Dearomatisation of 2-Naphthol by Oxidative Nucleophilic Substitution and Oxidative Electrophilic Substitution

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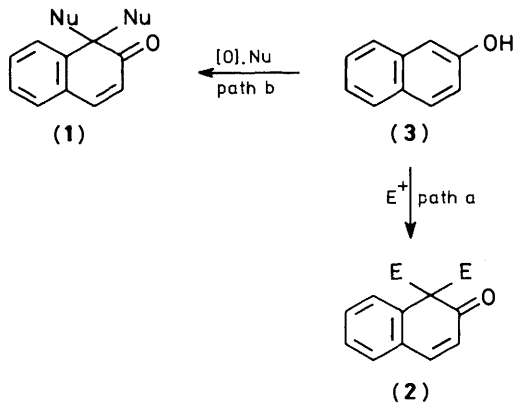
2-Naphthol has been dearomatised by oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in the presence of methanol, ethylene glycol, and 2,2-dimethylpropane-1,3-diol to give 1,1-alkoxynaphthalen-2(1*H*)-ones in moderate yield. The reaction of 2-naphthol with 5,5'-ethylene bis(toluene-*p*-sulphonate) (Woodward's reagent) gives a good yield of 1,1-dithioacetal. Finally 2-naphthol is dearomatised by t-butyl perbenzoate. The smooth Michael addition of nitromethane to most of these 1,1-disubstituted naphthalen-2(1*H*)-ones has been demonstrated.

Quinone monoacetals are versatile intermediates in organic synthesis.[1] This is evident from the elegant use of such compounds in the elaboration of a variety of natural products.[2] An entry to this class of compounds is most often provided by oxidation of the corresponding hydroquinone monoether by a number of methods.[2] A particular example of such a reaction is the thallium trinitrate oxidation[3] of an *o*-hydroquinone monoether in the elegant total synthesis of napelline.[4] More recently, quinone monoacetals have been obtained by selective hydrolysis of quinone acetals derived, in turn, from the corresponding hydroquinone mono- or bis-ethers by electrochemical oxidation.[1] Quinone monoacetals have also been prepared by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) oxidation of sterically hindered phenols.[5] However, there are few examples of the direct conversion of naphthols into naphthoquinone monoacetals. We chose to study this transformation in connection with a synthetic project and report here the results of our investigation.

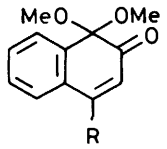
The direct conversion of 2-naphthol into the corresponding quinone monacetal can be envisaged to proceed by electrophilic or nucleophilic substitution reactions (see Scheme 1). In the



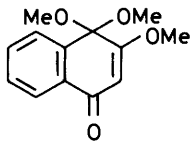
Scheme 1.

former case the substrate may be regarded as a potential nucleophile owing to the presence of π and unshared electron pairs and in the latter case as an easily oxidised electron donor which gives rise to intermediates that may be trapped by external nucleophiles. These substitution products can be regarded as arising from what is formally an oxidative electrophilic reaction (path a) or an oxidative nucleophilic reaction (path b). This class of compounds is of interest since it provides a functionalised bicyclic system which can be readily elaborated, by conjugate addition and subsequent transformation at C-1 and C-2, into more complex products. For this reason, it was desirable that the functionality at C-1 should be in the form of an ether or a thioether. We have prepared a certain number of derivatives representing structures (**1**) and (**2**) from 2-naphthol and have also investigated their ability to undergo conjugate addition with nitromethane.

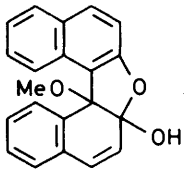
Oxidative Nucleophilic Substitution.—In view of the reported conversion of certain hydroquinone monoethers into the corresponding quinone bisethers in the presence of a suitable oxidant and an alcohol, we have investigated the application of this reaction to 2-naphthol. Treatment of 2-naphthol (**3**) with 2 equiv. of DDQ in anhydrous methanol afforded the dimethoxy acetal (**4**) in an 11% yield together with two isomeric trimethoxylated derivatives (**5**) (20%) and (**6**) (10%) and a product of a coupling reaction (**7**) (1%). The derivatives (**4**), (**5**), and (**6**) have been described previously by Swenton and co-workers[6] and exhibit the same characteristics. The structure of (**7**) was deduced from its high-resolution mass spectrum and ^{1}H n.m.r. spectrum. In separate experiments it was demonstrated that (**5**) was derived from (**4**) upon treatment with DDQ in methanol and that (**5**) and (**6**) underwent interconversion in the presence of methanol and $DDQH_2$. It would appear then that (**5**) is in fact formed in a yield of 41% in the original reaction. Attempts to limit the quantity of methanol by conducting the reaction in benzene containing methanol (10 equiv.) did not result in an increase in the yield of (**4**) although the trimethoxylated derivatives were not observed. In this case a number of unidentified aromatic compounds were predominant. The action of DDQ (2.2 equiv.) on 2-naphthol in ethylene glycol at ambient temperature yielded a mixture containing the bisacetal (**12**) as the major component and the desired monoacetal (**8**) as the minor component. Fractional crystallisation gave (**12**) in a 50% yield. In refluxing benzene, in the presence of 5 equiv. of ethylene glycol and 2.2 equiv. of DDQ, 2-naphthol yielded four components, isolated by high-performance liquid chromatography (h.p.l.c.). These were identified as being the monoacetal (**8**) (14%), the bisacetal (**12**) (8%), the bisacetal (**13**) (10%), and the bisacetal (**14**) (4%) on the basis of their spectral data. The differentiation of the bisacetals (**12**) and (**13**) deserves comment. These two derivatives can be distinguished by their rates of hydrolysis. Thus, in the presence of oxalic acid in a mixture of tetrahydrofuran and water, (**13**) hydrolysed slowly and, after one week, yielded a mixture of starting material and the monoacetal (**8**) where (**12**) remained unchanged under identical conditions. The latter compound was, however, hydrolysed at 65 °C in the presence of



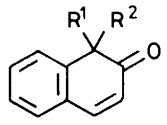
(4) R = H
(5) R = OMe



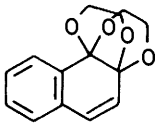
(6)



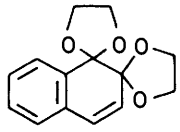
(7)



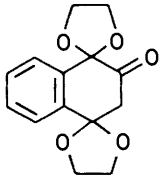
(8) $R^1.R^2 = (O-CH_2)_2$
(9) $R^1.R^2 = (O-CH_2-CMe_2-CH_2-O)$
(10) $R^1 = R^2 = OCMe_3$
(11) $R^1.R^2 = (S-CH_2)_2$



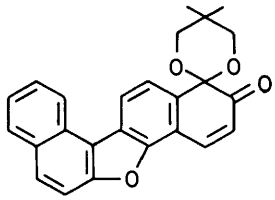
(12)



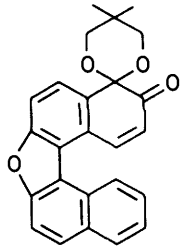
(13)



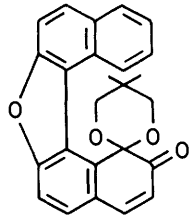
(14)



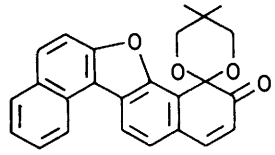
(15a_1)



(15a_2)



(15b_2)



(15b_1)

trifluoroacetic acid to give the monoacetal (**8**) as well as 1,2-naphthoquinone. On the basis of the reported[2] selective hydrolysis reactions of 1,1,2,2-quinonebisacetals under similar conditions to those employed here, it would appear that (**13**) is in fact the isomer shown. This conclusion is corroborated by the ^{13}C n.m.r. data for (**12**) and (**13**). It has been established[7] that, in general, the value of the one-bond geminal coupling constant, $^1J_{^{13}C-H}$, in acetals increases with decreasing ring size. The observe values of $^1J_{^{13}C-H}$ for the methylene carbons in (**12**) and (**13**), 146 and 150 Hz, respectively, are therefore in agreement with the proposed structures.

