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143. Primary Photophysical and Photochemical Processes in the Photoreduction of a Naphthoquinone methide: 2-Phenylnaphtho[1,8-*bc*]furan-5-one

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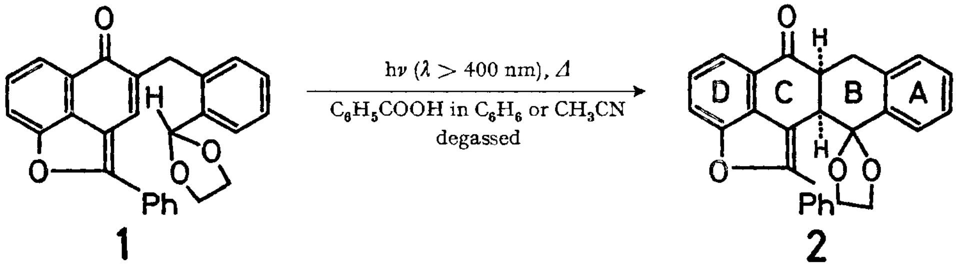
(3. IV. 74)

Summary. The photochemical reactivity of the title compound **3** was studied in the context of a novel acid catalysed photocyclisation reaction recently discovered by *Barton et al.* [1b]. The following results were obtained by flash photolysis methods and steady state irradiations in the presence and absence of quenchers and sensitisers combined with luminescence measurements: The fluorescence of **3** in benzene is very weak and short-lived ($\phi_{Fl} \leq 10^{-4}$, $\tau_{Fl} \leq 10^{-9}$ s) due to efficient intersystem crossing ($\phi_T = 0.8 \pm 0.15$). On the other hand, the conjugate acid **4** exhibits an intense green fluorescence ($\phi_{Fl} = 0.9_7 \pm 0.1$) with a lifetime of $(4. \pm 1.) \cdot 10^{-9}$ s. Acidity constants of **4** in the ground and first excited triplet state were estimated in acetic/trifluoroacetic acid mixtures by comparison with *Hammett* indicators: $pK(S_0) = -0.3$, $pK(T_1) = +1$.

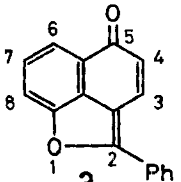
The *Förster* cycle yields $pK(S_1) = +6$, however, adiabatic protonation of S_1 (**3**) to produce fluorescent **4** is not efficient. The lowest $\pi\pi^*$ triplet state of **3** ($E_T = 45 \pm 1$ kcal/mol, ${}^3\tau = 8 \cdot 10^{-4}$s in dilute, degassed benzene solution) is an intermediate in the photoreduction of **3** by oxidisable substrates. Hydrogen abstraction from 2-propanol by T_1 (**3**) yields the semiquinone methide radical **5** which dimerises to **6**. On readmission of air after irradiation, **6** is reoxidised to the starting material **3**. Predictions derived from PPP SCF CI calculations are in accord with the observed spectroscopic and photochemical properties of **3**.

In the course of their experiments on the synthesis of tetracycline *Barton et al.* [1a] have achieved the cyclisation of ring B [1b] by irradiation of the ethylene acetal of 4-(2-formylbenzyl)-2-phenyl-naphtho[1,8-bc]furan-5-one **1** in the presence of benzoic acid.

Scheme 1



The kinetics of the photophysical decay and the photochemical reactivity of the parent chromophore **3** and its conjugate acid **4** have now been investigated to provide a starting point for the elucidation of the mechanism of the photocyclisation (*Scheme 1*).



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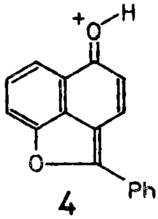

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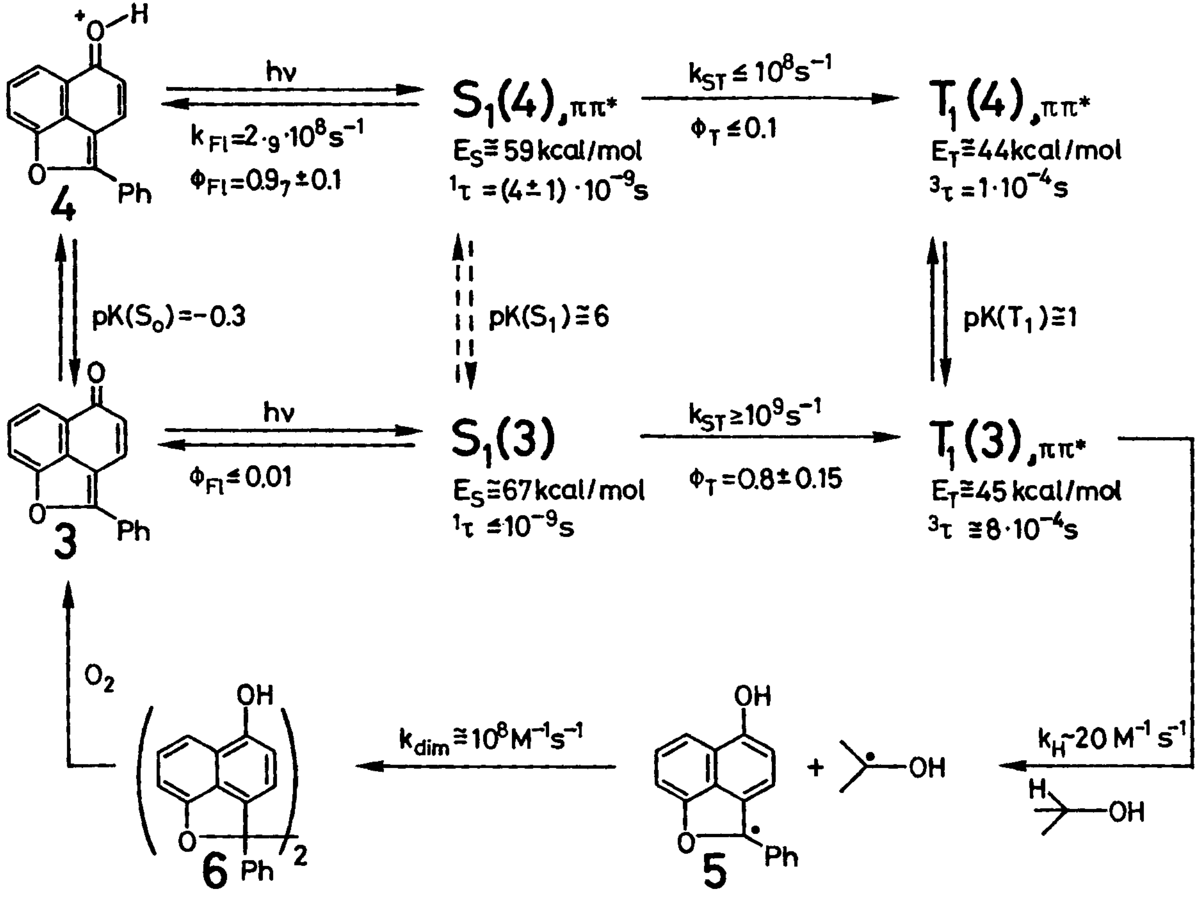
In a recent paper *Barton et al.* [1a] have shown that this type of photocyclisation is open to considerable structural variation. The authors suggest that it will be of general synthetic utility in the creation of linear carbocyclic structures that would otherwise require circuitous procedures. A detailed knowledge of the mechanism of this novel photoreaction is, therefore, of practical importance.

