Some Photoproducts from the Photochemical Cycloaddition Reactions between Acrylonitrile and 1-Methyl-, 2-Methyl- and 2,6-Dimethyl-naphthalenes

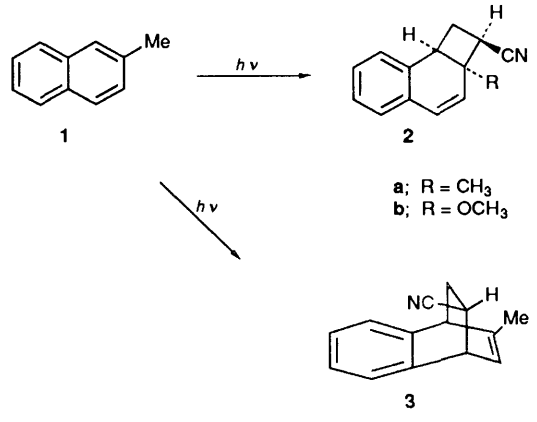
John J. McCullough,[a]† T. Brian McMurry[b]* and D. Neil Work[b]
[a] *Chemistry Department, Queen's University, Belfast BT9 5AG, Northern Ireland, UK*
[b] *University Chemical Laboratory, Trinity College, Dublin 2, Ireland*

Some photoadducts formed between 2-methyl-, 1-methyl- and 2,6-dimethyl-naphthalenes and acrylonitrile are described. 2-Methylnaphthalene gives one main product, 2a-methyl-1,2,2a,8b-tetrahydrocyclobuta[*a*]naphthalene-*endo*-2-carbonitrile, but on one occasion a second adduct, 1,4-dihydro-3-methyl-1,4-ethanonaphthalene-*endo*-10-carbonitrile was isolated, the product of 1,4-addition to the naphthalene ring. 1-Methylnaphthalene gives a complex mixture from which two products were isolated, only one 8-methyl-1,2,2a,8b-tetrahydrocyclobuta[*a*]naphthalene-*endo*-1-carbonitrile in a pure state. This was formed by addition of acrylonitrile to the unsubstituted ring. The second was a [2 + 2] adduct of acrylonitrile across the 1,2-double bond of the naphthalene. 2,6-Dimethylnaphthalene gives only one product 2a-methyl-1,2,2a,8b-tetrahydrocyclobuta[*a*]naphthalene-*endo*-2-carbonitrile. The regio- and stereo-chemistry of this was proved by a novel method, converting the nitrile into an acid, which readily formed a mixture of γ and δ iodolactones with iodine–hydrogen carbonate.

There has been considerable interest in the photochemical cycloaddition of acrylonitrile with substituted naphthalenes, and the subject was recently reviewed by the authors.[1] Additions of 1- and 2-naphthols and their derivatives are apparently quite useful in synthesis.[2–6] The initially formed cyclobutanes can, in some cases, be converted into related, useful compounds.[2–5] The addition of 2-methylnaphthalene and acrylonitrile was briefly mentioned in the review,[1] but this is the only record of any such addition reaction. Interest in these additions is clearly continuing, and we now report our joint efforts on some photoadditions of methylnaphthalenes and acrylonitrile.

Photolysis of acrylonitrile and 2-methylnaphthalene **1** in benzene or ethanol for 9.5 h affords one photoproduct **2a** in 8% yield. The presence in the NMR spectrum of the product of signals from four aromatic protons, two olefinic protons, an aliphatic methyl group and four other protons indicates that the addition of the acrylonitrile is to the 1,2-bond of the naphthalene. The pattern of coupling constants (see Experimental section) suggests that the nitrile group is attached to the carbon next to the 2-carbon of the original 2-methylnaphthalene, and the symmetry of the signals further suggests that the nitrile is *endo*. This is confirmed by the close resemblance of the coupling constant pattern in the ^{1}H NMR to that of the adduct **2b** formed from acrylonitrile and 2-methoxynaphthalene,[2] which we have remeasured, and also to the similar adduct formed from 2,6-dimethylnaphthalene. The latter's stereochemistry was proved by lactone formation (see below).

