

## Spirans. Part VIII.<sup>1</sup> 1,2-Naphthoquinone 1-Methide and its Spiro-dimer in Chroman Syntheses

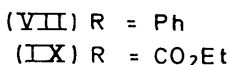
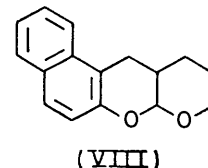
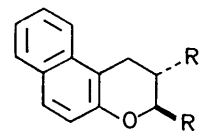
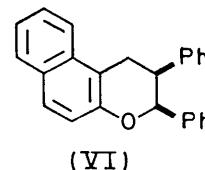
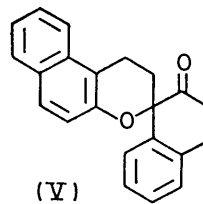
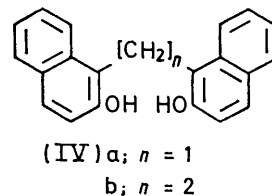
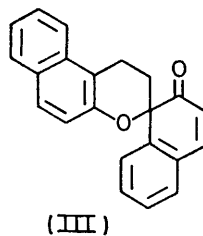
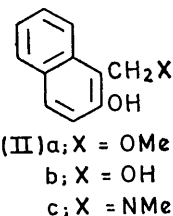
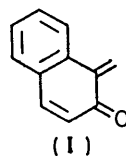
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Fully characterised for the first time, 1-hydroxymethyl-2-naphthol is an unsatisfactory source of 1,2-naphthoquinone 1-methide (I) because heat rapidly changes it into 1,1'-methylene-2-naphthol. 1-Dimethylaminomethyl-2-naphthol, heated with alkenes, gives chroman derivatives mixed with the naphthoquinone spiro-dimer (III). The spiro-dimer dissociates sufficiently at 160–200° to provide a good source of the naphthoquinone methide with the additional advantages that the absence of bases and protic molecules reduces side reactions and allows the reaction to be prolonged for higher yields.

1,2-NAPHTHOQUINONE 1-METHIDE (I) is usually obtained by thermal eliminations of HX from the naphthol derivatives (II). The methoxymethylnaphthol (IIa) has been used to prepare the quinone methide itself,<sup>2</sup> but where this has been merely an intermediate in chroman syntheses the common practice has been to use the hydroxymethylnaphthol<sup>3,4</sup> (IIb) or the Mannich base<sup>4</sup> (IIc). In our experience these methods are not entirely satisfactory because of side reactions, especially those induced by the eliminated species (water, dimethylamine), and we now show that a better source of the quinone methide is provided by thermal dissociation of its dimer (III).†

For our purposes the hydroxymethylnaphthol (IIb) proved to be a poor source, mainly because of its tendency to change into the methylenedinaaphthol (IVa) with the extrusion of formaldehyde. Indeed, the wide range of m.p.s quoted for the compound makes it probable that earlier workers<sup>5-10</sup> have described and worked with various mixtures of the alcohol with the dinaaphthol. Although the alcohol is formed by the

methods reported, it must be purified without the use of even moderate heat and without the use of chromatographic columns. Silica appears to be an effective



† This and other structures designate racemates.

<sup>1</sup> Part VII, D. J. Bennett, F. M. Dean, and A. W. Price, *J. Chem. Soc. (C)*, 1970, 1557.

<sup>2</sup> S. B. Cavitt, H. Sarrafzadeh R., and P. D. Gardner, *J. Org. Chem.*, 1962, **27**, 1211.

<sup>3</sup> K. Hultsch, *J. prakt. Chem.*, 1941, **158**, 275; **159**, 180; *Angew. Chem.*, 1948, **60**, 179; H. Euler, E. Adler, and J. O. Cedwall, *Arkiv Kemi*, 1941, **14A**, 1.

<sup>4</sup> J. Brugidou and H. Christol, *Compt. rend.*, 1963, **256**, 3149, 3323.

<sup>5</sup> A. H. Cook, J. Downer, and B. Hornung, *J. Chem. Soc.*, 1941, 502.

<sup>6</sup> D. Shirley and W. C. Sheehan, *J. Amer. Chem. Soc.*, 1955, **77**, 4606.

<sup>7</sup> P. W. Clutterbuck and J. B. Cohen, *J. Chem. Soc.*, 1923, **123**, 2507.