The monoacetal (**8**) when treated with 4 equiv. of ethylene glycol and 2 equiv. of DDQ in refluxing benzene for 18 h gave a mixture of unchanged starting material and the two bisacetals (**12**) and (**13**).

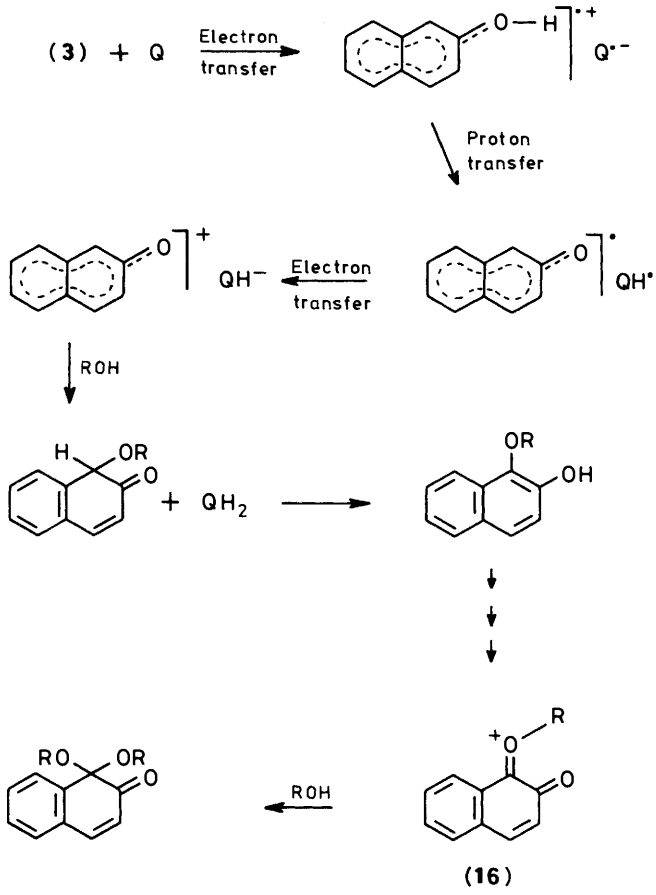
The reaction of 2-naphthol with 2,2-dimethylpropane-1,3-diol (10 equiv.) and DDQ (2 equiv.) in refluxing benzene was also investigated. After 20 h, a mixture consisting of the monoacetal (**9**) (39%), and a product of a coupling reaction, were obtained. The spectral characteristics of the latter component were compatible with any of the structures (**15a**$_1$), (**15a**$_2$), (**15b**$_1$), and (**15b**$_2$). Thus, for example, the ^1H n.m.r. spectrum at 400 MHz showed two doublets at δ 6.18 and 7.99 (*J* 10 Hz), characteristic of an α,β-unsaturated system and two mutually isolated AB systems at δ 8.06, 8.39 (*J* 8.6 Hz) and δ 7.76, 7.96 (*J* 9 Hz). The remaining four aromatic protons appeared as a mutually coupled doublet, triplet, triplet, doublet system. In fact, as established further, (**15a**$_1$) can be retained on mechanistic and steric grounds.

As a further extension, the method of McKillop and co-workers[3] was investigated as a means of synthesising the dimethoxy acetal (**4**). Thus, reaction of 2-naphthol with thallium(III) nitrate in methanol afforded the desired compound (**4**) but only in 29% yield. The major products of this reaction were phenolic in nature and were not identified; they presumably resulted from phenolic coupling reactions.

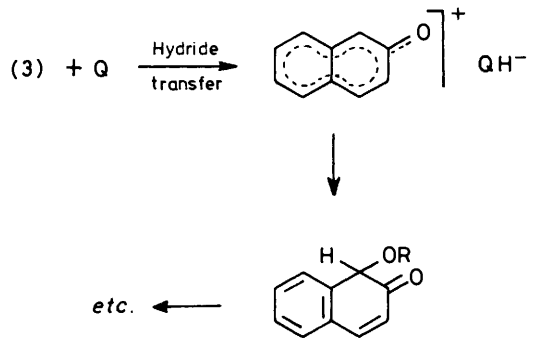
The oxidation of a phenol by a quinone of high oxidation potential can be regarded as proceeding *via* one-electron transfers. According to this interpretation, the radical cation formed initially is transformed into a radical by loss of a proton and the latter can either undergo dimerisation or coupling reactions or can itself be oxidised to a carbocation which can, in turn, be trapped by a nucleophile in the medium. An alternative interpretation in terms of a two-electron transfer to give the carbocation directly has also been considered.[5]

These concepts are illustrated for the oxidation of 2-naphthol by DDQ in Schemes 2 and 3. There also exists a variation of the first hypothesis, namely that the radical does not transfer an electron to the semiquinone to give the carbocation but adds to it instead (see Scheme 4). This species could then be oxidised to the radical as before and the ether function at C-1 would then favour the conversion of this radical into the corresponding carbocation. Regardless of the exact details of the reaction mechanism, the key elements in the DDQ oxidation of 2-naphthol are the formation of the oxocarbocation (**16**) and its reaction either with alcohols to give the monoacetals or alternatively with other nucleophiles in the medium to give the coupled products. The same key elements are present in the thallium(III) nitrate oxidation of 2-naphthol in methanol. The results described in the preceding section can now be discussed in terms of this hypothesis.

The formation of the condensation product (**7**) in the reaction of 2-naphthol with DDQ in methanol can be rationalised in terms of an initial attack of 2-naphthol, also present in the medium, on the intermediate (**16**), as shown in Scheme 5. The formation of the 'dimer' in the reaction of 2,2-dimethylpropane-1,3-diol with 2-naphthol can be interpreted in

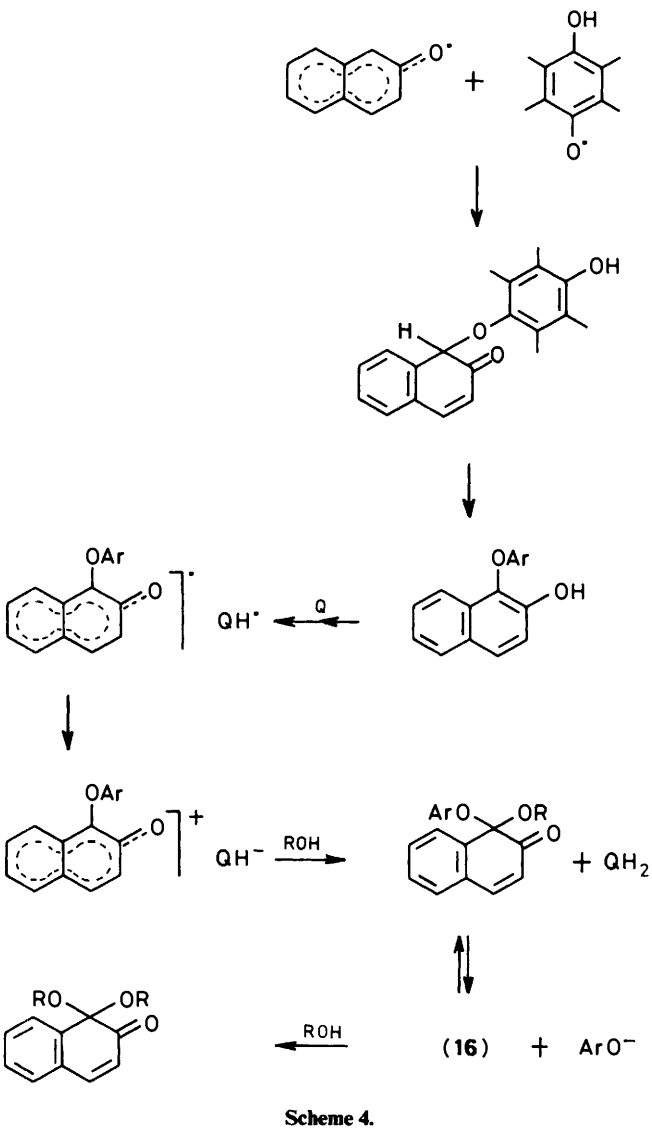


Scheme 2.

