

PROPELLANES—XIV

THE THERMAL BEHAVIOUR OF A BICYCLO[4.2.2]DECA-2,4,7,9-TETRAENE ETHER DERIVATIVE AND ITS REACTION WITH IRONPENTACARBONYL

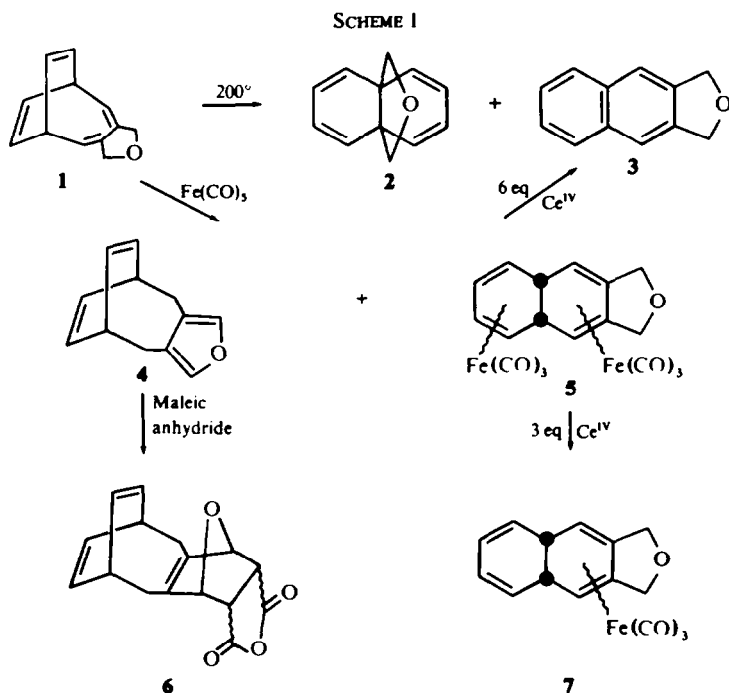
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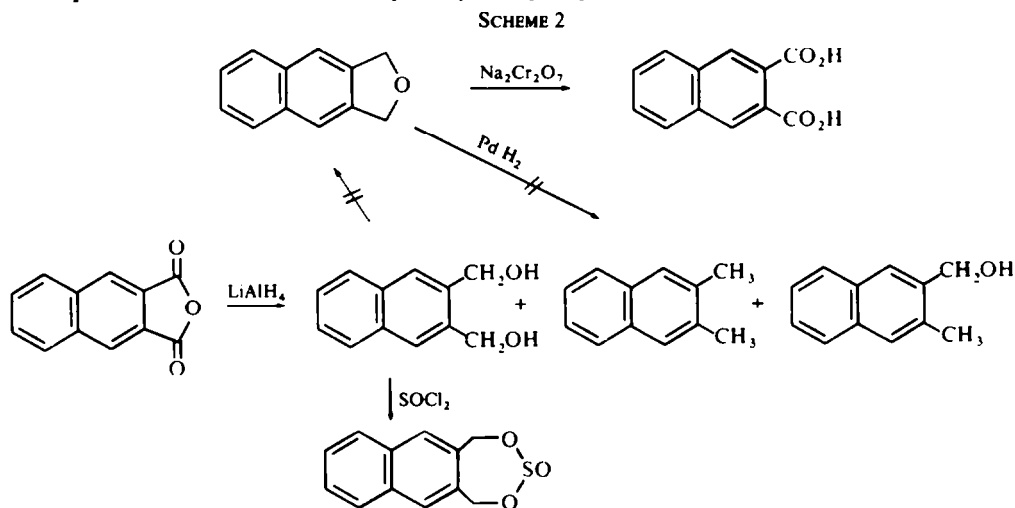
Abstract—The thermal behavior of the prebullvalene ether **1** and its reaction with ironpentacarbonyl has been studied. The structures of the various reaction products are elucidated.

