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SYNTHETIC APPLICATION OF LITHIATION REACTIONS—VII[a]

NEW SYNTHESES OF LINEAR AND ANGULAR NAPHTHOFURANS AND BENZOCOUMARINS[b]

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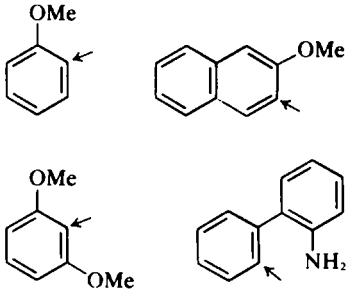
Abstract—Using lithiation reaction, four methoxy and hydroxynaphthaldehydes have been synthesised. Three of these have been converted into the corresponding naphthofurans and benzocoumarins.

The orientation in the lithiation reactions is characteristically different from those in acid catalysed electrophilic aromatic substitution reactions. Thus, in contrast to the latter, lithiation occurs specifically at *ortho* or other sterically close positions with respect to groups like –OMe, $-NH_2$, $-CH_2NMe_2$, –CONHMe, etc.[1] Further when two or more such sterically accessible positions are present, the reaction occurs at that position which is less active in electrophilic reactions.[1]

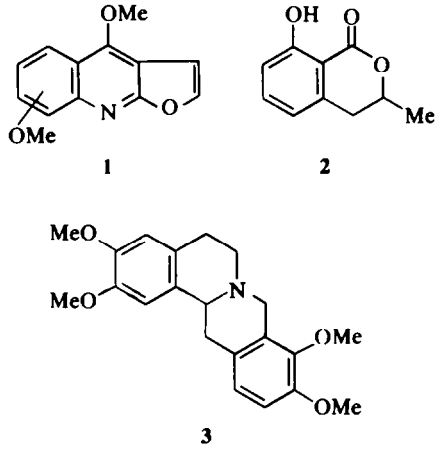
These trends in lithiation reactions are illustrated by the following examples where the arrows indicate the positions most favoured in lithiation reactions.[2-5]



Mechanistically the orientation is explained by a sequence which involves first complexation of the lithiating agent with the electron donor groups present, followed by removal of the most acidic hydrogen from *ortho* or other sterically close position.[6,7]

The above characteristic feature of the lithation reaction can lead to the substitution pattern not available by acid catalysed methods and could be of immense utility in organic synthesis. In earlier papers we have illustrated the usefullness of lithiation reactions by achieving new synthesis of several heterocyclic compounds in simple steps and in better over all yields. Among the natural products synthesised were the furoquinoline alkaloids (1),[8,9] mellein (2),[10] tetrahydropalmatine (3),[11] which were available only by lengthy acid catalysed methods.

The present paper further illustrates the versatility of lithiation reactions in organic synthesis. Thus, starting with methoxynaphthalenes the lithiation reaction gave, in one step, four of the methoxynaphthaldehydes. Three of



the methoxyaldehydes were then converted into the corresponding naphthofurans and benzocoumarins.

Methoxy naphthaldehydes

The methoxy naphthaldehydes were obtained according to Scheme 1.

The methoxynaphthalenes were lithiated. Treatment of the organometallic compound with N-methylformanilide furnished the formyl derivatives.

From 2-methoxynaphthalene the lithiation route gave the 3-formyl derivative as the major compound in 67% yield. The 1-isomer was obtained in only 7% yield. However the latter was obtained in 77% yield, as the exclusive product, by Vilsmeier Haack reaction on 2-methoxynaphthalene.

From 1-methoxynaphthalene the lithiation route furnished the 2-formyl derivative in 38% yield, while the 8-isomer was obtained only in 9% yield. Vilsmeier Haack reaction furnished only the 4-formyl derivative, and none of the desired isomers. Although the yield of the 8-isomer obtained by lithiation reaction is poor, the method is still vastly superior to the recently reported[12] multistep synthesis of the compound.

