## Notiz / Note

# ω-Hydroxy-*ortho*-quinodimethane: Trapping with Trifluoroacetone and Photocyclization

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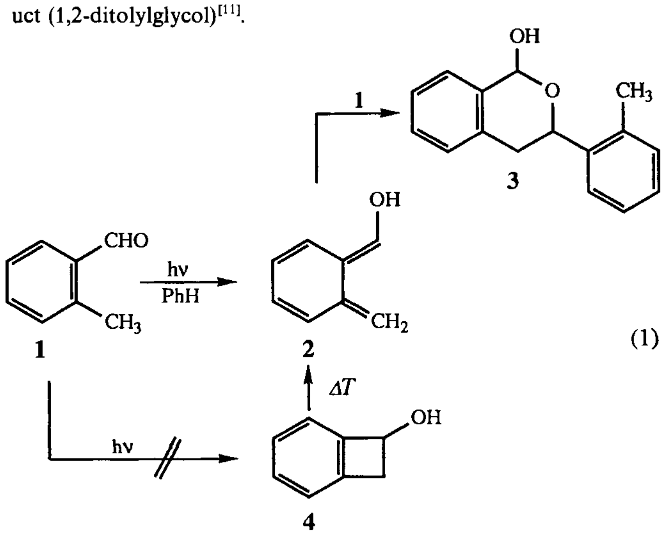
ω-Hydroxy-ortho-quinodimethane (**2**), generated by photoenolization of 2-methylbenzaldehyde (**1**) in benzene, is quantitatively trapped with trifluoroacetone to give the bicyclic hemiacetal **6** and the hydroxy aldehyde **7**. A less effective trapping reaction is observed with benzaldehyde with the formation of the bicyclic hemiacetal **5**. The formation of benzocyclobutenol **4** is probable due to a two-photon process involving electronically excited **2**.

Photoinduced enolization of aromatic carbonyl compounds bearing *ortho*-alkyl substituents is a general phenomenon, which was already utilized for the synthesis of a variety of annulated products from inter- and intramolecular trapping of the intermediary ω-hydroxy-*ortho*-quinodimethanes (QDM)[1,2].

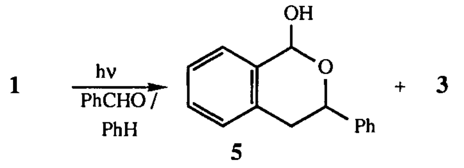
2-Methylbenzaldehyde (**1**) serves as a source for the parent (*Z*)- and (*E*)-ω-hydroxy-QDM (**2**) generated photochemically via two triplet states ($\tau_T = 1.1$ and 95 ns[3]) and subsequently a common triplet 1,4-diradical ($\tau_B = 310$ ns[4]). (*E*)-**2** could be trapped with a variety of dienophiles such as dimethyl butynedioate[5], maleic anhydride[6], tetracyanoethylene[7], and even with triplet oxygen[8,9]. In the absence of trapping reagents the photolysis of **1** leads to a dimerization product (hemiacetal **3**) besides a photoreduction product (1,2-ditolylglycol)[11].



(1)

The dimerization product **3**, however, was not observed when (*E*)-ω-hydroxy-QDM (**2**) was generated by thermolysis of the benzocyclobutenol **4**[12]. A plausible explanation for this result given in the literature is the assumption of a two-photon process for the photochemical reaction, i.e. the reaction of triplet-excited 2-methylbenzaldehyde (**1***) with the photochemically generated *o*-QDM **2**[12,1]. In contrast to the behavior of 2,6-dialkylphenylketones[1,13] or 2-alkylphenylketones[14] a thermal electrocyclic ring closure of **2** to the benzocyclobutenol **4** was observed only as a minor pathway[12].

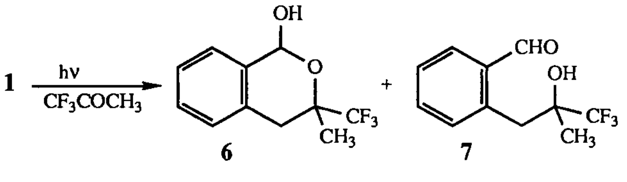
During our investigations of spin inversion control of stereoselectivity in photocycloaddition reactions[15] we now found that the QDM **2** from 2-methylbenzaldehyde (**1**) could be trapped with different carbonyl compounds. In the presence of a fivefold molar excess of benzaldehyde, irradiation of **1** in benzene led to 5% of the known hemiacetal **3**[10] and 46% of the mixed trapping product **5**. Additionally, about 40% of 1,2-diphenylglycol was formed in a photoreduction step as already known from benzaldehyde photolysis[16].