FLUXIONAL isomerism is known to exist in prebullvalene (bicyclo[4.2.2]deca-2,4,7,9-tetraene)¹ and in its derivatives.² Since certain (CH)₁₀ derivatives, e.g. **1** were available to us through the irradiation of the corresponding tetraenic propellanes followed by a thermal dark reaction,^{2e} we decided to study the thermal behavior of **1** at relatively high temperature. In addition it was thought that perhaps organometallic derivatives of **1** might be induced to take part in fluxional isomerizations. Alternatively, the metallic ligands might stabilize the (CH)₁₀ derivative and such isomerization might be avoided. We wish to report our results using the prebullvalene ether **1** as our starting point.

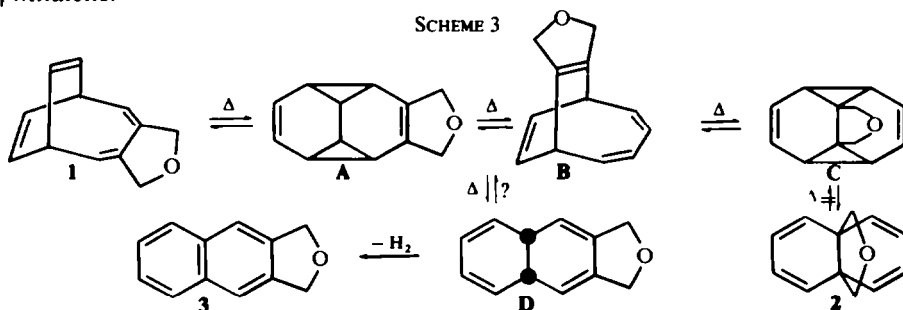


When **1** was heated in a sealed tube at 200°, rearrangement took place and the tetraenic propellane **2** was obtained in *ca* 75% yield, accompanied by the naphthalenic ether **3** (*ca* 15%) and recovered starting material (10%). The naphthalenic product **3** clearly must have resulted from its 9,10-dihydro derivative which is an isomer of **1** and **2**. The formation is not due to the presence of oxygen as an acceptor for the H atoms at the 9 and 10 positions as repetition of the above experiment after degassing and in the presence of oxygen, respectively, afforded the same mixture of products (Scheme 1).

The structure of **3** was proved by oxidation to naphthalene-2,3-dicarboxylic acid and comparison with an authentic specimen. It must be parenthetically noted that **3** has not been reported to date. Like its simpler aromatic analogue, phthalan,³ it is unstable and rapidly turns yellow in air. All our attempts to synthesize **3** by dehydration of 2,3-dihydroxymethylnaphthalene failed. Although the latter could be catalytically hydrogenolysed to give 2,3-dimethylnaphthalene, we were unable to effect the analogous hydrogenolysis of **3**. Similarly, all attempts failed to obtain **3** via the cyclic sulphite formed when 2,3-dihydroxymethylnaphthalene was heated with thionyl



chloride (Scheme 2). Other authors⁴ have reported the preparation of 2,3-dihydroxymethylnaphthalene by LAH reduction of 2,3-naphthalene-carboxylic anhydride (56% yield), but they did not report the presence of two hydrogenolysis products, the known 2,3-dimethylnaphthalene and the heretofore unknown 2-hydroxymethyl-3-methylnaphthalene.

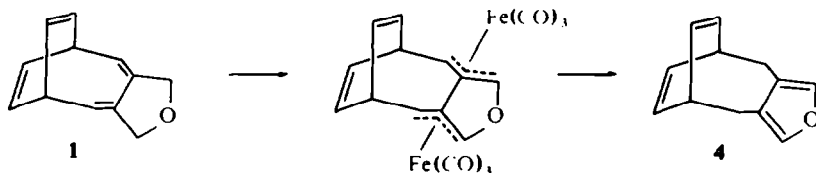


We have ample evidence for the existence of fluxional isomerism between the molecules whose structures are given in Scheme 3.^{2e,f} The possibility of writing structure **A** arises from an analogy with the corresponding lactone whose presence in an analogous equilibrium mixture of fluxional isomers has been demonstrated.^{2f}

