Photochemical Production of Sugar-like Interconvertible Anomeric Naphthopyranylhemiacetals from Acenaphthylene and Chloranil

Naoki Haga,* Hiroaki Takayanagi,† and Katsumi Tokumaru††
Department of Environmental and Natural Resource Science, Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183-8509
†*School of Pharmaceutical Sciences, Kitasato University, Minato-ku, Tokyo 108-0073*
††*University of Tsukuba, Tsukuba, Ibaraki 305-8577*

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Irradiation of acenaphthylene (ACN) and *p*-chloranil with > 420 nm light in 1,2-dichloroethane gives two interconvertible anomeric naphthopyranylhemiacetals in high yields (> 70%), whereas irradiation of ACN with other 1,4-benzoquinones does not afford this type of products. The above products will result from photochemical formation of an oxetane followed by its hydration. These products are stereoselectively converted into an identical naphthopyranylacetal in primary alcohols.

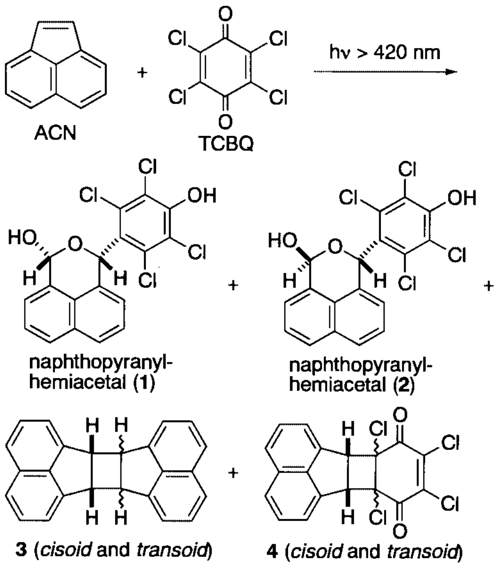
In the series of study on photochemical reactions of acenaphthylene (ACN) with various electron acceptors,[1,2] we now wish to report that the irradiation of ACN and *p*-chloranil (TCBQ) with >420 nm light[3] in solution affords unique products, that is, two anomeric naphthopyranylhemiacetals which are interconvertible like sugars and further converted into a naphthopyranylacetal on treatment with primary alcohols, whereas other benzoquinones such as unsubstituted, chloro-, dichloro-, and tetramethyl-1,4-benzoquinone give ordinarily expected products such as cyclobutanes and oxetanes.

When an equimolar (2.0×10^{-2} M) solution of ACN and TCBQ in 1,2-dichloroethane (DCE) was irradiated with light of > 420 nm [4] for 24 h, 80% of ACN was disappeared (with quantum yield of 0.11 ± 0.01 under irradiation of 435.8 nm light[5]) with concurrent appearance of new components. Chromatographic isolation of the reaction mixture gave two major components **1** (33.2%) and **2** (39.0%) as colorless powder together with the isomeric dimers of ACN, *cisoid*- and *transoid*-**3** (10.0% with the *cisoid/transoid* ratio of 2.9), and two isomeric cyclobutane-type adducts between ACN and TCBQ, *cisoid*- and *transoid*-**4**, (9.1% in a ratio of 6.5) as minor products (Scheme 1).[5] Reaction in acetonitrile gave essentially the same products, however, with reducing yields of **1** (22.5%), **2** (33.8%), and **4** (5.2%) instead of increasing yield of **3** (23.2% with the *cisoid/transoid* ratio of 4.5).

The major products (**1** and **2**) were shown to be two isomeric naphthopyranylhemiacetals based on elemental analysis and spectral properties. X-ray crystallography of a single crystal composed by **2** and ethanol as a crystallization solvent in a 1:1 ratio showed that the hydroxy group and the aryl group of the naphthopyran ring of **2** are suited in *trans* configuration (Figure 1).[6] Accordingly, the configuration of these two groups in **1** was necessarily assigned to *cis*.

