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CAN Mediated oxidative addition of 2-hydroxynaphthoquinone to dienes: a facile synthesis of naphthofurandiones

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Abstract—2-Hydroxy-1,4-naphthoquinone undergoes CAN mediated oxidative addition to various dienes followed by ring closure yielding corresponding furoquinones.

1. Introduction

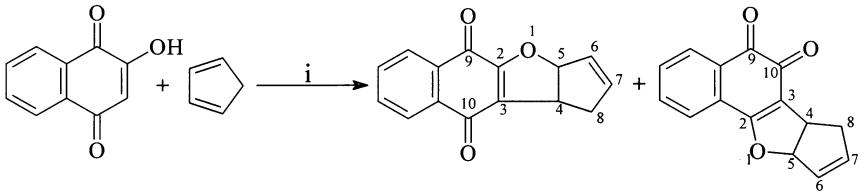
Synthetic transformations, especially C–C bond forming reactions, mediated by cerium(IV) ammonium nitrate (CAN) are in vogue.[1–3] Recently, we have demonstrated that CAN mediated oxidative addition of 1,3-dicarbonyl compounds to alkenes and dienes constitutes an excellent method for the synthesis of dihydrofurans.[4] In the context of this work, we were interested in examining the CAN mediated oxidative addition of 2-hydroxynaphthoquinone **1** to alkenic substrates, potentially leading to furano-annulated compounds. Except for the report on the reaction of **1** with acyclic alkenes,[5] there has not been any work in this direction.[6] With this background, we have carried out an investigation of the CAN mediated addition of 2-hydroxy-naphthoquinone to cyclic and acyclic dienes and our results are presented here.

2. Results and discussion

Our studies were initiated by the reaction of 2-hydroxy-1,4-naphthoquinone **1** with cyclopentadiene **2a**. When a solution of **1** and **2a** in acetonitrile was treated with a solution of CAN in acetonitrile at 0°C, two products **3a** and **4a** were obtained, the structures of which were assigned on the basis of spectral analysis (Scheme 1).

The IR spectrum of **3a** showed characteristic strong carbonyl absorption at 1676 cm^{-1}. In ^1H NMR spectrum, the proton on C-4 resonated as double triplet at δ 4.18 (J=2.2, 8.5 Hz) and the one on C-5 as a double triplet at δ 5.95 (J=2.2, 7.9 Hz). The olefinic proton on C-6 and C-7 appeared as a doublet at δ 6.10 (J=8.9 Hz) and as a triplet at δ 6.19 (J=2.6 Hz), respectively. The characteristic peaks corresponding to the carbonyl carbons C-9 and C-10 were observed in ^{13}C NMR spectrum at δ 182.43 and 178.64, respectively. The signal due to C-2 was seen at δ 158.51 and C-5 signal was visible at δ 96.09. The final proof for the structure was obtained from single crystal X-ray analysis (Fig. 1).[†]

The naphtho[2,1-*d*]dihydrofuran-5,6-dione **4a** exhibited the carbonyl absorption peak at 1694 cm^{-1} in the IR spectrum.



Scheme 1. (i) CAN, CH_3CN, 0–5°C, 30 min.

Keywords: cerium(IV); diene; radical reactions; quinonoid compounds.
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[†] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 159911.