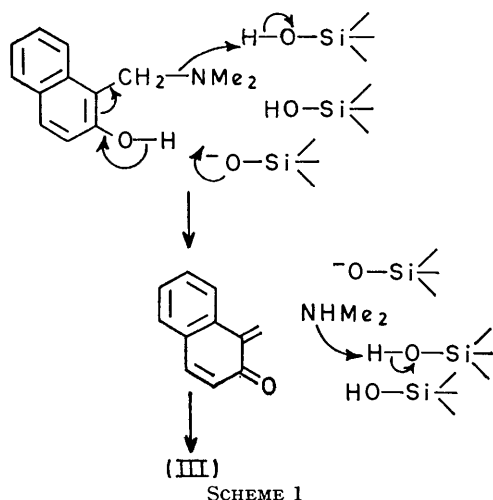
<sup>8</sup> R. N. Sen and N. N. Sarkar, *J. Amer. Chem. Soc.*, 1925, **47**, 1079.

<sup>9</sup> R. Fosse, P. de Graeve, and P. E. Thomas, *Compt. rend.*, 1935, **200**, 1450; **201**, 105.

<sup>10</sup> D. A. Sultanova, *Materially Nauchn.-Konf. Aspirantov, Azerb. Gos. Univ.*, 1964, 83 (*Chem. Abs.*, 1966, **64**, 17,505d).

catalyst for the change, and silica columns transform the Mannich base (IIc) into the methylenedinaaphthol

(IVa) equally easily. This catalytic activity may be related to the amphoteric character of silica and represented as in Scheme 1.



In non-protic media, however, the Mannich base (IIc) is not unduly sensitive and thermal elimination of dimethylamine occurs satisfactorily in dodecane, decalin,

unsaturated esters. Prolonged reaction, especially at the higher temperatures, induces resinification and the formation of by-products, including the methylenediphenol (IVa). Encountered twice only, another by-product appears to be a dihydro-derivative of spiro-dimer (III) and to have structure (V); attempts to obtain this compound by reducing spiro-dimer (III) catalytically and in other ways led only to ring fission giving the (known) ethylenediphenol (IVb).

All the chromans (Table 1) are assumed to be formed by [4 + 2] cycloadditions with *cis* geometry. In agreement, *cis*- and *trans*-stilbene give distinct products (VI) and (VII), respectively, while dihydropyran gives an adduct (VIII) with a chroman nucleus where the coupling constant ( $J_{2,3}$ ) is 2 Hz, a value too small to agree with a *trans*-fused ring system. One exception occurs, with ethyl maleate, which affords the same adduct (IX) as ethyl fumarate; in this case there is evidence (see later) that the reaction mixture induces geometrical isomerisation before addition occurs.

Notwithstanding the non-ionic mechanism usually attributed to the cycloaddition, unsymmetrical alkenes yield but one adduct; as Bolon<sup>11</sup> has noted, the orientation can often be predicted on the assumption that the

TABLE I  
Chroman derivatives from 1-dimethylaminomethyl-2-naphthol

Reactant		Method <sup>a</sup>	Temp. (°C)	Time (h)	Product	Yield <sup>b</sup> (%)
Compound	Wt. (g)					
<i>trans</i> -Stilbene	12	T	208	2.0	(VII)	89
<i>cis</i> -Stilbene	10	R	215	1.8	(VI)	10 <sup>c</sup>
Cyclohexene (i)	23	S	155	2.5	(XX)	4.2 <sup>d</sup>
(ii)	12	S	175	3.5	(XX)	10.5
Cyclo-octa-1,5-diene (i)	15	S	135	4.0	(XXI)	3 <sup>d</sup>
(ii)	15	S	200	1.0	(XXI)	46 <sup>e</sup>
(iii)	15	R	148	7.5	(XXI)	30
Indene	30	R	195	1.3	(XXII)	85
Ethyl crotonate	26	R	118	23.0	(XII)	36 <sup>d,e</sup>
Ethyl cinnamate	26	R	220	2.0	(XV)	76 <sup>f,g</sup>
Ethyl fumarate	50	R	200	2.3	(IX)	49 <sup>f</sup>
Ethyl maleate	50	R	210	2.5	(IX)	
Coumarin (i)	8.4	T	140	20.0	(XVIII)	8.8 <sup>e,h</sup>
(ii)	8.4	T	208	1.3	(XVII)	22 <sup>e,i</sup>
Dodecyl vinyl ether	24	R	220	1.0	(XXIII)	99
Benzofuran (i)	21	S	135	4.5	(XIV)	15
(ii)	21	R	170	3.0	(XIV)	97
Dihydropyran (i)	12	S	140	4.5	(VIII)	24 <sup>d</sup>
(ii)	12	S	175	3.5	(VIII)	59
Indole	7.5	T	200	1.0	(XIX)	74 <sup>f</sup>

<sup>a</sup> Conditions are designated thus: T, refluxing tetralin; R, reflux without solvent but under nitrogen; S, sealed tube without solvent. In all cases compound (III) was produced, especially when the yield of chroman derivative was low. <sup>b</sup> Related to base. <sup>c</sup> *trans*-Stilbene isolated in traces. <sup>d</sup> 1,1'-Methylenedi-2-naphthol formed. <sup>e</sup> Compound (V) produced. <sup>f</sup> 2-Naphthol isolated in traces. <sup>g</sup> Phenol (XVI) found (3.1%). <sup>h</sup> Phenol (XVII) found (2.7%). <sup>i</sup> Adduct (XVIII) was only the minor product (3%). <sup>j</sup> A polymer (6.8%) was separated chromatographically.