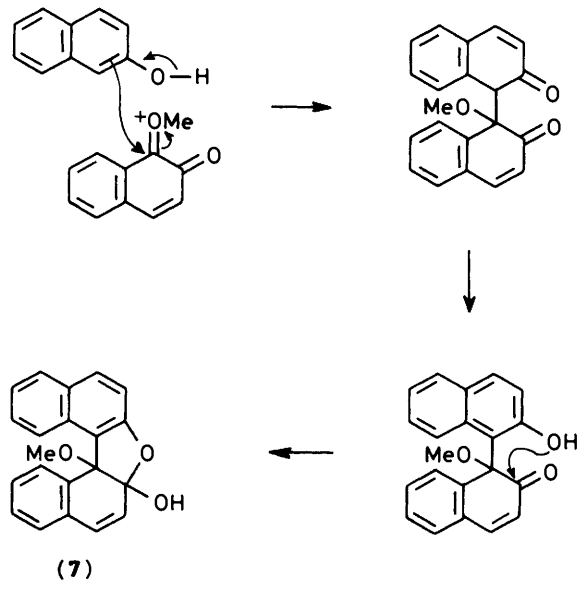


Scheme 3.

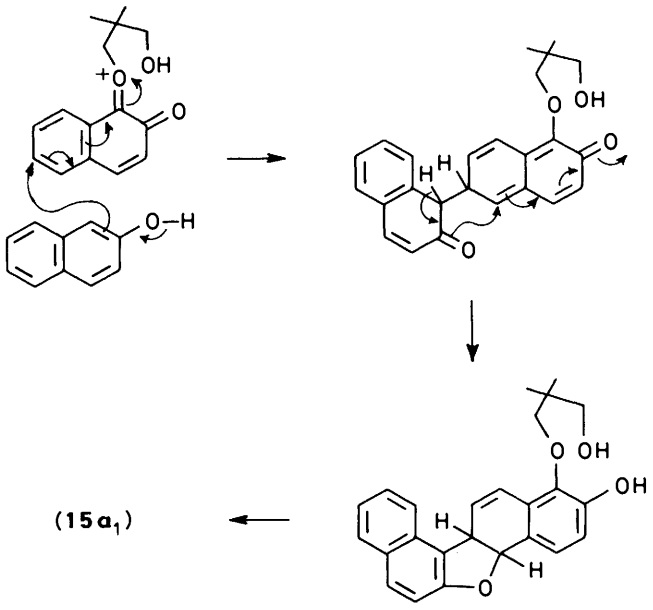
a similar manner. However, in this instance, the condensation product does not arise from attack of 2-naphthol at C-1 but rather on the aromatic moiety of the intermediate (**16**) (see Scheme 6). On the basis of the proposed mechanism it would appear that only the two isomeric structures (**15a**$_1$) and (**15b**$_2$), compatible with the spectral data, could be retained, (**15a**$_1$) being the most probable on steric grounds. The reactions obtained in the presence of ethylene glycol are somewhat more complex. In this case, products resulting from both intramolecular and intermolecular attack of the alcohol function on the intermediate (**16**) were obtained, as indicated in Scheme 7. The bisacetal (**12**) is then derived by intermolecular attack of ethylene glycol on (**16**) followed by acetalation in the acidic medium. In agreement with this interpretation, this reaction becomes predominant in the presence of an excess of



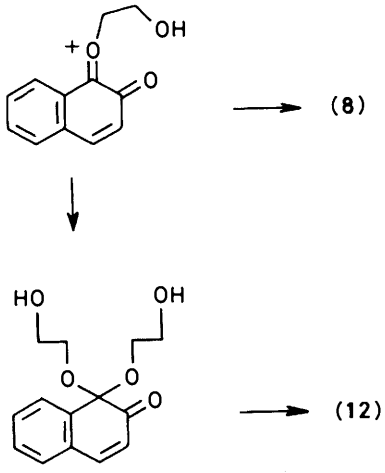
Scheme 4.



Scheme 5.



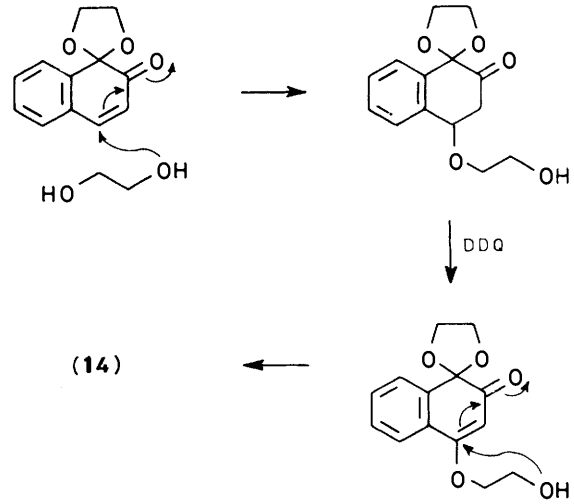
Scheme 6.



Scheme 7.

ethylene glycol and with ethylene glycol as solvent compound (**12**) was obtained in a yield of 50%. The other products of the reaction are derived from the monoacetal (**8**). Thus, (**13**) is formed by acetalation of (**8**), and (**12**) can also arise from (**8**) by opening of the dioxolane ring and subsequent attack by ethylene glycol, as described earlier. The bisacetal (**14**) is formed by conjugate addition of ethylene glycol with (**8**) followed by dehydrogenation with DDQ and a second conjugate addition (see Scheme 8).

In summary, the results may be adequately explained in the following manner, 2-naphthol, upon treatment with an oxidant of high oxidation potential in the presence of an alcohol gives rise to an electrophilic intermediate (**16**). This intermediate can then react with nucleophiles present in the medium, that is the excess of alcohol or 2-naphthol itself. The monoacetals themselves can undergo further reactions such as conjugate addition followed by oxidation [*e.g.*, (**5**), (**6**), and (**14**)] or acetalation [*e.g.*, (**12**) and (**13**)]. The relative proportions of the various products are governed by the relative rates of these reactions as well as by the nature and concentration of the



Scheme 8.

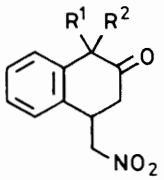
alcohol component. With 2,2-dimethylpropane-1,3-diol the secondary reactions were not observed and this presumably results from the steric hindrance of this moiety. On the other hand, with methanol or ethylene glycol as the alcohol component, the secondary reactions seem to be as rapid as the initial oxidation of 2-naphthol and the monoacetal was only obtained in low yield.

Oxidative Electrophilic Substitution.—The formation of a quinone monoacetal such as (**2**) by an oxidative electrophilic process (path a, Scheme 1), in which the functionality at C-1 is in the form of ethers, requires the use of an $^{+}$OR equivalent. We turned to the possible use of peroxyethers and peroxyesters for the generation, at least formally, of this $^{+}$OR equivalent. The reaction of Grignard reagents with MeO–OMe[8] can be regarded formally as proceeding *via* an $^{+}$OR species. However, the potential danger involved in the use of this reagent prompted us to examine other alternative sources, namely the peresters.

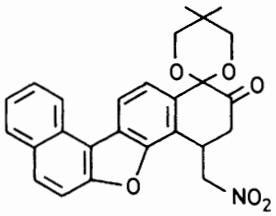
Treatment of 2-naphthol with t-butyl perbenzoate in refluxing benzene was without effect, the unchanged starting material being recovered. However, in the presence of sodium hydride a reaction was observed at ambient temperature and the di-t-butyl acetal (**10**) was isolated as a yellow solid in 30% yield. The remaining components of the mixture were phenolic in nature and were not investigated further.