We have previously shown that the interconversion $2 \rightarrow 1$ proceeds photochemically at its initial stage to yield **C** which subsequently forms **1** in a thermal (dark) reaction, i.e. $2 \xrightarrow{h\nu} C \xrightarrow{\Delta} 1$.^{2d,e} Indeed, although heating of **1** to 200° gives **2** in 75% yield, similar treatment of **2** demonstrated its stability under these conditions although above 200° it begins to decompose and to give naphthalene.*

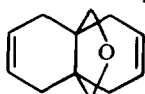
The question presents itself as to whether we may consider **D** as a partner in the mixture of fluxional isomers **1**, **A**, **B** and **C**. As implied above, the presence of **D** was not directly demonstrated but its intermediacy may perhaps be surmised in view of the isolation of its dehydrogenation product **3**. We thus decided to try to prepare organometallic derivatives of **1** in the hope that **D** might lend itself to isolation in the form of a stabilized organometallic derivative, particularly in view of the reported isolation of a *bis*-irontricarbonyl derivative of prebullvalene itself and its conversion at 180° to the *bis*-irontricarbonyl derivative of *cis*-9,10-dihydronaphthalene.⁷ In this particular case it was reported⁷ that triphenylphosphine at 140° removes the two irontricarbonyl groups from the prebullvalene complex, leading to bullvalene. Other authors⁸ have been unable to confirm this.

The prebullvalene ether **1** reacted with diiron-nonacarbonyl in boiling benzene and gave a *bis*-irontricarbonyl derivative in low (*ca* 10%) yield. The same *bis*-derivative was obtained in 41% yield when **1** was heated with ironpentacarbonyl in refluxing di-*n*-butyl ether. A by-product in this reaction (*ca* 20%) was compound **4** which contains a furan ring. Presumably the rearrangement of double bonds involved in the conversion $1 \rightarrow 4$ occurs via the intermediacy of a double π -allylic complex followed by its decomposition (Scheme 4). That this had occurred was indicated by disappearance of absorption bands in the vicinity of 270 nm, characteristic for the conjugated diene



in the prebullvalene ether **1** with extinctions of the order of 1000 and the appearance of the relative weak maximum at 260 nm (ϵ , 51.5) for the product **4**. The NMR spectrum of **4** no longer had the four CH_2O protons near τ , 5.0 but exhibited instead 2 aromatic $=\text{CH}-\text{O}$ protons at τ , 3.08 corresponding to the two hydrogen atoms in the furan

* It must be noted that when **2** is prepared from the corresponding diene

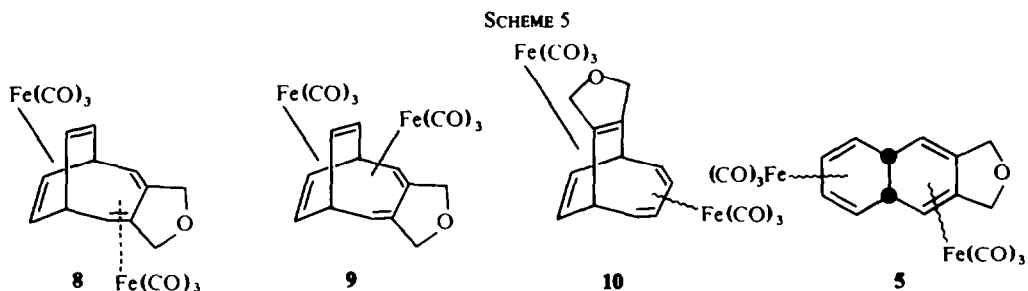


by bromination followed by dehydrobromination in DMF at 140° naphthalene is already obtained as a by-product at this (lower) temperature.³ However, this is not the case when **2** is heated "neat" at temperatures up to 200°. Further, no dimerization of **2** was observed at these temperatures in contradistinction to the thermal behavior of other tetraenic propellanes.⁶

