

## Electronic Supplementary Information

# Photochemical reactions of tetrachloro-1,4-benzoquinone (chloranil) with tricyclo[4.1.0.0<sup>2,7</sup>]heptane (Moore's hydrocarbon) and bicyclo[4.1.0]hept-2-ene (2-norcarene)

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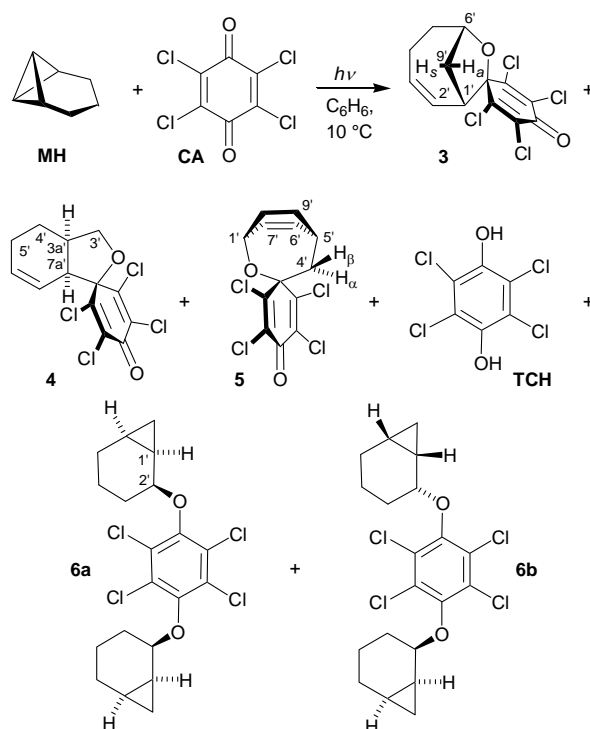
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## General details and general conditions for the photochemical reactions

See ref. 9.

### Irradiation of chloranil (CA) in the presence of tricyclo[4.1.0.0<sup>2,7</sup>]heptane (Moore's hydrocarbon, MH)



In a photolysis vessel, a solution of **CA** (1.00 g, 4.07 mmol) and **MH**<sup>25,41</sup> (770 mg, 8.18 mmol) in anhydrous benzene (150 cm<sup>3</sup>) was thoroughly purged with nitrogen and then irradiated by utilising a pyrex immersion well containing a Hanovia mercury lamp (medium pressure, 450 W), which was surrounded by a special glass filter supposed to prevent the passage of light of  $\lambda < 400$  nm, at 10 °C. After **CA** had been completely consumed (7 h), the solvent was evaporated *in vacuo* and the brown residue was subjected to flash chromatography (SiO<sub>2</sub>, pentane–ethyl acetate 25:1), with two fractions being collected. The first one was a yellow oil (670 mg) and consisted of 2,3,5,6-tetrachloro-1,4-bis(*endo*-bicyclo[4.1.0]hept-2-yloxy)benzene (**6**, most probably a 1:1 mixture of the achiral isomer **6a** and its racemic diastereomer **6b**) and impurities. Dissolution of this oil in the minimum quantity of ethyl acetate and storage of this solution at –35 °C over several days provided pure **6** as colourless crystals (541 mg, 30%). The second fraction contained a mixture of three components, the separation of which was attempted by medium pressure chromatography (SiO<sub>2</sub>, pentane–ethyl acetate 9:1, 15 bar). In the order of elution, the following fractions were obtained: a 3:1 mixture of (3a'*R*, 7a'*S*)-*rel*-2,3,5,6-tetrachloro-3a', 4', 5', 7a'-

tetrahydrospiro[2,5-cyclohexadiene-1,1'(3'*H*)-isobenzofuran]-4-one (**4**) and 2,3,5,6-tetrachlorospiro[2,5-cyclohexadiene-1,3'-[2]oxabicyclo[3.2.2]non[6]en]-4-one (**5**) (203 mg, 15%) and 2,3,5,6-tetrachlorospiro[2,5-cyclohexadiene-1,8'-[7]oxabicyclo[4.2.1]non[2]en]-4-one (**3**) (231 mg, 17%), both as colourless oils, which gave crystals after dissolution in the minimum quantity of ethyl acetate and storage of this solution at  $-35\text{ }^{\circ}\text{C}$ . Within the crystals, the ratio of **4:5** was 6:1.

