Dienone–Phenol Rearrangements of Bicyclic Cyclohexa-2,5-dienones; Confirmation of a Multistage Mechanism

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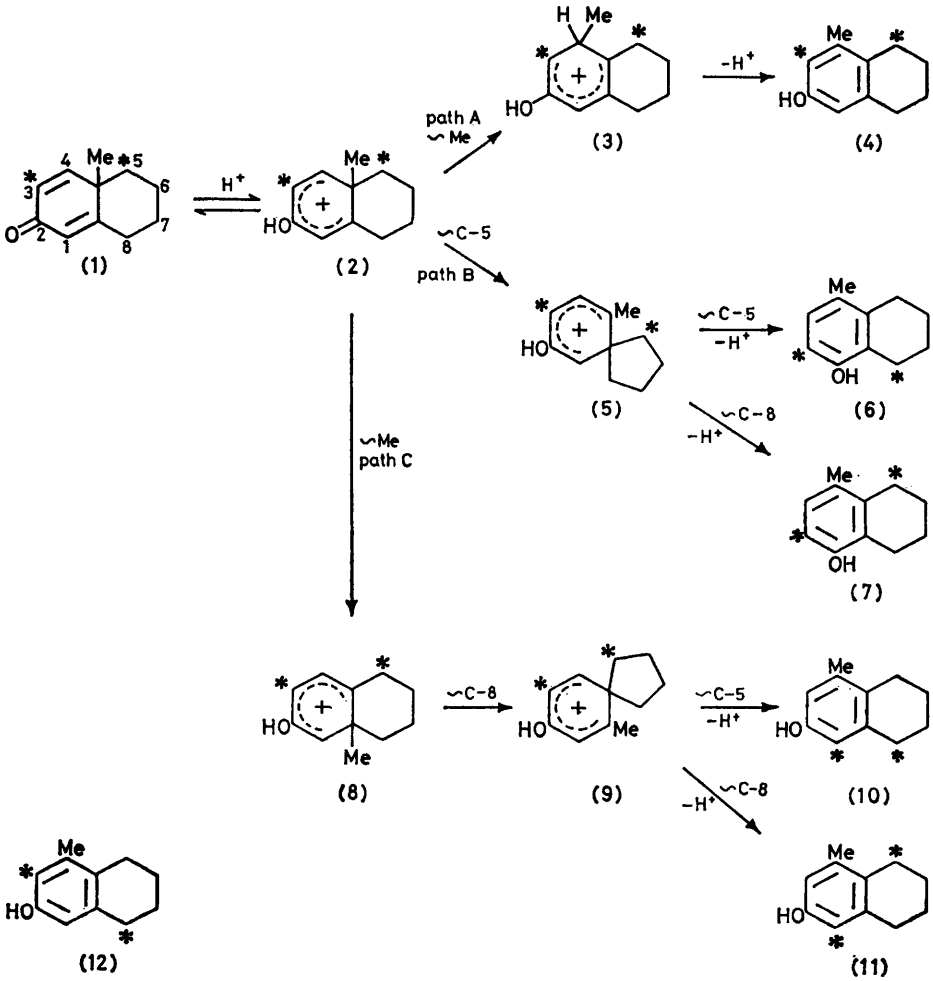
Two mechanisms are well established for the dienone–phenol rearrangements of bicyclic cyclohexadienones of the 4a-alkyl-5,6,7,8-tetrahydronaphthalen-2(4a*H*)-one type, of which the 4a-methyl compound (1) and the steroidal 1,4-dien-3-ones are examples. They involve, for (1), either a direct alkyl shift from C-4a to C-4 and deprotonation to give a 4-alkyl-5,6,7,8-tetrahydro-2-naphthol or a shift of the 4a,5-bond from C-4a to C-8a with formation of a spiran intermediate and further ring migration from C-8a to C-1 to form a 4-alkyl-5,6,7,8-tetrahydro-1-naphthol. A further mechanism, for which there was little strong evidence, involves an alkyl shift from one angular position, C-4a, to the other, C-8a, followed by further ring migrations *via* a spiran intermediate to give an additional route to the 4-alkyltetrahydro-2-naphthol product. The products of rearrangement of 3,4a- and 1,4a-dimethyl-5,6,7,8-tetrahydronaphthalen-2(4a*H*)-ones in aqueous sulphuric acid, and in acetic anhydride with sulphuric acid catalysis, have been studied critically. The use of quantitative ^{13}C n.m.r. spectroscopy confirms the identity and ratios of products deduced using ^{1}H n.m.r. spectroscopy and other techniques. The results show that the third, suspect, mechanism does indeed operate, and that it contributes significantly to the formation of 4-alkyltetrahydro-2-naphthol products from both dienones.