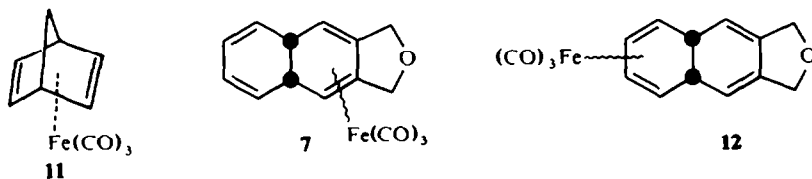
ring of **4**. Additional support for the structure **4** was obtained from the fact that it added to maleic anhydride in refluxing benzene to give the Diels-Alder adduct **6** whereas **1** does not add maleic anhydride under these conditions or in refluxing toluene.

In contrast to the literature report⁷ our *bis*-irontricarbonyl complex did not react with triphenylphosphine at about 140° (boiling di-*n*-butyl ether) to afford the bullvalene ether whose properties we have reported earlier.^{2e} Nor did the *bis*-complex change upon heating to 180° (*cf* Ref. 7).

Of the fluxional isomers listed in Scheme 3, the structures **A** and **C** need not be considered seriously as the organic portion of the *bis*-irontricarbonyl complex. However, **1**, **B** and possibly **D** are, in principle, capable of affording such a *bis*-deriva-



tive these corresponding substances, listed in Scheme 5. Structures **8** or **9** are immediately ruled out on the grounds of the NMR spectrum of the complex obtained. Central vinylic protons (*c*) characteristic of the central portion of a conjugated diene, $\text{CH}=\text{CH}-\text{CH}=\text{CH}$, are present in the region τ 4.6-4.8. Neither **8** nor **9** contains such central protons. The vinylic protons in a non-conjugated diene in a 6-membered ring in the boat-conformation, e.g. *nor*-bornadiene-irontricarbonyl, **11**, do not absorb in this region.⁹



Thus structures of type **10** and **5** remain to be considered. A decision between them may be reached on the basis of the following evidence. When the *bis*-derivative is treated under very mild conditions with 3 equivalents of ceric ion, one of the irontricarbonyl ligands is selectively removed.¹⁰ The NMR spectrum of the monoirontricarbonyl derivative thus obtained points to structure **7** for this compound rather than the isomeric structure **12** or an isomeric one based on the prebullvalene skeleton. The 100 MHz spectrum exhibits a symmetrical multiplet (4H) characteristic for the AA'BB' conjugated six-membered ring diene in the unsubstituted ring of **7** (τ 4.4-4.7), two terminal vinylic protons in the conjugated diene of the ether-substituted 6-membered ring (τ 6.54) and the two angular protons (τ , 7.15); the latter protons in *cis*-9,10-dihydronaphthalene itself appear at τ , 6.75.¹¹

The selectivity in removal of one irontricarbonyl ligand from **5** indicated the apparent relative stability of a substituted diene complex towards oxidation as

compared to the diene complex in the unsubstituted ring. Curiously, there appear to be no reports in the literature on this question. Our result would imply, for example, that if butadiene irontricarbonyl and 2,3-dimethylbutadieneirontricarbonyl were allowed to compete in removal of the ligand through oxidation by ceric ion, the former compound would be more readily oxidized than the latter.

Compound 7 was stable up to 180° and no rearrangement to 12 or to another substance was observed (*cf* 12). Nor was there any ligand exchange when 7 and an excess of 2 were refluxed together in di-n-butyl ether solution.

Returning to Scheme 3, it appears that we would be justified in removing the question mark regarding the involvement of D in the equilibrium mixture of fluxional isomers. Apparently D has two routes for further reaction. It may dehydrogenate and yield 3 or, in the presence of ironpentacarbonyl 1 → A → D, and D affords 5.