By using other light sources, namely a light bulb (Osram, 200 W) in one case and a Rayonet photochemical reactor, radiating at 350 nm, in the other, the experiment was repeated two times. The results were similar to that described above. Because of a number of very broad signals, the  $^1\text{H}$  NMR spectra of the crude photolysates (prior to chromatography) did not provide much information, but the  $^{13}\text{C}$  NMR spectra unambiguously indicated the presence of the compounds **3–6**. In addition, 2,3,5,6-tetrachlorohydroquinone (**TCH**) turned out to be a major product, which might have been overlooked in the workup of the above experiment due to its low solubility. The ratio of **3:4:5:6:TCH** was determined to be approximately 5:8:1:3:7 by comparing the height of the signals. Further, a number of signals remained unassigned and thus originated from unidentified products. Among them, a set of seven weak lines matches the  $^{13}\text{C}$  NMR chemical shifts of 2-norcarene (**NC**,  $\delta = 9.7, 10.0, 13.9, 18.5, 20.6, 122.7$  and  $128.8$  ppm), but a rigorous identification was not attempted.

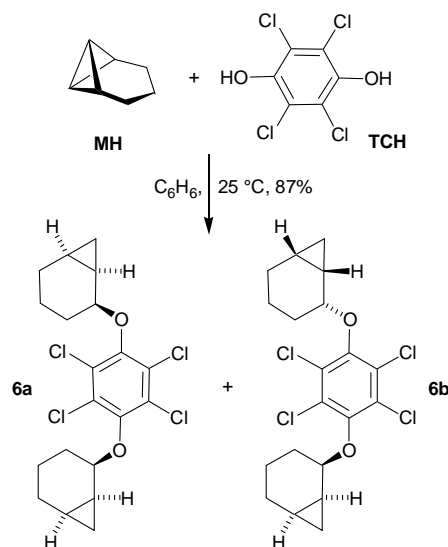
Compound **3**: Colourless crystals, m.p.  $193\text{--}195\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.06$  (m, 1 H), 2.29 (d,  $J_{9',\text{anti},9',\text{syn}} = 12.8$  Hz, 1 H, *syn*-9'-H), 2.30–2.51 (m, 3H), 2.90 (dddd,  $J_{9',\text{anti},9',\text{syn}} = 12.8$ ,  $J_{6',9',\text{anti}} = 8.4$ ,  $J_{1',9',\text{anti}} = 7.0$ ,  $J_{2',9',\text{anti}} = 1.6$  Hz, 1 H, *anti*-9'-H), 3.14 (br. t,  $J_{1',2'} = J_{1',9',\text{anti}} = 7.0$  Hz, 1 H, 1'-H), 5.15 (br. dd,  $J_{6',9',\text{anti}} = 8.4$ ,  $J_{5',6'} = 6.3$  and  $< 1$  Hz, 1 H, 6'-H), 5.38 (ddd,  $J_{2',3'} = 11.3$ ,  $J_{1',2'} = 7.0$ ,  $J_{2',4'} = 2.5$  and  $1.6$ ,  $J_{2',9',\text{anti}} = 1.6$  Hz, 1 H, 2'-H), 5.93 (ddd,  $J_{2',3'} = 11.3$ ,  $J_{3',4'} = 6.9$  and  $3.8$  Hz, 1 H, 3'-H) ppm; as far as specified, the assignments are based on NOE and decoupling experiments.  $^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ ):  $\delta = 25.6, 33.7, 34.3$  (3  $\text{CH}_2$ ), 58.6 (C-1'), 84.6 (C-6'), 90.6 (C-1  $\equiv$  C-8'), 125.1, 137.5 (HC=CH), 128.5, 129.9 (C-3, C-5), 155.6, 159.0 (C-2, C-6), 171.1 (C-4) ppm. IR (KBr):  $\nu_{\text{max}} = 2936$  (w), 2920 (w), 1689 (s), 1601 (w), 1570 (m), 1472 (w), 1273 (w), 1121 (s), 1070 (w), 1049 (w), 1013 (m), 996 (w), 953 (w), 942 (m), 798 (m), 750 (m), 740 (m)  $\text{cm}^{-1}$ . MS (EI, 70 eV):  $m/z$  (%) = 250 (13), 248 (35), 246 (31), 94 (67), 93 (33), 92 (26), 91 (66), 87 (16), 79 (100), 77 (23), 66 (12), 65 (12), 44 (14), 40 (54), 39 (11).  $\text{C}_{13}\text{H}_{10}\text{Cl}_4\text{O}_2$  (340.0): calcd. C 45.92, H 2.96; found C 45.34, H 2.61.