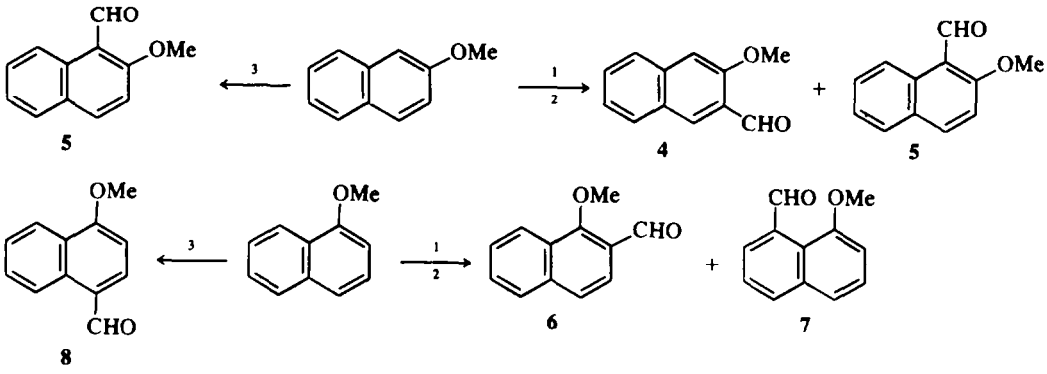
Naphthofurans

The synthesis of naphthofurans was according to Scheme 2.

The methoxynaphthaldehydes obtained earlier were reacted with methoxymethylenetriphenylphosphonium chloride and KOt-Bu. A mixture of enol ethers was obtained in 70–80% yield. Only the enol ether from 2-

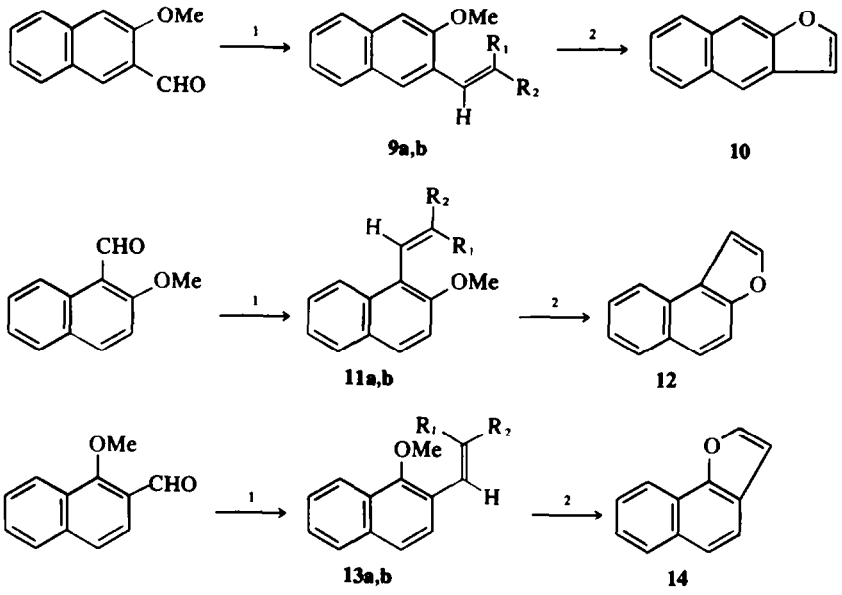
[a] Part VI: N. S. Narasimhan and R. S. Mali, *Tetrahedron* **30**, 4153 (1974).

[b] For a preliminary communication, see *Tetrahedron Letters* 843 (1973).



Reagents: 1. n-BuLi; 2. $PhN(CH_3)CHO$; 3. $PhN(CH_3)CHO/POCl_3$

Scheme 1.



a: $R_1 = H$; $R_2 = OMe$
b: $R_1 = OMe$; $R_2 = H$

Reagents: 1. $Ph_3\overset{+}{P}CH_2OMeCl^-$/KOt-Bu; 2. Py.HCl

Scheme 2.

methoxy-1-naphthaldehyde could be separated into its *cis* and *trans* isomers by simple chromatography. Since a separation of the mixtures into their *cis* and *trans* constituents was not obligatory for the further synthesis, no serious attempt was made to separate the mixture obtained in other reactions. The mixtures were demethylated as such when the naphthofurans were directly obtained.

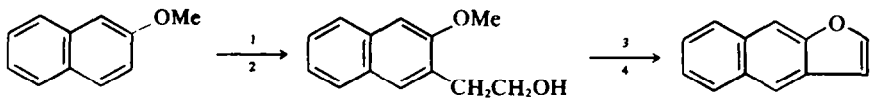
It may be mentioned that earlier[13] we had described another synthesis of the linear naphthofuran. The key step in that was also lithiation of 2-methoxynaphthalene. The organometallic compound was treated with ethylene oxide. Demethylation of the hydroxyethyl derivative furnished the dihydronaphthofuran, which was dehydrogenated to the naphthofuran (Scheme 3).