When 5 is treated with 6 equivalents of ceric iron, both irontricarbonyl ligands are removed, further oxidation takes place and the naphthalenic ether 3 is isolated. Again, since this removal of ligands is effected under very mild conditions, the obtention of 3 supports the deduction that the 9,10-dihydronaphthalene rather than the prebullvalene skeleton is already present in 5 (and in 7).

EXPERIMENTAL

UV spectra were measured on a Cary 15 spectrophotometer. IR spectra were measured on a Perkin-Elmer model 237 grating spectrophotometer. 60 MHz and 100 MHz nmr spectra were measured on the corresponding Varian spectrophotometers.* Mass spectra were measured on an Atlas CH 4 mass spectrometer using the heated inlet system at 200°. The electron energy was maintained at 70 eV and the ionization current at 20 μ A. All m.p.s are uncorrected.

Thermal reaction of the prebullvalene ether 1. A sol of 1 (70 mg) in dioxan (0.5 ml) was degassed in a pressure tube, the tube was sealed in a vacuum and heated at 200–205° for 15 hr. After cooling, the tube was opened, the solvent was removed and the NMR spectrum (CDCl_3) of the reaction mixture was determined and compared to those of pure 1 and 2.^{2a,5} The mixture contained *ca* 70% of 2, *ca* 10% of 1 and an aromatic component shown below to be 3. GLC analysis on an SE 30 column, 1 m by $\frac{3}{8}$ in at 185°, He flow rate 150 ml/min showed 4 components to be present: naphthalene (trace; retention time 1.8 min), 2 (76%; 3.4 min), 1 (9%; 6.8 min), 3 (15%; 9.4 min). Several components were isolated by preparative GLC and identified in the cases of 1 and 2 by comparison with authentic samples^{2a,5} and as shown below for 3.

The same results were obtained for an undegassed sol of 1 under analogous conditions. At higher temp e.g. 210–220° the amount of naphthalene rises, that of 2 falls and 3 decomposes.

Analogous treatment of 2 at 200–205° affords recovered 2 accompanied by a trace of naphthalene. GLC does not show the presence of even a trace of 3. Analogous treatment at 210–220° gives 40% recovered 2 and 60% naphthalene. The GLC peak of 3 was identical to that of 4,5-benzophthalan, 3, m.p. 99° (sealed cap) obtained after removal of the ligands in 5. (Found: C, 85.02; H, 5.84; M.W. 170. $\text{C}_{12}\text{H}_{10}\text{O}$ requires: C, 84.68; H, 5.92%; M.W. 170.20); UV (MeOH): λ_{max} , ϵ 318 nm, 850; 314 (min), 478; 311 (sh), 532; 304, 744; 301 (min), 691; 286, 2340; 283 (min), 2230; 277, 3400; 271 (min), 2970; 267, 3240; 258 (sh), 2570; 250 (sh), 1960; 246 (min), 1840; 223, 32,200; 219 (sh), 30,600; 217 (sh), 30,100; 205 (end); 14,100; NMR (CDCl_3): τ multiplet of sym AA'BB' system (2.65–2.08 centred at 2.40) with superimposed singlet for C protons (2.32); total of 6H; singlet (4H; CH_2O). The pattern of aromatic protons is identical to that of the aromatic protons in 2,3-dimethylnaphthalene. The UV spectra of the two are also very similar.

Oxidation of 3 to naphthalene-2,3-dicarboxylic acid. A mixture of 3 (30 mg), sodium bichromate (150 mg) and water (0.5 ml) was heated in a sealed tube at 200° for 24 hr. After cooling and opening the tube, water (5 ml) and conc HCl (1 ml) were added, the green ppt was removed by filtration, washed with water, dried and dissolved by shaking with ether. Removal of ether afforded the diacid, m.p. 238–241° (23 mg; 60.5%), lit.¹³ m.p. 239–241°. There was no m.p. depression on admixture with authentic naphthalene-2,3-dicarboxylic acid (Fluka) and the respective IR spectra were identical.