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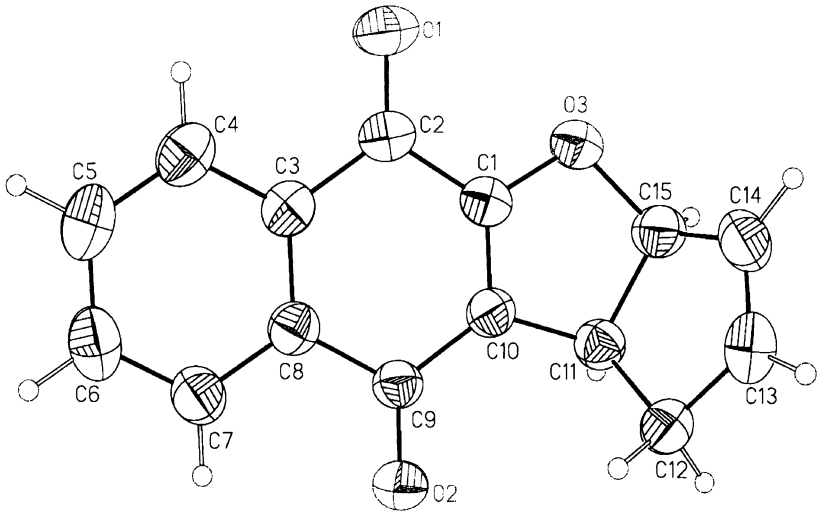
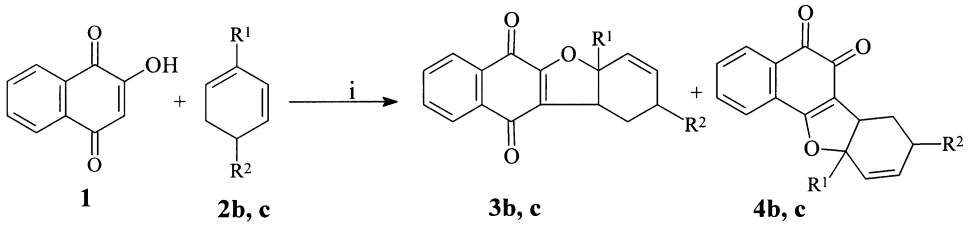


Figure 1. X-Ray structure of **3a**.



1 **2b, c** **3b, c** **4b, c**

2b, $R^1 = R^2 = H$ **3b** (49%) **4b** (46%)

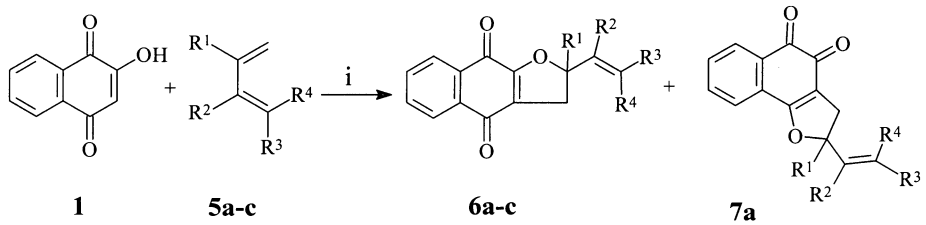
2c, $R^1 = Me$, $R^2 = CHMe_2$ **3c** (54%) **4c** (24%)

Scheme 2. (i) CAN, CH_3CN, 0–5°C, 30 min.

Examination of ^1H NMR showed the proton on C-4 as doublet of a triplet at δ 4.23 (J=2.2, 8.2 Hz) and the C-5 proton as a multiplet at δ 6.02. The signal due to the carbonyl carbons C-9 and C-10 were observed in ^{13}C NMR spectrum at δ 180.70 and 175.30, respectively. The signal due to C-2 was discernible at δ 168.51 and C-5 showed a peak at δ 97.55.

Other cyclic dienes also showed similar reactivity towards 2-hydroxynaphthoquinone in the presence of CAN as shown in Scheme 2.

The products were characterized on the basis of spectroscopic analysis. Additional evidence for the regio-chemistry of the products was drawn from the proton connectivity established by the 2D-COSY ^1H NMR of **3b**. The ring junction proton at δ 5.15 (m) is connected to the olefinic proton at δ 6.05 (m) and the ring junction proton at δ 3.60 (m), which in turn is connected to the methylenic protons at δ 2.15 (m). The DEPT-135 spectra of **3c** and **4c** were used to ascertain the structures of these products. The DEPT-135 spectrum of **3c** clearly established that the sp^3 carbon adjacent to the furan oxygen is a quaternary centre, which cannot be true in the other possible regio-isomer. A similar conclusion could be drawn from the DEPT-135 spectrum of **4c**.