We next turned our attention to the preparation of compounds of type (**2**) bearing functionality at C-1 in the form of thioethers. For this purpose we utilised Woodward's reagent, namely *S,S'*-ethylene bis(toluene-*p*-thiosulphonate).[9] Thus, 2-naphthol when treated with sodium hydride and *S,S'*-ethylene bis(toluene-*p*-thiosulphonate) in benzene afforded the dithioacetal (**11**). A yield of 84% was obtained provided that a solution of 2-naphthol was added to a suspension of the bis(toluene-*p*-thiosulphonate) and sodium hydride.

Addition of Nitromethane to the Enones derived from 2-Napthol.—As a final point of interest we chose to examine the conjugate addition of nitromethane with the enone systems prepared in this study. The four monoacetals (**4**), (**9**), (**10**), and (**15**) when treated with nitromethane in the presence of a base afforded the products of conjugate addition (**17**), (**18**), (**19**), and (**20**), respectively. In the cases of (**9**) and (**15**) triethylamine was used as the base. However, under similar conditions, the derivatives of (**4**) and (**10**) underwent significant decomposition.



(**17**) $R^1 = R^2 = OMe$
(**18**) $R^1, R^2 = (O - CH_2 - CMe_2 - CH_2 - O)$
(**19**) $R^1 = R^2 = OCMe_3$



(**20**)

In these cases use of a strong, hindered base such as tetramethylguanidine or t-butyltetramethylguanidine[10] which accelerate the reaction, gave the corresponding addition products (**17**) and (**19**) in high yield. Owing to its instability, compound (**19**) could not be fully characterised. Treatment of the dithioacetal (**11**) under the conditions described above resulted in the formation of a rearomatised compound that was not investigated further. It would appear then that attack of nucleophiles at the sulphur atom of the dithoacetal function is preferred to conjugate addition in these systems. This undoubtedly reflects the relative stabilities of the naphthol systems and the corresponding quinone monoacetal systems.

Experimental

Melting points were determined in capillary tubes with a Büchi melting-point apparatus and are uncorrected. The i.r. spectra were recorded on a Perkin-Elmer 297 spectrophotometer. U.v. spectra were recorded on a Jobin Yvon Duospec 203 spectrophotometer. Mass spectra under electron-impact conditions were recorded on a AEI MS 50 mass spectrometer at 70 eV ionizing voltage. Chemical ionization (CI) mass spectra were measured with an AEI MS 59 mass spectrometer modified for CI mass spectrometry. Isobutane or ammonia was used as reagent gas at 0.5 Torr pressure. ^{1}H N.m.r. spectra were recorded on a Bruker WP 80 or Bruker WM 400 spectrometer. ^{13}C N.m.r. spectra were recorded on a Cameca 250 spectrometer at 62.86 MHz or on a Bruker WM 400 spectrometer at 100.6 MHz. Spectra were measured in the appropriate solvent with tetramethylsilane (TMS) as internal standard. Chemical shifts are given in p.p.m. downfield from TMS. Chemical shifts and coupling constants were obtained from a first-order analysis of the n.m.r. spectra. Assignments were confirmed by means of double irradiation experiments.

Analytical t.l.c. was performed on pre-coated glass plates with Merck silica gel 60F-254 as the adsorbent. The developed plates were air-dried, and exposed to u.v. light and/or sprayed with 60% aqueous sulphuric acid, and heated at 150 °C. Preparative t.l.c. was performed on 20 × 20 cm glass plates coated with silica gel (Kieselgel 60PF 254) as adsorbent (layer thickness 1.5 mm). Column chromatography was performed on silica gel (Kieselgel 60H, Merck) under nitrogen pressure or on neutral aluminium oxide 90 (Activity I, Merck). High performance liquid chromatography (h.p.l.c.) was performed on a Waters Associates Prep LC/System 500 instrument with two Prep PAK-500 silica gel normal-phase columns and a refractive index detector. The chromatographic solvent systems (v/v) are as follows: A methylene chloride; B hexane–ether, 70:30; C 80:20; D 50:50; E toluene–methylene chloride, 9:1; F hexane–methylene chloride, 8:1; G ethyl acetate–toluene, 2:1; H 1:1; I 1:2; J 1:4; K toluene; L ethyl acetate–hexane, 10:90. Ether refers to diethyl ether throughout.

Solvents were distilled before use and were dried, as necessary, by literature procedures. Solvents were evaporated under reduced pressure and below 40 °C.

Reactions performed under nitrogen were also carried out in deoxygenated solvents. Transfers under nitrogen were effected by means of standard Schlenck tube techniques.

Reaction of 2-*Naphthol* (**3**) *with* 2,3-*Dichloro*-5,6-*dicyanobenzoquinone in Methanol.*—To a solution of 2,3-dichloro-5,6-dicyanobenzoquinone (35.0 g, 0.15 mol) in anhydrous methanol (500 ml) under nitrogen was added 2-naphthol (10.0 g, 0.069 mol) in portions and the mixture was stirred at ambient temperature for 20 h. The mixture was concentrated to a volume of 200 ml and then diluted with ether. The ether layer was washed thoroughly with 10% aqueous sodium hydroxide until the washings were colourless and then with saturated aqueous sodium chloride until neutral. The organic layer was dried (Na_2SO_4) and the solvent evaporated to yield a partially crystalline mass (7.5 g). Chromatography on silica gel using solvent E as eluant afforded three components having R_F values of 0.56, 0.48, and 0.20 (solvent A). The component having a R_F value of 0.48 was isolated as a yellow liquid and was identified as being 1,1-dimethoxynaphthalen-2(1*H*)-one (**4**) (1.5 g, 11%). Distillation (Kugelrohr, oven temp. 130 °C, 1 mmHg, lit.,[1] 116—120 °C, 0.7 mmHg) afforded an analytical sample, $\nu_{max.}(CH_2Cl_2)$ 1 670 cm^{-1} (CO); $\lambda_{max.}$(ethanol) 234 (ε 17 870) and 322 nm (7 790); δ_H (400 MHz; $CDCl_3$) 3.27 (6 H, s, 2 × OCH_3), 6.10 (1 H, d, *J* 10 Hz, 3-H), 7.29 (1 H, d, *J* 10 Hz, 4-H), 7.30 (1 H, d, *J* 7 Hz, 5-H), 7.39 (1 H, dt, *J* 7, 1 Hz, 7-H), 7.44 (1 H, dt, *J* 7, 1 Hz, 6-H), and 7.71 (1 H, br d, *J* 7.5 Hz, 8-H); *m/z* 204 ($M^{+\cdot}$, 47%), 173 ($M^{+\cdot}$ − OCH_3, 25), 145 (100), 121.5 [metastable $(145)^2/173$], and 103 [metastable $(145)^2/201$] (Found: C, 70.6; H, 5.85; O, 23.3. Calc. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92; O, 23.50%). The component having a R_F value of 0.56 was obtained as a white foam and was identified as being the dimer 13a-methoxy-7a,13a-dihydrodinaphtho[2,1-*b*:1′,2′-*d*]furan-7α-ol (**7**) (0.23 g, 1%), $\nu_{max.}(CH_2Cl_2)$ 3 475 cm^{-1} (OH); δ_H (80 MHz; $CDCl_3$) 3.18 (3 H, s, OCH_3), 5.07 (1 H, br s, OH), 6.17 (1 H, d, *J* 10 Hz, 3-H), 6.52 (1 H, d, *J* 10 Hz, 4-H), 6.87—8.12 (9 H m's, 9 × ArH), and 8.37 (1 H, m, ArH); *m/z* 316 ($M^{+\cdot}$, 87%), 283 (100), and 255 (33) (Found: *M*, 316.1088. Calc. for $C_{21}H_{16}O_3$: 316.1099). The component having a R_F value of 0.2 was further separated into two components by chromatography on silica gel using solvent I as eluant (R_F 0.47 and 0.62). The component having a R_F value of 0.62 was obtained as a white solid and was identified as being 1,1,4-trimethoxynaphthalen-2(1*H*)-one (**5**) (3.2 g, 20%). Recrystallisation from methylene chloride–hexane or sublimation afforded white needles, m.p. 100—101 °C (lit.,[2] 101.9—102.8 °C); $\nu_{max.}(CH_2Cl_2)$ 1 650 cm^{-1} (CO); $\lambda_{max.}$ (ethanol) 231 (ε 21 100), 234sh (20 164), and 317 nm (8 040); δ_H (80 MHz; $CDCl_3$) 3.26 (6 H, s, 2 × OCH_3), 3.92 (3 H, s, OCH_3), 5.60 (1 H, s, 3-H), and 7.20—7.90 (4 H, m's, 4 × ArH); *m/z* 234 ($M^{+\cdot}$, 17%), 219 (53), 204 (93), 175 (100), and 139.8 [metastable $(175)^2/219$] (Found: C, 66.8; H, 6.0; O, 27.42. Calc. for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02; O, 27.32%). The component having a R_F value of 0.47 was also obtained as a white solid and was identified as being 3,4,4-trimethoxynaphthalen-1(4*H*)-one (**6**) (1.6 g, 10%). Recrystallisation from ethanol or sublimation afforded white needles, m.p. 99—99.5 °C (lit.,[2] 100.5—101.7 °C); $\nu_{max.}(CH_2Cl_2)$ 1 650 cm^{-1} (CO); $\lambda_{max.}$(ethanol) 240 (ε 15 592) and 283 nm (9 600); δ_H (80 MHz; $CDCl_3$) 3.07 (6 H, s,

