5. The Photoenol Tautomer of 5-Methyl-1,4-naphthoquinone

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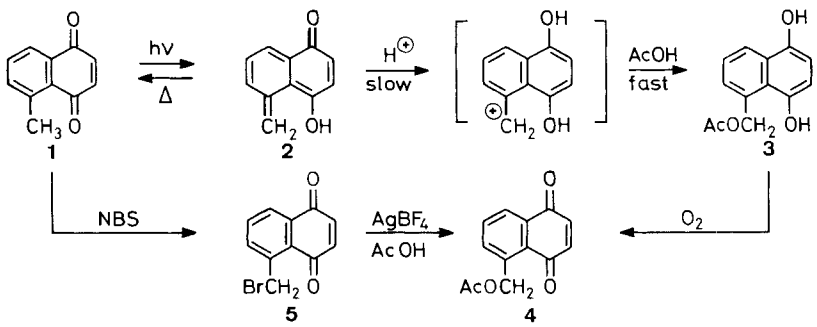
Summary

Irradiation of pale yellow 5-methyl-1,4-naphthoquinone (**1**, *Scheme 1*) yields the blue photoenol 4-hydroxy-5-methylidene-1(5*H*)-naphthalenone (**2**) which is stable at 77 K. At room temperature the enol retautomerizes to starting material, the reaction rate being strongly dependent on the hydrogen-bond-acceptor basicity of the solvent. The enol is trapped in the presence of acid by protonation at the remaining carbonyl oxygen atom and subsequent electrophilic reaction of the exocyclic methylene group.

The introduction of a methyl substituent in *peri*-position of 1,4-naphthoquinone was expected to suppress its photochemical reactivity towards intermolecular hydrogen abstraction due to the concomitant introduction of an effective desactivation channel *via* reversible intramolecular photoenolization. We report here a study of this reaction which has potential interest as a photochromic system and which provides the first unambiguous example for the formation of a (*Z*)-dienol by photoinduced [1.5]-hydrogen-shift.

Scheme 1



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Results. – 5-Methyl-1,4-naphthoquinone (**1**) was obtained by *Diels-Alder* addition of piperylene to *p*-benzoquinone [1]. Its light-sensitivity is strongly solvent-dependent: The quantum yield of disappearance of **1** upon 365 nm irradiation is less than *ca.* 10^{-3} in dry de-aerated benzene and rises to near unity in glacial acetic acid ($\phi = 0.70 \pm 0.04$) or ethanol ($\phi = 1.2 \pm 0.2$). Flash photolysis of **1** indicated that the primary photochemical process, intramolecular hydrogen transfer to form the photoenol 4-hydroxy-5-methylidene-1(5*H*)-naphthalenone (**2**) as a transient intermediate (λ_{max} 550 nm in apolar to 580 nm in polar solvents), occurs with essentially unit efficiency[2]) in all solvents investigated. Hence, the apparent photostability of **1** in aprotic solvents must be due to rapid retautomerization of **2** to **1**. Our assignment of the naphthoquinone methide structure to the transient species **2** rests on the following evidence: (*i*) In rigid glasses at 77 K (ethanol/methanol 8:2, methyl tetrahydrofuran, or polymethyl methacrylate) **2** is stable indefinitely. This excludes its identification with an excited state of **1**. (*ii*) The absorption spectrum of **2** is in excellent agreement with the predictions of standard PPP SCF CI calculations for the assumed structure (Fig. 1). (*iii*) The retardation of the reaction **2** → **1** by more than four orders of magnitude upon changing from hydrocarbon to aprotic hydrogen-bond acceptor [2] solvents (Table 1) is readily understood as being due to solvation of the enolic proton [3]. (*iv*) Trapping of **2** by acetic acid gives a quantitative yield of 5-(acetoxymethyl)-1,4-naphthalenediol (**3**) which was characterized by spectroscopic data and identified by independent synthesis of its oxidation product **4** (*Scheme 1*). The product(s) obtained by irradiation of **1** in ethanol were not analysed.