1 **5a-c** **6a-c** **7a**

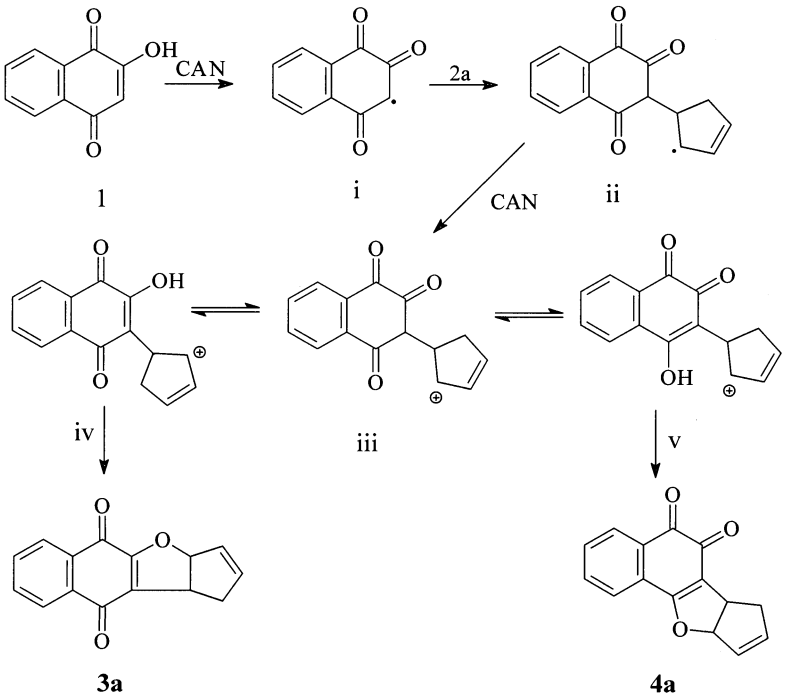
5a, $R^1 = R^2 = Me$, $R^3 = R^4 = H$ **6a** (20%) **7a** (61%)

5b, $R^1 = R^3 = R^4 = Me$, $R^2 = H$ **6b** (75%) nil

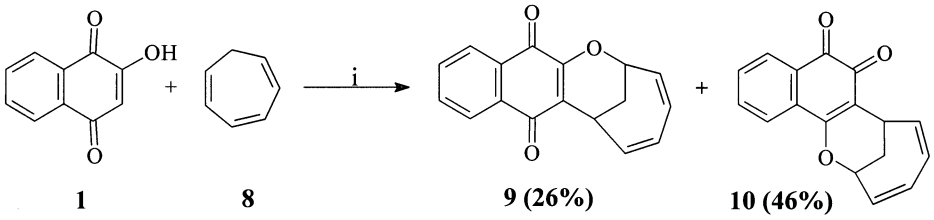
5c, $R^1 = R^3 = Me$, $R^2 = R^4 = H$ **6c** (69%) nil

5d, $R^1 = R^2 = R^4 = H$, $R^3 = Ph$ **6d** (50%) nil

Scheme 3. (i) CAN, CH_3CN, 0–5°C, 30 min.



Scheme 4.



Scheme 5. (i) CAN, CH_3CN, 0–5°C, 30 min.

Subsequently, **1** was treated with acyclic dienes under similar experimental conditions and the results are summarized in Scheme 3.

It is noteworthy that all the products are formed regioselectively with respect to the olefinic double bond. A mechanistic rationalization for the formation of the above products can be drawn by analogy with that suggested for similar reactions of other dicarbonyl compounds.[3] Oxidation of **1** by CAN would lead to the radical (**i**), which is trapped by the diene **2a** to yield the reactive intermediate (**ii**). The latter is further oxidized by CAN to the cation (**iii**), which in turn undergoes rearrangement yielding (**iv**) and (**v**). The cyclization of (**iv**) leads to **3a** whereas (**v**) affords **4a** (Scheme 4).

Interestingly, when **1** was treated with CAN and cycloheptatriene, the dienofuroquinones **9** and **10** were obtained (Scheme 5).

The structures of the products were established on the basis of spectroscopic data. The proton connectivity between the different sets of protons, revealed by $^1H-^1H$ relayed COSY spectrum of **9**, affirmed the assigned structure and these connectivities are illustrated in Fig. 2. The methine proton (δ 5.31) on the ring junction carbon C-1 is connected to the olefinic proton on C-2 and the methylenic protons on C-7. Similarly, the ring junction proton on C-6 is connected to the methylenic protons on C-7 as well as the olefinic proton on C-5. The COSY spectrum revealed the connectivity between the olefinic protons also.

A mechanistic postulate, similar to that outlined for the formation of **3a** and **4a** may be invoked for the formation of **9** and **10** also.