2 × OCH_3), 3.90 (3 H, s, OCH_3), 5.95 (1 H, s, 2-H), 7.32—7.80 (3 H, m's, 3 × ArH), and 7.97—8.17 (1 H, m, 8-H); *m/z* 234 ($M^{+\cdot}$, 8%), 219 (56), 203 (100), 175 (23), 157 (28), and 205 [metastable $(219)^2/234$] (Found: C, 66.80; H, 5.99; O, 27.36. Calc. for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02; O, 27.32%).

The basic aqueous layer obtained during the processing was acidified and then extracted with methylene chloride. The extracts were dried (Na_2SO_4) and concentrated to afford a dark brown solid. T.l.c. of this residue revealed the presence of very polar components and the absence of 2-naphthol. The ^1H n.m.r. spectrum indicated only the presence of signals in the aromatic region.

In another experiment the reaction was monitored by withdrawing aliquots at various intervals and by processing them as described above. This analysis revealed the initial formation of the dimethoxy acetal (**4**) and the subsequent formation of (**5**) within 2.5 h and (**7**) within 12 h.

Interconversion of 1,1,4-*Trimethoxynaphthalen*-2(1H)-*one* (**5**) *and* 3,4,4-*Trimethoxynaphthalen*-1(4H)-*one* (**6**).—(a) A mixture of 1,1,4-trimethoxynaphthalen-2(1*H*)-one (**5**) (0.067 g) and 2,3-dichloro-5,6-dicyanohydroquinone (0.13 g, 2.2 equiv.) in dry methanol (5 ml) was stirred at ambient temperature for 70 h. The mixture was diluted with ether and washed successively with 10% aqueous sodium hydroxide and saturated aqueous sodium chloride. The organic layer was dried (Na_2SO_4) and concentrated to give a solid whose ^1H n.m.r. spectrum indicated the presence of (**5**) and (**6**) in the ratio 80:20.

(b) A mixture of 3,4,4-trimethoxynaphthalen-1(4*H*)-one (**6**) (0.04 g) and 2,3-dichloro-5,6-dicyanohydroquinone (0.085 g, 2.2 equiv.) in dry methanol (5 ml) was stirred at ambient temperature for 19 days. The mixture was processed as described above to give a solid whose ^1H n.m.r. spectrum indicated the presence of (**6**) and (**5**) in the ratio 73:26.

Reaction of 1,1-*Dimethoxynaphthalen*-2(1H)-*one* (**4**) with 2,3-*Dichloro*-5,6-*dicyanobenzoquinone*.—To a solution of 1,1-dimethoxynaphthalen-2(1*H*)-one (**4**) (0.043 g, 0.21 mmol) in anhydrous methanol (4 ml) was added 2,3-dichloro-5,6-dicyanobenzoquinone (0.1 g, 0.44 mmol) and the mixture was stirred at ambient temperature. T.l.c. (solvent I) indicated the progressive formation of the trimethoxy compound (**5**) (R_F 0.6) and the subsequent formation of the isomer (**6**) (R_F 0.45). After 16 h the mixture was diluted with ether and the organic layer was washed successively with 10% aqueous sodium hydroxide and saturated aqueous sodium chloride. The organic layer was dried (Na_2SO_4) and the solvent evaporated to afford a solid (0.046 g). The ^1H n.m.r. spectrum indicated the presence of (**4**):(**5**):(**6**) in the ratio 26:46:28.

Reaction of 2-*Naphthol with* 2,3-*Dichloro*-5,6-*dicyanobenzoquinone in Ethylene Glycol*.—To a stirred solution of 2,3-dichloro-5,6-dicyanobenzoquinone (14.0 g, 0.062 mol) in ethylene glycol (70 ml) under nitrogen was added 2-naphthol (4.0 g, 0.028 mol) in portions and the mixture was stirred at ambient temperature for 24 h. The brown mixture was taken up in ether and washed successively with 5% aqueous sodium hydroxide and saturated aqueous sodium chloride until neutral. The organic layer was then dried (Na_2SO_4) and the solvent evaporated to afford a solid (4.1 g). Recrystallisation from ethanol yielded white needles which were identified as being 1,2,1,2-*bis*(*ethylenedioxy*)-1,2-*dihydronaphthalene* (**12**) (3.45 g, 50%), m.p. 124—125 °C; $\lambda_{max.}$(ethanol) 250 nm (ε 6 840); δ_H (80 MHz; $CDCl_3$) 3.40—3.90 (4 H, m, 2 × CH_2O), 3.90—4.35 (4 H, m, 2 × CH_2O), 5.80, 6.75 (two 1 H, d's, 3-H, 4-H), 6.95—7.45 (3 H, m's, 3 × ArH), and 7.45—7.80 (1 H, m, 8-H); δ_C (62.86 MHz; $CDCl_3$) 60.99, 61.20 (CH_2O, $^1J_{^{13}C-H}$ 147 Hz), 92.15; 92.98 (C-1, C-2), 125.19, 127.87, 128.58, 129.08, 129.40, 132.08. 132.34, and 132.58 (C-3, C-4, Ar); *m/z* 246 ($M^{+\cdot}$, 30%), 186 (14), 158 (26), 130 (100), 118 (25), and 102 (46%) (Found: C, 68.4: H, 5.75; O, 25.85. $C_{14}H_{14}O_4$ requires C, 68.28; H, 5.73; O, 25.99%).

1,1-*Ethylenedioxynaphthalen*-2(1H)-*one* (**8**).—To a solution of the bisacetal (**12**) (0.94 g, 3.8 mmol) in tetrahydrofuran (18 ml) was added trifluoroacetic acid (2.8 ml, 38.0 mmol) and water (8 ml) and the mixture was heated at 65 °C for 0.75 h. The solvent was evaporated and the residue was dissolved in ether. The ether layer was washed successively with aqueous sodium hydrogen carbonate and saturated aqueous sodium chloride and was then dried over anhydrous sodium sulphate. Evaporation of the solvent afforded a dark brown residue which was chromatographed on silica gel using gradient elution (solvent K—solvent J). The fraction having a R_F value of 0.51 (solvent H) was isolated as a yellow solid and was identified as being the title *compound* (**8**) (0.18 g, 23%). Recrystallisation from pentane afforded yellow prisms, m.p. 86—87 °C; $\nu_{max.}$(CH_2Cl_2) 1 670 cm^{-1} (CO); $\lambda_{max.}$(ethanol) 235 (ε 18 422) and 323 nm (7 124); δ_H (80 MHz; $CDCl_3$) 4.15—4.35 (4 H, m, 2XCH_2O), 6.06 (1H, d, J 10 Hz, 3-H), 7.31 (1H, d, *J* 10 Hz, 4-H), 7.05—7.52 (3 H, m's, 5-, 6-, and 7-H), and 7.52—7.77 (1 H, m, 8-H); *m/z* 202 ($M^{+\cdot}$, 79%), 174 (18), 130 (27), 119 (100), and 102 (34) (Found: C, 71.5; H, 4.95; O, 23.85%; *M*, 246.0879. $C_{12}H_{10}O_3$ requires C, 71.28; H, 4.98; O, 23.74%; *M*, 246.0892).

