A First Approach to the *cis-trans-cis*-Photocyclodimers of 1,2-Naphthoquinone

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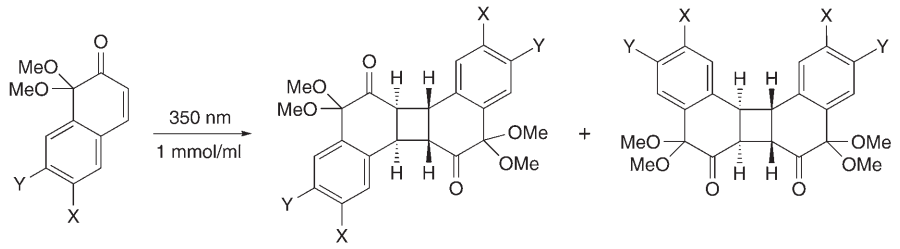
On irradiation ($\lambda = 350$ nm), 1,2-naphthoquinone (= naphthalene-1,2-dione) monoacetals **1** are converted quantitatively to mixtures of the *cis-trans-cis*-photocyclodimers **2** and **3**. Careful hydrolysis of each of the (parent) pentacyclic diacetals **2a** and **3a** affords the – rather unstable – compounds **4** and **5**, respectively.

1. Introduction. – It is well known that 1,4- and 1,2-quinones differ strongly in their photochemical behavior [1][2]. The former undergo [2 + 2] photocycloadditions to alkenes in solution to afford cyclobutanes, and photodimerization within self-assembled coordination cages – again to cyclobutanes [3]. In contrast, the latter undergo H-abstraction by an excited carbonyl group exclusively, and it is, therefore, not surprising that photodimerization to a cyclobutane type dimer of, *e.g.*, 1,2-naphthoquinone (= naphthalene-1,2-dione) never has been observed. Here, we report a straightforward access to such '*1,2-quinone cyclobuta-photodimers*'.

2. Results. – Irradiation of 1,1-dimethoxy-1,2-dihydronaphthalen-2-one (**1a**), easily accessible by oxidation of naphthalen-2-ol [4], quantitatively afforded mixtures (1:2 in benzene, 1:4 in MeCN) of dibenzobiphenylenediones **2a** and **3a**, respectively. Chromatographic separation of these dimers (SiO_2; pentane/Et_2O 2:1) was straightforward, affording **2a** as the first, and **3a** as the second fraction. Both compounds (colorless crystals) were fully characterized spectroscopically, and the structure assignments were confirmed by X-ray crystal-structure determinations. Similarly, irradiation of the 6-Br derivative **1b** in benzene afforded a 1:3 mixture of dimers **2b** and **3b**, respectively. Separation in this case was even easier, as **2b** turned out to be insoluble in MeCN and could, therefore, be obtained by simple filtration. Finally, irradiation of the 7-MeO derivative **1c** afforded dimer **3c** selectively, and only minor amounts (< 10%) of two other – unidentified – dimers were formed (*Scheme 1*).

Hydrolytic deprotection of bisacetals **2** and **3** in order to obtain dibenzobiphenylenetetraones **4** and **5**, respectively, turned out to be quite tricky, as follows in detail for the unsubstituted dimers **2a** and **3a**. No reaction at all occurred using wet or slightly acidified SiO_2, as proposed by *Conia* and co-workers [5], while another 'classic' approach using TsOH/acetone [6] led to rapid total decomposition. By far the best results were achieved by performing the hydrolysis in CH_2Cl_2 in the presence of 8N aq.