When acrylonitrile and 2-methylnaphthalene were irradiated for a longer period, a second product **3** (5% yield) in addition to **2a** (5% yield) was isolated on one occasion. The NMR spectrum again reveals the presence of four aromatic protons, a proton and methyl both attached to an alkene bond, and five aliphatic protons. Decoupling experiments show that the olefinic proton (δ 6.00) is coupled to two aliphatic protons (δ 3.70 and 4.03) which in their turn are coupled to two and one aliphatic protons, respectively. The coupling constant between the 3-olefinic proton and the proton giving a signal at δ 3.70 is only 2 Hz, indicating an allylic coupling, while that with the proton giving a signal at δ 4.03 is 6 Hz (vicinal coupling).[7] The 1,4-adduct **3** is the only structure consistent with this evidence.



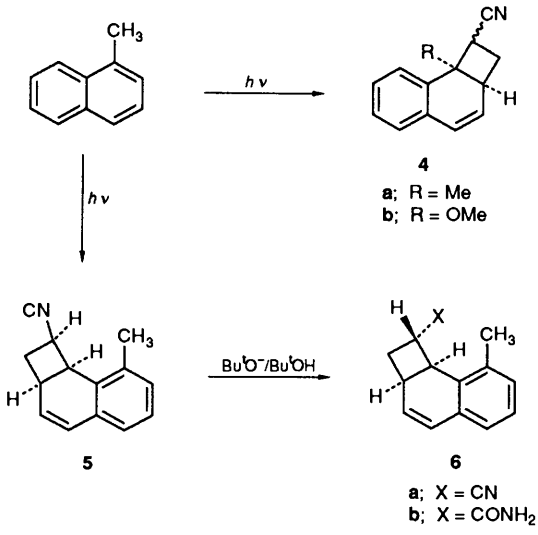
The nitrile group is placed in the *endo*-position, because of the absence of W-coupling between the 3- and 5-protons. This is the *first* example of the 1,4-addition of acrylonitrile to any naphthalene.

The photolysis of a mixture of 1-methylnaphthalene and acrylonitrile leads to a much more complex mixture. Careful flash chromatography affords three fractions. The first of these (6.7%) contains mainly one component, but this could not be obtained in an absolutely pure state. Nevertheless, the ^{1}H NMR suggests that this compound is **4a** though we are unable to determine the stereochemistry of the cyano group. We may predict that this will be *endo* as the NMR spectrum resembles that of the photoadduct **4b** of acrylonitrile with 1-methoxynaphthalene.[3]

The second fraction (12.8%) is very complex, and from GC–MS and ^{1}H NMR it contains five components. At least one of these (partially) decomposes during GC, as GC–MS reveals the presence of 1-methylnaphthalene, not present (NMR) in the original mixture.

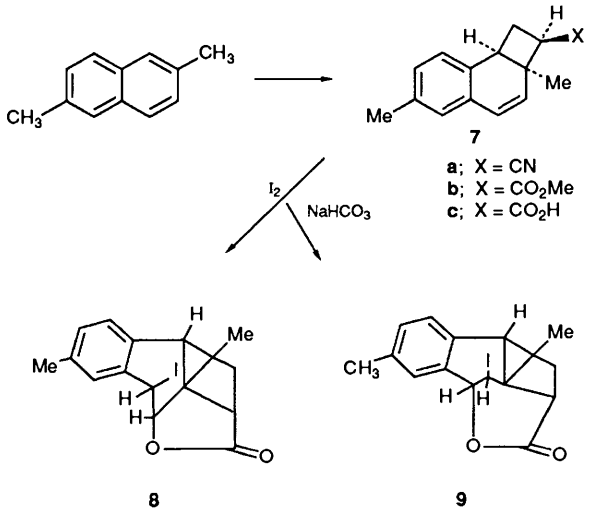
The third fraction affords a solid adduct **5** (7%). The ^{1}H NMR reveals the presence of three aromatic protons, an

† On leave of absence from Chemistry Department, McMaster University, Hamilton, Ontario, Canada L8S 4M1. *Present address:* University Chemical Laboratory, Trinity College, Dublin 2.



aromatic methyl group, two olefinic protons and five aliphatic protons. The pattern of these five protons suggests the presence of an *endo*-cyanocyclobutane ring. The COSY spectrum, shows that the 2-*exo* proton is coupled to the 2a,1- and 8b-H protons, the 2-*endo* proton to the 2a- and 1-H protons and the 8b-proton to the 1,2a, and weakly to the methyl group. This suggests the location and regiochemistry of the cyclobutane ring, which is also supported by the 3.5% NOE observed in the 8b-proton signal when the methyl group is irradiated and the 10% NOE observed at the neighbouring aromatic proton when the 4-H is irradiated. Treatment of the *endo*-nitrile **5** with potassium t-butoxide in t-butyl alcohol[2,3] affords the *exo*-nitrile **6a** and the corresponding amide **6b**. These structures are supported by their ^{1}H NMR spectra. Spin decoupling and a deuteriation experiment were used to interpret the spectra of **5** and **6b** (see Experimental section).