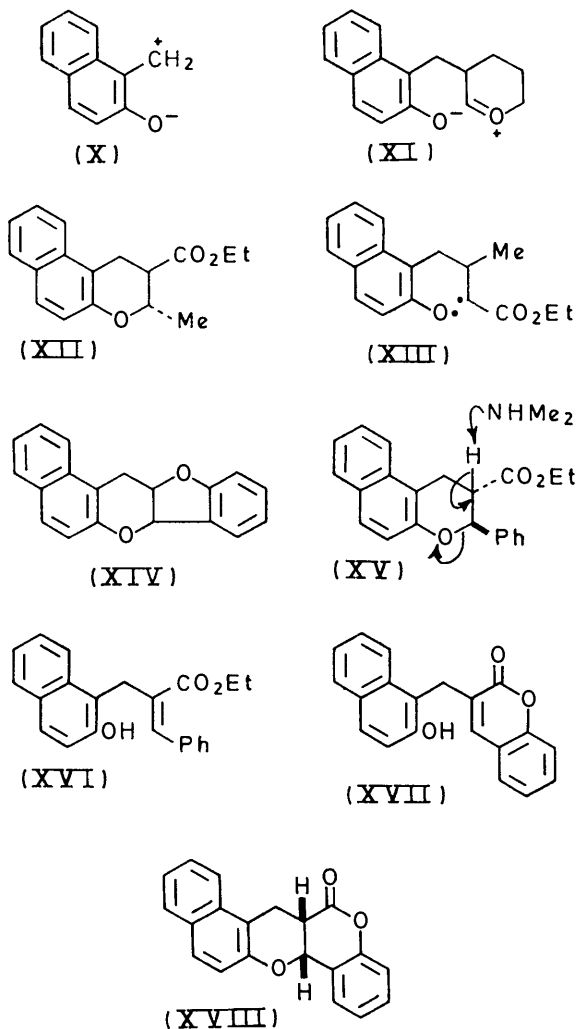
tetralin, xylene, or mesitylene, as described by Brugidou and Christol.<sup>4</sup> Provided that moisture is strictly excluded, such eliminations afford the 1,2-quinone methide as the dimer (III) in yields in excess of 75%, the reaction improving with increasing dilution.

When generated with alkenes present, the quinone methide (I) usually adds to them, giving chroman derivatives (Table 1). The spiro-dimer (III) is also formed, especially with alkenes that do not add the quinone methide readily, e.g. ethyl crotonate and other

quinone methide is strongly polarised in the sense indicated in (X) so that (XI), for example, could be supposed to contribute in some measure to the formation of the pyranopyran (VIII), thus explaining both orientation and the facility with which dihydropyran and other vinyl ethers add. In agreement, esters such as ethyl fumarate and ethyl crotonate react less easily and the latter gives the adduct (XII). The orientation of this adduct is not easily explained in terms of an

<sup>11</sup> D. A. Bolon, *J. Org. Chem.*, 1970, **35**, 3666.

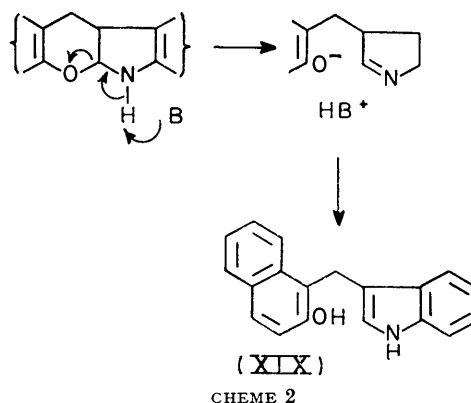
alternative hypothesis<sup>12</sup> which attributes to the transition state something of a diradical character; here, the more stable of the two possible diradicals would presumably be (XIII), which would not lead to (XII). In sharp contrast, the orientation seen in spiro-dimer (III) has to be explained in diradical terms because dimerisation of the ionic species (X) is most improbable.



Presumably *ortho*-quinone methides are highly polarisable and react in the form most suited to the addendum.<sup>13</sup>

Thus it is difficult to predict the behaviour of many alkenes. Benzofuran gives compound (XIV), thus perhaps favouring the diradical hypothesis, whereas ethyl cinnamate gives (XV) which is more easily explained on the ionic hypothesis. The basicity of the mixture induces much ring fission of adduct (XV) to the phenol (XVI) as indicated. Similarly, coumarin yields mainly the phenol (XVII) along with some of the initial adduct (XVIII) which appears to retain the *cis*-fusion thus indicating that deprotonation is followed by ring fission rather than by epimerisation. Indole affords a phenol (XIX) and indole-formaldehyde resin: the

orientation ascribed to the phenol is mainly based on the need to provide a mechanism for ring opening (Scheme 2).