When **1** or **2** was independently treated with 30% aqueous acetonitrile at 50 °C, both of them were anomerized to give a mixture of **1** and **2** with an equilibrium ratio of 2.8 certainly by the way of aldehyde form (**6** in Scheme 2) as in anomerization of sugars. This interconversion was accelerated in the presence of 10^{-3} M of hydrochloric acid.

Scheme 1.



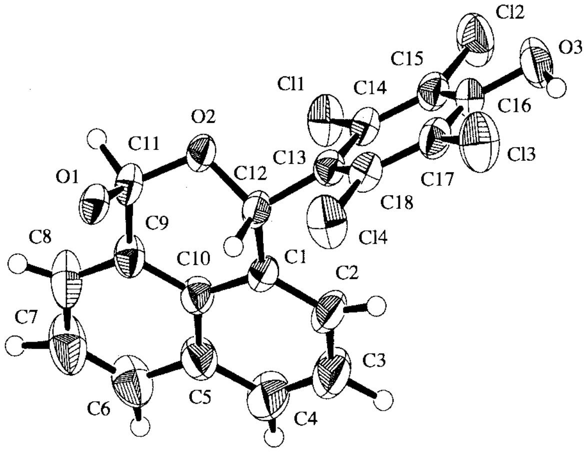
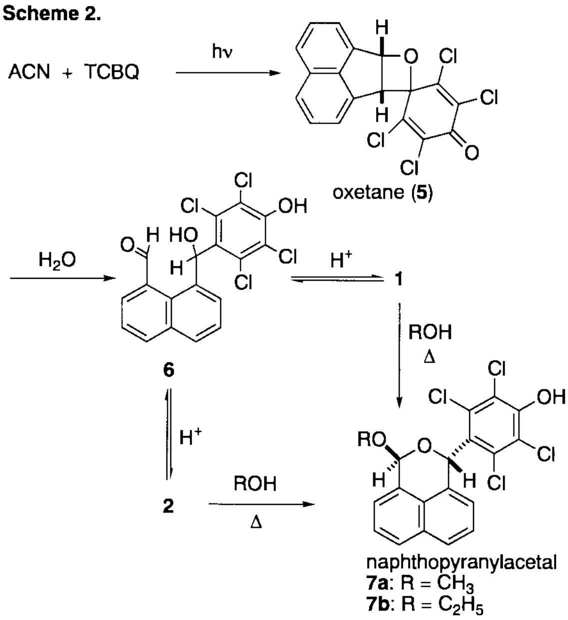


Figure 1. ORTEP drawing of compound **2**.

Mechanism for production of **1** and **2** is at present not entirely clear. A rational pathway leading to **1** and **2** is photochemical formation of oxetane (**5**) from ACN and TCBQ and its subsequent hydration by eventually present water leading to 8-(arylhydroxymethyl)-1-naphthylaldehyde (**6**) as depicted in Scheme 2. Facile cleavage of photochemically or thermally

Scheme 2.



labile oxetanes produced on irradiation of styrene and 1,4-benzoquinone gives dihydrobenzofuran.[7]

Furthermore, on treatment with primary alcohols such as methanol and ethanol but not with *tert*-butyl alcohol, both **1** and **2** were quantitatively converted into an identical naphthopyranylacetal (**7**) carrying with *trans* configuration between the alkoxy group and the aryl group on the naphthopyran ring (Scheme 2).[8] The structure of **7a** (R = CH_3) was unambiguously established by X-ray crystallography of a single crystal composed by **7a** and dichloromethane as a crystallization solvent in a ratio of 1:1.[9]

In conclusion, direct excitation of ACN and TCBQ with > 420 nm light in solution gives two anomeric naphthopyranylhemiacetals between ACN and TCBQ. These hemiacetals facilely anomerize each other like sugars in aqueous solutions, and both of these are converted solely into an identical naphthopyranylacetal in primary alcohol. To the best of our knowledge, formation of products with naphthopyran skeleton is the first finding in photochemical reactions of benzoquinones with unsaturated compounds, which are known to give cyclobutanes, oxetanes or ethers.[10,11]

References and Notes

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3 At 432 nm, both ACN and TCBQ have comparable molar absorption coefficients. Therefore, under > 420 nm irradiation, both of ACN and TCBQ will be nearly equally excited.