1. Results. – *Scheme 2* summarises the results of the present investigation. Details are given in the following Sections.

1.1. *UV./Vis. Spectra, MO Calculations.* The absorption spectra of the naphthofuranone **3** and its conjugate acid **4** are shown in Fig. 1. The position of the first absorption band of **3** is not sensitive to solvent polarity but is shifted to the red in protic solvents (λ_{max} 390, 390, 397, and 403 nm in benzene, acetonitrile, ethanol, and glacial acetic acid, respectively). In trifluoroacetic acid or concentrated sulfuric acid compound **3** is protonated at the carbonyl oxygen (NMR.: τ 1.0 and 2.4 – [AB quartet, J_{AB} 9 Hz] in CF_3COOD *vs.* ext. TMS).

The position and intensity of the first absorption bands of **3** and **4** are reproduced quite well by π-electron PPP SCF CI calculations (Fig. 1). The semiempirical parameters used (Table 1) were adopted from recent studies of related compounds [2]. Within the framework of configuration interaction the lowest $\pi\pi^*$ excited singlet

Scheme 2. Photodynamics of **3** in degassed solutions. Solvents: CH_3CN/H_2SO_4 (top line), CF_3COOH/CH_3COOH (p*K*-values), C_6H_6 (middle line), $(CH_3)_2CHOH$ (bottom line).



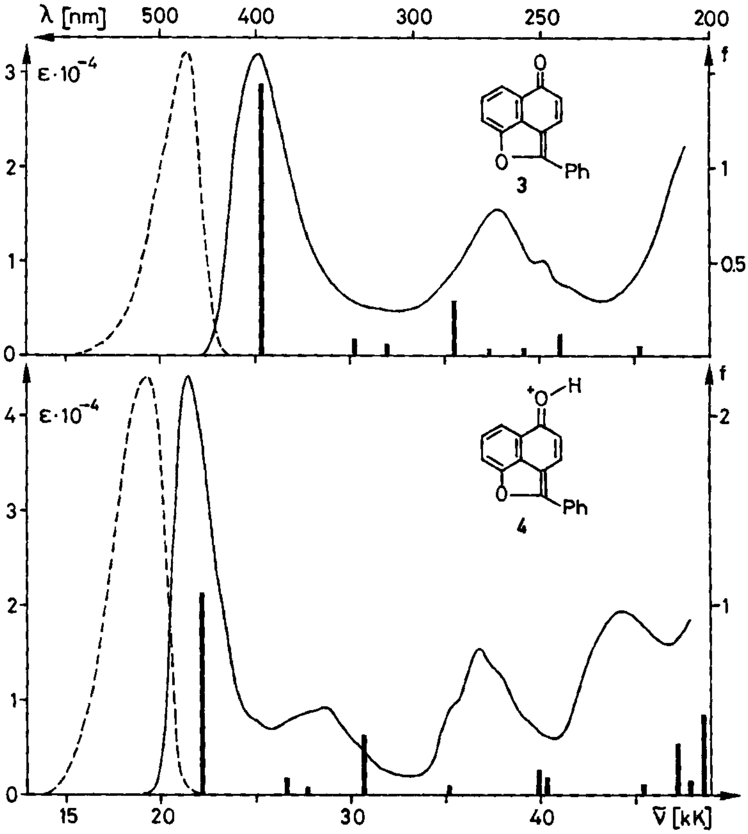


Fig. 1. *Absorption* (———) *and corrected fluorescence* (– – –) *spectra of* **3** (in ethanol) *and* **4** (in 5% H_2SO_4/acetonitrile). $\pi\pi^*$ transitions predicted by the PPP calculation are indicated by vertical bars (oscillator strength f on right-hand scale).