In the above scheme, although the steps till the dihydroderivative proceed satisfactorily, the dehydrogenation did not give the naphthofuran in reproducibly good yield. In the present synthesis, the final dehydrogenation is obviated, which then represents a definite improvement over the previous one.

Benzocoumarins

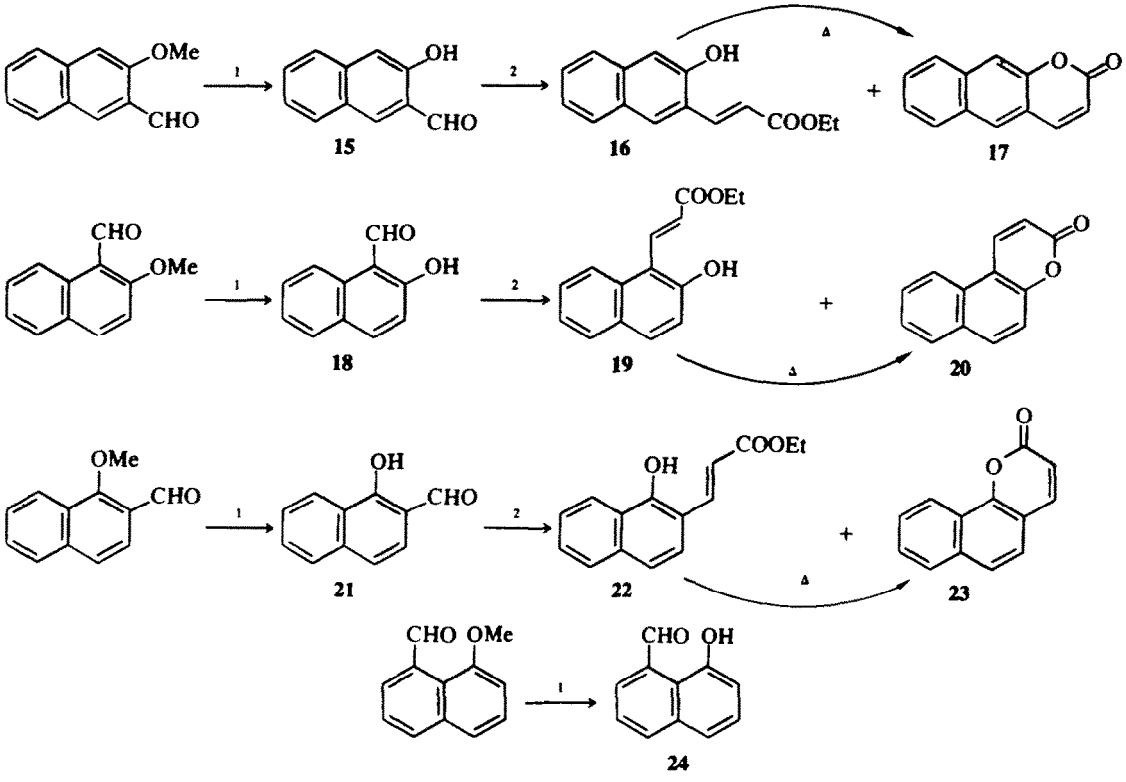
The synthesis of the three possible benzocoumarins is shown in Scheme (4).

The methoxynaphthaldehydes were demethylated with



Reagents: 1. n-BuLi; 2.  ; 3. HBr/AcOH; 4. Pd/C

Scheme 3.



Reagents: 1. $AlCl_3$ in CH_2Cl_2; 2. $Ph_3P{=}CHCOOEt$

Scheme 4.

$AlCl_3$. The hydroxyaldehydes were condensed with the stable carbethoxymethylenetriphenylphosphorane. Mixtures of the benzocoumarins and the uncyclised *trans* ($J = 16$ Hz) unsaturated esters were obtained which were separated by chromatography. The uncyclised esters were also converted into the benzocoumarins in excellent yield. The overall yields obtained were far superior to all known methods. Neutral reaction condition, high yield, stability and ready availability of the phosphorane, enhance the utility of the synthesis for obtaining the benzocoumarins.