Irradiation of 2,6-dimethylnaphthalene and acrylonitrile affords a single product **7a** in a reasonable yield (17%). The NMR spectrum shows the presence of three aromatic protons, an aromatic and an aliphatic methyl group, two olefinic protons and four aliphatic protons. The latter signals show a very similar pattern to those in **2a**, and suggest the related structure **7a**. We have confirmed this structure as follows. Compound **7a** can be converted into the corresponding ester **7b** using ether–methanol–hydrogen chloride,[8] and this on acid hydrolysis gives the acid **7c**. This acid on treatment with iodine–sodium hydrogen carbonate[8] affords a mixture of an iodo-γ-lactone **8**



(85%) and an iodo-δ-lactone **9** (15%), as demonstrated by the IR carbonyl absorption at 1780 and 1740 cm^{-1}. We were unable to free the γ-lactone from traces of the δ-lactone, but the ^{1}H NMR and an accurate mass spectrum proves its structure. This reaction sequence has been used for the first time to prove the structure of an acrylonitrile photoproduct, and should be applicable to other cases.

Discussion

The photoadditions of 2-methyl- and 2,6-dimethyl-naphthalene to acrylonitrile are routes to the methyl-substituted cyclobutanes **2a** and **7a**. The additions are regio- and stereo-specific; addition occurs at the methyl-substituted double bond of the naphthalene, and the nitrile group is *endo*. This stereochemistry has now been demonstrated unambiguously for the adducts of naphthalene,[1] 1-methoxynaphthalene[3] and the above methylnaphthalenes, and is consistent with the intermediacy of an exciplex. Support for exciplexes also comes from fluorescence quenching of a series of methylnaphthalenes by acrylonitrile.[10]

The 1,4-adduct **3** was only isolated after a long irradiation time, presumably because it is stable to photolysis. It was found difficult to repeat this experiment, and it is possible that the yield and reproducibility could be improved after careful study of reaction conditions. Photolysis of the adduct **2a** afforded only 2-methylnaphthalene, showing that the cycloaddition reaction achieved a photostationary state in which the isolation of adduct depended on an excess of acrylonitrile.

Addition of 1-methylnaphthalene and acrylonitrile gives a more complex product mixture. Adduct **4a** is analogous to one product from the 1-methoxynaphthalene–acrylonitrile addition.[3] Adduct **5** is interesting in that addition has occurred to the unsubstituted naphthalene ring. This is an unusual pathway, which has not been observed previously in intermolecular cases.

Experimental

Irradiations were carried out under nitrogen in benzene or isopropyl alcohol–t-butyl alcohol (1:1) using a Hanovia 450 W medium pressure lamp and a Pyrex filter. IR spectra were measured using a Perkin-Elmer 298 as liquid films or Nujol mulls. NMR spectra were recorded in [^{2}H]chloroform on either a Bruker WP80, a QE 300 or a JEOL GX 270 machine, in ppm from TMS. All *J* values are in Hz. Mass spectra were measured on a Finnegan MAT 5100 quadropole mass spectrometer, with GC attachment using a capillary column packed with Chrompack CP Sil 8 CB at 135 °C. Solvents were purified and dried before use. Preparative TLC (PLC) were carried out using Merck Kieselgel PF_{254}.