THE acid-induced rearrangement of cyclohexadienones to phenols has been well studied. When the dienone has structure (1) (with or without alkyl substituents on either ring) two rearrangement paths are firmly established.[1,2] In path A (Scheme 1) the *O*-protonated dienone (2)[3] undergoes a 1,2-methyl shift to form (3) which can



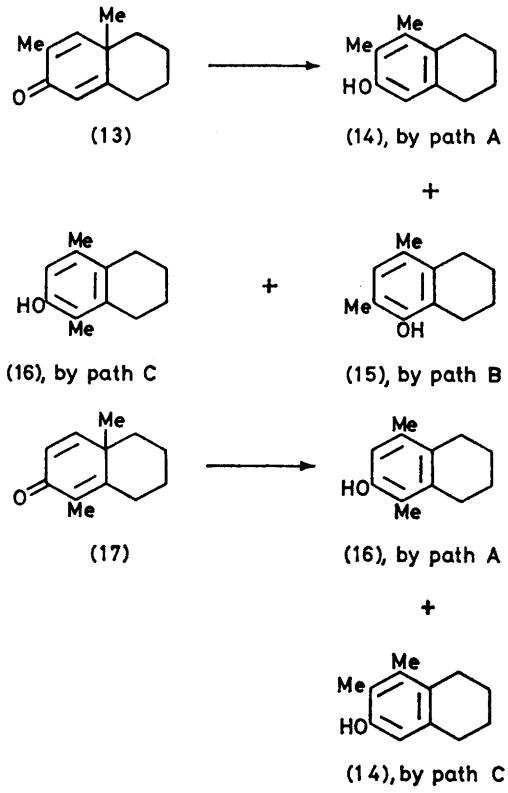
SCHEME 1

deprotonate to form a '*meta* methyl phenol' (4).[4] An alternative, path B, has migration of the ring-carbon C-5 to C-8a to form a spiran intermediate (5). Subsequent migration of C-5 or C-8 to C-1 gives the cations which deprotonate to the '*para* methyl phenols' (6) and (7).[5] This path was established by Woodward and Singh for compound (1)[6] and explains the major product formed by rearrangement of many steroidal 1,4-dien-3-ones.[1,2] A further mechanism, path C, has been proposed which provides an alternative, and more complex path to '*meta* methyl phenol' products.[7,8,9] In this, cation (2) suffers first a 1,2-methyl shift to the other angular position, C-8a, to form (8). This can then undergo migration of C-8 to form a spiran intermediate (9) which, by further migration of C-5 and deprotonation can give (10), or by similar migration of C-8 can give (11). The '*meta* methyl phenol' products of path C, (10) and (11), differ only subtly from the product (4) of path A.

The occurrence of path C has been subject to some experimental tests. However, for a number of reasons we had reservations about their ability to distinguish between path C and path A. In particular, if the cation (2) can equilibrate with cation (5) the distinction between C-5 and C-8 (or C-6 and C-7) would be lost, and path A could then give a '*meta* methyl phenol' product (12) as well as (4). We have given experimental evidence which suggests that this sort of equilibration of (2) and (5) should occur,[4] and so treat with caution tests for path C which depend on labelled C-5 in the dienone (1) ending up at both C-5 and C-8 in the 4-methyl-2-tetralol products,[9] or on a substituent at C-7 in (1) ending up partly at C-6 and partly at C-7.[7]

We see the essential feature of path C as being the methyl shift from C-4a to C-8a in the step (2) ⟶ (8) which makes C-3 of the dienone (1) end up as C-1 in the 4-methyl-2-tetralol product, and C-1 of (1) end up as C-3 in the tetralol [follow the labelled C-3 of (1) as (10) and (11) are formed]. This can be probed best by suitably labelling or substituting the carbon atoms of the dienone ring of (1). A study by Kropp is important here.[8] He rearranged the 3-methyl-dienone (13) in aqueous mineral acids and obtained three phenolic products, (14), (15), and (16), which should confirm the existence of path C. However, the brief report of this work left open some questions. Particularly important is the fact that (14) and (16) could not be separated by chromatography, and analysis of the product mixtures depended heavily on the chemical shift and integration of the single aromatic proton in the ^{1}H n.m.r. spectrum. A rearrangement of a steroidal 1,4-dien-3-one labelled at C-4 with ^{14}C showed the '*meta* methyl phenol' product to be formed only by path A (retaining the label at C-4).[10]

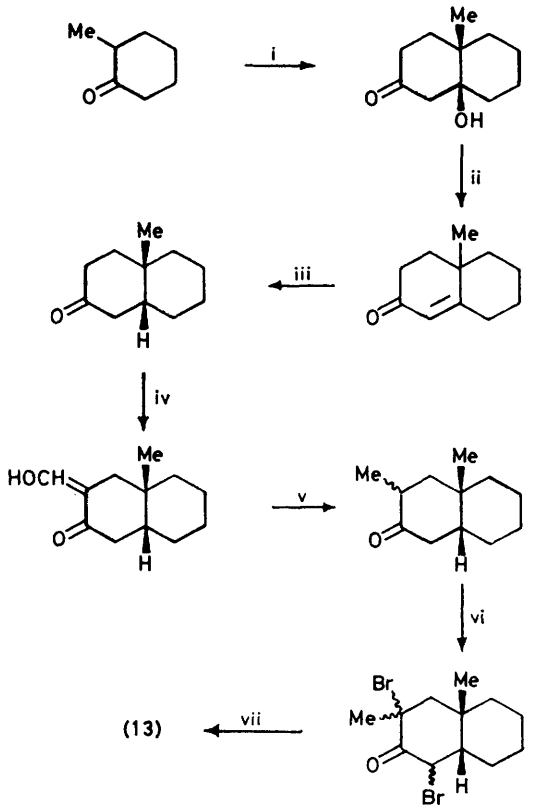
We have critically reinvestigated the rearrangement of Kropp's dienone (13) and used newer techniques to prove the presence or absence of the three products (14), (15), and (16). We have also investigated the rearrangements of the isomeric dienone (17). This has a number of important advantages. Reaction by the normal path A should give the phenol (16), which is produced from (13) by path C. Similarly, reaction of (17) by path C should give phenol (14), which arises from (13) by path A. If both dienones (13) and (17) give both phenols (14) and (16) as kinetic products, then both paths A and C operate. Furthermore, reaction of dienone (17) by path B would form a spiran intermediate, analogous to (5), which cannot aromatise after further migration of C-5 or C-8 to C-1. This path should then only allow equilibration of