Table 1. *Lifetime of enol* **2** *in various solvents*[a])

aprotic		protic	
cyclohexane[b])	8 μs	ethanol abs.	0.8 ms
benzene[b])	40 μs	acetonitrile[b]) + 1% water	0.8 ms
diethyl ether[b])	2 ms	acetonitrile[b]) +30% water	1.3 ms
acetonitrile[b])	3 ms	acetic acid[d])	26 μs
tetrahydrofuran[b])	7 ms		
dimethyl sulfoxide[c])	11 ms		
HMPA[b])[e])	90 ms		

[a]) Lifetimes are given as the reciprocals of the first-order decay rates at room temperature and should be taken as lower limits, since they may be determined by solvent impurities.
[b]) Spectrograde quality solvents (*Merck*, Uvasol).
[c]) *Merck, p. a.*, dried over CaH_2 and redistilled.
[d]) *Fluka, puriss.*
[e]) Hexamethyl phosphoric acid triamide, de-aerated.

The photoenolization of **1** occurs upon either π–π^* (313, 365 nm) or n–π^* (> 400 nm) excitation. It is not quenched appreciably by saturating the solutions with oxygen (1 atm) and the addition of nearly 0.1 M of anthracene is needed to halve the yield of **2** in benzene solution. At such high concentrations changes in the absorption spectrum of **1** indicate complex formation. These data do not allow any conclusion

[2]) Details of this measurement are given in the Exper. Part.

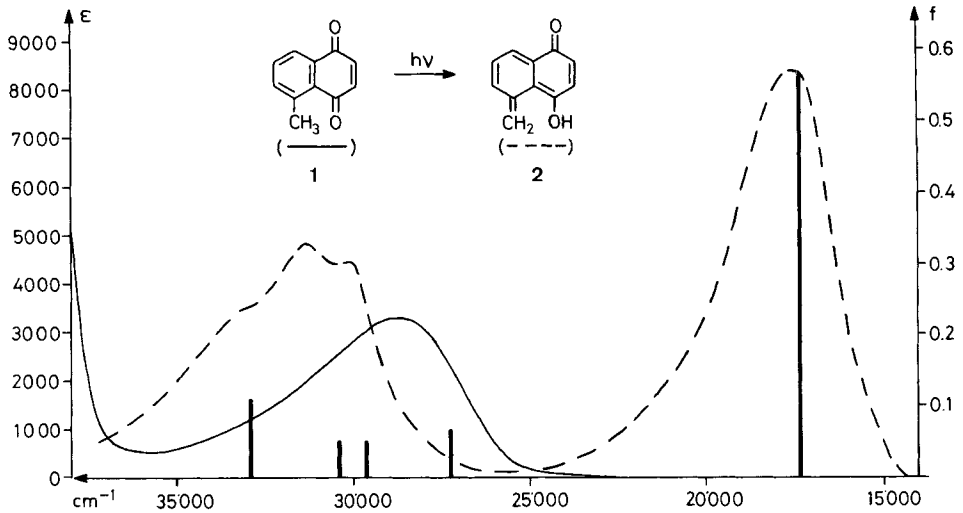


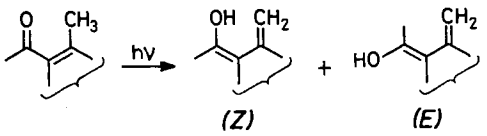
Fig. 1. *Absorption spectrum of* **1** *and its photoenol* **2** (≥ 80 percent conversion, ethanol/methanol glass, 77 K). Vertical bars indicate oscillator strengths *f* predicted by PPP SCF CI for **2**.

about the multiplicity of the reactive excited state but it follows that the rate of hydrogen transfer must be very fast ($k \gtrsim 10^9\ s^{-1}$).

As indicated in *Scheme 1*, the rate-determining step of the reaction **2** → **3** in glacial acetic acid appears to be the protonation of **2** since addition of sodium acetate does not influence the lifetime of **2** whereas traces of mineral acid quench **2** without affecting the overall reaction **1** → **3**. Only in HMPA solution is the lifetime of **2** sufficient to be markedly reduced when air oxygen is admitted (τ = 90 ms and 25 ms in degassed and aerated HMPA, respectively). The lifetime of **2** in HMPA decreases with increasing concentrations of **1** present suggesting the occurrence of an addition reaction between **2** and **1** with a rate of *ca.* $1000\,M^{-1}\,s^{-1}$. The bimolecular rate constant for the quenching of **2** by maleic anhydride was determined to be *ca.* $2000\,M^{-1}\,s^{-1}$ in HMPA or acetonitrile solution. We cannot, however, be certain that the observed quenching rates correspond to chemical consumption of **2** by the added dienophiles since preparative irradiations and product analyses were not attempted.