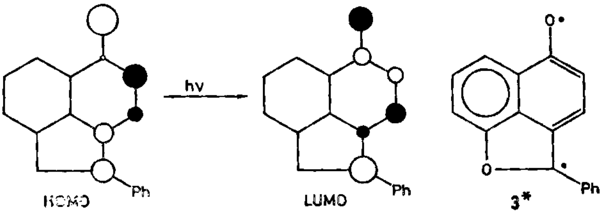
Table 1. *Semiempirical Parameters of the SCF Calculation*

Group	Atom μ	I_μ, eV	$\gamma_{\mu\mu}$, eV	$\beta_{C\mu}$, eV	Z_μ	$r_{C\mu}$, Å
	C	11.22	10.98	−2.39	1	1.40
C=O	O	16.1	14.00	−2.30	1	1.23
$C{=}\overset{+}{O}H$	O	34.3	23.00	−2.10	2	1.40
C—OC	O	34.3	23.00	−2.10	2	1.40

I_μ = Valence state ionisation potential.
$\gamma_{\mu\mu}$ = One-center electron repulsion integral.
$\beta_{C\mu}$ = Core resonance integral.
Z_μ = Number of π-electrons taking part in conjugation.
$r_{C\mu}$ = Bond lengths; idealised geometries (all atoms in plane, bond angles in six-membered rings 120°).

Two center electron repulsion integrals $\gamma_{\mu\nu}$ calculated by the *Mataga* approximation [3].
42 singly excited configurations included for CI.

and triplet states of both **3** and **4** are well described ($\geq 80\%$) by the lowest excited configuration corresponding to the HOMO → LUMO transition. These states are thus labeled ^1L_a and ^3L_a respectively. The HOMO (*h*ighest *o*ccupied *m*olecular *o*rbital) and the LUMO (*l*owest *u*noccupied *m*olecular *o*rbital) of **3** obtained by the SCF calculation are both essentially localised (70%) on the dienone part of the chromophore as shown in the diagram below. The excited resonance structure **3*** may thus be



regarded as a suggestive but by no means exhaustive description of the lowest $\pi\pi^*$ excited singlet and triplet state of **3**. The dipole moments calculated for **3** in the S_0 and ^1L_a states differ by only 1 Debye, hence the small effect of solvent polarity. The charge density on the carbonyl oxygen is virtually identical in the two states. Yet, when the hydrogen bonding of protic solvents is simulated in the calculation by increasing the ionisation potential I_μ of the carbonyl oxygen a red shift of the ^1L_a band is correctly predicted. In the ^3L_a state the carbonyl oxygen carries a partial charge of $+0.2$ with reference to the ground state.

An $n\pi^*$ transition is not discernible in the absorption spectrum of **3** and the strong absorption band at 400 nm is clearly due to the allowed $S_0 \rightarrow {}^1L_a$ transition. Nevertheless, the possible presence of a nearly degenerate $n\pi^*$ excited singlet state needs to be considered (*cf.* Sect. 1.3.).

1.2. *Acidity of* **4** *in the Electronic Ground State.* The acid **4** is insensitive to oxygen but decomposes rapidly in the presence of water or alcohol. In order to estimate the acidity constant of **4** an approximate acidity function H_0 was constructed for trifluoroacetic/acetic acid solvent mixtures using the *Hammett* indicators [4] *p*-nitroaniline, *o*-nitroaniline, and 4-chloro-2-nitroaniline. The ratio I of the concentration of the acid form of the indicators to that of the base form was measured spectrophotometrically as a function of solvent composition. Plots of log I against percent trifluoroacetic acid are shown in Fig. 2. It is seen that the differences in the log I values between successive indicators are not quite constant within the regions of overlap. Yet, the mean differences in log I values within the overlap regions of 1.4 and 0.7 agree rather well with the values 1.28 and 0.74 obtained in aequeous sulfuric acid [4]. The log I values determined for **3** (filled circles, Fig. 2) yield an estimate of $pK = -0.3$, *i.e.* the acidity of **4** and *o*-nitroanilinium ion are identical within the limits of error in the trifluoroacetic/acetic acid solvent system.

1.3. *Fluorescence Spectra, Quantum Yields, and Lifetimes.* The corrected fluorescence spectra of the naphthofuranone **3** in ethanol and its conjugate acid **4** in acetonitrile containing 5% sulfuric acid are given in Fig. 1. The corresponding excitation spectra (uncorrected) were in satisfactory agreement with the absorption spectra.

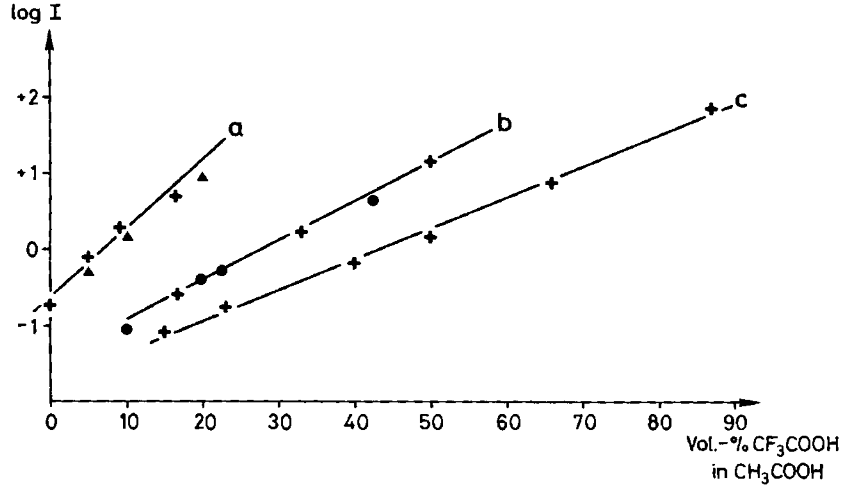


Fig. 2. *Acidity of nonaqueous trifluoroacetic/acetic acid mixtures.* Values of log I (I = ratio of acid form to base form) of three *Hammett*-indicators (+) and of the naphthofuranone **3** in its ground (●) and lowest triplet (▲) state. (a) *p*-nitroaniline (pK = 0.99 [4]), (b) *o*-nitroaniline (pK = – 0.29 [4]), (c) 4-chloro-2-nitroaniline (pK = – 1.03 [4]).