* We are grateful to Dr. A. Eisenstradt of Tel Aviv University for the 100 MHz spectra.

Reaction of 1 with ironpentacarbonyl. A mixture of **1** (344 mg) and iron-pentacarbonyl (1.6 ml) was heated under reflux in di-n-butyl ether (10 ml) at 155–160° (bath temp) for 15 hr under N₂. After cooling part of the product precipitates together with decomposition products of Fe(CO)₅. The ppt was removed by filtration and dissolved in chloroform. Decomposition products were removed by filtration. After removal of chloroform the pure bis-complex **5** was obtained (330 mg; 36.5%). The dibutyl ether mother liquor was treated to remove solvent at room temp (0.2 mm). After removal of solvent the residue was heated to 50°, leading to sublimation of the furan derivative **4** (68 mg; 20%). The residue in the flask after crystallization afforded additional bis-complex **5** (41 mg; total yield 41%).

The bis-complex **5** had m.p. 204° (sealed cap, dec, from MeOH or light petroleum-benzene). (Found: C, 47.58; H, 2.60; M.W. 452. C₁₈H₁₂O₂Fe₂ requires: C, 47.83; H, 2.68%; M.W. 451.98); UV(MeOH): λ_{max}, ε 310 nm, 9080; 280 (min), 6360; 231, 31,600; 221 (min), 29,700; 211, 38,800; 205 (end), 37,800. IR(CHCl₃): 2050 (sharp s), 2044 (sharp s), 1990 cm⁻¹ (broad s); NMR (CDCl₃): τ 4.67–4.85 (m, 2 central vinylic H); 5.13–5.45 (AB quartet, J = 11 cs, 4 CH₂O); 7.02 (v br) and 7.16 (v br m; terminal vinylic H); 7.32 (v br, angular H); total 6H. These assignments were proved by decoupling experiments showing that the peak at 7.16 belongs to terminal protons coupled with central protons at 4.67–4.85. The other assignments in the high field region were made on the basis of comparison with the nmr spectrum of **7**.

The furan derivative **4** formed colourless needles, m.p. 63–66° (sublimed; r.t./0.05 mm) which turn yellow upon contact with air. (Found: M.W. 172. C₁₂H₁₂O requires: M.W. 172.22); UV(MeOH): λ_{max}, ε 260 nm, 51.5; 225 (sh), 6360; 210 (end), 8600; NMR (CCl₄): τ 3.08 (s, 2H, C=CH–O); 4.00 (v br m; 4 vinylic H); 7.02 (br s; 6 allylic H). Irradiation at 7.02 sharpens the peak at 4.00 and vice versa.

Reaction of 4 with maleic anhydride. A mixture of freshly prepared **4** (57 mg; 0.33 mmol), maleic anhydride (80 mg; 0.82 mmol) and benzene (7 ml) was heated under reflux for 15 hr under N₂. After cooling a colourless precipitate of the Diels–Alder adduct **6** was obtained (60 mg; 67%), m.p. 205–206° (chloroform). (Found: C, 71.30; H, 4.87; M.W. 270. C₁₆H₁₄O₄ requires: C, 71.10; H, 5.22%; M.W. 270.27); IR (KBr): 1874 (m), 1835 (w), 1780 (s) cm⁻¹ (CO of anhydride). Nmr (DMSO-d₆): τ 3.95–4.15 (m; 4 vinylic H); 5.09 (s, CHO, 2H); 6.76 (s, CHCO, 2H); 7.04 (m, 2 angular allylic CH); 7.37 (m, 4 allylic H).

No reaction was obtained when **1** was subjected to similar reaction conditions with maleic anhydride in refluxing benzene or toluene.