4 Light from a 400 W high-pressure mercury lamp was passed through a color-glass filter.[11]

5 Preparative photolysis and determination of quantum yield were done according to the previous method.[1,12] Naphthopyranylhemiacetal (**1**): colorless fine prisms. mp 202.5–203.0 °C (dec). Anal. Calcd for $C_{18}H_{10}Cl_4O_3$: C, 51.96; H, 2.42; Cl, 34.08; O, 11.53%. Found: C, 52.32, H, 2.80, Cl, 33.70%. FAB-MS (*m*-nitrobenzylamine (*m*-NBA) as a matrix) *m/z* 397 (M^++H). HRMS (EI): Calcd for $C_{18}H_8Cl_4O_2$ (M–H_2O) 395.9278. Found 395.9286. ^1H NMR (400 MHz, acetone-d_6): δ 7.93 (d, 1H, *J* = 8.2 Hz), 7.85 (d, 1H, *J* = 8.0 Hz), 7.57 (dd, 1H, *J* = 8.2, 8.0 Hz), 7.45 (d, 1H, *J* = 8.2 Hz), 7.41 (s, 1H), 7.40 (dd, 1H, *J* = 8.2, 8.0 Hz), 6.87 (d, 1H, *J* = 8.0 Hz), 6.75 (s, 1H), 5.5–6.7 (br s, 1H). ^{13}C NMR (100 MHz, acetone-d_6): δ 151.8, 134.7, 134.1, 133.8, 133.6, 133.4, 130.1, 128.6, 127.2, 126.6, 126.43, 126.37, 123.8, 122.8, 120.6, 120.5, 93.3, 70.2. Naphthopyranylhemiacetal (**2**): colorless prisms. mp 198.5–200.0 °C (dec). Anal. Calcd for $C_{18}H_{10}Cl_4O_3$: C, 51.96; H, 2.42; Cl, 34.08; O, 11.53%. Found: C, 52.35, H, 2.78, Cl, 33.72%. FAB-MS (*m*-NBA as a matrix) *m/z* 397 (M^++H). HRMS (EI): Calcd for $C_{18}H_8Cl_4O_2$ (M–H_2O) 395.9278. Found 395.9267. ^1H NMR (400 MHz, acetone-d_6): δ 7.95 (d, 1H, *J* = 8.1 Hz), 7.85 (d, 1H, *J* = 8.1 Hz), 7.73 (d, 1H, *J* = 7.8 Hz), 7.63 (dd, 1H, *J* = 8.1, 7.8 Hz), 7.43 (s, 1H), 7.41 (dd, 1H, *J* = 8.1, 7.8 Hz), 6.87 (d, 1H, *J* = 7.8 Hz), 6.37 (s, 1H), 5.3–6.8 (br s, 1H). ^{13}C NMR (100 MHz, acetone-d_6): δ 152.2, 134.7, 134.1, 133.4, 132.7, 130.5, 129.5, 129.2, 127.5, 126.8, 126.7, 126.3, 124.6, 123.0, 121.1, 120.7, 94.9, 71.5.

6 A colorless single crystal with dimension of 0.20 × 0.30 × 0.20 mm was collected on a Rigaku AFC5R diffractometer using graphite monochromatic Cu Kα radiation (λ = 1.54178 Å) and 12 kW rotating anode generator at 23 °C. The structure was elucidated by a direct method using TEXSAN.[13] Crystal data for $\mathbf{2}\cdot C_2H_5OH$ ($C_{20}H_{16}Cl_4O_4$): MW = 430.07, monoclinic, space group *C*2/*c* (#15), *a* = 12.799 (3) Å, *b* = 11.909 (3) Å, *c* = 27.843 (4) Å, β = 99.67 (2)°, *V* = 4183 (1) $Å^3$, *Z* = 8, D_{calc}/g cm^{-3} = 1.366, μ = 53.17 cm^{-1}, 3937 reflections measured, 3586 unique (R_{int} = 0.025), *R*I (I > 3σ), = 0.075, *R* = 0.136, *R*w = 0.228.