Photolyses of 2-*Methylnaphthalene and Acrylonitrile*.—(*a*) 2-Methylnaphthalene (1.52 g) and acrylonitrile (7.51 g) were irradiated in degassed benzene (250 ml) for 9.5 h. The solvent was removed under reduced pressure and the residue extracted with ether, dried ($MgSO_4$) and concentrated. Flash chromatography [ethyl acetate–hexane (1:1)] followed by crystallisation from ethyl acetate–hexane gave 2a-*methyl*-1,2,2a,8b-*tetrahydrocyclobuta*[*a*]*naphthalene*-endo-2-*carbonitrile* **2a** (180 mg, 8%) m.p. 103–104 °C (Found: C, 85.9; H, 6.6; N, 6.9. $C_{14}H_{13}N$ requires C, 86.1; H, 6.7; N, 7.2%); ν_{max}/cm^{-1} 2210; δ_H 1.27 (3 H, s, Me), 2.41 (1 H, ddd, J_{gen}12, $J_{1\text{-}exo,8b} = J_{1\text{-}exo,2}$ 10, 1-H$_{exo}$), 2.44 (1 H, ddd, J_{gem} 12, $J_{1\text{-}endo,8b} = J_{1\text{-}endo,7}$ 8, 1-H$_{endo}$), 3.12 (1 H, dd, $J_{2,1\text{-}exo}$ 10 and $J_{2,1\text{-}endo}$ 8, 2-H), 3.23 (1 H, ddd, $J_{8b,1\text{-}exo}$ 10, $J_{8b,1\text{-}endo}$ 8 and $J_{8b,3}$ 1, 8b-H), 5.82 (1 H, dd, $J_{3,4}$ 10 and $J_{3,8b}$ 1, 3-H), 6.59 (1 H, d, $J_{4,3}$ 10, 4-H) and 6.91–7.24 (4 H, m, ArH).

(*b*) In one experiment, 2-methylnaphthalene (1.50 g) and acrylonitrile (7.59 g) in benzene were irradiated for 45 h.

Aliquots of acrylonitrile (7.6 g) were added after 6, 22 and 38 h. The solvent was removed and the residue was extracted with ether. The extract was dried ($MgSO_4$) and concentrated. Flash chromatography gave two products, the photoproduct **2a** (105 mg; 5%), m.p. 103–104 °C, and 1,4-dihydro-3-methyl-1,4-ethano-naphthalene-*endo*-9-carbonitrile **3** (100 mg; 5%), ν_{max}/cm^{-1} 2230; δ_H 1.65 (1 H, ddd, J_{gem} 12, $J_{10-endo,9}$ 5 and $J_{10-endo,4}$ 3, 6-H_{endo}), 1.83 (3 H, d, $J_{Me,2}$ 2, Me), 1.98 (1 H, ddd, J_{gem} 12, $J_{10-exo,9}$ 10 and $J_{10,4}$ 3, 10-H_{exo}), 2.72 (1 H, ddd, $J_{9,10-exo}$ 10, $J_{9,10-endo}$ 5 and $J_{9,1}$ 2, 9-H), 3.70 (1 H, ddd, $J_{4,10-endo} = J_{4,10-exo}$ 3, and $J_{4,2}$ 2, 4-H), 4.03 (1 H, dd, $J_{1,2}$ 6 and $J_{1,9}$ 3, 1-H), 6.00 (1 H, ddq, $J_{2,1}$ 6 and $J_{2,4} = J_{2,Me}$ 2, 2-H) and 7.08–7.37 (4 H, m, ArH).

Photolysis of the Carbonitrile **2a**.—The carbonitrile 680 mg in degassed benzene (250 ml) was irradiated for 9 h. The solvent was removed to give 2-methylnaphthalene (510 mg, 100%), δ_H 2.50 (3 H, s, Me) and 6.97–7.60 (7 H, m, ArH).

Photolysis of 1-*Methylnaphthalene and Acrylonitrile*.—1-Methylnaphthalene (1.15 g) and acrylonitrile (8.03 g) in degassed isopropyl alcohol–t-butyl alcohol (250 ml, 1:1) were irradiated for 6 h. The solvent was removed and the residue dissolved in ether. The ether extract was dried ($MgSO_4$) and concentrated. Flash chromatography afforded three fractions: (*a*) an oil (106 mg, 6.7%) which decomposed on GC–MS. The ^1H NMR spectrum showed that the main component of the oil was 8b-methyl-1,2,2a,8b-tetrahydrocyclobuta[*a*]naphthalene-1-carbonitrile **4a**, ν_{max}/cm^{-1} 2230; δ_H 1.76 (3 H, s, Me), 1.08–2.17 (1 H, m, 2-H), 2.58–2.80 (2 H, m, 2-H and 2a-H) 3.31 (1 H, dd, $J_{1,2}$ 9 and 7, 1-H), 5.78 (1 H, dd, $J_{3,4}$ 10 and $J_{3,2a}$ 4, 3-H), 6.39 (1 H, d, $J_{4,3}$ 10, 4-H) and 7.16–7.62 (4 H, m, ArH).