Fluorescence quantum yields were determined at room temperature by comparison of the sample fluorescence intensity with that of fluorescein and quinine sulfate as quantum yield standards (Eq. 1).

$$\phi_{\mathrm{Fl}}\,(\mathrm{sample}) = \frac{\mathrm{I\,(sample)} \cdot \mathrm{D\,(ref.)}}{\mathrm{I\,(ref.)} \cdot \mathrm{D\,(sample)}} \cdot \frac{\mathrm{n_D^2\,(sample)}}{\mathrm{n_D^2\,(ref.)}} \cdot \phi_{\mathrm{Fl}}\,(\mathrm{ref.}) \qquad (1)$$

I = integrated fluorescence intensity using corrected spectra
D = optical density at exciting wavelength
n_D = index of refraction for sodium light.

The fluorescence quantum yield of **4**, $\phi_{\mathrm{Fl}} = 0.9_7 \pm 0.1$, was measured with $1 \cdot 10^{-6}$ M solutions of **4** in acetonitrile containing 5% sulfuric acid ($n_D = 1.354$) using 436 nm excitation and $3 \cdot 10^{-6}$ M fluorescein in 0.1 N sodium hydroxide as a standard (ϕ_{Fl} = 0.90 [5]). It is not sensitive to oxygen or acid concentration. The quantum yield of the parent naphthofuranone **3** is strongly solvent dependent but always much lower than that of **4**. In cyclohexane solution the emission was below the detection limit of the fluorescence spectrophotometer. Quantum yields of **3** in benzene (with or without 10^{-3} M benzoic acid), ethanol, and water for 405 nm excitation were obtained as $\leq 10^{-4}$, $(5 \pm 2) \cdot 10^{-3}$, and 0.21 ± 0.03, respectively, by reference to the fluorescein standard. Fluorescence enhancement in polar solvents is a well known phenomenon with aromatic compounds possessing low lying $n\pi^*$ excited states and a number of explanations have been offered [6] [7]. The $\sim 10^4$ fold increase in ϕ_{Fl} (**3**) is presumably due to a near degeneracy of the lowest $n\pi^*$ and $\pi\pi^*$ excited singlet states of **3** which is lifted in highly polar protic solvents.

The fluorescence rates, k_{Fl} (**3**) $= 4._0 \cdot 10^8 s^{-1}$ and k_{Fl} (**4**) $= 2._9 \cdot 10^8 s^{-1}$, were estimated by graphical integration of the ^1L_a absorption band according to the simple formula [8]

$$k_{Fl} = 2.9 \cdot 10^{-9}\, n_D^2\, \tilde{\nu}_0^2 \int_{^1L_a} \varepsilon(\tilde{\nu})\, d\tilde{\nu} \qquad (2)$$

where $\tilde{\nu}_0$ is the wavenumber in cm^{-1} of the maximum of the absorption band. However, the value for k_{Fl} (**3**) will be much too high if the lowest excited singlet state S_1 (**3**) is $n\pi^*$ in character or a mixed state of nonplanar geometry.

The fluorescence lifetime of **4** in acetonitrile containing 5% sulfuric acid was measured at room temperature by the single photon counting technique¹): τ_{Fl} (**4**) $= (4 \pm 1) \cdot 10^{-9}$s. This value agrees, within the limits of error, with the calculated value, τ_{Fl} (**4**) $= 3._4 \cdot 10^{-9}$s, obtained from the relation

$$\tau_{Fl} = \phi_{Fl}/k_{Fl}. \qquad (3)$$

The fluorescence lifetime of **3** was too short-lived to be measured directly ($\leq 10^{-9}$s). Application of Eq. 3 to compound **3** (benzene solution) yields an estimate of $\tau_{Fl} \leq 2.5 \cdot 10^{-13}$s. Since the triplet yield of **3** in benzene is near unity (Sect. 1.8.) this implies an enormous rate of intersystem crossing, $k_{ST} \geq 4 \cdot 10^{12} s^{-1}$. It appears that k_{Fl} (**3**), which was calculated assuming $S_1 = {}^1L_a$, is too high and that the lowest excited singlet state of **3** cannot be adequately described when the existence of an $n\pi^*$ excited state is ignored.

1.4. *Acidity of* **4** *in the Lowest Excited Singlet State.* The acidity constant in the state S_1 was estimated on the basis of the *Förster* cycle [9]:

$$pK(S_1) = pK(S_0) - \frac{0.625}{T}\left[\tilde{\nu}_{0-0}(4) - \tilde{\nu}_{0-0}(3)\right],\ [\tilde{\nu}] = cm^{-1}. \qquad (4)$$

The energies of the 0–0 transitions, $\tilde{\nu}_{0-0}$, were taken as the arithmetic mean of the positions of the absorption and fluorescence maxima. These values – transformed to kcal/mol – are given in *Scheme 2* as singlet state energies, E_S, of **3** and **4**, respectively. Eq. 4 yields a p*K* value of *ca.* +6 for the first excited singlet state of **4**. However, the short lifetime of S_1 (**3**) effectively prevents the establishment of this hypothetical equilibrium. If adiabatic protonation of **3** did occur to a significant extent in mildly acidic solutions this process could easily be detected by the fluorescent emission from S_1 (**4**), λ_{max} 490 nm. The fluorescence spectrum of **3** in glacial acetic acid exhibits a shoulder at 490 nm which disappears upon dilution with ethanol. Addition of chloroacetic acid to a glacial acetic acid solution of **3** affords a strong increase in the fluorescence intensity at 490 nm only when the acidity becomes high enough to protonate **3** in the ground state. It is concluded that adiabatic protonation of S_1 (**3**) is inefficient in dilute solutions of weak acids and occurs to an extent of less than 1% in glacial acetic acid although the basicity of **3** in its first excited singlet state should be greater than that of pyridine in the ground state.