EXPERIMENTAL

All mps and bps are uncorrected. IR spectra were measured as nujol mulls, and UV in MeOH soln. Chemical shifts are expressed in ppm downfield from TMS. n-BuLi used was in ether solution prepared according to Gilman.[14]

Methoxynaphthaldehydes

2-Methoxy-3-naphthaldehyde (**4**) *and 2-methoxy-1-naphthaldehyde* (**5**). A soln of 2-methoxynaphthalene (9·3 g) in ether (100 ml) was treated with *n*-BuLi in ether (from 2·7 g Li and 13·5 ml *n*-BuBr). After refluxing for 18 hr, it was treated with a soln of N-methylformanilide (17·5 ml) in ether (25 ml), refluxed for 30 min, and hydrolysed by pouring over crushed ice containing dil HCl. The residue (9·8 g), obtained after ether extraction, on chromatography over silica gel gave a solid from the initial light petroleum eluates, which on crystallisation furnished **4** (7·1 g, 64·8%), light yellow needles from hexane, m.p. 93° (Lit.[15] m.p. 92°) (Found: C, 76·96; H, 5·45. $C_{12}H_{10}O_2$ requires; C, 77·43, H, 5·37%).

Further elution with the same solvent gave **5** (0·75 g, 7%) light yellow needles from hexane, m.p. 85° (Lit.[16] m.p. 84°) (Found: C, 77·49; H, 5·10. $C_{12}H_{10}O_2$ requires; C, 77·43; H, 5·37%).

1-Methoxy-2-naphthaldehyde (**6**) *and 1-methoxy-8-naphthaldehyde* (**7**). 1-Methoxynaphthalene (9·3 g) was lithiated, refluxed for 1 hr after addition of N-methylformanilide, and hydrolysed. The residue obtained after ether extraction, on chromatography over silica gel in light petroleum gave the starting compound (1·8 g) from the initial eluates and then **6** (3·3 g, 37·4% on the basis of compound reacted), white prisms from light petroleum, m.p. 58° (Lit.[17] m.p. 47°) (Found: C, 77·2; H, 5·48. $C_{12}H_{10}O_2$ requires; C, 77·43; H, 5·37%).

Further elution with the same solvent gave **7** (0·8 g, 9%, on the basis of compound reacted), white needles from hexane, m.p. 91–2°; (Lit.[12] m.p. 88–90°). ν_{max} (nujol) 1662 cm^{-1} (–CHO). ν_{max} ($CHCl_3$) 2800, 1680, 1622 cm^{-1}; λ_{max} 251·5 and 330 nm (log ϵ 4·42 and 3·68); NMR (CCl_4), δ 3·95 (3H, *s*, –OMe); 6·8 (1H, *dd*, $J = 7$ and 2 Hz, C_2H), 7·35 (3H, *m*, C_3H, C_4H and C_6H); 7·8 (2H, *dd*, $J = 7$ and 2 Hz, C_5H and C_7H); 10·85 (1H, *s*, –CHO). (Found: C, 77·13; H, 5·67. $C_{12}H_{10}O_2$ requires; C, 77·43; H, 5·37%).

IR, UV and NMR were in agreement with reported[12] values.

2-Methoxy-1-naphthaldehyde (**5**). N-Methylformanilide (6·5 g) and $POCl_3$ (4·7 ml) were mixed and kept at room temp for 1 hr. 2-Methoxynaphthalene (7·5 g) was added with stirring, heated on waterbath for 3 hr, and the mixture poured over crushed ice. The solid obtained, on crystallisation, furnished **5**, (6·8 g, 77%) light needles from hexane, m.p. 84–5°, undepressed with authentic sample.

1-Methoxy-4-naphthaldehyde (**8**). 1-Methoxynaphthalene (7·5 g) was reacted with N-methylformanilide and $POCl_3$ as in the previous experiment. The residue (8·5 g) obtained after ether extraction, on distillation yielded **8** (6·5 g, 73·6%), b.p. 160°/0·2 mm, (Lit.[16] b.p. 212°/40 mm) ν_{max} 1680 cm^{-1} (Found: C, 77·28; H, 5·72. $C_{12}H_{10}O_2$ requires; C, 77·43; H, 5·37%).