It is supported by the n.m.r. spectrum. In 3-methylindole the 2-proton resonates at  $\tau$  3.22 and in 2-methylindole the 3-proton resonates at 3.90; but the corresponding values for a benzylindole would be raised by shielding because such molecules would adopt a propellor-like conformation similar to that found in comparable diarylmethane derivatives in which one ring is capable of shielding the nearest protons of the other.<sup>14</sup> Consequently, the fact that the phenol (XIX) shows a resonance at  $\tau$  3.59 (slight splitting by the adjacent methylene group is seen) confirms the presence of a 2-proton. The formation of the other chromans (XX)—(XXIII) raises no new points.

In the mass spectra of most of the chromans the chief fragments correspond to reversed cycloadditions, exceptions occurring with those esters, (IX) and (XII), that were not readily formed. These esters are stripped of their ester and methyl groups giving an ion *m/e* 181 that we formulate as the pyrylium ion (XXIV). The normal fragmentation need not occur of necessity in the molecular ion, since thermal dissociation of the adducts at the source temperature has to be taken into account. As a corollary, it seemed that thermal dissociation of the spiro-dimer (III) should provide a useful method of generating the quinone methide (I) and would also account for the increase in yields (Table I) at the expense of spiro-compound by-product often observed in reactions run at the higher temperatures or for the longer periods.

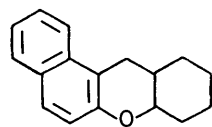
In practice, spiro-dimer (III) forms an excellent source of the quinone methide (I) at 160–210° and, since basic and protic groups and small molecules (water, dimethylamine) are absent, formation of by-products such as methylenedindanthol (IVa) is minimal. The adduct (XVIII) from coumarin is obtainable in high yields free from the phenol (XVII), and 1,4-naphthoquinone gives small quantities of the (oxidised) adduct (XXV) though only a black tar had been obtained before. Indole still yielded the phenol (XIX), since in this case the reaction mixture is not free from bases *etc.*, but no polymer was

<sup>12</sup> A. B. Turner, *Quart. Rev.*, 1964, **18**, 347.

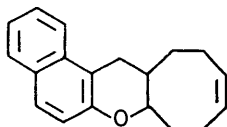
<sup>13</sup> N. D. Epiotis, *J. Amer. Chem. Soc.*, 1972, **94**, 1924, 1935.

<sup>14</sup> G. Montaudo, S. Caccamese, P. Finocchiaro, and F. Bottino, *Tetrahedron Letters*, 1970, 877.

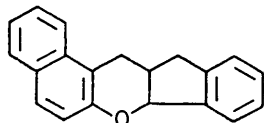
produced. Of the reactants examined, diphenylethyne gave no chroman derivative; presumably this derivative (XXVI) would dissociate easily so as to relieve the



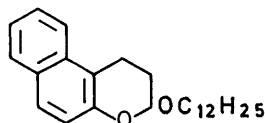
(XX)



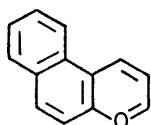
(XXI)



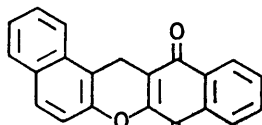
(XXII)



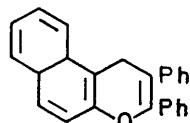
(XXIII)



(XXIV)



(XXV)



(XXVI)

compression between the two phenyl substituents and its concentration in the reaction mixture would therefore remain low. Ethyl fumarate gave the expected adduct (IX) whereas ethyl maleate did not react; evidently the

have an arrangement of  $\pi$ -orbitals that is associated with resonance energies larger than those in acyclic but otherwise comparable arrangements;<sup>15</sup> indeed, the tendency of the quinone methide (I) to react in the form (X) can be taken as a reflection of this. Compound (III) dissociates relatively easily, therefore, because the loss of resonance energy as the benzenoid system becomes quinonoid is partly counterbalanced by a gain as the other portion becomes quinonoid. Although a rise in temperature should increase the reaction rate, a point should be reached at which the adducts would also dissociate readily and the method would lose its effectiveness. This and other limitations have yet to be explored.

#### EXPERIMENTAL

Unless stated otherwise, i.r. spectra were determined for dispersions in potassium bromide. N.m.r. spectra were determined for solutions in [<sup>2</sup>H]chloroform, and only those resonances are given that could be assigned unambiguously. Molecular weights were determined mass spectroscopically. Light petroleum refers to the fraction of b.p. 60–80°.