(2)

Obviously, **1** as well as the trapping reagent benzaldehyde could be electronically excited during photolysis. Aliphatic aldehydes which did not absorb light under the photolysis conditions, were found to be unreactive, and mainly **3** was isolated. Negative results were also obtained with acetone and acetophenone. Trifluoroacetone, however, proved to be an exception. This highly electrophilic compound quantitatively reacted with ω-hydroxy-QDM, when applied in a fivefold molar excess. Not even traces of the hemiacetal **3** was detected in the product mixture [irradiation of a solution of **1** (0.15 M) and trifluoroacetone (0.45 M) in benzene, λ = 300 nm, 5°C, 16 h].

In the $^{19}$F-NMR spectrum of the crude reaction mixture three signals appeared in a ratio of 38:18:44. HH and CH COSY revealed the structure of two diastereomeric hemiacetals **6** (d.r. = 68:32) and that of the hydroxy aldehyde **7** (total yield 91%). The products **6** and **7** (formally the [4 + 2] cycloaddition product



(3)

and the vinylogous aldol addition product, respectively) are in rapid equilibrium with each other and could therefore not be separated.

In this type of addition reaction the trapping reagent trifluoroacetone clearly must act in its electronical ground state, because it cannot be directly excited or sensitized under the reaction conditions[17]. Further excitation of the photodienol **2** cannot be a relevant pathway in conventional (low photon flux) photolysis either. This was demonstrated by an experiment performed under high-photon flux conditions (laser jet[18,19]). Thus, whereas irradiation of a 80 mM solution of **1** under conventional conditions gave mainly **3** and photoreduction products, irradiation with an argon ion laser under jet conditions gave mainly the benzocyclobutenol **4**. This accounts for a two-photon process **1**→**4** in sharp contrast to the results obtained for the photocyclization of hydroxy-QDM generated from aromatic ketones[14].

The excellent mass balance (> 95%) for the trifluoroacetone trapping reaction accounts for a highly efficient process without competing photoreduction reactions. This is the first example[20] of a photochemically generated hydroxy-QDM trapped by a *ketone* and should also stimulate further work for synthetic applications. From these experiments the postulated photochemical formation[1,12] of the hemiacetal **3** seems to be unlikely. Obviously, a rather low bimolecular reaction rate constant for dimerization must be responsible for the exclusive formation of **1** during *thermolysis* of benzocyclobutenol **4**.

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## Experimental

IR: Perkin-Elmer 1420 spectrometer. – $^{1}$H NMR: Bruker AC 250 (250 MHz). – $^{13}$C NMR: Bruker AC 250 (63.4 MHz). – MS: Finnigan MAT 8200. – $^{19}$F NMR: Jeol FX 90Q (89.5 MHz). – Irradiations were performed in Rayonet photoreactors (RPR 3000-Å lamps, pyrex tubes) under nitrogen at 10°C.

1. *Irradiation of* **1** *in the Presence of Benzaldehyde:* A solution of 1.00 g (8.3 mmol) of **1** and 2.65 g (25.0 mmol) of benzaldehyde in 80 ml of benzene was irradiated ($\lambda = 300$ nm) for 16 h. After removal of the solvent (rotary evaporator), the crude reaction mixture (3.60 g, $^{1}$H-NMR analysis of this mixture indicated a ratio of **3** to **5** of 9:91 besides ca. 40% of the photoreduction product diphenylglycol) was purified by silica gel column chromatography (PE/EA, 10:1) to give 600 mg (32%) of **5** as a 90:10 mixture of *trans* and *cis* isomer. – **5** [90:10 diastereomeric mixture, spectral data for major (*trans*) diastereomer]: $^{1}$H NMR (CDCl$_3$, 250 MHz): $\delta = 2.79$ (dd, $J = 3.5$, 16.5 Hz), 1H), 2.93 (dd, $J = 11.3$, 16.5 Hz, 1H), 3.67 (br. s, 1H, OH), 5.15 (dd, $J = 3.5$, 11.4 Hz, 1H), 6.03 (s, 1H), 7.15–7.50 (m, 9H). – $^{13}$C NMR (CDCl$_3$, 63 MHz): $\delta = 36.5$ (t), 69.7 (d), 92.7 (d), 126.7, 127.1, 128.2, 128.4, 128.9, 129.0, 129.1 (all d), 134.9 (s), 142.0 (s), 142.1 (s). – IR (film): $\tilde{\nu} = 3660$, 3080, 2950, 1615, 1595, 1505, 1465, 1390, 1270, 1000 cm$^{-1}$. – $C_{15}H_{14}O_2$ (226.3): calcd. C 79.62, H 6.24; found C 79.45, H 5.99.