Naphthofurans

Methoxyvinylnaphthalenes. Detailed procedure is described for **11a** and **11b**. The others were obtained by similar procedure. Chromatography was done over silica gel and the columns eluted successively with light petroleum and light petroleum-benzene (1:1).

2-*Methoxy*-cis *and* trans-1-(2-*methoxyvinyl*) *naphthalenes* **11a** *and* **11b**. To an ice cold suspension of methoxymethyltriphenylphosphonium çhloride (6·86 g) in ether (70 ml, N_2 atm) was added t-BuOK (2·24 g) in *t*-BuOH (20 ml, freshly distilled over calcium hydride). After 20 min, when the red colour of the ylide had fully developed, a solution of **5** (1·86 g) in ether (25 ml) was introduced at an even rate (5 min). The mixture was stirred for 3 hr and decomposed with water. The residue (10 g), obtained after extraction, on chromatography over silica gel in light petroleum gave a liquid from initial eluates, which on distillation yielded **11a** (0·9 g, 42%); b.p. 165°/0·4 mm; ν_{max} 1635 cm^{-1} (enol ether); NMR (CCl_4), δ 3·7 and 3·77 (3H each, *s*, 2X-OMe); 5·98 and 7·02 (1H each, *d*, J = 13 Hz, *trans* –CH=CH–), 7·1–8·1 (6H, *m*, aromatic H's). (Found: C, 78·52; H, 7·02. $C_{14}H_{14}O_2$ requires; C, 78·48; H, 6·59%).

Further elution with light petroleum-benzene (1:1), gave another liquid, which on distillation furnished **11b**, (0·800 g, 37·4%) b.p. 160°/0·4 mm; ν_{max} 1650 cm^{-1} (enol ether); NMR (CCl_4), δ 3·45 and 3·77 (3H each, *s*, 2*x*-OMe); 5·45 and 6·15 (1H each *d*, J = 7 Hz, *cis* –CH=CH–), 6·9–7·9 (6H, *m*, aromatic H's); (Found: C, 78·49; H, 6·57. $C_{14}H_{14}O_2$ requires; C, 78·48; H, 6·59%).

2-*Methoxy*-cis *and* trans-3-(2-*methoxyvinyl*) *naphthalenes* **9a** *and* **9b**. 2-Methoxy-3-naphthaldehyde (1·86 g) gave a residue (10·5 g). Chromatographic separation gave in the light petroleum benzene (1:1) fraction, a liquid, which on distillation furnished a mixture of **9a** and **9b** (1·55 g, 72·4%), b.p. 145°/0·1 mm; ν_{max} 1652 cm^{-1} (*cis* enol ether), 1635 cm^{-1} (*trans* enol ether); NMR (CCl_4), δ 3·63 and 3·7 (3H each, *s*, –OMe); 3·83 (6H, *s*, 2*X*-OMe); 5·98 and 7·0 (1H each, *d*, J = 13 Hz, *trans* –CH=CH–); 5·67 and 6·11 (1H each, *d*, J = 7 Hz, *cis* –CH=CH–), 7·0–8·35 (12H, *m*, aromatic H's). (Found: C, 78·84; H, 6·31. $C_{14}H_{14}O_2$ requires; C, 78·48; H, 6·59%).

1-*Methoxy*-cis *and* trans-2-(2-*methoxyvinyl*) *naphthalenes* **13a** *and* **13b**. 1-Methoxy-2-naphthaldehyde (1·86 g) gave a residue (9·8 g) which on chromatographic separation furnished in light petroleum benzene (1:1) fraction, a liquid which was distilled to yield a mixture of **13a** and **13b** (1·42 g, 66·4%); b.p. 220° (bath)/0·2 mm ν_{max} 1648 cm^{-1} (*cis* enol ether) and 1630 cm^{-1} (*trans* enol ether); NMR (CCl_4), δ 3·65 (6H, *s*, 2X-OMe); 3·81 (6H, *s*, 2X-OMe); 6·1 and 7·11 (1H each, *d*, J = 13 Hz, *trans* –CH=CH–); 5·65 and 6·05 (1H each, *d*, J = 7 Hz, *cis* –CH=CH–), 7·23–8·1 (12H, *m*, aromatic H's). (Found C, 78·08; H, 6·27. $C_{14}H_{14}O_2$ requires; C, 78·48; H, 6·59%.)