(*b*) The second fraction (200 mg, 12.8%) was an oil purified by distillation (b.p. 170–172 °C at 3mmHg). The distillate was shown by ^1H NMR spectroscopy to have 5 components. GC–MS confirmed the presence of 5 components plus 1-methylnaphthalene.

(*c*) A solid (103 mg; 7%) which on crystallisation from ether–hexane gave 8-*methyl*-1,2,2a,8b-*tetrahydrocyclobuta*[*a*]-*naphthalene*-endo-1-*carbonitrile* **5**, m.p. 66–67 °C (Found: C, 86.4; H, 6.6; N, 6.9. $C_{14}H_{13}N$ requires C, 86.1; H, 6.7; N, 7.2%); ν_{max}/cm^{-1} 2235; δ_H 2.16 (3 H, s, Me), 2.36 (1 H, dddd, J_{gem} 12, $J_{2-exo,2a} = J_{2-exo,1}$ 5 and $J_{2-exo,8b}$ 1, 2-H_{exo}), 2.96 (1 H, ddd, J_{gem} 12, $J_{2-endo,2a} = J_{2-endo,1}$ 9 Hz, 2-H_{endo}), 3.32–3.40 (1 H, m, 2a-H), 3.63 (1 H, dddd, $J_{1,2-endo} = J_{1,8b}$ 10, $J_{1,2-exo}$ 5 and $J_{1,2a}$ 1, 1-H), 4.19 (1 H, dd, further split, $J_{8b,2a} = J_{8b,1}$ 10, 8b-H), 5.80 (1 H, dd, $J_{3,4}$ 10 and $J_{3,2a}$ 4, 3-H), 6.40 (1 H, dd, $J_{4,3}$ 10 and $J_{4,2a}$ 2, 4-H) and 6.91–7.22 (3 H, m, ArH); δ_C 18.6 (q, Me), 30.2 (d, C-1), 33.2 (d, C-2a), 33.7 (t, C-2), 35.0 (d, C-8b), 120.8 (s, CN) 125.7, 127.8, 130.2 (d, Ar-C), 127.1 (d, C-3), 127.6 (d, C-4), 128.4 and 132.5 and 135.3 (s, Ar-C).

In the ^1H spectrum, NOE measurements showed enhancement (3.5%) of the 1-H signal on irradiation of the methyl group, and (10%) of the neighbouring aromatic-H signal on irradiation of the 4-H.

Isomerisation of the Carbonitrile **5**.—The carbonitrile (160 mg) in t-butyl alcohol was added to a solution of potassium t-butoxide (from 610 mg potassium) in t-butyl alcohol (20 ml), under N_2. The mixture was heated under reflux for 2 h, cooled, diluted with water and acidified with hydrochloric acid (1 mol dm^{-3}; 20 ml). The resulting aqueous solution was extracted with ether (3 × 100 ml). The combined ether layers were washed successively with aqueous sodium hydrogen carbonate and water, and dried ($MgSO_4$). Removal of solvent and flash chromatography of the residue gave starting material (20 mg, 12%), followed by 8-*methyl*-1,2,2a,8b-*tetrahydrocyclobuta*[a]-*naphthalene*-exo-1-*carbonitrile* **6a** (90 mg, 56%), m.p. 84–86 °C (from ethyl acetate–hexane) (Found: C, 86.0; H, 6.7; N, 7.1. $C_{14}H_{13}N$ requires C, 86.1; H, 6.7; N, 7.2%); ν_{max}/cm^{-1} 2230; δ_H 2.25–2.48 (1 H, m, 2-H_{endo}), 2.38 (3 H, s, Me), 2.86 (1 H, ddd, J_{gem} 11 and $J_{2-exo,2a} = J_{2\ exo,1}$ 8, 2-H_{exo}), 3.19–3.29 (1 H, m, 2a-H), 3.35 (1 H, ddd, $J_{1,8b}$ 9 and $J_{1,2-endo}$ 8, 1-H), 4.22 (1 H, dd, $J_{8b,2a} = J_{8b,1}$ 9, 8b-H), 5.77 (1 H, $J_{3,4}$ 10 and $J_{3,2a}$ 3, 3-H), 6.42 (1 H, dd, $J_{4,3}$ 10 and $J_{4,2a}$ 2, 4-H) and 6.93–7.25 (3 H, m, ArH). A final fraction contained the corresponding *exo*-amide **6b** (20 mg, 11%), m.p. 168–171 °C; ν_{max}/cm^{-1} 3200–3600 (NH_2) and 1640 (CO); δ_H 2.10 (1 H, m, 2-H_{endo}), 2.22 (3 H, s, CH_3), 2.82 (1 H, ddd, J_{gem} 11 and $J_{2-exo,1}$ 8, 2-H_{exo}), 3.10–3.20 (1 H, m, 2a-H), 3.29 (1 H, ddd, $J_{1,8b}$ 9 and $J_{8,2-endo} = J_{1,2-exo}$ 8, 1-H), 4.11 (1 H, dd, $J_{8b,2a} = J_{8b,1}$ 9, 8b-H), 5.85 (1 H, dd, $J_{3,4}$ 10 and $J_{3,2a}$ 3, 3-H), 6.38 (1 H, dd, $J_{4,3}$ 10 and $J_{4,2a}$ 2, 4-H) and 6.93–7.25 (3 H, m, ArH).