In conclusion, we have developed a simple and rapid one step procedure for the synthesis of naphthofurandiones. It is noteworthy that there are a number of biologically active natural products which contain, both linear and angular

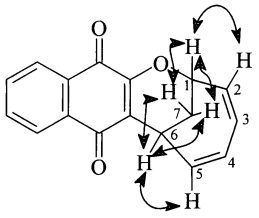


Figure 2. Selected COSY data of **9**.

furanoquinone framework.[7] The protocol described in this paper may be applicable to the synthesis of such compounds.

3. Experimental

All reactions were carried out in oven-dried glassware (120°C). Analytical thin layer chromatography was performed on silica gel TLC plates. 1-Phenyl butadiene was prepared from cinnamaldehyde by Wittig olefination. All the other dienes and 2-hydroxynaphthoquinone were purchased from Aldrich. On completion of the reaction, the mixture was stirred with water (20 mL) and extracted with dichloromethane (4×15 mL). The extract was dried over anhydrous Na_2SO_4 and concentrated. The crude product was then purified by column chromatography on silica gel (100–200 mesh). Mixtures of ethyl acetate and hexane were used as eluents. All melting points were recorded on a Thoshniwal or Büchi-530 melting point apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet impact 400p FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on JEOL-EX-90 and Bruker 300 MHz NMR spectrometers using chloroform-d as solvent and tetramethylsilane as internal standard. The chemical shifts are given in δ scale. High-resolution mass spectra were run on a Kratos MS 50 instrument at 70 eV. Elemental analyses were done using Perkin–Elmer CHN analyser. All solid products were purified by recrystallization from dichloromethane/hexane solvent system.

3.1. General procedure for the reaction of 2-hydroxynaphthoquinone with dienes

A solution of CAN (1.260 g, 2.3 mmol) in distilled acetonitrile (20 mL) was added dropwise to an ice-cooled solution of 2-hydroxy-1,4-naphthoquinone (0.174 g, 1 mmol) and diene (2 mmol) in acetonitrile (15 mL). The reaction mixture was stirred for 30 min and then it was diluted with water (20 mL) and extracted with dichloromethane (4×15 mL). The solvent was evaporated off and the crude product was then purified by column chromatography on silica gel (100–200 mesh) using 5% ethyl acetate in hexane as eluent. All solid products were purified by recrystallization from dichloromethane/hexane solvent system.

3.2. Dihydronaphthofurandiones 3a and 4a

A solution of CAN (1.260 g, 2.3 mmol) in acetonitrile (20 mL) was added dropwise to an ice-cooled solution of 2-hydroxy-1,4-naphthoquinone (0.174 g, 1 mmol) and cyclopentadiene (0.132 g, 2 mmol) in acetonitrile (15 mL). The aqueous work up and chromatographic purification using 5% ethyl acetate in hexane afforded **3a** (0.054 g, 23%) and **4a** (0.136 g, 57%).

3.2.1. 3a,10b-Dihydrocyclopenta[2,3]naphtho[2,3-*d*]furan-5,10-dione (3a). Yellow solid, recrystallized from CH_2Cl_2–hexane, mp 191–193°C. IR (KBr) ν_{max}: 1676, 1639, 1613, 1587, 1449, 1385, 1365, 1244, 1195 cm^{-1}. ^{1}H NMR: δ 8.20–8.05 (m, 2H), 7.81–7.60 (m, 2H), 6.19 (t, J=2.6 Hz, 1H), 6.10 (d, J=8.9 Hz, 1H), 5.95 (dt, J=7.9, 2.2 Hz, 1H), 4.18 (dt, J=8.5, 2.2 Hz, 1H), 2.99–2.89 (m, 2H). ^{13}C NMR: δ 182.43, 178.64, 158.51, 137.66, 134.23, 133.26, 132.99, 121.66, 127.84, 127.04, 126.31, 126.06, 96.09, 42.19, 38.32. EIMS, *m/z*: 238 (M$^+$, 100), 210 (50), 182 (18), 181 (60), 152 (40), 104 (60), 76 (65), 66 (65), 63 (18), 50 (25), 39 (15). HRMS calcd for $C_{15}H_{10}O_3$: 238.0632. Found: 238.0629.

X-Ray crystal data: $C_{15}H_{10}O_3$. F_w: 238.23. Crystal size: 0.40×0.40×0.20 mm^3, monoclinic, space group: $P2_1/c$. Unit cell dimensions a=8.1663(2) Å, α=90°; b=11.1884(2) Å, β=105.473(1) °; c=12.6039(2) Å, γ=90° R indices (all data) $R1$=0.0821, $wR2$=0.1261. Volume, Z=1109.85(4) Å^3, D_{calcd}=1.426 mg/m^3. F(000)=496. Absorption coefficient=0.100 mm^{-1}. Reflections collected=2424. λ=0.71073 Å (Sheldrick, G. M., Siemens, Analytical X-ray Division, Madison, WI, 1995).