Naphthofurans

These were prepared according to the procedure described for **10** except for the modification mentioned against individual compounds.

Naphtho (**2,3-b**) *furan* (5:6-*benzocoumarone*) (**10**). A mixture of **9a** and **9b** (130 mg), obtained from the total light petroleum-benzene (1:1) eluates, was heated with pyridinehydrochloride (800 mg) at 160–70° for 2 hr and poured over crushed ice. Acidification (HCl) and extraction with ether gave a brown solid, which on chromatography over neutral alumina in benzene gave a white solid from the benzene eluates. Crystallisation from EtOH followed by sublimation *in vacuo* gave **10** (30 mg, 29·4%), m.p. 119° identical (m.p., mixed m.p., UV and IR) with an authentic sample.

Naphtho (**2,1-b**) *furan* (4:5-*benzocoumarone*) (**12**). The heating with pyridine hydrochloride was for 6 hr at 200–10°. The reddish oil, obtained from 1 g of the mixture of **11a** and **11b**, on chromatography over silica gel in benzene gave a low melting solid, which on crystallisation furnished **12** (0·350 g, 46·6%), white needles from light petroleum, m.p. 61° (Lit.[18] m.p. 60–1°), λ_{max} 229·5, 236·5, 252, 258·5, 261·5, 281·5, 288, 296, 301, 308, 315 and 323 nm (log ϵ 4·21, 4·17, 3·52, 3·37, 3·34, 3·81, 3·86, 3·79, 3·66, 3·62, 3·46 and 3·67); NMR (CCl_4), δ 7·15 (1H, *d*, J = 2 Hz furan βH), 7·7 (1H, *d*, J = 2 Hz, furan αH); 7·3–8·1 (6H, *m*, aromatic H's). (Found: C, 86·04; H, 5·00. $C_{12}H_8O$ requires; C, 85·69; H, 4·79%). UV and NMR were in agreement with reported[23,24] values.

Naphtho (**1,2-b**) *furan* (6:7-*benzocoumarone*) (**14**). The heating with pyridine hydrochloride was for 2 hr at 130–40°. The reddish oil, obtained from 0·5 g of the mixture of **13a** and **13b**, on chromatography over silica gel in benzene gave a liquid, which on distillation furnished **14** (0·120 g, 28·0%), b.p. 200° (bath)/1·5 mm, (Lit.[19] b.p. 282–4°/755 mm). λ_{max} 237·5, 244, 261, 270·5, 280, 291, 306, 315, 322, 330 and 358 nm (log ϵ 4·62, 4·79, 3·80, 3·74, 3·69, 3·51, 3·14, 3·16, 3·05, 3·10 and 2·59). (Found: C, 85·52, H, 5·08. $C_{12}H_8O$ requires; C, 85·69; H, 4·79%), Picrate m.p. 113–4° (Lit.[19] m.p. 113°).

Benzocoumarins

Hydroxynaphthaldehydes: *General procedure for the demethylation of methoxy naphthaldehydes*. A suspension of anhyd $AlCl_3$ (2 g, powdered) in CH_2Cl_2 (10 ml) was stirred at room temp for 2 hr. The methoxynaphthaldehyde (1 g) in CH_2Cl_2 (10 ml) was added and stirred for 2 hr. The mixture was poured in dil HCl and extracted with chloroform. The residue obtained, after removal of solvent, on crystallisation from hexane furnished the hydroxyaldehyde.

2-*Hydroxy*-3-*naphthaldehyde* (**15**). Demethylation of 2-methoxy-3-naphthaldehyde (1 g) gave **15**, (0·85 g, 92%), yellow needles from hexane, m.p. 99–100° (Lit.[9] m.p. 99–100°) (Found: C, 76·88; H, 4·81. $C_{11}H_8O_2$ requires: C, 76·73; H, 4·68%).

2-*Hydroxy*-1-*naphthaldehyde* (**18**). Demethylation of 2-methoxy-1-naphthaldehyde (1 g) gave **18**, (0·89 g, 96%), light yellow needles from hexane, m.p. 82° (Lit.[5], m.p. 81°). (Found: C, 76·68; H, 4·44. $C_{11}H_8O_2$ requires: C, 76·73; H, 4·68%).