Compounds **4** and **5** as a 6:1 mixture: Colourless crystals, m.p.  $139\text{--}142\text{ }^{\circ}\text{C}$ . IR (KBr):  $\nu_{\text{max}} = 2956$  (w), 2935 (m), 2891 (w), 1686 (s), 1678 (s), 1608 (m), 1581 (s), 1575 (s), 1280

(m), 1136 (m), 1116 (s), 1061 (w), 1050 (w), 1034 (m), 981 (m), 968 (w), 752 (m), 735 (s), 692 (w)  $\text{cm}^{-1}$ . MS (EI, 70 eV):  $m/z$  (%) = 307, 305, 303 (7, 23, 23)  $[\text{M}-\text{Cl}]^+$ , 94 (53), 93 (15), 91 (9), 87 (8), 79 (100), 78 (6), 77 (21), 66 (11), 39 (8).  $\text{C}_{13}\text{H}_{10}\text{Cl}_4\text{O}_2$  (340.0): calcd. C 45.92, H 2.96; found C 46.14, H 2.88.  $^1\text{H}$  NMR of **4** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.79 ( $\approx$ dq,  $J_{4',4'} = 13.2$ ,  $J_{3a',4'}$  and  $2 J_{4',5'} \approx 5.7$  Hz, 1 H) and 1.90 ( $\approx$ td,  $J_{4',4'} = 13.2$ ,  $J_{3a',4'} = 8.1$ ,  $2 J_{4',5'} = 8.1$  and 5.0 Hz, 1 H) ( $4'$ - $\text{CH}_2$ ), 1.99 (dm,  $J_{5',5'} = 17.4$ ,  $2 J_{4',5'} = 8.1$  and 5.7,  $J_{5',6'} = 3.6$ ,  $J_{5',7a'} = 2.6$ ,  $J_{5',7'} = 2.0$  Hz, 1 H) and 2.11 (dm,  $J_{5',5'} = 17.4$ ,  $2 J_{4',5'} = 5.7$  and 5.0,  $J_{5',6'} = 4.5$ ,  $J_{5',7'} = 2.0$  Hz,  $J_{5',7a'} = 1.9$ , Hz, 1 H) ( $5'$ - $\text{CH}_2$ ), 2.91 (m,  $J_{3a',7a'} = 9.1$ ,  $2 J_{3a',4'} = 8.1$  and 5.7,  $2 J_{3',3a'} = 7.8$  and 6.2 Hz, 1 H,  $3a'$ -H), 3.32 ( $\approx$ ddq,  $J_{3a',7a'} = 9.1$ ,  $J_{7',7a'} = 3.9$ ,  $2 J_{5',7a'} = 2.6$  and 1.9,  $J_{6',7a'} = 2.5$  Hz, 1 H,  $7a'$ -H), 4.23 (dd,  $J_{3',3'} = 8.5$ ,  $J_{3',3a'} = 6.2$  Hz, 1 H) and 4.58 (dd,  $J_{3',3'} = 