C-5 with C-8 in the dienone, but cannot itself give a phenolic product. Thus the products from (17) should be only (14) and (16). In fact, both our studies confirm that path C does operate and is a major pathway for rearrangement. Kinetic studies, reported in a later paper,[11] show that its importance is not due to default of the alternatives. However, the relative importance of the three paths changes significantly as the reaction medium is changed from aqueous mineral acid to acetic anhydride with catalysis by sulphuric acid, an effect which is commonly found for this class of rearrangement.

Preparation of Compounds.—The two dienones, 3,4a-dimethyl-5,6,7,8-tetrahydronaphthalen-2(4a*H*)-one (13)[12,13] and 1,4a-dimethyl-5,6,7,8-tetrahydronaphthalen-2(4a*H*)-one (17)[14] were made by variants[15-20] of published routes[12,14] (see Schemes 2 and 3). They were purified by column chromatography or distillation followed in each case by recrystallisation [for (13)], or by recrystallisation alone [for (17)]. Evidence of purity and structure is given in the Experimental section.

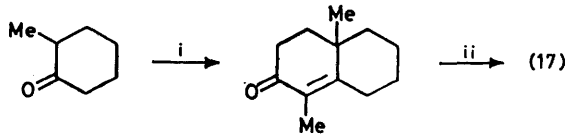
Samples of the dimethyltetrahydronaphthol products were made by established routes or minor variants of



SCHEME 2 *Reagents:* i, $AcCH{=}CH_2$, NaOEt, EtOH (ref. 15); ii, OH^- or $(CO_2H)_2$ (ref. 15); iii, H_2, Pd–C, EtOH (refs. 12 and 16); iv, HCO_2Et, NaOMe, C_6H_6 (ref. 17); v, H_2, Pd–C, MeOH (ref. 18); vi, Br_2, $CHCl_3$, 0 °C (ref. 18); vii, $CaCO_3$, DMF, reflux (ref. 19)

them. The methyl ethers of 2,3-dimethylphenol, 2,4-dimethylphenol, and 2,5-dimethylphenol were acylated with succinic anhydride (at C-4, except for 2,4-dimethylphenol which is known to react at C-5; [21] we confirm this), and subjected to Clemmensen reduction to give the 4-arylbutanoic acids. These were cyclised in polyphosphoric or sulphuric acid, and the resulting tetralones reduced (Clemmensen) and the methyl ethers demethylated to give the authentic phenols (14),[22] (15),[12,21] and (16).[22] The structures of the phenols were confirmed using their ^1H n.m.r. and, particularly, their ^{13}C n.m.r. spectra; the latter agree well with predictions from established empirical rules. The relevant data, and critical ^1H n.m.r. data for intermediates in the preparations of (14), (15), and (16), are given in the Experimental section.

Analysis of Rearrangement Products.—The phenol (15) was easily distinguished and separated from its isomers (14) and (16), and from the dienones (13) and (17) using



SCHEME 3 *Reagents:* i, $EtCOCH_2CH_2Cl$ (ref. 17), H_2SO_4, C_6H_6 (ref. 20); vii, DDQ, C_6H_6 (ref. 14)

g.l.c. on a variety of columns, and by chromatography on silica. However, like Kropp,[8] we found (14) and (16) could not be separated or distinguished in these ways, or even by h.p.l.c. on long silica, alumina, or reverse-phase columns. Mixtures of only (14) and (16) were satisfactorily analysed by mixed-melting-point comparisons with standard mixtures of the pure components. When reliable spectra of the authentic phenols were available, mixtures of (14), (15), and (16) were analysed by ^1H n.m.r. spectroscopy in two solvents, but only the aryl proton peak allows a clear distinction to be made and the peaks for (14) and (16) are very close. Much more convincing results are given by ^{13}C n.m.r. spectroscopy. The three phenols show only minor coincidences, giving 32 clearly assignable peaks out of a total of 36. This allows one to decide unambiguously whether (14), (15), or (16) are present in their mixtures. Moreover, by using gated decoupling and long pulse intervals, with integrations of peaks in the ^{13}C n.m.r. spectra, we were able to analyse product mixtures quantitatively (compare ref., 23). The results of these measurements were all consistent. When they were present, small amounts of unchanged dienones could be detected and measured by g.l.c., h.p.l.c., and ^1H and ^{13}C n.m.r. spectroscopy, and did not affect analyses of the phenols.