Scheme 1

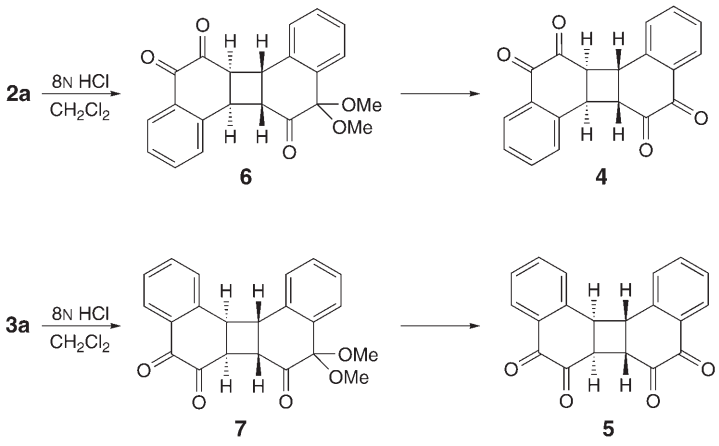


1 **2** **3**

a X = Y = H
b X = Br, Y = H
c X = H, Y = MeO

HCl as a second phase at room temperature [7][8] in a well-defined time period (10–12 h). At shorter reaction times, the (mono-deprotected) acetals **6** and **7** were still present in substantial amounts as determined by ^{1}H-NMR monitoring of the hydrolysis, whereas, at prolonged reaction times, decomposition of both **4** and **5** occurred (*Scheme 2*). Indeed, running the reaction for 72 h led to their total disappearance. The crude (*ca.* 90%) products **4** and **5** were also fully characterized by ^{1}H- and ^{13}C-NMR spectroscopy, (*cf. Exper. Part*) but attempts to further purify them, *e.g.*, by chromatography, led again to their rapid decomposition.

Scheme 2



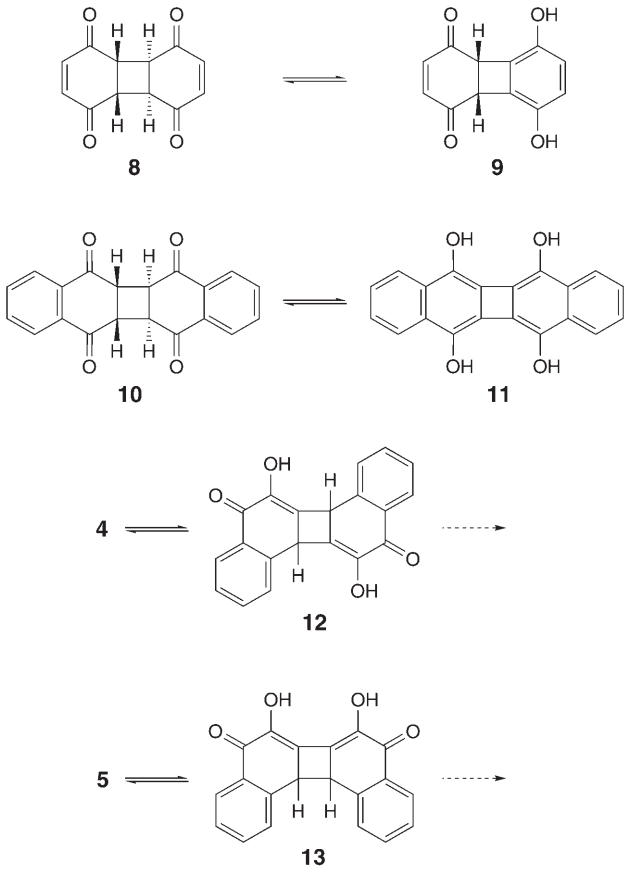
6 **4**

7 **5**

3. Discussion. – The behavior of unsaturated ketones **1** regarding photodimerization is very similar to that of 1,1-dimethylnaphthalen-2-one, where the preferentially formed *cis-trans-cis*-dimer possesses the same constitution as **3** [9][10]. However,

whereas this compound was not further investigated, photodimers **2** and **3** represent interesting synthetic intermediates for further transformation to (the unknown) 'bis-1,2-diketones'. Indeed, the reported (isomeric) 1,4-quinone photodimers have been rather poorly characterized. On irradiation, 1,4-benzoquinone affords a *cis-trans-cis* tricyclic dimer **8** in very low (< 2%) yield [11][12], which tautomerizes to bis-phenol **9** on prolongued contact with AcOH. Similarly, the photodimer **10** of 1,4-naphthoquinone isomerizes to the – apparently more stable dibenzobiphenylene **11** [13]. Now, cyclohexane-1,2-diones are known to tautomerize readily to 2-hydroxycyclohex-2-enones [14], which, in turn, can be readily oxidized to 5-oxoalkanoic acids [15], whereas cyclohexane-1,4-diones exist almost up to 100% as dicarbonyl compounds and do not undergo oxidative ring opening. It is, therefore, not surprising that the dibenzobiphenylenetetraones **4** and **5** are extremely sensitive to both acid and base, their decomposition probably involving tautomerization to dihydroxy derivatives **12**/**13** as a first step (*Scheme 3*). In summary, compounds **4** and **5** represent the first

Scheme 3



cyclobutane-type photodimers of 1,2-quinones ever to be isolated and fully characterized by both ^{1}H- and ^{13}C-NMR spectroscopy.