3.2.2. 6b,9a-Dihydrocyclopenta[8,9]naphtho[2,1-*d*]furan-5,6-dione (4a). Red solid, recrystallized from CH_2Cl_2–hexane, mp 144–146°C. IR (KBr) ν_{max}: 1694, 1641, 1615, 1567, 1488, 1442, 1401, 1353, 1281, 1220, 1144, 1042 cm^{-1}. ^{1}H NMR: δ 8.10 (t, J=9.0 Hz, 1H), 7.67–7.53 (m, 3H), 6.20–6.12 (m, 2H), 6.03–6.01 (m, 1H), 4.23 (dt, J=8.2, 2.2 Hz, 1H), 2.94–2.83 (m, 1H), 2.74–2.64 (m, 1H). ^{13}C NMR: δ 180.70, 175.30, 168.00, 138.50, 134.51, 132.21, 131.30, 129.30, 127.52, 127.31, 124.53, 119.46, 97.54, 41.46, 38.37. Anal calcd for $C_{15}H_{10}O_3$: C, 75.61; H, 4.23. Found: C, 75.53; H, 4.19.

3.3. Naphthofurandiones 3b and 4b

A solution of CAN (1.260 g, 2.3 mmol) in acetonitrile (20 mL) was added dropwise to an ice-cooled solution of 2-hydroxy-1,4-naphthoquinone (0.174 g, 1 mmol) and cyclohexadiene (0.160 g, 2 mmol) in acetonitrile. The aqueous work up followed by chromatographic purification on silica gel column afforded the product **3b** (0.123 g, 49%) and **4b** (0.116 g, 46%).

3.3.1. 1,2,4a,10b-Tetrahydrobenzo[*b*]naphtho[2,3-*d*]furan-5,10-dione (3b). Yellow solid, recrystallized from CH_2Cl_2–hexane, mp 145–147°C. IR (KBr) ν_{max}: 1677, 1637, 1612, 1584, 1390 1366 1227, 1190, 963 cm^{-1}. ^{1}H NMR: δ 8.09–8.05 (m, 2H), 7.76–7.64 (m, 2H), 6.29–6.24 (m, 1H), 6.09–6.03 (m, 1H), 5.19–5.17 (m, 1H), 3.65–3.55 (m, 1H), 2.25–2.11 (m, 2H), 2.06–1.98 (m, 1H), 1.66–1.53 (m, 1H). ^{13}C NMR: δ 182.42, 178.40, 159.89, 135.24, 134.21, 133.24, 132.98, 131.60, 127.77, 126.33, 126.04, 122.63, 81.53, 38.84, 23.92, 22.76. HRMS calcd for $C_{16}H_{12}O_3$: 252.0786. Found: 252.0789.

3.3.2. 6b,7,8,10a-Tetrahydrobenzo[*c*]naphtho[2,1-*d*]furan-5,6-dione (4b). Red semisolid IR (neat) ν_{max}: 1697, 1642, 1567, 1493, 1405, 1280, 1218, 1161, 1080 cm^{-1}. ^{1}H NMR: δ 8.05 (d, J=7.1 Hz, 1H), 7.63–7.56 (m, 3H), 6.29 (brs, 1H), 6.06 (d, J=9.9 Hz, 1H), 5.25 (d, J=7.7 Hz, 1H), 3.55–3.47 (m, 1H), 2.20–2.14 (m, 2H), 1.99–1.93 (m, 1H), 1.60–1.53 (m, 1H). ^{13}C NMR: δ 181.25, 175.42, 169.71, 135.95, 134.47, 131.85, 130.50, 129.29, 128.29, 124.58, 122.45, 119.56, 82.86, 37.78, 23.76, 22.59. EIMS, *m/z*: 253 (M$^+$+1, 4), 252 (M$^+$, 15), 250 (25), 165 (28), 89 (25), 76 (45), 39 (44), 28 (80), 14 (100). HRMS calcd for $C_{16}H_{12}O_3$: 252.0786. Found: 252.0776.