The unchanged bisacetal (**12**) was also isolated (R_F 0.49, solvent H) (0.06 g, 6%).

Reaction of 2-*Naphthol* (**3**) *with* 2,3-*Dichloro*-5,6-*dicyanobenzoquinone and Ethylene Glycol*.—To a stirred solution of 2-naphthol (5.0 g, 0.035 mol) in anhydrous benzene (300 ml) under nitrogen was added 2,3-dichloro-5,6-dicyanobenzoquinone (17.0 g, 0.076 mol) and ethylene glycol (9.8 ml, 0.175 mol) and the mixture was heated at reflux for 20 h. The mixture was filtered and the solvent was evaporated. The residue was dissolved in ether and the solution was washed successively with 10% aqueous sodium hydroxide and saturated aqueous sodium chloride. The ether layer was dried (Na_2SO_4) and the solvent was evaporated to yield a dark red syrup (4.1 g). T.l.c. (solvent H) indicated the presence of four major components having R_F values of 0.51, 0.49, 0.43, and 0.36. H.p.l.c. using solvent L as eluant afforded the pure components. The component having a R_F value of 0.51 was obtained as a yellow solid and was identified as being 1,1-ethylenedioxynaphthalen-2(1*H*)-one (**8**) (0.868 g, 14%). Recrystallisation from pentane afforded yellow prisms identical with the product prepared from the bisacetal (**12**) (m.p., i.r., ^1H n.m.r.). The component having a R_F value of 0.49 was isolated as a white solid. Recrystallisation from ethanol afforded white needles (0.661 g, 8%) identified as 1,2,1,2-bis(ethylenedioxy)-1,2-dihydronaphthalene (**12**) obtained independently by the reaction of 2-naphthol in ethylene glycol. The component having a R_F value of 0.43 was isolated as a white solid (0.304 g, 4%). Recrystallisation from ethanol yielded white prisms which were identified as 1,1,4,4-*bis*(*ethylenedioxy*)-3,4-*dihydronaphthalen*-2(1H)-*one* (**14**), m.p. 171—172 °C; $\nu_{max.}$(CH_2Cl_2) 1 690 cm^{-1} (CO); δ_H (80 MHz; $CDCl_3$) 3.12 (2 H, s, CH_2), 3.37—3.95 (4 H, m, 2 × CH_2O), 3.95—4.42 (4 H, m, 2 × CH_2O), and 7.25—8.15 (4 H, m, 4 × ArH); δ_C (100.6 MHz; $CDCl_3$) 44.32 (C-3), 61.26 (CH_2O), 94.04, 94.09 (C-1, C-4), 125.99, 126.66, 129.59, 134.53 (C-5, C-6, C-7, C-8), 132.43, 139.64 (C-9, C-10), and 194.29 (C-2); *m/z* 246 ($M^{+\cdot}$, 42%), 202 (14), 147 (26), 104 (24), and 86 (100) (Found: C, 64.2; H, 5.45; O, 30.35. $C_{14}H_{14}O_5$ requires C, 64.12; H, 5.38; O, 30.50%). The component having an R_F value of 0.36 was obtained after distillation under reduced pressure (0.5 mmHg) as a colourless syrup and was identified as 1,1,2,2-*bis*(*ethylenedioxy*)-1,2-*dihydronaphthalene* (**13**) (0.766 g, 10%); $\lambda_{max.}$(ethanol) 268 nm (ε 6 280); δ_H (80 MHz; $CDCl_3$) 3.75—4.27

(8 H, m, 4 × CH_2O), 5.81, 6.45 (two 1 H, d's, 3-H, 4-H), and 6.82—7.45 (4 H, m's, 4 × ArH); δ_C (100.6 MHz; $CDCl_3$) 65.83, 66.16 (CH_2O, $^1J_{^{13}C-H}$ 150 Hz), 106.70, 107.73 (C-1, C-2), 123.93, 127.09, 127.70, 129.04, 129.86, 130.62, 132.54, and 136.32 (C-3, C-4, Ar); *m/z* 246 ($M^{+\cdot}$, 68%), 202 (12), 174 (86), and 118 (100) (Found: C, 68.38; H, 5.67; O, 26.10. $C_{14}H_{14}O_4$ requires C, 68.28; H, 5.73; O, 25.99%).

Selective Hydrolysis of 1,2,1,2,*Bis*(*ethylenedioxy*)-1,2-*dihydronaphthalene* (**13**).—To a solution of the bisacetal (**13**) (0.023 g) in tetrahydrofuran (0.5 ml) containing water (0.25 ml) was added oxalic acid (8 mg) and the mixture was left to stand at room temperature for one week. The mixture was diluted with ether and washed successively with aqueous sodium hydrogen carbonate and saturated aqueous sodium chloride. The ether layer was dried (Na_2SO_4) and the solvent evaporated to yield a solid (0.02 g) whose ^1H n.m.r. spectrum indicated the presence of the bisacetal (**13**) and the monoacetal (**8**) in the ratio 3:2.

Reaction of 1,1-*Ethylenedioxynaphthalen*-2(1H)-*one* (**8**) *with* 2,3-*Dichloro*-5,6-*dicyanohydroquinone and Ethylene Glycol*.—To a solution of the monoacetal (**8**) (0.132 g, 0.655 mmol) in benzene (8 ml) was added 2,3-dichloro-5,6-dicyanohydroquinone (0.3 g, 1.3 mmol) and ethylene glycol (0.15 ml, 2.62 mmol) and the mixture was heated at reflux for 18 h. The mixture was diluted with ether and washed successively with 10% aqueous sodium hydroxide and saturated aqueous sodium chloride. The ether layer was dried (Na_2SO_4) and the solvent was evaporated to give a solid (0.152 g) whose ^1H n.m.r. spectrum indicated the presence of the unchanged monoacetal (**8**), the bisacetal (**13**), and the bisacetal (**12**) in the ratio 72:20:8.

Reaction of 2-*Naphthol with* 2,3-*Dichloro*-5,6-*dicyanobenzoquinone and* 2,2-*Dimethylpropane*-1,3-*diol*.—To a stirred solution of 2,3-dichloro-5,6-dicyanobenzoquinone (3.5 g, 0.015 mol) in anhydrous benzene (50 ml) under nitrogen was added 2,2-dimethylpropane-1,3-diol (7.2 g, 0.07 mol) and the mixture was heated at reflux until the diol was completely dissolved. A solution of 2-naphthol (1.0 g, 0.007 mol) in anhydrous benzene (50 ml) was then added dropwise over a period of 6 h and the mixture was heated at reflux for an additional 14 h. The precipitate was removed by filtration and the filtrate was diluted with ether. The organic layer was washed successively with 10% aqueous sodium hydroxide and saturated aqueous sodium chloride and dried over anhydrous sodium sulphate. Evaporation of the solvent afforded a solid (2.52 g) which was chromatographed rapidly on silica gel using solvent C as eluant. A fraction having a R_F value of 0.55 (solvent D) was isolated as a solid and was shown by ^1H n.m.r. spectroscopy to consist of two components. The solid was triturated with hot ethanol and the insoluble material was collected by filtration. The filtrate was concentrated to give a solid which was subsequently recrystallised from ethanol to yield 1,1-(2,2-*dimethyltrimethylenedioxy*)*naphthalene*-2(1H)-*one* (**9**) as yellow needles (0.65 g, 39%), m.p. 76—77 °C; $\nu_{max.}$(CH_2Cl_2) 1 680 cm^{-1} (CO); $\lambda_{max.}$(ethanol) 233 (ε 19 208) and 322 nm (7 193); δ_H (400 MHz; $CDCl_3$) 0.84 (3 H, s, CH_3), 1.38 (3 H, s, CH_3), 3.54 (2 H, d, *J* 11.2 Hz, OCH_2), 4.39 (2 H, d, *J* 11.2 Hz, OCH_2), 5.99 (1 H, d, *J* 10 Hz, 3-H), 7.21 (1 H, d, *J* 10 Hz, 4-H), 7.24 (1 H, br d, *J* 7.2 Hz, 5-H), 7.37 (1 H, dt, *J* 8, 2 Hz, 7-H), 7.45 (1 H, dt, *J* 8, 2 Hz, 6-H), and 7.94 (1 H, br d, *J* 8 Hz, 8-H); *m/z* 244 ($M^{+\cdot}$, 86%), 216 (20), 173 (23), 147 (19), 130 (100), 118 (71), 102 (37), and 191.2 [metastable $(216)^2/244$] (Found: C, 73.6; H, 6.55; O, 19.65. $C_{15}H_{16}O_3$ requires C, 73.75; H, 6.60; O, 19.65%).