Experimental Part

1. *General.* Photolyses were conducted in a *Rayonet RPR-100* photoreactor equipped with (16) 350-nm lamps and solvents of spectrophotometric grade. Column chromatography (CC): silica gel *60* (*Merck*; 230–400 mesh). ^{1}H- and ^{13}C-NMR spectra (including two-dimensional plots): in $CDCl_3$ at 500.13 and 125.8 MHz, resp., δ in ppm, J in Hz. GC/EI-MS: at 70 eV; 30-m *SE-30* cap. column. X-Ray analyses were performed on an *Bruker APEX CCD* three-circle diffractometer at 153 K with MoK_α radiation ($\lambda = 0.71073$ Å).

2. *Starting Materials.* Quinone acetals **1** were synthesized from the corresponding, commercially available naphthalen-2-ols according to [4].

3. *Photolyses.* Ar-degassed solns. of **1** (1 mmol) in benzene (1 ml) are irradiated for 18 h up to >95% conversion (monitoring by ^{1}H-NMR).

3.1. *Photodimerization of* **1a**. CC of the residue (SiO_2; pentane/Et_2O 2:1) afforded first 38 mg (19%) *(6a*R**,6b*R**,12a*S**,12b*S**)-6b,11,12a,12b-tetrahydro-5,5,11,11-tetramethoxydibenzo[*a,g*]biphenylene-6,12(5*H*,6a*H*)-dione* (**2a**). M.p. 213–215°. ^{1}H-NMR: 7.70 (*d*, J = 8.4); 7.40 (*t*, J = 8.4); 7.32 (*d*, J = 8.2); 7.28 (*t*, J = 8.3); 4.40, 3.62 (*AA′XX′*, J_{AX} = 9.8, $J_{AX'}$ = 6.5, $J_{AA'} = J_{XX'} = 0$); 3.61, 2.97 (*s*, MeO). ^{13}C-NMR: 207.0 (*s*); 141.1 (*s*); 137.2 (*s*); 129.1 (*d*); 127.5 (*d*); 127.2 (*d*); 126.4 (*d*); 100.1 (*s*); 50.5 (*q*); 49.6 (*q*); 49.5 (*d*); 39.2 (*d*). The second fraction consisted of 119 mg (59%) *(6a*S**,6b*S**,12b*S**,12c*S**)-5,6a,6b,8,12b,12c-hexahydro-5,5,8,8-tetramethoxydibenzo[*a,i*]biphenylene-6,7-dione* (**3a**). M.p. 218–220°. ^{1}H-NMR: 7.77 (*d*, J = 8.4); 7.48 (*t*, J = 8.4); 7.48 (*d*, J = 8.2); 7.33 (*t*, J = 8.3); 4.15, 3.82 (*AA′XX′*, J_{AX} = 8.8, $J_{AX'}$ = 0, $J_{AA'}$ = 8.5, $J_{XX'}$ = 3.0); 3.54, 2.94 (*s*, MeO). ^{13}C-NMR: 205.5 (*s*); 141.0 (*s*); 137.1 (*s*); 130.2 (*d*); 128.1 (*d*); 127.4 (*d*); 126.9 (*d*); 99.7 (*s*); 50.5 (*q*); 49.6 (*q*); 47.1 (*d*); 43.0 (*d*).

X-Ray Crystal-Structure Determination of **2a**[1]). Transparent colorless needles (0.50 × 0.17 × 0.05 mm) from Et_2O, $C_{20}H_{24}O_6$, M_r 408.43: triclinic, space group $P\bar{1}$, $Z = 1$, $a = 5.602(3)$, $b = 8.937(4)$, $c = 10.811(5)$ Å, $\alpha = 68.880(8)°$, $\beta = 87.910(8)°$, $\gamma = 73.286(7)°$; $V = 482.2(4)$ Å^3, $D_x = 1.407$ g cm^{-3}.