8.5$ ,  $J_{3',3a'} = 7.8$  Hz, 1 H) ( $3'$ - $\text{CH}_2$ ), 5.30 (ddt,  $J_{6',7'} = 10.2$ ,  $J_{7',7a'} = 3.9$ ,  $2 J_{5',7'} = 2.0$  Hz, 1H,  $7'$ -H), 5.98 (dddd,  $J_{6',7'} = 10.2$ ,  $2 J_{5',6'} = 4.5$  and 3.6,  $J_{6',7a'} = 2.5$  Hz, 1 H,  $6'$ -H) ppm; as far as specified, the assignments are based on decoupling experiments.  $^1\text{H}$  NMR of **5** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.24 (ddm,  $J = 13.4$  and 8.6 Hz, 1 H), 2.31 (dd,  $J_{4',4'} = 15.0$ ,  $J_{4',5'} = 3.4$  Hz, 1 H,  $4'$ - $\text{H}_\alpha$ ), 2.35 (ddd,  $J_{4',4'} = 15.0$ ,  $J_{4',5'} = 4.1$ ,  $J_{4',9'anti} = 1.2$  Hz, 1 H,  $4'$ - $\text{H}_\beta$ ), 2.73–2.81 (m, 2 H), 4.68 ( $\approx$ ddt,  $J \approx 5.9$ , 3.7 and 2.2 Hz, 1 H,  $1'$ -H), 6.41 ( $\approx$ td,  $J = 7.2$  and 1.6 Hz, 1 H) and 6.43 ( $\approx$ td,  $J = 7.5$  and 1.7 Hz, 1 H) ( $6'$ -H and  $7'$ -H) ppm; the missing signals are superimposed by multiplets of **4**.  $^{13}\text{C}$  NMR of **4** (63 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 21.5, 22.5 (C- $4'$ , C- $5'$ ), 37.1, 50.8 (C- $3a'$ , C- $7a'$ ), 77.5 (C- $3'$ ), 89.9 (C-1  $\equiv$  C- $1'$ ), 121.2, 131.4 (C- $6'$ , C- $7'$ ), 128.8, 130.5 (C-3, C-5), 154.1, 155.9 (C-2, C-6), 170.2 (C-4) ppm.  $^{13}\text{C}$  NMR of **5** (63 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 23.7, 28.2 (C- $8'$ , C- $9'$ ), 32.5 (C- $5'$ ), 39.7 (C- $4'$ ), 73.3 (C- $1'$ ), 132.2, 136.6 (C- $6'$ , C- $7'$ ) ppm; the intensities of the signals of the quaternary carbon atoms were too low to permit their detection.