3.4. Naphthofurandiones 3c and 4c

An ice-cooled mixture of 2-hydroxy-1,4-naphthoquinone (0.174 g, 1 mmol) and α-phellandrene (0.272 g, 2 mmol) in methanol (10 mL) was treated with CAN (1.260 g, 2 mmol) in methanol (10 mL) for 30 min. The aqueous work up followed by chromatographic purification afforded the compound **3c** (0.166 g, 54%) as a yellow semisolid and **4c** (0.068 g, 22%) was obtained as a red oil.

3.4.1. 1,2,4a,10b-Tetrahydro-4a-methyl-2-(1-methylethyl)-benzo[*b*]naphtho[2,3-*d*]furan-5,10-dione (3c). IR (neat) ν_{max}: 1681, 1649, 1614, 1595, 1387, 1367, 1270, 1206, 1038 cm^{-1}. ^1H NMR: δ 8.07–8.05 (m, 2H), 7.73–7.63 (m, 2H), 5.98 (d, J=13.8 Hz, 1H), 5.72 (dd, J=10.2, 1.5 Hz, 1H), 3.36–3.30 (m, 1H), 2.49–2.45 (m, 1H), 2.35–2.21 (m, 1H), 1.78 (m, 2H), 1.63 (s, 3H), 0.93 (d, J=2.6 Hz, 6H). ^{13}C NMR: δ 182.71, 178.37, 159.75, 136.24, 134.06, 133.50, 132.78, 131.00, 128.16, 125.88, 125.10, 90.65, 45.33, 37.00, 31.43, 30.90, 26.35, 25.65, 19.60. EIMS, *m/z*: 308 (M^+, 17), 266 (22), 247 (14), 219 (14), 165 (10), 91 (13), 77 (17), 43 (100), 41 (78). HRMS calcd for $C_{20}H_{20}O_3$: 308.1412. Found: 308.1400.

3.4.2. 6b,7,8,10a-Tetrahydro-10a-methyl-9-(1-methyl-ethyl)benzo[*c*]naphtho[2,1-*d*]furan-5,6-dione (4c). IR (neat) ν_{max}: 1702, 1661, 1613, 1371, 1222, 1054 cm^{-1}. ^1H NMR: δ 8.04 (d, J=7.3 Hz, 1H), 7.60–7.51 (m, 3H), 5.96 (d, J=10.2 Hz, 1H), 5.67 (dd, J=10.1, 2.0 Hz, 1H), 3.50 (q, J=4.4 Hz, 1H), 2.50–2.46 (m, 1H), 1.67 (s, 3H), 1.64–1.57 (s, 3H). 0.90 (d, J=2.6 Hz, 3H), 0.88 (d, J=2.5 Hz, 3H). ^{13}C NMR: δ 181.11, 175.47, 169.12, 136.97, 134.15, 131.66, 129.69, 128.06, 124.41, 117.29, 109.29, 104.70, 92.35, 83.94, 31.29, 26.41, 25.38, 19.50, 19.33. HRMS calcd for $C_{20}H_{20}O_3$: 308.1412. Found: 308.1398.

3.5. 2,3-Dihydronaphthofurandiones 6a and 7a

A solution of CAN (1.260 g, 2.3 mmol) in acetonitrile (20 mL) was added dropwise to an ice-cooled solution of 2-hydroxy-1,4-naphthoquinone (0.174 g, 1 mmol) and 2,3-dimethyl butadiene (0.164 g, 2 mmol) in acetonitrile (15 mL). The aqueous work up followed by chromatographic purification on silica gel afforded the products **6a** (0.051 g, 20%) and **7a** (0.155 g, 61%).

3.5.1. 2,3-Dihydro-2-methyl-2-(1-methylvinyl)naphtho [2,3-*b*]furan-4,9-dione (6a). Yellow solid, recrystallized from CH_2Cl_2–hexane, mp 103–105°C IR (KBr) ν_{max}: 1694, 1640, 1378, 1256, 1209, 1054, 960 cm^{-1}. ^1H NMR: δ 8.08–8.05 (m, 2H), 7.72–7.67 (m, 2H), 5.12 (s, 1H), 4.92 (s, 1H), 3.26 (d, J=16.1 Hz, 1H), 3.03 (d, J=16.1 Hz, 1H), 1.85 (s, 3H), 1.66 (s, 3H). ^{13}C NMR: δ 182.45, 178.03, 158.92, 145.55, 134.11, 133.04, 132.92, 132.06, 126.30, 125.97, 123.37, 111.28, 94.57, 38.68, 26.23, 18.43. HRMS calcd for $C_{16}H_{14}O_3$: 254.0943. Found: 254.0949.