The ethanol-insoluble material obtained above was recrystallised from methylene chloride–hexane to give the dimer (**15a**$_1$) as yellow needles (0.12 g, 4.5%), m.p. 200—201 °C; $\nu_{max.}$(CH_2Cl_2) 1 670 cm^{-1} (CO); $\lambda_{max.}$(ethanol) 223 (ε 32 078), 252 (36 332), 287 (7 783), 324 (13 140), and 355 nm (14 243); δ_H (400 MHz; $CDCl_3$) 0.90 (3 H, s, CH_3), 1.47 (3 H, s, CH_3), 3.63 (2 H, d, *J* 11 Hz, CH_2O), 4.46 (2 H, d, *J* 11 Hz, CH_2O), 6.18 (1 H, d, *J* 10 Hz, 3-H), 7.57 (1 H, t, *J* 8 Hz, 6′-H), 7.75 (1 H, t, *J* 8 Hz, 7′-H), 7.76 (1 H, d, *J* 9 Hz, 4′-H), 7.96 (1 H, d, *J* 9 Hz, 3′-H), 7.99 (1 H, d, *J* 10 Hz, 4-H), 8.03 (1 H, d, *J* 8 Hz, 5′-H), 8.06 (1 H, d, *J* 8.4 Hz, 7-H), 8.39 (1 H, d, *J* 8.4 Hz, 8-H), and 8.56 (1 H, d, *J* 8.4 Hz, 8′-H); *m/z* 384 ($M^{+\cdot}$, 91%), 356 (36), 313 (70), and 270 (100) (Found: C, 77.85; H, 5.2; O, 16.45. $C_{25}H_{20}O_4$ requires C, 78.11; H, 5.24; O, 16.65%).

1,1-*Di*-*t*-*butoxynaphthalen*-2(1H)-*one* (**10**).—To a mixture of t-butylperbenzoate (8.35 ml, 0.044 mol) and sodium hydride (50% mineral dispersion; 2 g, 0.044 mol) in anhydrous benzene (50 ml) under nitrogen was added 2-naphthol (2.48 g, 0.017 mol) in portions over a period of 5 min and the mixture was stirred at ambient temperature for 12 h. The mixture was poured into cold saturated aqueous ammonium chloride (150 ml) with stirring and then extracted with ether. The extracts were washed with aqueous sodium hydrogen carbonate and water and then dried over anhydrous sodium sulphate. The solvent was evaporated and the residue was chromatographed on neutral alumina using solvent F as eluant. The component having a R_F value of 0.19 was isolated as a yellow solid and was identified as being the *title compound* (**10**) (1.48 g, 30%). Recrystallisation from ethanol yielded yellow prisms upon cooling, m.p. 83—84 °C; $\nu_{max.}$(CH_2Cl_2) 1 670 cm^{-1} (CO); $\lambda_{max.}$(ethanol) 238 (ε 15 844) and 321 nm (7 298); δ_H (80 MHz; $CDCl_3$) 1.21 [18 H, s, 2 × $C(CH_3)_3$], 6.15 (1 H, d, *J* 10 Hz, 3-H), 7.24 (1 H, d, *J* 10 Hz, 4-H), 7.19—7.55 (3 H, m's, 3 × ArH), and 7.84 (1 H, m, 8-H); *m/z* 288 ($M^{+\cdot}$, <1%), 175 ($M^{+\cdot}$ − $2Me_3C$, 100%), 159 [$M^{+\cdot}$ − $Me_2C{=}CH_2$ + CMe_3O), 87], 148 (71), 131 ($C_9H_7O^+$, 49), and 57 (38); *m/z* (CI, isobutane) 159 ($C_{10}H_7O_2^+$) (Found: C, 74.85; H, 8.45. $C_{18}H_{24}O_3$ requires C, 74.97; H, 8.39%).

Reaction of 2-*Naphthol with Thallium*(III) *Nitrate in Methanol*.—To a stirred solution of 2-naphthol (0.8 g, 5.5 mmol) in methanol (40 ml) containing powdered sodium carbonate (5.0 g) at −78 °C under nitrogen was added thallium(III) nitrate trihydrate (5.0 g, 11.0 mmol) in portions. The mixture was allowed to warm to room temperature gradually. After 0.5 h, water was added and the mixture was extracted with ether. The extracts were washed with saturated aqueous sodium chloride, dried (Na_2SO_4), and concentrated to give a syrupy residue. Chromatography on silica gel using solvent A as eluant yielded 1,1-dimethoxynaphthalen-2(1*H*)-one (**4**) as a yellow liquid (0.326 g, 29%).

Reaction of 1,1-*Dimethoxynaphthalen*-2(1H)-*one* (**4**) *with Nitromethane*.—To a solution of 1,1-dimethoxynaphthalen-2-(1*H*)-one (**4**) (1.0 g, 0.005 mol) in benzene (20 ml) was added nitromethane (10 ml) and tetramethylguanidine (0.2 ml) and the mixture was stirred under nitrogen for 1 h at ambient temperature. Acetic acid was added and the mixture was diluted with ether. The ether layer was washed successively with water, aqueous sodium hydrogen carbonate, and saturated aqueous sodium chloride and then dried over anhydrous sodium sulphate. Evaporation of the solvent afforded a liquid which was chromatographed rapidly on silica gel using solvent E initially and then solvent A as eluants. The component having a R_F value of 0.77 (solvent A) was isolated as a light yellow liquid and was identified as 1,1-*dimethoxy*-4-*nitromethyl*-3,4-*dihydronaphthalen*-2(1H)-*one* (**7**) (1.2 g, 93%); $\nu_{max.}$(neat) 1 730 cm^{-1} (CO); δ_H (80 MHz; $CDCl_3$) 2.62 (1 H, dd, *J* 18, 4.4 Hz, 3-H), 2.95 (1 H, dd, *J* 18, 7.0 Hz, 3′-H), 3.20 (3 H, s, OCH_3), 3.42 (3 H, s, OCH_3), 4.11 (1 H, m, 4-H), 4.70 (2 H, m, CH_2NO_2), 7.0—7.5 (3 H, m's, 3 × ArH), and 7.70 (1 H, m, 8-H); *m/z* (CI, NH_3) 283 (MNH_4^+) and 222 (MNH_4^+ − CH_3NO_2), 219; *m/z* (CI,

isobutane) 234 ($MH^+ - CH_3OH$) and 173 (234 − CH_3NO_2) (Found: M, 283.1306. Calc. for $C_{13}H_{15}NO_5 + NH_4$: 283.1292).