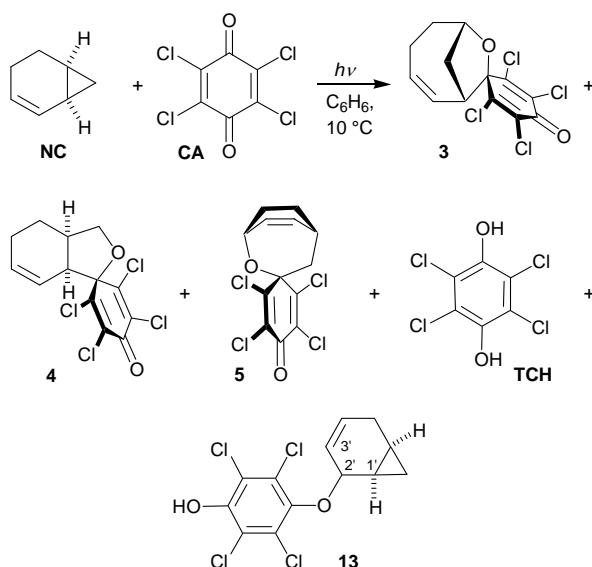
Compounds **6**: Colourless crystals, m.p. 112–113 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.68 [q, (average of  $J_{1',7'endo}$ ,  $J_{6',7'endo}$  and  $J_{7'endo,7'exo}$ ) = 5.5 Hz, 1 H,  $endo$ - $7'$ -H), 0.75 (td,  $J_{1',7'exo} = J_{6',7'exo} = 8.7$ ,  $J_{7'endo,7'exo} = 5.0$  Hz, 1 H,  $exo$ - $7'$ -H), 1.10–1.57 (m, 6 H), 1.72 (dtm,  $J \approx 13$  and 6 Hz, 1 H), 1.87 (m, 1 H), 4.91 (dt,  $2 J_{2',3'} = 9.5$  and 5.8,  $J_{1',2'} = 5.8$  Hz, 1 H,  $2'$ -H) ppm.  $^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.8 (C- $7'$ ), 13.6, 15.0 (C- $1'$ , C- $6'$ ), 21.6, 22.9, 26.8 (C- $3'$ , C- $4'$ , C- $5'$ ), 82.3 (C- $2'$ ), 127.9 (C-2, C-3, C-5, C-6), 148.2 (C-1, C-4) ppm. IR (KBr):  $\nu_{\text{max}}$  = 2958 (m), 2870 (m), 1421 (s), 1387 (w), 1370 (m), 1348 (m), 1330 (w), 1128 (w), 971 (s), 952 (s), 926 (w), 718 (m)  $\text{cm}^{-1}$ . MS (CI, isobutane, 150 eV):  $m/z$  (%) = 254, 252, 250, 248, 246 (0.03, 0.22, 1.21, 2.35, 1.88)  $[\text{C}_6\text{H}_2\text{Cl}_4\text{O}_2]^+$ , 96 (5), 95 (100)  $[\text{C}_7\text{H}_{11}]^+$ , 94 (15), 93 (6), 91 (3), 79 (3), 67 (5).  $\text{C}_{20}\text{H}_{22}\text{Cl}_4\text{O}_2$  (436.2): calcd. C 55.07, H 5.08; found C 55.10, H 4.53.

## Reaction of 2,3,5,6-tetrachlorohydroquinone (TCH) with tricyclo[4.1.0.0<sup>2,7</sup>]heptane (Moore's hydrocarbon, MH) without irradiation



To a suspension of **TCH** (300 mg, 1.21 mmol) in anhydrous benzene (50 cm<sup>3</sup>), **MH**<sup>25,41</sup> (141 mg, 1.50 mmol) was added, and the mixture was stirred at 25 °C for 2 d. The solvent was then evaporated *in vacuo* and the residue subjected to flash chromatography (SiO<sub>2</sub>, pentane–ethyl acetate 9:1) at –30 °C. The colourless oil obtained was dissolved in the minimum quantity of ethyl acetate, and the storage of this solution at –35 °C provided crystals of **6** (285 mg, 87%).