Reactions of 5. (a) Heating **5** in a sealed tube at 200° for 15 hr gave recovered **5** and a trace of **3**. (b) Heating of **5** with excess triphenylphosphine in di-n-butyl ether at 140° did not cause decomposition of the complex, nor was such decomposition caused with excess triphenylphosphine in a sealed tube at 160–170°. (c) To a solution of **5** (45.2 mg; 0.1 mmol) in MeOH (60 ml) was added a soln of ceric ammonium nitrate (328 mg ≡ 0.6 mmol Ce^{IV}) in MeOH (20 ml) at room temp. A quantitative evolution of CO was measured volumetrically (14.5 ml). The MeOH was removed at the water pump (bath temp 40°). Water and ether were added, the ether phase was washed thrice with water. Removal of ether afforded **3** (18 mg; quant) identical in all respects to **3** described above. (d) To a solution of **5** (190 mg; 0.42 mmol) in MeOH (90 ml) was added at room temp a soln of ceric ammonium nitrate (725 mg; 1.32 mmol) in MeOH. CO was evolved (28.5 ml; 92% based on 3 CO). After workup similar to the above a mixture (103 mg) of **7** and **3** was obtained. This was separated on a preparative TLC plate of neutral alumina affording **7** (71 mg; 54%) and **3** (12 mg; 17%). The mono-irontricarbonyl complex **7** had m.p. 88° MeOH. (Found: C, 57.61; H, 4.04; M.W. 312. C₁₅H₁₂O₄Fe requires: C, 57.72; H, 3.87%; M.W. 312.11); UV (MeOH): λ_{max}, ε 272 nm (sh), 7320; 226 23,100; 221 (min), 22,800; 205 (end), 37,000; IR (CHCl₃): 2059 (sh s), 1990 cm⁻¹ (br s) (CO); NMR 60 MHz (CDCl₃): τ 4.52 (s, 4 vinylic H), 5.1–5.7 (m, AB part of ABX system, 4 CH₂O); 6.52 (m, 2H); 7.12 (m, 2H); 100 MHz (CDCl₃): 4.4–4.7 (sym m of AA'BB' system, 4 vinylic H); 5.39, 5.50 (AB quartet, J_{HH} = 11 cs, 4 CH₂O); 6.54 (br s, 2 terminal vinylic H); 7.15 (2 ang H). Double irradiation experiments lead to these assignments.

Attempted synthesis of 3. A mixture of naphthalene-2,3-dicarboxylic anhydride (1.98 g), LAH (1.1 g) and THF (120 ml) was heated under reflux for 6 hr. After acidic workup in the usual way and extraction thrice with EtOAc (50 ml portions), the organic layers were combined, washed with water, with 10% NaHCO₃ aq, water and dried (MgSO₄). After removal of solvents the crude product mixture was obtained (1.8 g). Crystallization from benzene gave pure 2,3-dihydroxymethylnaphthalene (1.35 g; 72%), m.p. 160°. (Found: C, 76.43; H, 6.48; M.W. 188. Calc. for C₁₂H₁₂O₂: C, 76.75; H, 6.43%; M.W. 188.22), lit. m.p. 158°, 4 m.p. 160°, ¹⁴UV (MeOH): λ_{max}, ε 319 nm, 168; 317 (min), 132; 313, 182; 311 (min), 176; 306, 254; 302 (min), 222; 285 (sh), 2320; 275, 3610; 269 (min), 3350; 266, 3500; 256 (sh), 2680; 247 (sh), 1840; 241 (min), 1540; 226, 89,400; 219 (sh), 47,600; 217 (sh), 41,500; 208 (end), 5860; IR (CHCl₃): 3590, 3380 cm⁻¹ (OH); NMR (DMSO-d₆): τ 2.02–2.62 (sym m centred at 2.32 of AA'BB' of unsubst arom ring superimposed on s at 2.08 of 2 protons in substit arom ring; total 6H) 4.74 (t, 2H, OH, J_H = 5.5 cs); 5.26 (d, 4H, CH₂O; J_H = 5.5 cs).

Addition of D₂O causes disappearance of triplet of OH and the doublet at 5.26 is converted into a singlet.