EXPERIMENTAL

G.l.c. analyses were with a Pye 104 instrument with flame ionisation detector and glass columns (7 ft or 10 ft × ¼ in), specifically of silicone gum (E30), neopentyl glycol succinate (NGS), and polyethylene glycol adipate (PEGA), on silanised Supasorb (B.D.H.). Many other columns were tried, but did not separate the phenols (14) and (16). Alumina for chromatography was Type UGl (Laporte Industries Ltd.). High performance liquid chromatography were with Pye–Unicam or Waters Inc. instruments with u.v. detection at wavelengths close to the absorption maxima of the mixtures. M.p.s were measured on a microscope hot-stage using Anschutz thermometers. ^1H N.m.r. spectra were recorded at 100 MHz on a Varian XL instrument with tetramethylsilane as internal standard. ^{13}C N.m.r. spectra were measured at 15.03 MHz on a JEOL-FX60 Fourier Transform n.m.r. spectrometer with coherent noise cancelling. For quantitative measurements of peak intensities the 'Gated II' setting was used in which the CH decoupling was gated, and the pulse repetition time (90 s) was very long compared with the pulse interval (1 s), with suppression of the nuclear Overhauser effects on all the peaks. 8K Data points were taken over an observation range of 2.5 kHz; the resolution of each point was 0.61 Hz (*i.e.* 0.04 p.p.m.). After the accumulation of 900 or more scans appropriate peaks were electronically integrated to measure their intensities. The excellent agreement of integrations based on different types of carbon atoms in the molecules confirms the validity of the technique.

3,4a-*Dimethyl*-5,6,7,8-*tetrahydronaphthalen*-2(4a*H*)-*one* (13) (*see Scheme* 2).—The crude dienone from the dehydrobromination reaction was chromatographed on an alumina column (activity I—II), using light petroleum (b.p. 60—80 °C) and its mixture with increasing amounts of diethyl ether, to give material >95% pure. Recrystallisation

from hexane or pentane at −78 °C then gave material >99.5% pure, m.p. 36—37 °C (lit.,[13] 38—39 °C). (Found: *m/e* 176.120 ± 0.005. $C_{12}H_{16}O$ requires *M*, 176.120); $\nu_{max.}$ (CCl_4) 1 643 and 1 670 cm^{-1}; δ(CCl_4) 6.48 (1 H, m, 4-H), 5.92 (1 H, s, 1-H), 2.45—1.42 (8 H, m, 5—8-CH_2), 1.81 (3 H, d, *J* 1.5 Hz, 3-Me), and 1.22 (3 H, s, 4a-Me), δ(C_6D_6) 6.19 (4-H), 6.13 (1-H), 1.96 (3-Me), and 0.81 (4a-Me). The solvent shift values, Δ = δ(CCl_4) − δ(C_6D_6), for the various protons are 1-H, −0.21; 4-H, 0.29; 3-Me, −0.15; 4a-Me, 0.41; these, and the chemical shifts, are entirely consistent with the dienone structure.[5,13,18] The ^{13}C n.m.r. spectrum had δ_C($CDCl_3$) 187.71 (C-2), 167.37 (C-8a), 153.34 (C-4), 132.81 (C-3), 123.77 (C-1), 40.67 (C-4a), 38.53, 32.42, 28.13, and 20.99 (CH_2 groups), 23.06 (angular Me), and 15.59 (3-Me): the assignments were confirmed by off-resonance decoupling.

1,4a-*Dimethyl*-5,6,7,8-*tetrahydronaphthalen*-2(4a*H*)-*one* (17) (*see Scheme* 3).—The dienone, recrystallised from n-hexane at −78 °C, had m.p. 39—40 °C (lit.,[14] 40—40.5 °C), >99.5% pure (g.l.c.; 20% NGS at 190 °C), $\nu_{max.}$ (CCl_4) 1 615, 1 640, and 1 667 cm^{-1}; $\lambda_{max.}$ (EtOH) 240 nm (ε 11 350); δ(CCl_4) 6.58 (1 H, d, *J* 10 Hz, 4-H), 6.05 (1 H, d, *J* 10 Hz, 3-H), 2.91—1.18 (8 H, m, 5—8-CH_2), 1.81 (3 H, s, 1-Me), and 1.22 (3 H, s, 4a-Me); δ(C_6D_6) 6.26 (3- and 4-H), 1.90 (1-Me), and 0.90 (4a-Me). The solvent shift values, Δ, are: 1-Me, −0.09; 3-H, −0.21; 4-H, 0.32; 4a-Me, 0.32; these, and the chemical shifts confirm the dienone structure.[5,13,18] The ^{13}C n.m.r. spectrum had δ_C($CDCl_3$) 186.67 (C-2), 160.55 (C-8a), 157.04 (C-4), 128.84 (C-1), 126.05 (C-3), 40.67 (C-4a), 38.59 (C-5), 27.81, 27.48, and 21.05 (CH_2 groups), 23.52 (angular Me), and 10.52 (1-Me). The small shift of the last peak is explained by the synperiplanar interaction with the 8-CH_2 group, which also suggests that one of the peaks at δ 27—28 is due to the 8-CH_2 group. The spectrum is fully consistent with the structure.