X-Ray Crystal-Structure Determination of **3a**[1]). Transparent colorless blocks (0.50 × 0.50 × 0.40 mm) from Et_2O, $C_{20}H_{24}O_6$, M_r 408.43: monoclinic, space group $P2_1/n$, $Z = 4$, $a = 12.1648(9)$, $b = 12.0233(9)$, $c = 15.2212(11)$ Å, $\beta = 108.7610(10)°$; $V = 2108.0(3)$ Å^3, $D_x = 1.287$ g cm^{-3}.

3.2. *Photodimerization of* **1b**. After addition of MeCN (1 ml) to the residue, the insoluble material was filtered and washed with cold MeCN (1 ml). It consisted of 60 mg (21%) *(6a*R**,6b*R**,12a*S**,12b*S**)-2,8-dibromo-6b,11,12a,12b-tetrahydro-5,5,11,11-tetramethoxydibenzo[*a,g*]biphenylene-6,12(5*H*,6a*H*)-dione* (**2b**). M.p. 275–280°. ^{1}H-NMR: 7.59 (*d*, J = 8.2); 7.45 (*s*); 7.44 (*d*, J = 8.2); 4.35, 3.60 (*AA′XX′*, J_{AX} = 10.0, $J_{AX'}$ = 6.2, $J_{AA'} = J_{XX'} = 0$); 3.61, 2.95 (*s*, MeO). The filtrate was evaporated, and then cold acetone (1 ml) was added to the residue. The insoluble material was filtered and washed with cold acetone (0.5 ml). It consisted of 152 mg (53%) *(6a*S**,6b*S**,12b*S**,12c*S**)-2,11-dibromo-5,6a,6b,8,12b,12c-hexahydro-5,5,8,8-tetramethoxydibenzo[*a,i*]biphenylene-6,7-dione* (**3b**). M.p. 229–232°. ^{1}H-NMR: 7.63 (*d*, J = 8.4); 7.56 (*s*); 7.51 (*d*, J = 8.2); 4.11, 3.78 (*AA′XX′*, J_{AX} = 8.9, $J_{AA'}$ = 8.6, $J_{XX'}$ = 3.2, $J_{AX'}$ = 0); 3.56, 2.97 (*s*, MeO).

3.3. *Photodimerization of* **1c**. After evaporation of the solvent cold acetone (1 ml) was added to the residue, and the insoluble material was filtered and washed with cold acetone (0.5 ml) to afford 164 mg (71%) *(6a*S**,6b*S**,12b*S**,12c*S**)-5,6a,6b,8,12b,12c-hexahydro-3,5,5,8,8,10-hexamethoxydibenzo[*a,i*]biphenylene-6,7-dione* (**3c**). M.p. 249–252°. ^{1}H-NMR: 7.35 (*d*, J = 8.2); 7.27 (*d*, J = 2.5); 7.02 (*dd*, J = 2.8, 8.2); 4.02, 3.78 (*AA′XX′*, J_{AX} = 8.6, $J_{AA'}$ = 8.6, $J_{XX'}$ = 2.8, $J_{AX'}$ = 0); 3.84, 3.56, 2.97 (*s*, MeO).

4. *Hydrolysis of* **2a** *and* **3a**. 4.1. *Monitoring by ^{1}H-NMR.* To a soln. of **2a** or **3a** (20.4 mg, $5 \cdot 10^{-4}$ mol) in CH_2Cl_2 (2 ml) was added 1.5 ml 8N HCl, and the mixture was stirred at r.t. Every 2 h, 0.2-ml samples of the org. phase were taken, evaporated, and analyzed by ^{1}H-NMR. In the first 4 h, monoacetals **6** and **7** (characterized by eight aromatic CH signals, an *ABCD* pattern for the cyclobutane H-atoms, and two *s*s

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[1]) CCDC-639738 and CCDC-639739 contain the supplementary crystallographic data for **2a** and **3a**, respectively. This data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

for (only) six MeO H-atoms) were formed and then vanished, whereas the signals of the (symmetric) tetraones appeared continuously to reach a maximum (85–90%) after 10–12 h. Further stirring then led to slow degradation without build-up of any assignable signal/compound.