3.5.2. 2,3-Dihydro-2-methyl-2-(1-methylvinyl)naphtho [1,2-*b*]furan-4,5-dione (7a). Red solid, recrystallized from CH_2Cl_2–hexane (mp 112–114°C). IR (KBr) ν_{max}: 1708, 1620, 1364, 1256 cm^{-1}. ^1H NMR: δ 8.10–8.08 (m, 1H), 7.69–7.59 (m, 3H), 5.11 (s, 1H), 4.95 (s, 1H), 3.16 (d, J=15.4 Hz, 1H), 2.98 (d, J=15.4 Hz, 1H), 1.85 (s, 3H), 1.68 (s, 3H). ^{13}C NMR: δ 181.14, 175.57, 168.70, 145.70, 134.58, 131.99, 130.85, 129.43, 127.69, 124.53, 114.88, 111.12, 96.24, 37.87, 26.28, 18.46. HRMS calcd for $C_{16}H_{14}O_3$: 254.0943. Found: 254.0949.

3.5.3. 2,3-Dihydro-2-methyl-2-(2-methylpropenyl)naphtho-[2,3-*b*]furan-4,9-dione (6b). A solution of CAN (1.260 g, 2.3 mmol) in acetonitrile (20 mL) was added dropwise to an ice-cooled solution of 2-hydroxy-1,4-naphthoquinone (0.174 g, 1 mmol) and 2,4-dimethyl-1,3-pentadiene (0.192 g, 2 mmol) in acetonitrile. The aqueous work up followed by chromatographic purification on silica gel afforded the title compound **6b** as a yellow solid (0.201 g, 75%), recrystallized from CH_2Cl_2–hexane, mp 83–85°C. IR (KBr) ν_{max}: 1682, 1651, 1620, 1370, 1264, 1201 cm^{-1} ^1H NMR: δ 8.08–8.03 (m, 2H), 7.71–7.65 (m, 2H), 5.59 (s, 1H), 3.24 (d, J=16.9 Hz, 1H), 3.18 (d, J=16.9 Hz, 1H), 1.76 (s, 3H), 1.75 (s, 3H), 1.62 (s, 3H). ^{13} C NMR: δ 182.21, 177.90, 158.57, 136.44, 133.87, 133.15, 132.67, 131.64, 128.74, 126.18, 125.89, 123.22, 92.63, 41.17, 28.60, 26.52, 19.23. HRMS calcd for $C_{17}H_{16}O_3$: 268.1099. Found: 268.1094.

3.5.4. 2,3-Dihydro-2-methyl-2-propenylnaphtho[2,3-*b*]-furan-4,9-dione (6c). An ice-cooled mixture of 2-hydroxy-1,4-naphthoquinone (0.174 g, 1 mmol) and 2-methyl-1,3-pentadiene (0.164 g, 2 mmol) in acetonitrile was treated with a solution of CAN (1.260 g, 2.3 mmol) in the same solvent. The aqueous work up followed by chromatographic purification afforded the title compound **6c** as a yellow solid (0.175 g, 69%). It was recrystallizsed from CH_2Cl_2–hexane, mp 79–81°C. IR (KBr) ν_{max}: 1681, 1634, 1384, 1249, 1202, 960 cm^{-1}. ^1H NMR: δ 8.06–8.02 (m, 2H), 7.71–7.63 (m, 2H), 5.78 (m, 2H), 3.19 (d, J=17.0 Hz, 1H), 3.00 (d, J=17.0 Hz, 1H), 1.71 (d, J=5.4 Hz, 3H), 1.61 (s, 3H). ^{13}C NMR: δ 182.45, 178.15, 158.83, 134.07, 133.27, 133.01, 132.85, 131.00, 126.26, 126.09, 125.95, 123.33, 92.50, 39.17, 26.79, 17.66. Anal. calcd for $C_{16}H_{14}O_3$: C, 75.56; H, 5.55. Found: C, 75.71; H, 5.76.