3,4-*Dimethyl*-5,6,7,8-*tetrahydro*-2-*naphthol* (14).—Prepared by the method of Nilsson and his co-workers,[22] this phenol was sublimed repeatedly (100 °C at 1 mmHg) and recrystallised from light petroleum (b.p. 40—60 °C) to m.p. 113—116 °C (lit., 114—115,[22] 114—115,[24] 116—118 °C [14]); δ(CCl_4) 6.180 ± 0.002 (1 H, s, 1-H), 4.36br (1 H, OH), 2.086 (3 H, s, 3-Me), 2.068 (3 H, s, 4-Me), 2.57 (4 H, q, 5- and 8-CH_2), and 1.73 (4 H, 6- and 7-CH_2); δ($CDCl_3$) 6.392 ± 0.002 (1-H), 4.42 (OH), 2.60 (5- and 8-CH_2), 2.16 (4-Me), 2.14 (3-Me), and 1.73 (6- and 7-CH_2). These data agree closely with those published, but the uncertainty in the aryl proton position should be noted [lit., δ($CDCl_3$) 6.36,[13] 6.33,[22] 6.38 [8]]. The high field at which this resonance occurs is typical of a proton *ortho* or *para* to a phenolic hydroxy-group.[4,13,25,26] The ^{13}C n.m.r. spectrum had δ_C($CDCl_3$) 151.13 (C-2), 136.44 (C-1), 135.15 (C-8a), 127.61 C-4a), 120.13 (C-3), 112.80 (C-1), 30.08, 27.03, 23.84, and 22.87 (CH_2 groups), 15.14 (Me-4), and 11.76 (Me-3). The chemical shifts agree well with expectation based on empirical additive rules,[27] and data for other simple phenols:[28] in particular, there is one methyl group *ortho* to the hydroxy-group,[28] and the position and high intensity of the resonance at δ 112.80 confirm that this is due to an aromatic CH group, *ortho* to the hydroxy-group. Only structures (14) or (16) are consistent with these data; the method of synthesis indicates (14), of course, but the conclusions of this paper would be unchanged even if the structures were to be reversed.

2,4-*Dimethyl*-5,6,7,8-*tetrahydro*-1-*naphthol* (15).—2,4-Dimethylphenol was methylated using dimethyl sulphate and sodium hydroxide. The resulting methyl ether was treated with succinic anhydride and aluminium chloride in tetrachloroethane and nitrobenzene:[29] this gave more reliable results than the method of ref. 12.* The product, 3-(5-methoxy-2,4-dimethylbenzoyl)propionic acid[21] has δ($CDCl_3$) 7.14 (1 H, s, aryl 6-H), 7.00 (1 H, s, aryl 3-H), 3.83 (3 H, s, OMe), 3.20 (2 H, m, 3-CH_2), 2.77 (2 H, m, 2-CH_2), 2.40 (3 H, s, 2- or 4-Me), and 2.22 (3 H, s, 4- or 2-Me). Calculated[26] chemical shifts for the aryl protons of this isomer are δ 7.30 and 6.93, whereas for the alternative isomer, 3-(2-methoxy-3,5-dimethylbenzoyl)propionic acid the values are 7.47 and 7.14. Clemmensen reduction, modified as in ref. 22, gave 4-(5-methoxy-2,4-dimethylphenyl)butanoic acid, m.p. 120—121 °C (lit.,[21] 92 and 120 °C, for two modifications); δ($CDCl_3$) 6.90 (1 H, s, aryl 3-H), 6.60 (1 H, s, aryl, 6-H), 3.79 (3 H, s, OMe), 2.61 (2 H, t, *J* 7.1 Hz, 4-CH_2), 2.40 (2 H, t, *J* 7 Hz, 2-CH_2), 2.18 and 2.14 (each 3 H, s, 2- and 4-Me), and 2.90 (2 H, mult., 3-CH_2). The calculated[26] chemical shifts for this structure's aryl protons are 6.78 and 6.51, whereas for the alternative, 4-(2-methoxy-3,5-dimethylphenyl)butanoic acid, the shifts should be 6.82 for both aryl protons. Cyclisation of this acid in polyphosphoric acid[22] was unsatisfactory, but the use of sulphuric acid[12,21] gave 8-methoxy-5,7-dimethyl-1-oxo-1,2,3,4-tetrahydronaphthalene; δ($CDCl_3$) 7.18 (1 H, s, 6-H), 3.77 (3 H, s, OMe), 2.72 (2 H, t, *J* 6 Hz, 4-CH_2), 2.46 (2 H, t, *J* 6 Hz, 2-CH_2), 2.22 and 2.20 (each 3 H, s, 5- and 7-Me), and 2.09 (2 H, m, 3-CH_2). The calculated[26] shift for the aryl proton was δ 7.08, and for the alternative isomer, 5-methoxy-6,8-dimethyl-1-oxo-1,2,3,4-tetrahydronaphthalene, δ 6.75. Clemmensen reduction[22] and demethylation with HBr in acetic acid[12] gave 2,4-dimethyl-5,6,7,8-tetrahydro-1-naphthol, purified by sublimation at 100 °C and 1 mmHg, and recrystallisation from light petroleum (b.p. 40—60 °C), m.p. 75—77 °C (lit., 76—76.5,[21] 78 °C [12]); δ(CCl_4) 6.56 (1 H, s, 3-H), 2.51 (4 H, m, 5- and 8-CH_2), 2.08 and 2.04 (each 3 H, s, 2- and 4-Me), 1.74 (4 H, m, 6- and 7-CH_2), and 4.27br (1 H, s, OH); δ($CDCl_3$) 6.75 (3-H), 2.58 (5- and 8-CH_2), 2.16 and 2.09 (2- and 4-Me), 1.76 (6- and 7-CH_2), and 4.50 (OH). The low-field position of the aryl proton is characteristic of a proton *meta* to a phenolic hydroxy-group[4,13,25,26] and agrees closely with the value quoted for this compound.[13] The ^{13}C n.m.r. spectrum had δ_C($CDCl_3$) 149.70 (C-1), 134.24 (C-4a), 128.97 (C-4), 127.93(C-3), 122.73 (C-8a), 119.29 (C-2), 26.96, 23.45, 22.80, and 22.41 (CH_2 groups), 18.71 (Me-4), and 15.46 (Me-2). The chemical shifts agree well with predicted values.[27,28] In particular, the position of the very strong peak owing to the aryl C-H at δ 128.97 shows it to be *meta* to the hydroxy-group, and the peak at δ 15.46 is typical for one methyl group *ortho* to a hydroxy-group: these define the structure.