4.2. *Preparation of* **4**. To a soln. of **2a** (40.8 mg, 1 mmol) in CH_2Cl_2 (2 ml) was added 8N HCl (1.5 ml), and the mixture was stirred at r.t. for 11 h. The org. phase was washed with sat. aq. NaCl and dried ($MgSO_4$). After evaporation of the solvent, 21 mg (66%) (*6a*R*,*6b*R*,*12a*S*,*12b*S*)-*5,6,6a,6b,11,12,12a,12b-octahydrodibenzo[*a,g*]*biphenylene-5,6,11,12-tetraone* (**4**) were obtained as an orange-colored solid residue. M.p. 163–169°. ^{1}H-NMR: 8.22 (*d*, *J* = 8.4); 7.72 (*t*, *J* = 8.4); 7.55 (*t*, *J* = 8.2); 7.52 (*d*, *J* = 8.3); 4.47, 3.69 (*AA′XX′*, J_{AX} = 9.5, $J_{AX'}$ = 6.2, $J_{AA'} = J_{XX'} = 0$). ^{13}C-NMR: 195.2 (*s*); 180.5 (*s*); 144.7 (*s*); 135.3 (*d*); 133.1 (*s*); 129.1 (*d*); 128.7 (*d*); 128.1 (*d*); 51.5 (*d*); 40.1 (*d*).

4.3 *Preparation of* **5**. From **3a** as described above (same amounts, concentration, reaction time, workup), 17 mg (53%) (*6a*S*,*6b*S*,*12b*S*,*12c*S*)-*5,6,6a,6b,10,11,12b,12c-octahydrodibenzo[*a,i*]*biphenylene-5,6,7,8-tetraone* (**5**) were obtained as a dark-greyish solid residue. M.p. 173–179°. ^{1}H-NMR: 8.25 (*d*, *J* = 8.4); 7.73 (*t*, *J* = 8.4); 7.57 (*t*, *J* = 8.2); 7.23 (*d*, *J* = 8.3); 4.05, 3.95 (*AA′XX′*, J_{AX} = 9.5, $J_{AA'}$ = 8.2, $J_{XX'}$ = 3.5, $J_{AX'} = 0$). ^{13}C-NMR: 194.9 (*s*); 179.5 (*s*); 144.3 (*s*); 135.1 (*d*); 133.2 (*s*); 128.6 (*d*); 128.3 (*d*); 128.1 (*d*); 47.0 (*d*); 46.7 (*d*).

REFERENCES

[1] A. Gilbert, in 'Handbook of Organic Photochemistry and Photobiology', 2nd edn., Eds. W. Horspool and F. Lenzi, CRC Press, Boca Raton, 2004, p. 87–1.
[2] M. Oelgemoeller, J. Mattay, in 'Handbook of Organic Photochemistry and Photobiology', 2nd edn., Eds. W. Horspool and F. Lenzi, CRC Press, Boca Raton, 2004, p. 88–1.
[3] M. Yoshizawa, Y. Takeyama, T. Kusukawa, M. Fujita, *Angew. Chem., Int. Ed.* **2002**, *41*, 1347.
[4] D. Mal, H. N. Roy, N. K. Hazra, S. Adhikari, *Tetrahedron* **1997**, *53*, 2177.
[5] F. Huet, A. Lechevallier, M. Pellet, J. Conia, *Synthesis* **1978**, 63.
[6] H. Muxfeldt, M. Weigele, V. van Rheenen, *J. Org. Chem.* **1965**, *30*, 3573.
[7] N. De Kimpe, R. Verhé, L. De Buyck, N. Schamp, *J. Org. Chem.* **1978**, *43*, 2933.
[8] K. A. Tehrani, M. Boeykens, V. I. Tyvorskii, O. Kulinkovich, N. De Kimpe, *Tetrahedron* **2000**, *56*, 6541.
[9] J. Carnduff, J. Iball, D. G. Leppard, J. N. Low, *J. Chem. Soc. D* **1969**, 1218.
[10] T. Mukai, T. Oine, H. Sukawa, *J. Chem. Soc. D* **1971**, 271.
[11] E. H. Gold, D. Ginsburg, *J. Chem. Soc. C* **1967**, 15.
[12] U. v. Gizycki, *Liebigs Ann. Chem.* **1971**, *753*, 1.
[13] J. M. Bruce, *J. Chem. Soc.* **1962**, 2782.
[14] M. Utaka, M. Hojo, A. Takeda, *Chem. Lett.* **1984**, 445.
[15] M. Utaka, M. Nakatani, A. Takeda, *Tetrahedron Lett.* **1983**, *24*, 803.

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