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¹) The author is grateful to Dr. *G. S. Beddard*, The Royal Institution, for the performance of these measurements.

1.5. *Phosphorescence.* The naphthofuranone **3** gave rise to an unstructured phosphorescent emission above 620 nm (λ_{max} 653 nm, uncorr.) with a half-life of *ca.* 20 ms in diethyl ether glass at 77° K. The emission maximum was not shifted significantly upon changing the matrix polarity from hydrocarbon to ethanol glass. In polymethylmethacrylate (PMMA) glass the phosphorescence was observable at room temperature with a lifetime of $(4.3 \pm 0.2) \cdot 10^{-3}$s. The excitation spectra (uncorr.) did not indicate the presence of a phosphorescent impurity. In the absence of a well-defined high energy emission maximum, the 0–0 transition was taken to lie in the range of 620 to 655 nm corresponding to a triplet energy $E_T = 45 \pm 1$ kcal/mol. The singlet-triplet splitting, $E_S - E_T$, then amounts to *ca.* 22 kcal/mol or 7700 cm^{-1}. Since the singlet-triplet splitting for $n\pi^*$ excited states of aromatic ketones is generally less than 3000 cm^{-1} the $n\pi^*$ excited triplet state of **3** is expected to lie at least 10 kcal/mol above the ^3L_a state T_1 (**3**).

With hydrocarbon solvents containing **3** an intense, shortlived emission (λ_{max} 510 nm) in addition to the phosphorescence appeared on freezing which was accompanied by a red shift in the absorption spectrum. From ethanol glass no such emission was observed and with diethyl ether as solvent it appeared only when the solution was cooled down slowly. This phenomenon is attributed to aggregation of solute molecules.

No phosphorescence was detected from the conjugate acid **4** dissolved in phosphoric acid glass.

1.6. *Flash Photolysis, Acidity of* **4** *in the Lowest Triplet State.* Spectrographic flash photolysis of 10^{-5}M solutions of **3** in degassed benzene, acetonitrile, or acetic acid yielded an intense, structureless absorption in the visible (λ_{max} 490 nm) which decayed within a few ms. The transient absorption observed after flash photolysis of the conjugate acid **4** in acetonitrile containing 5% sulfuric acid was much weaker and shifted to the red (λ_{max} 580 nm). These transients (Fig. 3) are assigned to the lowest triplet state T_1 of **3** and **4**, respectively, based on the observations outlined below.

The risetime of the absorptions by T_1 (**3**) and T_1 (**4**) did not exceed the duration of a Q-switched, frequency doubled ruby laser photolysis flash, *i.e.* the transients are formed within a time period of less than 10^{-8}s after excitation. The decay of T_1 (**3**) was monitored photoelectrically at several wavelengths on an apparatus equipped with conventional photolysis flash lamps. Below 420 nm the transmittance of the solutions was found to increase during the photolysis flash due to ground state depopulation (*cf.* Fig. 3). In PMMA glass doped with $2 \cdot 10^{-5}$M **3** both the buildup of the original ground state absorption (≤ 420 nm) and the decay of the transient absorption (≥ 420 nm) were strictly first order with a lifetime of $(4.3 \pm 0.1) \cdot 10^{-3}$s. Since the phosphorescence lifetime of the same sample measured under identical conditions was also $4.3 \cdot 10^{-3}$s (Sect. 1.5.), this strongly supports the assignment of the transient absorption to the lowest triplet state of **3**. In deaerated benzene solutions the decay of T_1 (**3**) initially followed second order kinetics when high flash intensities were used. A second order decay rate $k_{TT} = (6 \pm 2) \cdot 10^9$M^{-1}s^{-1} was obtained with a $3 \cdot 10^{-5}$M benzene solution of **3** using the extinction coefficient determined on the chopped beam apparatus (Sect. 1.7.). This near diffusion controlled second order decay process is attributed to triplet-triplet annihilation and should be unimportant under steady state irradiation conditions. The first-order decay rate at low concentrations of T_1 (**3**) was strongly dependent on solvent purity. A number of purification methods for benzene were tried (Exp. Sect.). The longest triplet lifetime, $^3\tau = (7.6 \pm 0.8) \cdot 10^{-4}$s (Sect. 1.7.), was obtained when the solvent was pre-irradiated in the presence of **3** and distilled before the measurement.