1,4-*Dimethyl*-5,6,7,8-*tetrahydro*-2-*naphthol* (16).—Prepared from 1-methoxy-2,5-dimethylbenzene, by the method of Nilsson and his co-workers,[22] and purified by twice subliming at 100 °C and 0.1 mmHg, this phenol had m.p. 103—105 °C (lit., 104—105,[22] 103—105 °C [13]); δ(CCl_4) 6.25 (1 H, s, 3-H), 4.82 (1 H, s, OH), 2.53 (4 H, m, 5- and 8-CH_2), 2.05 and 2.01 (3 H each, s, 4- and 1-Me), and 1.74 (4 H, m, 6- and 7-CH_2); δ($CDCl_3$) 6.488 ± 0.002 (3-H), 4.42 (OH), 2.58 (5- and 8-CH_2), 2.16 (4-Me), 2.10 (1-Me), and 1.77 (6- and 7-CH_2). These values agree with the reported ones,

* In ref. 12, the structures assigned all assume the Friedel–Crafts acylation to occur *ortho* to the methoxy-group rather than *meta* to it; the correct structures were established by Cocker's group[21] and are confirmed here.

within small limits, but for the aryl proton, $\delta(CDCl_3)$ is 6.46,[13] and 6.41,[22] or 6.48,[8] typical of a proton *ortho* to the phenolic hydroxy-group but not reliably different from the values reported for the isomer (14). The ^{13}C n.m.r. spectrum has $\delta_C(CDCl_3)$ 150.74 (C-2), 136.96 (C-8a), 134.56 (C-4), 128.00 (C-4a), 119.29 (C-1), 114.22 (C-3), 27.81, 26.83, 23.13, 23.00 (C-5 to -8), 19.36 (Me-4), and 10.78 (Me-1). The agreement with the values calculated from additive rules [27] and with data from other phenols [28] is excellent. In particular, the intense CH peak at δ 114.22 has a position typical for its being *ortho* to the hydroxy-group, and the methyl groups are shown to be *meta* or *para*, and *ortho* to the hydroxy-group: these alone define the structure.

Rearrangements of 3,4a-*Dimethyl*-5,6,7,8-*tetrahydronaphthalen*-2(4aH)-*one* (13).—(a). *In* 50% *sulphuric acid*. The dienone (400 mg) was heated at 100 °C for 30 min in 50% (by weight) aqueous sulphuric acid (25 cm^3). After rapid cooling and the addition of crushed ice (10 g) the mixture was extracted with dichloromethane (5 × 25 cm^3). The combined organic extracts were washed with saturated sodium hydrogencarbonate solution (20 cm^3), dried ($MgSO_4$), and evaporated to an oil (360 mg, 90%), ^1H and ^{13}C n.m.r. spectroscopy (in $CDCl_3$ solution) of which established the presence of only the phenolic products (14), (15), and (16). Integration of the separated aryl proton peaks in this ^1H n.m.r. spectrum, and in the spectrum in CCl_4, gave the product ratios shown in Table 1. Quantitative ^{13}C n.m.r. spectra were measured, and the peaks were electronically integrated at (151.23 and 150.86 p.p.m.) due to (14) plus (16), at 149.64 p.p.m. due to (15), at 122.96 p.p.m. due to (15), at 120.24 p.p.m. due to (14), at 119.43 p.p.m. due to (15) and (16), at 114.27 p.p.m. due to (16), at 112.89 p.p.m. due to (14), at (19.33 and 18.72 p.p.m.) due to (15) and (16), at (15.51 and 15.11 p.p.m.) due to (14) and (15), at 11.81 p.p.m. due to (14), and at 10.76 p.p.m. due to (16). The product ratios calculated are in Table 1. G.l.c. (20% NGS at 225 °C) gave the ratio of the peaks due to (15) and to [(14) plus (16)] as in Table 1. The phenolic mixture was then steam-distilled to remove traces of tarry materials. The distillate was extracted with dichloromethane, the dried extracts were evaporated, and the ^1H n.m.r. spectrum was re-measured in $CDCl_3$ solution. The product ratios are given in Table 1.