Isomerization and Deuterium Exchange of endo-**5**.—Potassium (25 mg) was dissolved in Bu^t OD (Aldrich) (2.5 ml), and *endo*-**5** (20 mg) was added. The mixture was stirred and heated (oil bath) at 90 °C for 1 h. The mixture was cooled, diluted with deuterium oxide (13 ml) and extracted with methylene dichloride (3 × 10 ml). The organic extracts were dried ($MgSO_4$), filtered and evaporated. A crystalline product (18 mg), m.p. 205–208 °C, was obtained, and identified as the *exo*-amide [^2H]-**6b**. *m/z* 214 (7.9%), M^+, $C_{14}H_{14}DNO$); 142 (100) (methylnaphthalene). In the NMR spectrum (300 MHz; $CDCl_3$), the resonance at δ 3.36 assigned to 1-H, was not observed, confirming the above assignment. The 8b-H signal at δ 4.11, was a doublet ($J_{8b,2a}$ 9.2), the splitting of the vinylic protons was the same as in unlabelled **6b**. The NMR spectrum also showed the presence of a minor amount (< 10%) of the corresponding *exo* amide.

Photolysis of 2,6-*Dimethylnaphthalene and Acrylonitrile*.—2,6-Dimethylnaphthalene (1.20 g) and acrylonitrile (12.90 g) in degassed isopropyl alcohol–t-butyl alcohol (1:1; 250 ml) was irradiated for 5 h. The solvent was removed and the residue extracted with ethyl acetate. The solution was dried ($MgSO_4$) and the solvent removed. The residue was purified by flash chromatography to give 2a,6-*dimethyl*-1,2,2a,8b-*tetrahydrocyclobuta*[a]*naphthalene*-endo-2-*carbonitrile* **7a** (270 mg, 17%), m.p. 87–89 °C (from ethanol–water) (Found: C, 86.1; H, 7.5; N, 6.7. $C_{15}H_{15}N$ requires C, 86.1; H, 7.2; N, 6.7%); ν_{max}/cm^{-1} 2230; δ_H 1.27 (3 H, s, 2a-Me), 2.30 (3 H, s, ArMe), 2.39 (1 H, ddd, J_{gem} 12, $J_{1-exo,8b} = J_{1-exo,2}$ 10, 1-H_{exo}), 2.45 (1 H, ddd, J_{gem} 12, $J_{1-endo,8b} = J_{1-endo,2}$ 8, 1-H_{endo}), 3.11 (1 H, dd, $J_{2,1-exo}$ 10 and $J_{2,1-endo}$ 8, 2-H), 3.26 (1 H, dd, $J_{8b,1-exo}$ 10 and $J_{8b,1-endo}$ 8, 8b-H), 5.82 (1 H, d, $J_{2,4}$ 10, 3-H), 6.56 (1 H, d, $J_{4,3}$ 10, 4-H) and 6.83–6.99 (3 H, m, ArH).