*1-Hydroxymethyl-2-naphthol* (IIb).—2-Hydroxy-1-naphthaldehyde (4.7 g) in ether (150 ml) was added dropwise to a suspension of lithium aluminium hydride (3.2 g) in ether (150 ml) that had been de-aerated by a stream of nitrogen for 30 min. After being stirred under nitrogen for 15 h, the mixture was treated with moist ether and then methanol until inert. 2*N*-Hydrochloric acid caused separation into two layers; the aqueous layer was washed well with ether and the washings were added to the ether layer, which was then washed with water and dried (MgSO<sub>4</sub>) thoroughly. Evaporation of the ether under reduced pressure left a red oil which crystallised when kept with benzene. The solid (0.75 g) could not be purified further but consisted of satisfactorily pure *1-hydroxymethyl-2-naphthol*, m.p. 85.5°

TABLE 2  
Chroman derivatives from spiro-compound (III)

Reactant		Wt. (g)	Method <sup>a</sup>	Temp. (°C)	Time (h)	Product	Yield <sup>b</sup> (%)
Compound							
Cyclo-octa-1,5-diene		120	R		30.0	(XXI)	60
Ethyl fumarate	(i)	3	R	210	2.0	(IX)	28
	(ii)	3	S	205	12.0	(IX)	56
Ethyl cinnamate		33	R	220	3.0	(XV)	85
Coumarin	(i)	7.8	M	165	2.0	(XVIII)	8
	(ii)	5.4	M	165	30.0	(XVIII)	91
Indole		15	M	165	2.0	(XIX)	85
1,4-Naphthoquinone		12	M	165	1.5	(XXV)	2.5

<sup>a</sup> Conditions are designated thus: R, spiran in refluxing neat reactant under nitrogen; S, spiran heated with neat reactant in sealed tube; M, spiran heated with reactant in refluxing mesitylene. <sup>b</sup> Based on compound (III) consumed.

maleate addition observed with the Mannich base was made possible by a preliminary geometrical inversion. The reason for the marked difference between the two esters is not clear.

The success of the method depends upon the fact that spiro-dimer (III) dissociates more readily than any of the chromans listed. Though they are not aromatic in the conventional sense, quinones and quinone methides

<sup>15</sup> C. A. Coulson and A. Streitwieser, 'Dictionary of  $\pi$ -Electron Calculations,' Pergamon, Oxford, 1965.

$\nu_{\max}$  3450, 3200 (OH), 1625, 1585, and 1520 cm<sup>-1</sup> (aromatic), giving an intense grey-purple colour with aqueous alcoholic iron(III) chloride (Found: C, 75.8; H, 6.0. C<sub>11</sub>H<sub>10</sub>O<sub>2</sub> requires C, 75.8; H, 5.8%). Obtained by using acetic anhydride and pyridine at 25° for 16 h, the diacetate formed needles, m.p. 72–74° (lit.,<sup>16</sup> 76°),  $\nu_{\max}$  1760 (ArOAc) and 1730 cm<sup>-1</sup> (CH<sub>2</sub>·OAc),  $\tau$  7.99 (3H, s, CH<sub>2</sub>·O·CO·CH<sub>3</sub>), 4.45 (2H, s, ArCH<sub>2</sub>·O), and 2.78–1.92 (ArH).

<sup>16</sup> J. Cornforth, O. Kaunder, J. Pike, and R. Robinson, *J. Chem. Soc.*, 1955, 3348.

Chromatography of the alcohol on silica gave 1,1'-methylenedi-2-naphthol, and so did attempts at recrystallisation from warm benzene or warm chloroform. After melting at 85.5°, the compound solidifies again at 87° and then re-melts at 185—188°, the m.p. of the methylenedipnaphthol. T.l.c. and i.r. checks show that the naphthol is stable in the solid state for 5 min at 60°, but at 100° changes completely into the methylenedipnaphthol. The same change occurs at 25° in aqueous ethanolic hydrochloric acid during 1 min but alkali has little effect.

1,1',2,2'-Tetrahydro-3H-benzo[f]chromen-3-spiro-1'-naphthalen-2'-one (III).—1-Dimethylaminomethyl-2-naphthol (1.0 g) was kept in refluxing dodecane (100 ml) under nitrogen until the evolution of dimethylamine was complete (ca. 1.5 h). The residue left after removal of the solvent under reduced pressure was purified by chromatography on a silica column eluted first with benzene and then with chloroform, or on an alumina column eluted with benzene-light petroleum. The product separated from ether-light petroleum as crystals (0.7 g), m.p. 142—143°, identical with an authentic specimen.<sup>17</sup> A later fraction from the silica column contained a small amount of 1,1'-methylenedi-2-naphthol. A similar experiment with xylene as the solvent required 24 h but gave a higher yield.