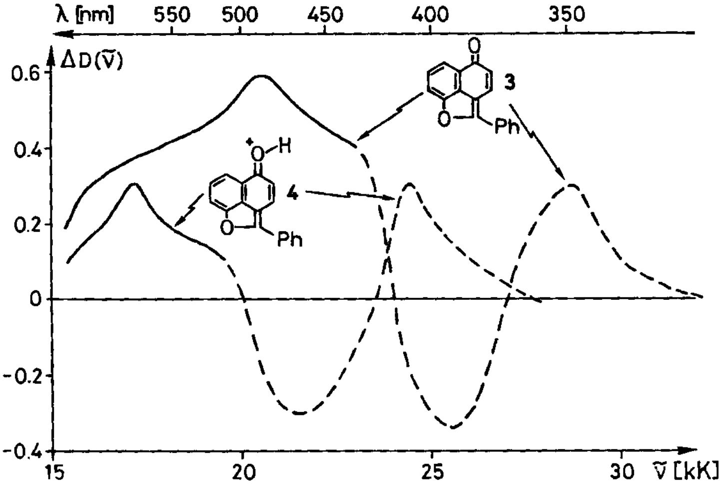

Fig. 3. *Triplet state* (T_1) *absorption spectra of* **3** *in benzene and* **4** *in acetonitrile/5% sulfuric acid taken at a delay of* 10^{-5}*s after the peak of the photolytic flash.* The relative change in optical density, $\Delta D(\tilde{\nu})$, is proportional to the difference of the extinction coefficients, $\varepsilon_{T_1} - \varepsilon_{S_0}$. The broken line (---) is used in the regions of overlap with the ground state (S_0) absorption spectra.

Near diffusion controlled quenching rates of T_1 (**3**) were observed with the following additives in benzene solution: oxygen ($E_S = 23$ kcal/mol [10]), azulene ($E_T = 34 \pm 5$ kcal/mol [11]), and anthracene ($E_T = 42$ kcal/mol [10]). The build-up of the characteristic triplet absorption of anthracene [12] after excitation of **3** was monitored at 430 nm and matched the first order decay of T_1 (**3**) as observed at 500 nm thus establishing energy transfer as a quenching mechanism. Naphthalene ($E_T = 61$ kcal/mol [10]), *cis*-piperylene ($E_T \cong 53$ kcal/mol [13]), and pyrene ($E_T = 48$ kcal/mol [10]) did not affect the decay rate of T_1 (**3**) appreciably at concentrations up to 10^{-4}M in benzene solution. This allows to bracket the excitation energy of T_1 (**3**) between 42 and 48 kcal/mol in further support of its assignment to the phosphorescent triplet state of **3**, $E_T = 45 \pm 1$ kcal/mol.

Sensitisation of **3** to form T_1 (**3**) by energy transfer was also directly observed by flash photolysis ($\lambda_{exc} > 430$ nm) of a $2 \cdot 10^{-4}$M benzene solution of **3** containing 10^{-3}M ethyl 1-thionaphthoate. The latter compound provides a convenient sensitiser for excitation in the visible ($n\pi^*$ absorption up to 480 nm) due to its small singlet-triplet splitting and low photochemical reactivity ($E_T \cong 56$ kcal/mol, $^3\tau^0 = 10^{-6}$s) [14].

The equilibrium T_1 (**3**) + $H^+ \rightleftharpoons T_1$ (**4**) was studied in trifluoroacetic/acetic acid solvent mixtures by the method of *Jackson & Porter* [15]. Protonation of T_1 (**3**), as observed by the relative intensities of the transient absorptions at 490 and 580 nm, took place in the 2 to 15% trifluoroacetic acid concentration range (Fig. 2). In 7% trifluoroacetic acid both T_1 and the *Hammett* indicator *p*-nitroaniline ($pK^{00} = +0.99$) [4] were found to be about half-protonated, assuming ε [T_1 (**3**), 490 nm] $\simeq$ ε [T_1 (**4**), 580 nm]. This yields an estimate of $pK(T_1) \simeq +1$ for the acidity and $E_T = 44 \pm 2$ kcal/mol for the excitation energy of **4** in the lowest triplet state.

1.7. *Triplet Quantum Yield Determination.* The extinction coefficient of T_1 (**3**) at 490 nm and the quantum yield of intersystem crossing ϕ_T (**3**) were measured[2] on a chopped beam apparatus constructed and described in detail by *Heinzelmann* & *Labhart* [16]. The method consists of measuring the small changes in optical density resulting from intermittent cross-illumination of the sample. $1.0 \cdot 10^{-5}$M solutions of **3** in degassed benzene (purified by preirradiation, Exp. Sect.) were used. Under these conditions second-order decay by triplet-triplet annihilation was found to be unimportant. The following results were obtained: ϕ_T (**3**) $= 0.8 \pm 0.15$, ${}^3\tau$ (**3**) $= (7.6 \pm 0.8) \cdot 10^{-4}$s, ε [T_1 (**3**), 490 nm] $= (1.8 \pm 0.3) \cdot 10^4 \text{M}^{-1}\,\text{cm}^{-1}$.

1.8. *Photoreduction of* **3** *by 2-Propanol.* In the absence of hydrogen or electron donators the naphthofuranone **3** is rather stable to irradiation. Measurements of the

