylene*-1,4-*naphtho*[2,3-b]*dioxin* (2c). According to the general procedure C, (1c) (2.5 mmol) yielded (2c) (215 mg, 43%) as a white solid, which was recrystallised from n-hexane to give colourless leaflets, m.p. 62—64 °C (Found: C, 78.6; H, 5.2. $C_{13}H_{10}O_2$ requires C, 78.8; H, 5.09%).

Attempts to cyclise (1d). Using the general procedure C, (1d) (4 mmol) was allowed to react and the course of the reaction was monitored by t.l.c. The amount of (1d) gradually decreased and after 20 h reflux it had almost disappeared. Compound (2d) could be detected by t.l.c., but the yield of pure (2d) was only 3 mg.

2,3-*Dihydro*-2-*methylene*-(N-*prop*-2-*ynyl*)-1,4-*benzoxazine* (2e). According to the general procedure C, (1e) (4 mmol) yielded (2e) (555 mg, 75%) as a red viscous oil. Compound (2e) is unstable and gradually decomposes even in the refrigerator.

N-*Benzyl*-2,3-*dihydro*-2-*methylene*-1,4-*benzoxazine* (2f). By the general procedure C, (1f) (3 mmol) was cyclised to give (2f) (468 mg, 66%) as an unstable orange viscous oil.

N-*Acetyl*-2,3-*dihydro*-2-*methylene*-1,4-*benzoxazine* (2g). According to the general procedure C, (1g) (3 mmol) was cyclised to afford (2g) (426 mg, 75%) as a yellow oil (Found: C, 69.4; H, 5.9; N, 7. $C_{11}H_{11}NO_2$ requires C, 69.8; H, 5.86; N, 7.40%).

N-*Benzoyl*-2,3-*dihydro*-2-*methylene*-1,4-*benzoxazine* (2h). According to the general procedure C, (1h) (4 mmol) was cyclised to afford (2h) (783 mg, 78%) as a yellow solid, which was recrystallised from benzene to give light yellow plates, m.p. 116—117 °C (Found: C, 76.6; H, 5.15; N, 5.3. $C_{16}H_{13}NO_2$ requires C, 76.5; H, 5.22; N, 5.57%).

N-*Benzoyl*-2,3-*dihydro*-2-*methoxy*-2-*methyl*-1,4-*benzoxazine* (4h). A solution of (2h) (537 mg) and toluene-*p*-sulphonic acid (8.3 mg) in methanol (50 ml) was refluxed for 4 h. After concentration the residue was purified by silica gel column chromatography [benzene–ethyl acetate (9 : 1)]. The desired oxazine (4h) was obtained as a solid (514 mg,

85%), which was recrystallized from benzene–n-hexane (2 : 1) to give colourless, needles, m.p. 154—155 °C (Found: C, 72.1; H, 6.0; N, 4.95. $C_{17}H_{17}NO_3$ requires C, 72.1; H, 6.05; N, 4.94%).

2-Benzoyl-1-oxo-1-phenylpent-4-yne (5a). By the general procedure A, dibenzoylmethane (5.15 g, 23 mmol) and prop-2-ynyl bromide (1.79 g, 15 mmol) were allowed to react. After addition was complete the reaction mixture was stirred at room temperature for 1 h, then refluxed for 4 h, and worked up as described for procedure A. Compound (5a) was obtained as a yellow solid which was recrystallised from n-hexane–benzene (2 : 1) to give light yellow cubes (2.04 g, 52%), m.p. 70—70.5 °C (Found: C, 82.2; H, 5.4. $C_{18}H_{14}O_2$ requires C, 82.4; H, 5.38%); i.r. (KBr); 2 110 [ν(C≡C)], 1 695, 1 660 [ν(C=O)], 1 600, and 690 cm^{-1} (phenyl); δ(CCl_4) 1.84 (t, 1 H, *J* 2.5 Hz), 2.90 (q, 2 H, *J* 2.5 and 7.0 Hz), 5.42 (t, 1 H, *J* 7.0 Hz), and 7.20—8.00 (m, 10 H); *m/e* 262 (M^+) (11%), 105 (100), 77 (44), and 51 (20).

3-Benzoyl-4-methyl-2-phenylfuran (8a). By the general procedure C, (5a) (524 mg, 2 mmol) and mercuric oxide (50 mg) in DMF (3 ml) were refluxed for 48 h. After purification by silica gel column chromatography [benzene–n-hexane (2 : 1)] compound (8a) (393 mg, 75%) was obtained as a yellow oil; i.r. (liquid film); 1 650 [ν(C=O)], 1 600, 1 495 (phenyl), and 1 380 cm^{-1} (methyl); δ(CCl_4) 2.32 (s, 3 H), 6.18 (s, 1 H), and 7.10—7.80 (m, 10 H); *m/e* 262 (M^+) (76), 185 (32), 105 (100), and 77 (76) (Found: C, 82.1; H, 5.3. $C_{18}H_{14}O_2$ requires C, 82.4; H, 5.38%).

The author thanks Mr. Michio Shido at the Analytical Centre in Kyushu University for combustion analyses, and the Japanese Ministry of Education for financial support.

[9/096 *Received*, 22*nd January*, 1979]

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