2. *Irradiation of* **1** *in the Presence of Trifluoroacetone:* A solution of 1.00 g (8.3 mmol) of **1** and 4.66 g (41.6 mmol) of trifluoroacetone in 80 ml of benzene was irradiated ($\lambda = 300$ nm) for 16 h. After removal of the solvent (rotary evaporator), the crude reaction mixture (1.85 g, $^{1}$H-NMR analysis of this mixture indicated a ratio of **6** to **7** of 56:44 besides 9% of the photoreduction product 1,2-ditolylglycol) was purified by silica gel column chromatography (PE/EA, 10:1) to give 1.20 g (32%) of a mixture of **6** (68:32 ratio of diastereomers) and **7**. – **6** (major diastereomer): $^{1}$H NMR (CDCl$_3$, 250 MHz): $\delta = 1.13$ (s, 3H), 2.77 (d, $J = 15.9$ Hz, 1H), 3.06 (d, $J = 15.9$ Hz, 1H), 3.80 (s, 1H, OH), 5.96 (s, 1H), 7.03–7.32 (m, 4H). – $^{13}$C NMR (CDCl$_3$, 63 MHz): $\delta = 19.3$ (q), 32.4 (t), 74.4 (q, CF$_3$), 91.8 (d), 125.9, 127.1, 128.9, 133.8 (all d), 135.8 (s). – $^{19}$F NMR (CDCl$_3$, 89.5 MHz): $\delta = -83.1$ (s); (minor diastereomer): $^{1}$H NMR (CDCl$_3$, 250 MHz): $\delta = 1.17$ (s, 3H), 2.61 (d, $J = 15.2$ Hz, 1H), 3.37 (d, $J = 15.2$ Hz, 1H), 3.52 (s, 1H, OH), 5.91 (s, 1H), 7.03–7.32 (m, 4H). – $^{13}$C NMR (CDCl$_3$, 63 MHz): $\delta = 20.3$ (q), 31.8 (t), 74.0 (q, CF$_3$), 92.8 (d), 125.7, 128.6, 129.1, 131.34, 23.8 (all d), 135.6 (s). – $^{19}$F NMR (CDCl$_3$, 89.5 MHz): $\delta = -82.8$ (s). – **7**: $^{1}$H NMR (CDCl$_3$, 250 MHz): $\delta = 1.36$ (s, 3H), 2.83 (d, $J = 13.5$ Hz, 1H), 3.69 (d, $J = 13.5$ Hz, 1H), 4.31 (s, 1H, OH), 7.03–7.32 (m, 1H), 7.38–7.55 (m, 2H), 7.68–7.75 (m, 1H), 9.92 (s, 1H). – $^{13}$C NMR (CDCl$_3$, 63 MHz): $\delta = 21.5$ (q), 36.6 (t), 74.6 (q, CF$_3$), 127.2, 128.0, 128.3, 134.4 (all d), 136.2 (s), 196.4 (d). – $^{19}$F NMR (CDCl$_3$, 89.5 MHz): $\delta = -83.5$ (s).

3. *Irradiation of* **1** *under Laser-Jet Conditions:* A solution of 100 mg (0.83 mmol) of **1** in 10 ml of acetone was irradiated for 1 h with all UV lines (3.6 W, 333, 351, 364 nm) of an INNOVA 100 argon ion laser. $^{1}$H- and $^{13}$C-NMR analysis of the crude reaction mixture indicated 50% conversion and the formation of ca. 35% benzocyclobutenol **4** [characteristic signals: $^{13}$C NMR: 42.2 (t), 70.9 (d). – $^{1}$H NMR: 3.01 (dd, 1H), 3.61 (dd, 1H), 5.27 (dd, 1H)]. – Conventional irradiation (Rayonet) of a reference sample gave <4% **4**.

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