Methyl endo-2a,6-*Dimethyl*-1,2,2a,8b-*tetrahydrocyclobuta*-[a]-*naphthalene*-2-*carboxylate* **7b**.—The *endo* nitrile **7a** (260 mg) in methanol (14 ml) and ether (14 ml) saturated with dry hydrogen chloride was stirred at 0 °C for 8 h. Crushed ice (*ca.* 100 g) was added, and stirring continued for 12 h. Further water (50 ml) was added, and the mixture extracted with chloroform (3 × 50 ml). The extracts were dried ($MgSO_4$) and the solvent removed to give the methyl ester (290 mg, 100%); *m/z* 156 (100%) and 242 (3.8); ν_{max}/cm^{-1} 1734 (C=O), 1605 (C=C), 1217 and 1193; δ_H 1.31 (s, 2a-Me), 2.28 (Ar*Me*), 2.24 (1 H, m, 1-H_{exo}), 2.41 (1 H, ddd, J_{gem} 10.5, 1-H_{endo}), 3.16 (2 H, m, 2a- and 2-H), 5.50 (1 H, dd, *J* 9.5 and 1.0, 3-H), 6.40 (1 H, d, *J* 9.5, 4-H) and 6.80–7.0 (3 H, m, Ar-H).

endo-2a,6-*Dimethyl*-1,2,2a,8b-*tetrahydrocyclobuta*[a]-*naphthalene*-2-*carboxylic Acid* **7c**.—The ester **7b** (290 mg) and hydrochloric acid (10%; 75 ml) containing 10% tetrahydrofuran were heated at reflux for 5 h. The solution was cooled and extracted with chloroform (3 × 50 ml). The combined

chloroform layers were extracted with aqueous sodium hydroxide (1 mol dm^{-3}; 2 × 50 ml). The aqueous layers were acidified (pH 1.0) and extracted with chloroform (3 × 70 ml). The extracts were dried ($MgSO_4$) and the solvent removed to give the *acid* **7c** (175 mg, 64%) which crystallised (ethyl acetate–cyclohexane) to give needles (61 mg), m.p. 118–120 °C. The residue from the crystallisation was purified by PLC to give more acid (43 mg) (Found: C, 78.5; H, 7.1. $C_{15}H_{10}O_2$ requires C, 78.9; H, 7.0%); δ_H 1.30 (2a-Me), 2.27 (3 H, s, ArMe), 2.10–2.40 (m, 1-CH_2), 3.20 (2 H, m, 8b- and 2-H), 5.65 (1 H, d, *J* 9.8, 3-H), 6.43 (1 H, d, *J* 9.8, 4-H), and 6.8–7.0 (3 H, m, Ar*H*).

1-*Iodo*-10,12-*dimethyl*-1,2,6,7-*tetrahydro*-2,5,7-*metheno*-3-*benzoxonin*-4(5*H*)-*one* **8** *and* 11-*Iodo*-9,12-*dimethyl*-5,6-*dihydro*-1,4,6-*ethanylylidene*-1H-2-*benzoxonin*-3(4H)-*one* **9**.—The acid **7c** (70 mg) in aqueous sodium hydrogen carbonate (0.5 mol dm^{-3}; 2.5 ml) was added to a solution of iodine (160 mg) and potassium iodide (320 mg) in water (1.2 ml) and the mixture stirred at room temperature and in the dark for 48 h. Water (15 ml) was added, and the mixture extracted with dichloromethane (3 × 15 ml). The combined organic layers were washed with aqueous sodium thiosulphate, dried ($MgSO_4$) and the solvent removed at room temperature to give the product (114 mg). Purification by PLC afforded the lactone mixture **8** and **9** (76 mg, 70%); ν_{max}/cm^{-1} 1780 (γ-lactone)[11] and 1740 (δ-lactone);[9] δ_H(γ-lactone) 4.95 (CHI) and 5.55 (C*H*O), (δ-lactone) 4.40 (CHI) and 5.60 (CHO). The ratio (by NMR) of γ- to δ-lactone was 85:15.

Crystallisation from ethanol gave the γ-lactone **8**, m.p. 95–103 °C (decomp.); *m/z* 354 (M^+, 1.4%) and 227 (100) (Found: M^+, 354.011 08. $C_{15}H_{15}IO_2$ requires M^+, 354.011 68); ν_{max}/cm^{-1} 1780, 1170 and 996; δ_H 1.88 and 2.30 (both s, 2 × Me), 2.06, 2.80, 3.10 and 3.20 (all m, cyclobutane-H), 4.95 (1 H, d, *J* 3.0, CHI), 5.55 (1 H, d, *J* 3.0, CHO) and 6.8–7.3 (m, ArH).

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