Discussion. – The photoenolization of aromatic ketones such as *ortho*-methyl aceto- or benzophenones has been thoroughly studied [4] but the results obtained by different workers are partly conflicting and details of the reaction mechanism are still a matter of debate [5] [6]. The rigid molecular framework of **1** eliminates one complicating feature, namely the conformational degree of freedom of the carbonyl group. *Sammes et al.* [4] [7] maintain the hypothesis that photoenolization by [1.5]-hydrogen-shift yields uniquely the (*E*)-dienol isomer and that 'ketones which cannot form (*E*)-photoenols for steric reasons do not form (*Z*)-photoenols.' The highly efficient photoreaction **1** → **2** provides an example to the contrary.

Our findings with the single compound **1** obviously do not warrant the conclusion that (*Z*)-dienols are formed in general from *ortho*-alkyl substituted aromatic ketones



such as those investigated by *Sammes et al.* If, for the sake of argument, we nevertheless assume that the data obtained with **1** are applicable *e.g.* to the related 5,8-dimethyl-1-tetralone we predict a quantum yield of less than 10^{-5} for the trapping of the corresponding enol by *Diels-Alder* addition under the conditions used in [7] (0.06 M dimethyl butynedioate in benzene solution). It is thus not surprising that the starting material is in fact consumed by a more efficient 'side reaction' and the absence of adduct formation does not exclude the occurrence of the (*Z*)-dienol. The strong dependence of the retautomerization rate $k(\mathbf{2} \rightarrow \mathbf{1})$ on the hydrogen-bond-acceptor basicity [2] of the solvent may prove to be a useful general criterion for the identification of transient (*Z*)-dienols by flash photolysis and suggests the use of highly polar aprotic solvents such as HMPA and more reactive dienophiles for attempts to trap (*Z*)-dienols by *Diels-Alder* addition.

Experimental Part. – UV./VIS. absorption spectra were recorded on a *Cary* 14 spectrophotometer equipped with a temperature-controlled quartz dewar as a sample holder for the low-temperature work (λ_{max} in nm, ε in parenthesis; λ_{min} especially mentioned). NMR. spectra were obtained with a *Varian* HA-100D spectrometer (chemical shifts are given as δ in ppm, coupling constants in Hz). Quantum yields were determined spectrophotometrically for conversions of $<20\%$ in dilute solutions ($c \cong 2 \cdot 10^4$ M) using the split-beam apparatus described earlier [8]. Quoted error limits are 90% confidence ranges but do not include possible systematic errors. The kinetic flash photolysis equipment was of conventional design [9]. The quantum yield for the formation of the enol **2** in various solvents was estimated from flash photolysis data as follows: The concentration of **2** immediately after the flash was obtained from the initial absorbance at 560 nm and the molar absorptivity ε (**2**, 560 nm) $\cong 8500\,M^{-1}\,cm^{-1}$ (Fig. 1). The light absorbed by **1** during the flash was determined from the permanent photochemical conversion $\mathbf{1} \rightarrow \mathbf{3}$ produced by the flash on a solution of **1** in acetic acid assuming that the quantum yield determined with 365 nm light is applicable to 'white' light in the range of 330 to 400 nm.

PPP SCF CI calculations [10] for **2** were carried out assuming an idealized geometry (bond lengths 1.4 Å, bond angles 120°) using the following standard set of parameters: Valence state ionization potential $I_\mu \equiv 0$ eV (-21.48 and -2.18 eV for –OH and =O, resp.), one-center repulsion integral $\gamma_{\mu\mu} = 10.84$ eV (22.9 and 11.3 for –OH and =O, resp.), core resonance integral $\beta_{\mu\nu} = -2.318$ eV, core charge $Z^c = 1$ (2 for –OH), two-center repulsion integrals $\gamma_{\mu\nu} = 14.395/(1.328 + R_{\mu\nu})$ eV. All 42 singly excited configurations were included for CI.