(b) *In* 72.7% H_2SO_4. The dienone (65 mg) in 72.7% sulphuric acid (10 cm^3) was kept at 25 °C for 240 h (*ca.* 4.4 half-lives). Aliquots were removed at 24, 71, and 186 h. The samples were diluted with ice–water (20 cm^3) and extracted with ether (5 × 25 cm^3). The ether extracts were washed with aqueous sodium hydrogencarbonate, then water, dried ($MgSO_4$), and evaporated. G.l.c. (E30 at 154 °C) showed 5% of dienone remained, with two product peaks. The product ratios are given in Table 1. The ratio of product peaks was essentially the same for all the samples. Analysis by ^1H n.m.r. in $CDCl_3$ and separately in CCl_4 solution gave the product ratios shown in Table 1.

(c) *In acetic anhydride*. To the dienone (120 mg) in acetic anhydride (7.2 cm^3) was added concentrated sulphuric acid (50 mg). After 6 h at room temperature, water (15 cm^3) was added and the mixture was left stirring overnight. Extraction with dichloromethane (4 × 20 cm^3) and work-up as in (a) gave an oily mixture of phenolic acetates (145 mg). G.l.c. (25% E30 at 170 °C) showed no dienone remaining. Hydrolysis with concentrated hydrochloric acid (1.0 ml) in ethanol (12 cm^3) and work-up [6] gave a mixture of crystalline phenols (110 mg, 92%). The normal ^{13}C n.m.r. spectrum showed peaks only for product (15). However, the ^1H n.m.r. spectrum (CCl_4) showed peaks due to small amounts of (14) and (16) also: the ratios deduced are given in Table 1. Similarly, careful g.l.c. analysis (20% PEGA column at 180 °C) confirmed the presence of the two peaks due to (15) and [(14) plus (16)] in the ratios recorded in Table 1.

TABLE 1

Products of rearrangements of 3,4a-dimethyl-5,6,7,8-tetrahydronaphthalen-2(4a*H*)-one (13)

Conditions	Yield (%) (14)	(15)	(16)	Method of analysis
50% H_2SO_4, 100 °C, 30 min	26.8 ± 1	40.3 ± 1	32.8 ± 1	*a*
	24.5 ± 1.5	39.6 ± 2	35.8 ± 1.3	*b*
	27 ± 1	40 ± 1	33 ± 1	*c*
		41		*d*
	24	43	33	*e*
72.7% H_2SO_4, 25 °C, 240 h	17 ± 3	37 ± 3	46 ± 3	*a*
		37 ± 2		*d*
Ac_2O + H_2SO_4, 20 °C, 6 h	5 ± 1	89 ± 1	5 ± 1	*a*
		88 ± 2		*d*
	Absent	Present	Absent	*f*

[a] ^1H N.m.r. in $CDCl_3$ and/or CCl_4. [b] ^{13}C N.m.r., gated decoupling, long pulse intervals. [c] ^1H N.m.r. after steam distillation of mixture. [d] Calibrated g.l.c.; (14) and (16) are not distinguished. [e] Values given by Kropp. [f] Normal ^{13}C n.m.r.; the small amounts of (14) and (16) would not be detected under the operating conditions used.

Rearrangements of 1,4a-*Dimethyl*-5,6,7,8-*tetrahydronaphthalen*-2(4aH)-*one* (17).—(a) *In* 50% *aqueous sulphuric acid*. Rearrangement for 30 min at 100 °C and work-up as described for the dienone (13) gave a mixture of phenols. The ^{13}C n.m.r. spectrum showed only (14) and (16) to be present (see Table 2). The ^1H n.m.r. spectrum (CCl_4) showed only the peaks expected for products (14) and (16) in the ratio shown in Table 2. A similar experiment for 5—6 h, and similar analysis by ^1H n.m.r. showed the product composition to be unchanged (Table 2).

(b) *In* 79.1% H_2SO_4. Rearrangement at 25 °C for 72 h (*ca.* 6 half-lives), and work-up as described above for (13), gave a white crystalline mixture (84%). G.l.c. (20% PEGA at 180 °C) showed dienone to be absent, but a peak due to (14) and/or (16) to be present. The normal ^{13}C n.m.r. spectrum failed to show peaks due to (14), but the ^1H n.m.r. spectrum (CCl_4) at high sensitivity showed both (14) and (16) to be in the ratio given in Table 2.