## Irradiation of chloranil (CA) in the presence of bicyclo[4.1.0]hept-2-ene (2-norcarene, NC)



A solution of **CA** (700 mg, 2.85 mmol) and **NC** (270 mg, 2.87 mmol) in anhydrous benzene (70 cm<sup>3</sup>) was thoroughly purged with nitrogen and then illuminated by several light bulbs (Osram, total power 1000 W) for 10 h at 10 °C. The solvent was then evaporated *in vacuo*, and the residue was subjected to flash chromatography [SiO<sub>2</sub>, light petroleum ether (b.p. 40–65 °C)–ethyl acetate 20:1 (400 cm<sup>3</sup>), then 10:1 (200 cm<sup>3</sup>) and finally pure ethyl acetate (50 cm<sup>3</sup>)]. Five fractions were collected, whose order of elution was: **4** (108 mg, 11%), a 4:5:1 mixture of **3**, **4** and **5** (60 mg, 6%), **3** (61 mg, 6%), 2,3,5,6-tetrachloro-4-(bicyclo[4.1.0]hept-3-en-2-yloxy)phenol (**13**, 130 mg 13%) and **TCH** (355 mg). The latter was heavily contaminated with unidentified compounds. The first four fractions contained only minor amounts of impurities, among them components of the adjacent fractions. On treatment of the first and the third fractions with light petroleum ether–ethyl acetate, crystals of **4** and **3**, respectively, were obtained, which proved to be suitable for X-ray structure analysis.<sup>29,30</sup> An attempt to gain crystals of **13** by treatment of the fourth fraction with glacial acetic acid resulted in the formation of **TCH**. The use of ethyl acetate as solvent and cooling of the solution to –35 °C gave a small amount of crystalline **13**, which still contained impurities to the extent of 20%. Possibly, these were stereo- and regioisomers of **13**. By utilising pentachlorobenzene as internal standard, the yields of **3**, **4**, **5**, **13** and **TCH** in the crude photolysate were determined to be 11, 11, 3, 14 and 2%, respectively.

Compound **13**: About 80% purity, colourless crystals, m.p. 110–112 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 0.73 (td,  $J_{1',7'_{exo}} = J_{6',7'_{exo}} = 8.3$ ,  $J_{7'_{endo},7'_{exo}} = 4.9$  Hz, 1 H, *exo*-7'-H), 0.81 [q, (average of  $J_{1',7'_{endo}}$ ,  $J_{6',7'_{endo}}$  and  $J_{7'_{endo},7'_{exo}}$ ) = 5.1 Hz, 1 H, *endo*-7'-H), 1.27 (m, 1 H) and 1.48 (ttd,  $J = 8.3, 5.4$  and 1.6 Hz, 1 H) (1'-H and 6'-H), 2.28 (ddq,  $J = 18.5, 5.3$  and 2.7 Hz, 1 H) and 2.34 (ddm,  $J = 18.5$  and 5.3 Hz, 1 H) (5'-CH<sub>2</sub>), 5.23 [dq,  $J = 5.1$  and 2.2 Hz, 1 H, 2'-H), 5.62 (ddq,  $J = 10.5, 4.8$  and 2.2 Hz, 1 H) and 5.73 (ddq,  $J = 10.5, 3.0$  and 1.8 Hz, 1 H) (3'-H and 4'-H) ppm; the OH signal was not found, probably due to extensive broadening. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ = 6.2 (C-7'), 10.3 (C-6'), 15.3 (C-1'), 23.7 (C-5'), 79.1 (C-2'), 124.2, 126.0 (C-3', C-4') ppm; the signals of the aromatic carbon atoms could not be unambiguously identified due to absorptions of impurities. IR (KBr):  $\nu_{max} = 3448$  (broad, w), 3008 (w), 2892 (w), 2830 (w), 1419 (s), 1395 (m), 1369 (m), 1350 (m), 1329 (m), 1313 (m), 986 (w), 951 (s), 899 (m), 706 (m) cm<sup>-1</sup>. MS (EI, 70 eV):  $m/z$  (%) = 250, 248, 246 (4, 8, 6) [C<sub>6</sub>H<sub>2</sub>Cl<sub>4</sub>O<sub>2</sub>]<sup>+</sup>, 93 (97), 92 (37), 91 (100), 77 (55), 65 (18), 43 (15), 39 (13).

### **Additional reference**

<sup>41</sup> P. G. Gassman and G. D. Richmond, *J. Am. Chem. Soc.*, 1970, **92**, 2090–2096.