3.5.5. 2,3-Dihydro-2-(2-phenylvinyl)naphtho[2,3-*b*]furan-4,9-dione (6d). An ice-cooled mixture of 2-hydroxy-1,4-naphthoquinone (0.174 g, 1 mmol) and 1-phenyl-1,3-butadiene (0.260 g, 2 mmol) in acetonitrile was treated with a solution of CAN (1.260 g, 2.3 mmol) in the same solvent. The aqueous work up followed by chromatographic purification yielded the title compound **6d** as a yellow solid product (0.152 g, 50%). Recrystallized from CH_2Cl_2–hexane, mp 145–147°C. IR (KBr) ν_{max}: 1672, 1650, 1624, 1452, 1392, 1373, 1232, 1195 cm^{-1}. ^1H NMR: δ 8.08 (brs, 2H), 7.75–7.65 (m, 2H), 7.40–7.30 (m, 5H), 6.74 (d, J=15.8 Hz, 1H), 6.32 (dd, J=15.7, 7.2 Hz, 1H), 5.61 (dd, J=17.3, 7.9 Hz, 1H), 3.47 (dd, J=17.3, 7.9 Hz, 1H), 3.10 (dd, J=17.1, 8.2 Hz, 1H). ^{13}C NMR: δ 182.05, 177.62, 159.81, 135.56, 134.47, 134.11, 133.13, 132.96, 131.65, 130.38, 128.73, 128.59, 126.90, 126.38, 126.11, 125.95, 123.87, 105.51, 86.35, 33.53. HRMS calcd for $C_{20}H_{14}O_3$: 302.0942. Found: 302.0949.

3.6. Naphthopyrandiones 9 and 10

An ice-cooled solution of 2-hydroxy-1,4-naphthoquinone (0.174 g, 1 mmol) and cycloheptatriene (0.184 g, 2 mmol)

in acetonitrile was treated with CAN (1.260 g, 2 mmol) in acetonitrile. After aqueous work up and chromatography **9** (0.068 g, 26%) was obtained as a yellow solid and **10** (0.121 g, 46%) was obtained as a red solid 115–117°C.

3.6.1. Naphthopyrandione 9. Recrystallized from CH_2Cl_2–hexane. mp 104–106°C (decomposed). IR (KBr) ν_{max}: 1682, 1647, 1607, 1367, 1292, 1190, 1082, 972 cm^{-1}. ^1H NMR: δ 8.08–8.02 (m, 2H), 7.71–7.66 (m, 2H), 6.53–6.47 (m, 1H), 6.11–5.98 (m, 2H), 5.91–5.85 (m, 1H), 5.31 (d, J=1.5 Hz, 1H), 3.78–3.76 (m, 1H), 2.45–2.40 (m, 1H), 2.12 (d, J=14.1 Hz, 1H). ^{13}C NMR: δ 183.90, 180.32, 154.34, 136.13, 134.02, 133.05, 132.12, 131.20, 130.00, 128.92, 126.33, 126.02, 124.93, 123.45, 72.80, 29.09, 26.98. HRMS calcd for $C_{17}H_{12}O_3$: 264.0786. Found: 264.0784.

3.6.2. Naphthopyrandione 10. Red solid, recrystallized from CH_2Cl_2–hexane, mp 115–117°C. IR (neat) ν_{max}: 1690, 1646, 1593, 1377, 1286, 1084, 971, 927 cm^{-1}. ^1H NMR: δ 8.01 (t, J=7.5 Hz, 1H), 7.83 (d, J=7.7 Hz, 1H), 7.65 (t, J=7.5 Hz, 1H), 7.50 (t, J=7.5 Hz, 1H), 6.57 (t, J=9.50 Hz, 1H), 6.14–6.00 (m, 2H), 5.89–5.82 (m, 1H), 5.35 (t, J=1.6 Hz, 1H), 3.74 (t, J=6.4 Hz, 1H), 2.47–2.42 (m, 1H), 2.09 (d, J=14.2 Hz, 1H). ^{13}C NMR: δ 179.88, 178.27, 162.05, 137.87, 134.89, 132.25, 131.85, 131.09, 130.32, 129.50, 128.60, 128.35, 124.58, 124.21, 116.72, 73.60, 29.08, 28.52. HRMS calcd for $C_{17}H_{12}O_3$: 264.0786. Found: 264.0779.

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