The mother liquor from which the diol was crystallised was concentrated to a volume of 20 ml and the soln was chromatographed on neutral alumina (Merck, 20 g). Elution with benzene afforded 2,3-dimethylnaphthalene (26 mg) m.p. 104°, mixed m.p. with authentic specimen (Fluka), 104°. The spectral properties of both specimens were identical. Elution with benzene (1)-chloroform (1) afforded 2-methyl-3-hydroxymethylnaphthalene, 90 mg) m.p. 93° (benzene-light petroleum). It sublimes at 85° (24 mm). Found: C, 83.77; H, 6.94; M.W. 172. C₁₂H₁₂O requires: C, 83.69; H, 7.02%; M.W. 172.22); UV (MeOH): $\lambda\lambda_{\max}$, $\epsilon\epsilon$ 350–327 nm (sh), 87.4; 320, 270; 317 (min), 208; 314, 257; 312 (min), 246; 307, 405; 304 (min), 380; 286 (sh), 2640; 277, 3800; 271 (min), 3440; 267, 3560; 261 (min), 2940; 249, 3920; 241 (min), 3440; 226, 83,300; 221 (sh), 52,800; 217 (sh), 44,200; 208 (end), 5200; IR (CHCl₃): 3590, 3400 cm⁻¹ (OH); NMR (CDCl₃): τ 2.10–2.70 (m, 6 arom H); 5.30 (s, 2H, CH₂O); 7.45 (s; 1H, OH, disappears after addition of D₂O); 7.62 (s, 3H, CH₃).

Hydrogenolysis of 2,3-dihydroxymethylnaphthalene. The diol (100 mg) was dissolved in MeOH (15 ml) and AcOH (1 ml) and Pd-C (30%: 50 mg) were added. H₂ was absorbed (2 moles) during 10 min. After removal of catalyst and solvents the product was dissolved in ether. After washing with water, 10% NaHCO₃aq, water and drying (MgSO₄), the solvent was removed. 2,3-Dimethylnaphthalene (67 mg; 82%), m.p. 104°, mixed m.p. 104° was obtained.

The naphthalenic ether 3 was not hydrogenolysed under similar conditions.

Attempted dehydration of 2,3-dihydroxymethylnaphthalene. Compound 3 was not obtained when the diol was refluxed in CH₂Cl₂ soln in the presence of *p*-toluenesulphonic acid. Replacement of this solvent by benzene led to Friedel-Crafts reaction. Higher boiling solvents also produced negative results. Heating the diol at 180–200° with NaHSO₄ failed. Pyrolysis at 200–350° did not lead to the ether although small quantities of 2,3-dimethylnaphthalene were isolated.

Treatment of a pyridine soln (10 ml) of the diol (188 mg; 1 mmol) at 0° with SOCl₂ (238 mg; 2 mmol) followed by standing overnight, pouring into water, EtOAc extraction, washing the EtOAc layers with water, 5% HCl, water, drying (MgSO₄) and removal of solvent afforded a cyclic sulfite (165 mg; 70.5%), m.p. 172° (benzene) (Scheme 2); (Found: C, 61.72; H, 4.20; M.W. 234. C₁₂H₁₀O₃S requires: C, 61.54; H, 4.30%; M.W. 234.20); IR (CHCl₃): 1175 (s; S=O); 1000 (m), 975 (sh), 958 (s), 935 (sh m), 897 (s) (S—O); NMR (CDCl₃): 2.08–2.60 (m, 6 arom H); 3.78, 4.55 (AB quartet, $J_{\text{HH}} = 14$ cs, 4H, CH₂O).

Pyrolysis of the cyclic sulphite also failed to give 3. It is of interest to note that selenium dioxide oxidation of the diol afforded a stable cyclic selenite *en route* to the corresponding dialdehyde.⁴

The mass spectrum exhibits strong M⁺-SO₂ and M⁺-SO₂H peaks, beyond which it is identical to that of 3. Thus, although we were unsuccessful in synthesizing 3, it apparently formed from the cyclic sulphite under electron impact.

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