Hydrogenation of the product over 10% palladium-charcoal gave only 1,1'-ethylenedi-2-naphthol (IVb), m.p. 252° (from ethanol-light petroleum) (lit.,<sup>17</sup> 252°). Oxidation of this with ethanolic iron(III) chloride regenerated compound (III), m.p. and mixed m.p. 142—143°.

1,1',2,2',3',4'-Hexahydro-3H-benzo[f]chromen-3-spiro-1'-naphthalen-2'-one (V).—Thermolysis of the Mannich base (IIc) (1.0 g) in tetralin (100 ml) on two occasions gave a black mixture, chromatography of which gave mainly compound (III) accompanied by the *hexahydrospiro-naphthalenone* which, purified from benzene-light petroleum, formed crystals (0.07 g), m.p. 175°,  $\nu_{\max}$  1693 (C=O), and 1620 and 1595  $\text{cm}^{-1}$  (aromatic) (Found: C, 84.2; H, 6.0%; M, 314.  $\text{C}_{22}\text{H}_{18}\text{O}_2$  requires C, 84.1; H, 5.8%; M, 314). The mass spectrum shows that the parent ion splits mainly into two complementary fragment ions at  $m/e$  168 ( $m^*$  89.9) and 146 ( $m^*$  67.9) though a fragment  $m/e$  157 ( $m^*$  78.5) is also important and appears to correspond to the type of fission typical of compound (III). The n.m.r. spectrum shows aromatic and alicyclic proton multiplets in accord with structure (V) but no vinylic resonances.

*General Methods for Chroman Syntheses.*—(i) The alkene (Table 1) was heated with 1-dimethylaminomethyl-2-naphthol (3 g) in refluxing tetralin (75 ml). After the time stated the solvent and other volatile materials were removed under reduced pressure and the residue was chromatographed on silica. Mixtures of benzene and light petroleum usually served to elute surviving alkene and then the desired adduct. Chloroform then eluted compound (III), 1,1'-methylenedi-2-naphthol, and other products. (ii) The same method was used but under nitrogen and with the tetralin omitted, the alkene itself acting as solvent. (iii) For alkenes of low b.p. the alkene and Mannich base were heated together in a sealed tube. (iv) The alkene was heated with compound (III) (Table 2) either alone or in mesitylene and the products isolated as in (i).

The compounds obtained are listed with their analytical and spectroscopic characteristics:

2,3-Dihydro-trans-2,3-diphenyl-1H-benzo[f]chromen (VII). This *chroman* separated from benzene-light petroleum as flat prisms, m.p. 166—167°,  $\tau$  4.91 (m, PhCHO) and 6.6 (m,

$\text{CH}_2\cdot\text{CH}$ ) (Found: C, 89.15; H, 5.9%; M, 336.  $\text{C}_{25}\text{H}_{20}\text{O}$  requires C, 89.25; H, 6.0%; M, 336).

2,3-Dihydro-cis-2,3-diphenyl-1H-benzo[f]chromen (VI). This *chroman* crystallised from light petroleum as needles, m.p. 139°,  $\tau$  4.53 (d,  $J$  2.5 Hz, PhCHO) (Found: C, 89.3; H, 6.0%; M, 336.  $\text{C}_{25}\text{H}_{20}\text{O}$  requires C, 89.25; H, 6.0%; M, 336).

8,9,10,11,11a,12-Hexahydro-7aH-benzo[a]xanthen (XX). This *xanthen* formed prisms, m.p. 77° (from light petroleum),  $\tau$  5.80 (m, CHO) and bands corresponding to the methylenic protons of an ABX system at 6.91 (dd,  $J$  7 and 17 Hz) and 7.24 (dd,  $J$  3 and 17 Hz) (Found: C, 85.65; H, 7.7%; M, 238.  $\text{C}_{17}\text{H}_{18}\text{O}$  requires C, 85.7; H, 7.6%; M, 238).

8,9,12,13,13a,14-Hexahydro-7aH-benzo[f]cyclo-octa[b]-chromen (XXI). This *chromen* formed needles, m.p. 114—115° (from light petroleum),  $\tau$  ca. 4.4 (m, vinylic protons), 5.61 (td,  $J$  8 and 2 Hz, OCH), 6.84 (dd,  $J$  15 and 7 Hz; one proton of ABX system  $\text{ArCH}_2\cdot\text{CH}$ , the others being overlaid) (Found: C, 86.3; H, 7.5%; M, 264.  $\text{C}_{15}\text{H}_{20}\text{O}$  requires C, 86.3; H, 7.6%; M, 264).