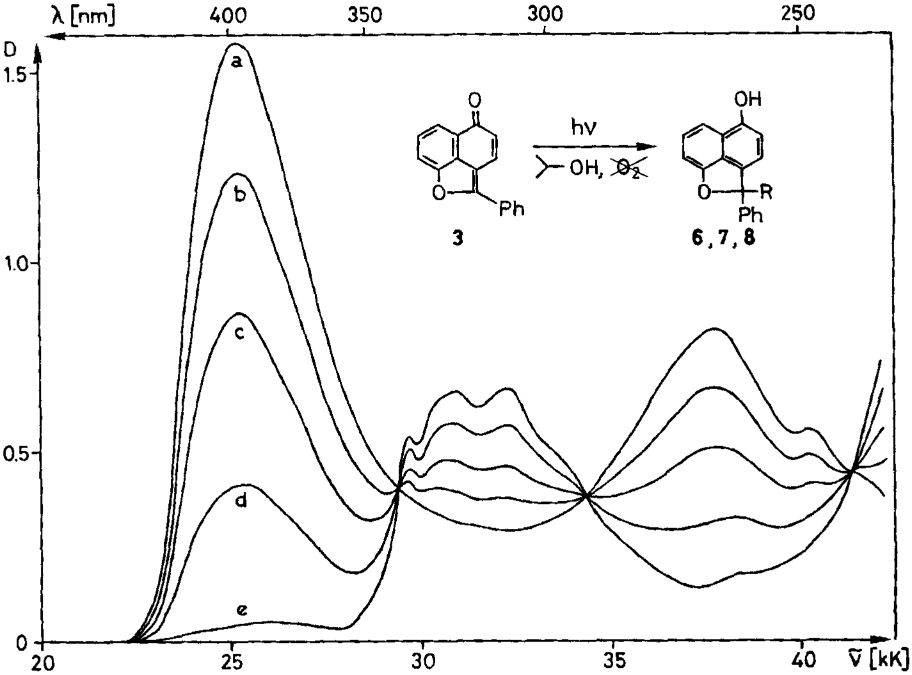

Fig. 4. *Photoreduction of* **3** *in 2-propanol* by irradiation at 405 nm in a deaerated optical quartz cell. Spectra were taken after the following irradiation times: (a) 0, (b) 45, (c) 60, (d) 90, and (e) 180 s.

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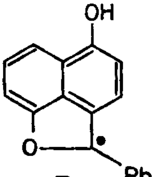
[2] The author is very grateful to Mr. *E. Wäckerlin*, Institute of Physical Chemistry, University of Zürich, for the careful performance of these measurements.

quantum yield of disappearance of **3** in degassed benzene were badly reproducible but always yielded values below 10^{-2}. The UV./Vis. spectral changes during continuous 405 nm irradiation of a $5 \cdot 10^{-5}$ M solution of **3** in deaerated 2-propanol are shown in Fig. 4. Readmission of oxygen to the irradiated solution resulted in nearly quantitative restoration of the original spectrum of **3** within a few days. The appearance of a new shoulder at 345 nm indicated that small amounts of side product(s) were also formed. The main product isolated from preparative runs after reoxidation of the photo-product was shown to be identical with the starting material **3** (mixed m.p., UV., NMR., IR., MS.). An air-sensitive white powder was isolated from the irradiated reaction mixture by fractional crystallisation and column chromatography under anaerobic conditions. It was characterised as the dimer **6** of the semiquinone methide radical **5** on the basis of spectral data and molecular weight determinations (Exp. Part). The possible presence of other compounds with the same chromophore (**7** or **8**) in the photolysed solution before work-up is not excluded.



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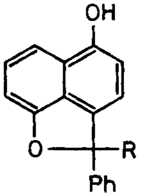
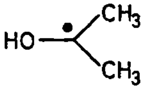


6,7,8,9

6: R = 5
7: R = H
8: R = 10
9: R = OH

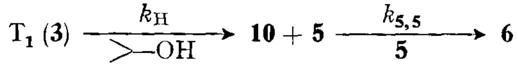


10

With solutions of **3** in purified benzene or in PMMA glass the lowest triplet state T_1 (**3**) was the only transient species observed by flash photolysis. Addition of up to 10^{-2} M benzoic acid to the benzene solutions had no effect. In unpurified benzene and in solutions to which oxidisable substrates such as 2-propanol, benzyl alcohol, or *p*-methoxytoluene had been deliberately added a second transient was formed from T_1 (**3**). The assignment of this transient species to the semiquinone methide radical **5** appears as an obvious interpretation which is to be justified by the following observations. The kinetics of formation of **5** were monitored at the isosbestic point of T_1 (**3**) and **3** (λ 417 nm, Fig. 3) where the absorption remained constant during the photolysis flash. At this wavelength **5** absorbed more strongly than both **3** and T_1 (**3**). The absorption by **5** was evident only up to about 450 nm allowing for a measurement of the triplet decay at 490 nm without interference by **5**. The formation of **5** was found to be a reaction first order in T_1 (**3**), the build-up rate of **5** matching the decay rate of T_1 (**3**) under a variety of conditions. The yield of **5** increased with increasing concentration of the added substrate. High yields of **5** were obtained with compounds containing C–H bonds of low dissociation energies. A reduction of the triplet state lifetime by oxygen quenching resulted in a proportional diminution of the amount of **5** formed. On a ms timescale the transient **5** decayed by a reaction appearing second order in **5** to a photoproduct which did not absorb above 360 nm as evidenced by irreversible photobleaching of the solutions in which **5** was formed.

Clearly, the above results from flash photolysis complement the observations from continuous irradiations. It is seen that **5** derives from a bimolecular reaction, presumably hydrogen abstraction, between T_1 (**3**) and the added substrates (*e.g.* 2-propanol, *Scheme 3*). The rôle of the ketyl radical **10** has so far been ignored. Although **10** has an absorption spectrum extending up to *ca.* 450 nm it is not expected to contribute significantly to the total absorption monitored at 417 nm, its molar extinction coefficient ε_{417} amounting to *ca.* 100 M^{-1} cm^{-1} [17], at least two orders of magnitude less than that of **5**. It will, however, affect the decay kinetics of **5** if it can effectively compete with the dimerisation of **5** to form the products **7** and/or **8**. The decay of **5** will appear second order in **5** both if $k_{5,5} \gg k_{5,10}$ or if $k_{5,5} \cong k_{5,10} \cong k_{10,10}$. Consequently, the fate of **10** cannot be deduced from the available kinetic data.

Scheme 3



The quantum yield ϕ_R of photoreduction of **3** in degassed 2-propanol using 405 nm irradiation was found to depend on the temperature of the solution. It was attempted to specify the effect of temperature in terms of the proposed reaction mechanism (*Scheme 3*) by evaluation of the effect on the individual observables in flash photolysis. The results are summarised in Table 2.