Reaction of 1,1-*Di-t-butoxynaphthalen*-2(1H)-*one* (**10**) *with Nitromethane*.—To a solution of 1,1-di-t-butoxynaphthalen-2(1*H*)-one (**10**) (0.05 g, 0.17 mmol) in nitromethane (1 ml) was added *N*-butyl-*N*′,*N*′,*N*″,*N*″-tetramethylguanidine[10] (0.05 ml). After 5 min t.l.c. (solvent A) indicated the presence of a less polar component (R_F 0.48) as the sole product. The mixture was diluted with methylene chloride and the organic layer was washed successively with 10% hydrochloric acid, water, aqueous sodium hydrogen carbonate, and water. The organic layer was dried over anhydrous potassium carbonate and the solvent evaporated to yield a light brown syrup that was homogeneous on t.l.c. The compound was identified as being 1,1-di-t-butoxy-4-nitromethyl-3,4-dihydronaphthalen-2(1*H*)-one (**19**) (0.055 g), $\nu_{max.}(CH_2Cl_2)$ 1 740 cm^{-1} (CO); δ_H (80 MHz; $CDCl_3$) 1.28 [18 H, s, 2 × $C(CH_3)_3$], 2.75 (1 H, dd, *J* 14, 4.5 Hz, 3-H), 3.27 (1 H, dd, *J* 14, 6 Hz, 3′-H), 4.07 (1 H, m, 4-H), 4.61 (2 H, m, CH_2NO_2), 7.00—7.57 (3 H, m's, 3 × ArH), and 7.81 (1 H, m, 8-H). Complete characterisation of this compound was not possible owing to its instability.

Reaction of 1,1-(2,2-*Dimethyltrimethylenedioxy*)*naphthalen*-2(1H)-*one* (**9**) *and the Dimer* (**15a**$_1$) *with Nitromethane*.—To a solution of the acetal (**9**) (4.75 g, 0.019 mol) in anhydrous methanol (5 ml) was added nitromethane (7 ml, 0.13 mol) and then triethylamine (2.7 ml, 0.019 mol) and the mixture was stirred at ambient temperature for 24 h. The mixture was evaporated to dryness and the residue was chromatographed on silica gel using solvent B as eluant. The component having a R_F value of 0.46 (solvent D) was isolated as a white solid and was identified as being 1,1-(2,2-dimethyltrimethylenedioxy)-4-nitromethyl-3,4-dihydronaphthalen-2(1*H*)-one (**18**) (3.75 g, 63%). Recrystallisation from methylene chloride–hexane yielded white needles, m.p. 108—109 °C; $\nu_{max.}(CH_2Cl_2)$ 1 725 cm^{-1} (CO); δ_H (400 MHz; $CDCl_3$) 0.80 (3 H, s, CH_3), 1.30 (3 H, s, CH_3), 2.68 (1 H, dd, *J* 17, 3.6 Hz, 3-H), 3.04 (1 H, dt, *J* 17, 8 Hz, ^4J *ca.* 2 Hz, 3′-H), 3.67 (1 H, dd, *J* 11, 2 Hz, CH_2O, $H_{eq.}$), 3.68 (1 H, dd, *J* 11, 2 Hz, CH_2O, $H'_{eq.}$), 3.89 (1 H, d, *J* 11 Hz, CH_2O, $H_{ax.}$), 4.10 (1 H, d, *J* 11 Hz, CH_2O, $H'_{ax.}$), 4.18 (1 H, m, 4-H), 4.68 (1 H, dd, *J* 12.6, 5 Hz, CH_2NO_2), 4.79 (1 H, dt, *J* 12.6, 10 Hz, ^4J *ca.* 2 Hz, CH_2NO_2), 7.24 (1 H, m, 5-H), 7.42 (2 H, m, 6-H, 7-H), and 7.89 (1 H, m, 8-H); *m*/*z* 305 ($M^{+\cdot}$, 2%), 277 (13%), 231 (100), and 145 (44) (Found: C, 63.05; H, 6.15; N, 4.8; O, 26.45. Calc. for $C_{16}H_{19}NO_5$: C, 62.93; H, 6.27; N, 4.61; O, 26.19%). The unchanged starting material was isolated as a solid (R_F 0.63, solvent D) (0.23 g, 5%).

In another preparation, a fraction containing a mixture of the monoacetal (**9**) and the dimer (**15a**$_1$) was subjected to the conditions described above. In this case, chromatography yielded, in addition to (**18**), compound (**20**), 11,11-(2,2-dimethyltrimethylenedioxy)-8-nitromethyl-8,9-dihydrodinaphtho[2,1-*b*:2,1-*d*]furan-10(11*H*)-one, identified as being the *product* of conjugate addition of nitromethane with (**15a**$_1$). Recrystallisation from methylene chloride–hexane afforded the compound as white needles, m.p. 198—199 °C; $\nu_{max.}(CH_2Cl_2)$ 1 725 cm^{-1} (CO); δ_H (400 MHz; $CDCl_3$) 0.84 (3 H, s, CH_3), 1.36 (3 H, s, CH_3), 2.91 (1 H, dd, *J* 16, 2 Hz, 3-$H_{eq.}$), 3.24 (1 H, dd, *J* 16, 6.6 Hz, 3-$H_{ax.}$), 3.71 (1 H, dd, *J* 11, 2 Hz, CH_2O, $H_{eq.}$), 3.74 (1 H, dd, *J* 11, 2.4 Hz, CH_2O, $H'_{eq.}$), 3.89 (1 H, d, *J* 11 Hz, CH_2O, $H_{ax.}$), 4.18 (1 H, d, *J* 11 Hz, CH_2O, H'_{ax}), 4.89 (2 H, m, CH_2NO_2), 4.97 (1 H, m, 4-H), 7.60 (1 H, t, *J* 7—8 Hz, 6′-H), 7.77 (1 H, t, *J* 7—8 Hz, 7′-H), 7.82 (1 H, d, *J* 9 Hz, 4′-H), 8.00 (1 H, d, *J* 8 Hz, 7-H), 8.01 (1 H, d, *J* 9 Hz, 3′-H), 8.06 (1 H, d, *J* 8 Hz, 5′-H), 8.44 (1 H, d, *J* 8 Hz, 8-H), and 8.61 (1 H, d, *J* 8 Hz, 8′-H); *m*/*z* 445 ($M^{+\cdot}$, 2%), 417 (4), 371 (54), 285 (23), 257 (31), and 231 (100) (Found: C, 69.65; H, 5.2; N, 3.1; O, 21.95. $C_{26}H_{23}NO_6$ requires C, 70.10; H, 5.20; N, 3.14; O, 21.55%).

1,1-*Ethylenedithionaphthalen*-2(1H)-*one* (**11**).—To a stirred suspension of *S*,*S*′-ethylene bis(toluene-p-sulphonate) (1.0 g, 2.49 mmol) and sodium hydride (0.15 g; 55—60% mineral dispersion) in dry benzene (15 ml) under nitrogen was added a solution of 2-naphthol (0.35 g, 2.43 mmol) in benzene (50 ml) dropwise over a period of 2 h. The mixture was stirred for an additional 15 min at ambient temperature and was then quenched by addition of ice–water. The mixture was extracted with ether and the extracts were washed with saturated aqueous sodium chloride and dried over anhydrous sodium sulphate. Evaporation of the solvent afforded a solid which was recrystallised from methanol to yield the *dithioacetal* (**11**) as light yellow needles (0.48 g, 84%), m.p. 71—72 °C; $\nu_{max.}$(Nujol) 1 650 cm^{-1} (CO); $\lambda_{max.}$(ethanol) 220 (ε 11 637), 239 (11 212), 290sh (3 746), and 318 nm (4 721); δ_H (80 MHz; $CDCl_3$) 3.62 (4 H, s, 2 × SCH_2), 6.22 (1 H, d, *J* 10 Hz, 3-H), 7.26 (1 H, d, *J* 10 Hz, 4-H), 7.07—7.50 (3 H, m's, 3 × ArH), and 8.16 (1 H, m, 8-H); *m*/*z* 234 ($M^{+\cdot}$, 87%), 178 (100), and 134 (82) (Found: C, 61.3; H, 4.3; S, 27.55. $C_{12}H_{10}OS_2$ requires C, 61.51; H, 4.30; S, 27.37%).

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