7a,12,12a,13-Tetrahydrobenzo[f]indeno[1,2-b]chromen (XXII). This *chromen* separated from benzene-light petroleum as needles, m.p. 105° (Found: C, 88.55; H, 6.1%; M, 272.  $\text{C}_{20}\text{H}_{16}\text{O}$  requires C, 88.2; H, 5.9%; M, 272). The nonaromatic protons resonated in a complex fashion near  $\tau$  6.9 ( $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$ ) except for a band at 4.43 (m, OCHAr).

Ethyl 2,3-dihydro-3-methyl-1H-benzo[f]chromen-2-carboxylate (XII). This *ester* crystallised as leaflets, m.p. 111°,  $\nu_{\max}$  1722  $\text{cm}^{-1}$  ( $\text{CO}_2\text{Et}$ ),  $\tau$  8.68 (t,  $J$  7 Hz,  $\text{O}\cdot\text{CH}_2\cdot\text{CH}_3$ ), 5.77 (q,  $J$  7 Hz,  $\text{O}\cdot\text{CH}_2\cdot\text{CH}_3$ ), 8.54 (d,  $J$  7 Hz,  $\text{CH}\cdot\text{CH}_3$ ), 7.29 (m,  $\text{CH}\cdot\text{CO}_2\text{Et}$ ), 6.23 (m,  $\text{ArCH}_2$ ), and ca. 5.8 (m,  $\text{O}\cdot\text{CH}\cdot\text{CH}_3$ ) (Found: C, 75.9; H, 6.7%; M, 270.  $\text{C}_{17}\text{H}_{18}\text{O}_3$  requires C, 75.5; H, 6.7%; M, 270).

Ethyl 2,3-dihydro-3-phenyl-1H-benzo[f]chromen-2-carboxylate (XV). This *ester* formed thick prisms, m.p. 111—112° (from light petroleum),  $\nu_{\max}$  1725  $\text{cm}^{-1}$ ,  $\tau$  8.98 (t,  $J$  7 Hz,  $\text{O}\cdot\text{CH}_2\cdot\text{CH}_3$ ), 6.02 (q,  $J$  7 Hz,  $\text{O}\cdot\text{CH}_2\cdot\text{CH}_3$ ), 4.49 (d,  $J$  3 Hz,  $\text{O}\cdot\text{CHPh}$ ), and a complex (ABC) band at 6.4—7.0 ( $\text{ArCH}_2\cdot\text{CH}$ ) (Found: C, 79.3; H, 5.9%; M, 332.  $\text{C}_{22}\text{H}_{20}\text{O}_3$  requires C, 79.5; H, 6.1%; M, 332).

Ethyl 2-(2-hydroxy-1-naphthylmethyl)-3-phenylpropenoate (XVI). This *ester* was obtained from ethyl cinnamate condensations (Table 1) and crystallised from benzene-light petroleum as columnar prisms, m.p. 170°,  $\nu_{\max}$  (mull) 3400 (OH) and 1700  $\text{cm}^{-1}$  (unsaturated ester),  $\tau$  ca. 4.3br (removed by  $\text{D}_2\text{O}$ , OH), 9.03 (t,  $J$  7 Hz,  $\text{CH}_3\cdot\text{CH}_2$ ), 6.10 (q,  $J$  7 Hz,  $\text{CH}_3\cdot\text{CH}_2$ ), and 6.77br (m,  $\text{ArCH}_2\cdot\text{C}\cdot\text{CH}$ ) (Found: C, 79.45; H, 6.1%; M, 332.  $\text{C}_{22}\text{H}_{20}\text{O}_3$  requires C, 79.5; H, 6.1%; M, 332).

Diethyl 2,3-dihydro-1H-benzo[f]chromen-2,3-dicarboxylate (IX). This *ester* crystallised slowly from light petroleum (b.p. 40—60°) to give squat prisms, m.p. 42°,  $\nu_{\max}$  1740  $\text{cm}^{-1}$  (ester),  $\tau$  8.76 (t,  $J$  7 Hz,  $\text{O}\cdot\text{CH}_2\cdot\text{CH}_3$ ), 5.8 (two overlapping quartets,  $J$  7 Hz,  $\text{O}\cdot\text{CH}_2\cdot\text{CH}_3$ ), 4.99 (d,  $J$  5 Hz, with signs of slight long-range coupling,  $\text{O}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ ), and ca. 6.6 (m, ABC system in  $\text{ArCH}_2\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ ) (Found: C, 69.6; H, 6.3%; M, 328.  $\text{C}_{19}\text{H}_{20}\text{O}_5$  requires C, 69.5; H, 6.1%; M, 328).

6a,14a-Dihydro-7H-benzo[f]chromeno[4,3-b]chromen-6-one (XVIII). This *chromenochromenone* separated from benzene as fibrous needles, m.p. 161—162°,  $\nu_{\max}$  1757  $\text{cm}^{-1}$  (lactone C=O),  $\tau$  4.72 (d,  $J$  3 Hz,  $\text{ArO}\cdot\text{CH}\cdot\text{CH}$ ), 6.2—7.0 (m, ABC system  $\text{ArCH}_2\cdot\text{CH}\cdot\text{CO}$ ) (Found: C, 79.7; H, 4.9%; M,

<sup>17</sup> R. Pummerer and E. Cherbuliez, *Ber.*, 1919, **52**, 1392.