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8 *trans*-1-Methoxy-3-(2,3,5,6-tetrachloro-4-hydroxyphenyl)-1*H*,3*H*-naphtho[1,8-*cd*]pyran (**7a**): colorless prisms. mp 182.0–183.0 °C. Anal. Calcd for $C_{19}H_{12}Cl_4O_3$: C, 53.06; H, 2.81; Cl, 32.97; O, 11.16%. Found: C, 52.88, H, 2.68, Cl, 32.75%. FAB-MS (*m*-NBA): *m/z* 428 (M^++1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (dd, 1H, *J* = 8.1, 1.2 Hz), 7.79 (d, 1H, *J* = 8.4 Hz), 7.55 (dd, 1H, *J* = 8.1, 7.2 Hz), 7.45 (dd, 1H, *J* = 7.2, 1.2 Hz), 7.36 (dd, 1H, *J* = 8.4, 7.2 Hz), 7.24 (s, 1H), 6.78 (dt, 1H, *J* = 7.2, 1.2 Hz), 6.25 (br s, 1H), 5.90 (s, 1H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, CD_3OD): δ 153.1, 125.3, 134.7, 134.1, 133.7, 131.6, 129.5, 129.4, 127.7, 126.91, 126.86, 126.8, 124.7, 121.0, 100.8, 71.0, 55.8. *trans*-1-Ethoxy-3-(2,3,5,6-tetrachloro-4-hydroxyphenyl)-1*H*,3*H*-naphtho[1,8-*cd*]pyran (**7b**): colorless prisms. mp 178.0–179.0 °C. Anal. Calcd for $C_{20}H_{14}Cl_4O_3$: C, 54.08; H, 3.18; Cl, 31.93; O, 10.80%. Found: C, 53.75, H, 3.12, Cl, 32.35%. EI-MS: *m/z* 442. ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (dd, 1H, *J* = 8.2, 1.2 Hz), 7.78 (d, 1H, *J* = 8.3 Hz), 7.55 (dd, 1H, *J* = 8.2, 7.2 Hz), 7.45 (dd, 1H, *J* = 7.2, 1.2 Hz), 7.36 (dd, 1H, *J* = 8.3, 7.2 Hz), 7.27 (s, 1H), 6.78 (dt, 1H, *J* = 7.2, 1.2 Hz), 6.26 (br s, 1H), 6.02 (s, 1H), 4.12 (dq, 1H, *J* = 10.0, 7.2 Hz), 3.84 (dq, 1H, *J* = 10.0, 7.2 Hz), 1.36 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 134.2, 133.7, 132.7, 132.1, 130.3, 129.3, 128.4, 126.6, 125.8, 125.6, 125.4, 123.3, 121.2, 119.9, 118.8, 98.3, 98.1.

9 A colorless single prism with dimension of 0.30 × 0.30 × 0.20 mm was used. Crystal data for $\mathbf{7a}\cdot CH_2Cl_2$ ($C_{20}H_{13}Cl_6O_3$): MW = 514.04, triclinic, space group, *P*$\bar{1}$ (#2); Lattice parameters, *a* = 10.789 (2) Å, *b* = 11.964 (2) Å, *c* = 8.388 (1) Å, α = 93.52 (2)°, β = 103.84 (1)°, γ = 85.22 (2)°, *V* = 1046.7 (6) $Å^3$, *Z* value, 2; D_{calc}/g cm^{-3}, 1.631, μ = 78.61 cm^{-1}, 3893 reflections measured, 3683 unique (R_{int} = 0.076), *R*I (I > 3σ), = 0.075, *R*, 0.070; *R*w, 0.080.

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