1-*Hydroxy*-2-*naphthaldehyde* (**21**). Demethylation of 1-methoxy-2-naphthaldehyde gave **21**, (0·86 g, 93%), white needles from hexane, m.p. 57–8° (Lit.[6] m.p. 59°) (Found: C, 76·93; H, 4·96. $C_{11}H_8O_2$ requires: C, 76·73; H, 4·68%).

1-*Hydroxy*-8-*naphthaldehyde* (**24**). 1-Methoxy-8-naphthaldehyde (500 mg) was demethylated to **24**, (402 mg, 87%); according to the procedure of Berry and Smith, orange plates from pentane, m.p. 90–3° (Lit.[12] m.p. 92–6°) (Found: C, 76·70, H, 4·36. $C_{11}H_8O_2$ requires: C, 76·73; H, 4·68%).

Benzocoumarins

The procedure is described in detail for 6:7 benzocoumarin **17**. The others were synthesised with the modifications described against individual compounds.

6: 7-*Benzocoumarin* (2H-*naphtho* [**2,3-b**] *pyran*-2 *one*) (**17**). A mixture of 2-hydroxy-3-naphthaldehyde (0·650 g) and carbethoxymethylenetriphenylphosphorane (1·30 g) in anhyd benzene (20 ml) was refluxed for 2 hr. The residue (1·9 g) obtained, after removal of solvent, on chromatography over silica gel gave in the initial benzene eluates **17** (30 mg, 3·5%), white needles from chloroform light petroleum, m.p. 165° (Lit.[21] m.p. 163–4°). ν_{max} 1720 cm^{-1} (lactone of the coumarin); λ_{max} 253, 264·5, 274, 318 and 363 nm (log ϵ 3·95, 4·22, 4·29, 4·13 and 4·96); NMR ($CDCl_3$), δ 6·4 (1H, *d*, J = 10 Hz, C_3H); 7·27–7·93 (7H, *m*, aromatic H's) (Found: C, 79·59; H, 4·38. $C_{13}H_8O_2$ requires: C, 79·58; H, 4·11%).

Further elution with the same solvent furnished **16**, (0·850 g, 84·3%) light yellow needles from chloroform, m.p. 187°. ν_{max} 3160 cm^{-1} (hydroxyl), 1660 cm^{-1} (conjugated ester); λ_{max} 262, 271·5, 311·5 and 364 nm (log ϵ 6·24, 6·33, 4·21 and 3·22), after addition of 2N NaOH it showed λ_{max} 237·5, 277, 326 and 424 nm (log ϵ 4·57, 4·70, 4·42 and 3·69); NMR (DMSO-d_6), δ 1·27 (3H, *t*, –O–CH_2–$\underline{CH_3}$), 4·17 (2H, *q*, –O–$\underline{CH_2}$–CH_3), 6·72 and 7·92 (1H each, *d*, J = 16 Hz, *trans* –CH=CH–), 10·22 (1H, *s*, phenolic OH), 7·1–8·1 (6H, *m*, aromatic H's) (Found: C, 73·98; H, 6·01. $C_{15}H_{14}O_3$ requires: C, 74·36; H, 5·83%).

Cyclisation of ethyl trans-β (2-*hydroxy naphth*-3*yl*) *acrylate* (**16**) *to* 6:7-*benzocoumarin* (**17**). The ester **16** (100 mg) was heated at 240–50° under N_2 for 15 hr. The crude solid dissolved in benzene was passed through the column of silica gel to furnish **17**, (60 mg, 84·4%), m.p. 164–5°, mixed m.p. undepressed with authentic sample.

5:6-*Benzocoumarin* (3H-*naphtho* [**2,1-b**] *pyran*-3-*one*) (**20**). A mixture of 2-hydroxy-1-naphthaldehyde (0·4 g) and carbethoxymethylenetriphenylphosphorane (0·8 g) in anhyd benzene (15 ml) was refluxed for 6 hr. Work up as in the previous case followed by chromatography over silica gel gave unreacted 2 hydroxy-1-naphthaldehyde (0·130 g) from the initial benzene eluates and then **20** (0·161 g, 52·4% on the basis of recovered starting compound) rosettes of needles from benzene-hexane, m.p. 118° (Lit.[22] m.p. 117–8°), ν_{max} 1720 cm^{-1} (lactone of the coumarin); λ_{max} 245, 251·5,

314·5 and 345 nm (log ε 3·97, 3·91, 4·07 and 4·11); NMR ($CDCl_3$), δ 6·47 (1H, *d*, J = 10 Hz, C_3H); 7·3–8·2 (6H, *m*, aromatic H's); 8·4 (1H, *d*, J = 10 Hz, C_4H); (Found: C, 79·75; H, 4·03. $C_{13}H_8O_2$ requires: C, 79·58; H, 4·11%). IR and UV were in agreement with reported[22] values.