TABLE 2

Products of rearrangements of 1,4a-dimethyl-5,6,7,8-tetrahydronaphthalen-2(4a*H*)-one (17)

Conditions	Yield (%) (14)	(16)	Method of analysis
50% H_2SO_4, 100 °C, 30 min	17 ± 2	83 ± 2	*a*
	18 ± 1	82 ± 1	*b*
50% H_2SO_4, 100 °C, 6 h	14 ± 2	86 ± 2	*a*
79.1% H_2SO_4, 25 °C, 72 h	7 ± 1	93 ± 1	*a*
	Absent	Present	*b*
79.1% H_2SO_4, 25 °C, 72 h, then 50% H_2SO_4, 100 °C, 30 min	8 ± 2	92 ± 2	*a*
Ac_2O + H_2SO_4, 20 °C, 6 h	30 ± 2	70 ± 2	*a*, *d*
Ac_2O + H_2SO_4, 20 °C, 6 h, then hydrolysis	30 ± 3	70 ± 3	*a*
	Present	Present	*b*
	31 ± 3	69 ± 3	*c*

[a] ^1H N.m.r. in $CDCl_3$ and/or CCl_4. [b] ^{13}C N.m.r. run normally, comparing intensities of peaks due to C-2 in both isomers, due to the aryl C-H in both isomers, and due to Me-4 in both isomers. [c] Using m.p. comparison with known mixtures. [d] As the acetates.

(c) *In acetic anhydride.* The dienone (250 mg) in acetic anhydride (15 cm^3) had concentrated sulphuric acid (100 mg) added. Reaction and work-up as described for the isomer (13), but with ether extraction, gave an oil (300 mg). No dienone remained (g.l.c.; 25% E30 at 170 °C) but peaks were present in the ^1H n.m.r. spectrum for two phenolic acetates (Table 2). Hydrolysis as described for (13) gave a crystalline product mixture (190 mg, 76% overall), ^{13}C and ^1H n.m.r. spectroscopy of which showed only products (14) and (16) to be present in the ratio shown in Table 2. One recrystallisation from light petroleum (b.p. 40—60 °C) gave white crystals, m.p. 74—89 °C, whose ^1H n.m.r. spectrum (in CCl_4) was identical with that of the crude product, and in which the isomer ratio was unchanged. Mixtures of pure (14) and (16) of known composition were prepared, for which m.p. (range) was plotted against composition. From this graph the composition of the product mixture was determined (see Table 2).

Attempts to Equilibrate Products and Product Mixtures.—The second experiment in (a) above is such an attempt. Also, the product mixture from (b) was treated with 50% sulphuric acid for 30 min further at 100 °C. Analysis was by ^1H n.m.r. spectroscopy (Table 2). Similarly, a sample of pure (15) was treated in 50% sulphuric acid at 100 °C for 6 h, and an aliquot withdrawn after 30 min. Work-up as before, and g.l.c. (20% NGS at 230 °C) showed that no trace (<0.3%) of the isomers (14) and (16) was formed: only (15) was recovered. These experiments show that the product phenols (14), (15), and (16) are not interconverted in 50% sulphuric acid at 100 °C, the conditions used for some of the rearrangements.

RESULTS AND DISCUSSION

The results summarised in Tables 1 and 2 establish unambiguously that all three rearrangement paths A, B, and C outlined previously do operate to significant extents for the dienone (13), and paths A and C apply to (17) for which path B is excluded. The different product ratios observed from the two dienones (13) and (17) suggest that they are not determined by equilibration between (14), (15), and (16), and specific attempts to equilibrate these individual isomers or their mixtures under the rearrangement conditions failed. We conclude, therefore, that the ratios given in Tables 1 and 2 represent kinetic control. The dienone (13) studied by Kropp does give the phenols (14), (15), and (16), which he claimed.[8] In aqueous sulphuric acids the contentious product (16) makes up a third to a half of the whole, but it is only present in trace amounts in the acetic anhydride rearrangement. In this, the normal product (15), derived *via* the spiran intermediate of type (5), predominates (*ca.* 90%). The product (14) of a direct 1,2-methyl migration is in all cases the least abundant. The usual [1,2,5] qualitative pattern is, however, found, *i.e.* that the '*meta* methyl phenol' products, (14) plus (16), predominate in aqueous acidic rearrangements. For the dienone (17), both paths A and C occur, to give up to *ca.* 17% of product (14) by path C in aqueous acids, and 30% in acetic anhydride. The predominance in aqueous acids of (16), formed by a direct 1,2-methyl migration, agrees with normal expectation.

Elsewhere [11] we present the results of kinetic studies which show that the observations reported here are not abnormal. That is, the methyl groups which are present in the dienone rings of (13) and (17) to label the ring carbon atoms do not greatly affect the rates of reaction by the various paths [apart from suppressing path B for (17)], and that they affect them in accordance with good analogy. We conclude that the '*meta* methyl phenol' products formed in dienone–phenol rearrangements of bicyclic dienones such as (1), (13), and (17) can be formed by both paths A and C, whose relative importance will depend on the substituents attached to the two rings and the size of the non-dienone ring.

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