302.  $C_{20}H_{14}O_3$  requires C, 79.45; H, 4.7; *M*, 302). This compound (0.1 g) was warmed with aqueous *N*-sodium hydroxide (15 ml) in a steam-bath for 0.5 h, which sufficed to dissolve all the solid. The cooled solution was acidified with dilute hydrochloric acid giving a precipitate that was washed with water, dried in air, and crystallised from benzene. Obtained thus, 3-(2-hydroxy-1-naphthylmethyl)-coumarin (XVII) formed tiny prisms, m.p. 232—233°, immediately soluble in dilute sodium hydroxide (Found: C, 79.4; H, 4.8%; *M*, 302).  $C_{20}H_{14}O_3$  requires C, 79.5; H, 4.7%; *M*, 302),  $\nu_{\max}$  3400 (OH) and 1690  $cm^{-1}$  (coumarin C:O),  $\tau$  [( $CD_3$ )<sub>2</sub>SO] 5.5 (s,  $CH_2$ ) (no other signals could be clearly distinguished). The same compound was obtained directly in some thermal condensations (Table 1).

3-Dodecyloxy-2,3-dihydro-1H-benzo[f]chromen (XXIII). This chromen formed an oil, b.p. 163° at 0.1 mmHg, purified by distillation; it had  $\tau$  4.88 (dd, *J* 2 and 3 Hz, O·CH·CH<sub>2</sub>) (other resonances could not be allocated with certainty) (Found: C, 81.5; H, 9.9%; *M*, 368).  $C_{25}H_{36}O_2$  requires C, 81.5; H, 9.9%; *M*, 368).

12a,13-Dihydro-7aH-benzo[f]benzofuro[3,2-b]chromen (XIV). This benzofurochromen separated from benzene-light petroleum as flat prisms, m.p. 156°,  $\tau$  4.31 (d, *J* 7 Hz, ArO·CHAr), 4.70 (m, 8 lines, O·CH·CH<sub>2</sub>Ar), 6.32 (dd, *J* 16 and 3 Hz, H<sub>A</sub> in ArCH<sub>2</sub>·CH), and 6.68 (dd, *J* 16 and 5 Hz,

H<sub>B</sub> in ArCH<sub>2</sub>·CH) (Found: C, 83.3; H, 5.1%; *M*, 274).  $C_{19}H_{14}O_2$  requires C, 83.2; H, 5.15%; *M*, 274).

cis-10,11,11a,12-Tetrahydro-7aH,9H-benzo[f]pyrano[2,3-b]chromen (VIII). After purification from light petroleum, this pyranochromen formed thin prisms, m.p. 78°,  $\tau$  4.67 (d, *J* 2 Hz, O·CH·O), ca. 6.1 (m, O·CH<sub>2</sub>·CH<sub>2</sub>), 6.83 (dd, *J* 16.5 and 5 Hz, H<sub>A</sub> in ArCH<sub>2</sub>·CH), and 7.11 (dd, *J* 16.5 and 4 Hz, H<sub>B</sub> in ArCH<sub>2</sub>·CH) (Found: C, 79.7; H, 6.5%; *M*, 240).  $C_{18}H_{16}O_2$  requires C, 80.0; H, 6.7%; *M*, 240).

2-(2-Hydroxy-1-naphthylmethyl)indole (XIX).—This indole separated from benzene-light petroleum as needles, m.p. 155°,  $\nu_{\max}$  3400 and 3500  $cm^{-1}$  (OH, NH),  $\tau$  5.59 (d, *J* ca. 1 Hz, ArCH<sub>2</sub>·C:CH), 3.59 (q, *J* ca. 1 Hz, ArCH<sub>2</sub>·C:CH), and 4.88 (removed by D<sub>2</sub>O, OH) (Found: C, 83.6; H, 5.7; N, 5.1%; *M*, 273).  $C_{18}H_{15}NO$  requires C, 83.5; H, 5.5; N, 5.1; *M*, 273).

14H-Dibenzo[a,i]xanthen-8,13-dione (XXV). From benzene this xanthen crystallised as yellow prisms, m.p. 211—214°,  $\nu_{\max}$  1678, 1646, 1615, and 710  $cm^{-1}$  (1,4-naphthoquinone bands),  $\tau$  5.95 (s, CH<sub>2</sub>) (Found: C, 81.0; H, 4.1; *M*, 312).  $C_{21}H_{12}O_3$  requires C, 80.8; H, 3.9%; *M*, 312).

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