Further elution with the same solvent furnished, **19** (0·090 g, 23·7% on the basis of compound reacted) long leaflets from hexane-acetone, m.p. 148°, ν_{max} 3340 cm^{-1} (OH) and 1670 cm^{-1} (conjugated ester); λ_{max} 251, 307, 317 and 353·5 nm (log ε 4·46, 4·19, 4·21 and 4·20); on addition of 2N NaOH it displayed λ_{max} 246, 260, 324 and 409 nm (log ε 4·35, 4·28, 3·97 and 4·11), NMR (DMSO-d_6), δ 1·25 (3H, *t*, $-O-CH_2-\underline{CH_3}$); 4·17 (2H, *q*, $-O\underline{CH_2}-CH_3$); 6·75 and 8·17 (1H each, *d*, J = 16 Hz, *trans*–CH=CH–); 10·57 (1H, *s*, phenolic –OH); 7·07–8·05 (6H, *m*, aromatic H's) (Found: C, 74·25; H, 5·72. $C_{15}H_{14}O_3$ requires: C, 74·36; H, 5·83%).

Cyclisation of ethyl trans *β-(2-hydroxynaphth-1-yl) acrylate to 5:6-benzocoumarin* (**20**). The ester **19** (100 mg) was heated at 160° under N_2 for 2 hr. Workup gave **20**, (62 mg, 87·3%), m.p. 118°, mixed m.p. undepressed with an authentic sample.

7:8-*Benzocoumarin* (2H-*naphtho* [1,2-b] *pyran-2-one* (**23**). Following the procedure for **17** a mixture of 1-hydroxy-2-naphthaldehyde (0·4 g) was refluxed with the phosphorane for 1 hr. Usual work up gave **23**, (15 mg, 3·3%) needles from chloroform-light petroleum, m.p. 142° (Lit.[22] m.p. 140–1°), ν_{max} 1725 cm^{-1} (lactone of the coumarin); λ_{max} 264, 274, 293·5, 305, 318·5 and 352 nm (log ε 4·5, 4·61, 3·81, 3·93, 4·06 and 3·72), NMR ($CDCl_3$), δ 6·43 (1H, *d*, J = 10 Hz, C_3H); 7·17–8·57 (7H, *m*, aromatic H's and C_4H). (Found: C, 79·69; H, 4·28. $C_{13}H_8O_2$ requires, C, 79·58; H, 4·11%.) IR and UV were in agreement with reported[22] values.

Further elution with the same solvent furnished **22**, (520 mg, 92·7%), white needles from benzene, m.p. 158°. ν_{max} 3280 (OH), 1665 (conjugated ester); λ_{max} 280·5, 309 and 358 nm (log ε 4·39, 4·17 and 3·98), after addition of 2N NaOH it exhibited λ_{max} 234, 299 and 420 nm (log ε 4·81, 4·93 and 4·71); NMR (DMSO-d_6), δ 1·25 (3H, *t*, $-O-CH_2-CH_3$), 4·14 (2H, *q*, $-O-\underline{CH_2}-CH_3$); 6·43 and 8·18 (1H, each, *d*, J = 16 Hz, *trans* –CH=CH–), (–OH exchanged with D_2O); 7·18–8·3 (6H, *m*, aromatic H's) (Found: C, 74·50; H, 6·15. $C_{15}H_{14}O_3$ requires: C, 74·36; H, 5·83%).

Cyclisation of ethyl trans-*β-(1-hydroxynaphth-2-yl) acrylate* (**22**) *to* 7:8-*benzocoumarin* (**23**). The ester **22** (100 mg) was heated at 200° under N_2 for 5 hr. Work up gave **23**, (57 mg, 70·4%), m.p. 142°, mixed m.p. undepressed with authentic sample.

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