5-Methyl-1,4-naphthoquinone (**1**). The preparation, purification and properties of **1** have been described [1]. – ^{1}H-NMR. (in $CDCl_3$, internal TMS.): 2.77 (*s*, 3H); 6.92 (*s*, 2H); 7.5 to 7.7 (*m*, 2H); 8.03 (*q*, $^3J = 7$, $^4J = 3$, 1H). – MS. (*m/e* (relative intensity)): 172 (*100*), 144 (20), 118 (25), 116 (31), 115 (32), 90 (15); broad peaks for metastable ions corresponding to 172-28, 144-28, 118-28.

Photolytic preparation of 5-(acetoxymethyl)-1,4-naphthalenediol (**3**). A de-aerated solution of 50 mg **1** in acetonitrile/glacial acetic acid 9:1 was irradiated through a UV. cut-off filter with light from an *Osram* HBO 200 W super pressure mercury arc. The absorption of **1** at wavelengths greater than 385 nm was by then reduced by more than 90% indicating virtually complete conversion to the photoproduct **3** whose absorption spectrum ($\lambda < 385$ nm, log ε calculated from log ε (**1**, 348 nm) = 3.53 assuming 100% conversion) was closely similar to that of 1,4-naphthalenediol (**6**)[3]).

[3]) The spectrum of **6** given in [11] was apparently obtained with a sample contaminated by nearly 50% 1,4-naphthoquinone. In our hands a purified sample of **6** gave the following UV. spectral data in acetonitrile solution: 336 (3.77), 324 (3.77), 312 sh. (3.69); λ_{min} 264 (2.67) in good agreement with a spectrum published earlier [12].

342 (3.83), 329 (3.83), 318 sh. (3.77); isosbestic points **1**/**3** at 352 (3.53) and 268 (3.09). An ^{1}H-NMR. spectrum of **3** was obtained by evaporating a photolysed solution to dryness and redissolving the residue in de-aerated acetonitrile-d_3 containing 5% TMS.: 2.06 (*s*, 3H); 2.5 (br., shifted by acid); 5.74 (*s*, 2H); 6.72 (*s*, 2H); 7.4 to 8.6 (*m*, *ca.* 3H). The isolation of **3** as a pure compound was not attempted due to its lability towards air oxidation and charring in conc. solution. Air oxydation in dilute solution (accelerated by the addition of Pd/C) yielded 5-(acetoxymethyl)-1,4-naphthoquinone (**4**) identical with the sample prepared by the method described below.

5-(Bromomethyl)-1,4-naphthoquinone (**5**). A suspension of 6.5 g *N*-bromosuccinimide in a solution of 6 g **1** in 160 ml of carbon tetrachloride was heated under reflux and treated with a trace of dibenzoyl peroxide every 15 min. After 2 h the hot mixture was filtered. Upon cooling, the raw product crystallized from the filtrate. Recrystallization from isooctane gave 6.5 g bright yellow **5**, m.p. *ca.* 145° (dec., slow dec. above 120°). – UV. (acetonitrile): 342 (3.43), 242 (4.31). – ^{1}H-NMR. ($CDCl_3$, internal TMS.): 5.15 (*s*, 2H); 6.98 (*s*, 2H); 7.6 to 7.9 (*m*, 2H); 8.16 (*q*, ^3J = 6, ^4J = 2, 1H). – MS. (*m/e* (relative intensity)): 252 and 250 (15 each), 171 (*100*), 115 (55).

5-(Acetoxymethyl)-1,4-naphthoquinone (**4**). A solution of 0.5 g **5** and 0.5 g silver tetrafluoroborate in 100 ml glacial acetic acid was stirred for 2 h at RT. The resulting dark green mixture was diluted with water and extracted with methylene chloride. The organic layer was washed until neutral, dried and evaporated to give a tarry residue which was extracted with several small portions of isooctane. The soluble extract was chromatographed on silica with carbon tetrachloride/acetonitrile 9:1. The product (**4**, 50 mg) was eluted second after the remaining starting material **5** and recrystallized from isooctane. M.p. 88°. – UV. (acetonitrile): 337 (3.48), 247 nm (4.28). – ^{1}H-NMR. ($CDCl_3$, internal TMS): 2.22 (*s*, 3H); 5.71 (*s*, 2H); 6.95 (*s*, 2H); 7.6 to 7.9 (*m*, 2H); 8.13 (*q*, ^3J = 7, ^4J = 2, 1H).

$C_{13}H_{10}O_4$ (230.22) Calc. C 67.82 H 4.38 O 27.80% Found C 67.55 H 4.42 O 27.61%

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