An *Arrhenius* plot (log k *vs.* T^{-1}) of the total first order rate of triplet decay, $k_T = ({}^3\tau)^{-1}$, yields a regression line with a slope not significantly different from that of the bimolecular diffusion rate, k_{diff}. This indicates that even in 2-propanol as solvent the triplet lifetime of **3** is essentially determined by diffusion controlled impurity quenching and not by the rate of hydrogen abstraction k_H. The low overall quantum yield, $\phi_R \leq 0.1$, is consistent with this view. The relative yield of radical **5**, ϕ_5^{rel}, was determined from the increase in optical density at 417 nm during the triplet decay. Both ϕ_R and ϕ_5^{rel} increase by a factor of nearly three over the temperature range investigated. It may be concluded that the product yield from **5** is not strongly affected by temperature. The increase of both ϕ_R and ϕ_5 are thus ascribed to a *ca.* twentyfold increase in the rate of hydrogen abstraction k_H by T_1 (**3**), corresponding to an activation energy $E_a \cong 10$ kcal/mol. The pseudo first order rates k_H given in table 2 were calculated as $k_H = \phi_R/{}^3\tau$ and thus represent lower limits. The upper

Table 2. *Flash photolysis and quantum yield data at various temperatures* (**3** *in degassed 2-propanol*) [a])

°K	$\phi_R \cdot 10^2$ –	ϕ_5 rel –	$({}^3\tau)^{-1} \cdot 10^{-3}$ s^{-1}	$k_{diff} \cdot 10^{-9}$ $M^{-1}s^{-1}$ [b])	k_H s^{-1}	$k_{dim} \cdot 10^{-3}/\varepsilon$ $s^{-1}cm$
278	3.9 ± 1.	≡ 1(±.2)	2.1 ± .3	1.7	80	1.3 ± .2
298	5.0 ± 1.	1.6 ± .3	4.3 ± 1.	3.3	220	2.5 ± .3
323	8.4 ± 2.	2.1 ± .4	10. ± 2.	7.1	840	4.4 ± .7
338	11. ± 2.	2.6 ± .4	15. ± 3.	11.	1700	6.3 ± .7

[a]) Error limits are standard errors of the mean of three measurements, explanation of symbols see text.

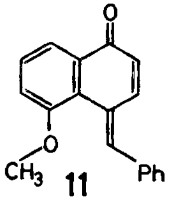
[b]) Calculated as $k_{diff} = 8RT/3000\ \eta$ [18] using tabulated values [19] for the viscosity η of 2-propanol.

limits are equal to $({}^3\tau)^{-1}$. A *caveat* is in order: The above analysis is based on the implicit assumption that each triplet abstracting a hydrogen from 2-propanol yields a free radical **5**. However, it cannot be excluded that an appreciable fraction of the radicals react in cage to form starting material or products although this process necessitates intersystem crossing at some stage. Finally, $k_{\mathrm{dim}}/\varepsilon$ is the observed second order disappearance rate of **5** divided by the unknown extinction coefficient of **5** at 417 nm. Using the inequality max $(\varepsilon) \simeq 2 \cdot 10^5 > \varepsilon_{417}$ (**5**) $> \varepsilon_{417}$ (**3**) $\simeq 10^4$ the rate k_{dim} may be estimated to lie in the range of $(9 \pm 7) \cdot 10^7 \mathrm{M}^{-1}\mathrm{s}^{-1}$ at room temperature.

In a number of preliminary experiments triethylamine and 1,4-diaza-bicyclo-[2.2.2]octane (DABCO) were added to solutions of **3** to explore the effect of amines on T_1 (**3**). The observed bimolecular rates of triplet quenching were of the order of $10^6 \mathrm{M}^{-1}\mathrm{s}^{-1}$, *i.e.* several orders of magnitude faster than that of 2-propanol. Electron transfer from the amine to T_1 (**3**) to form the anion of the radical **5** appears as a likely quenching mechanism. Indeed, the quenching results in the formation of a second transient which absorbs strongly up to 500 nm and slowly decays by a second order reaction. This topic was not further investigated.

Discussion. – The naphthofuranone **3** and its conjugate acid **4** differ strikingly in their fluorescent emission. While **4** exhibits a strong green fluorescence ($\phi_{\mathrm{Fl}} = 0.9_7$), the fluorescence yield of **3** is generally low but strongly solvent dependent (water: $\phi_{\mathrm{Fl}} = 0.2_1$, benzene: $\phi_{\mathrm{Fl}} \leq 10^{-4}$). The low fluorescence yield of **3** is due to rapid intersystem crossing. It was inferred from indirect evidence (Sect. 1.3.) that the lowest $\mathrm{n}\pi^*$ and $\pi\pi^*$ excited singlet states of **3** are nearly degenerate in nonpolar solvents. Taking ${}^1\mathrm{n}\pi^* - {}^3\pi\pi^*$ spinorbit coupling to be responsible for the rapid intersystem crossing of **3**, the fluorescent behaviour of **3** and **4** can be understood as a consequence of the hypsochromic shift of the ${}^1\mathrm{n}\pi^*$ state in protic solvents.

The lowest triplet state T_1 (**3**) has been identified as a potential photoreactive intermediate in the presence of hydrogen donators in solution. It is formed with near unit efficiency upon direct excitation of **3** and was observed and characterised both by its phosphorescent emission ($E_T = 45$ kcal/mol) and triplet-triplet absorption. Alternatively, T_1 (**3**) may be generated by triplet energy transfer using ethyl-1-thionaphthoate as a sensitiser. The assignment of T_1 (**3**) as a ${}^3L_a$ ($\pi\pi^*$) excited state on the basis of spectroscopic data and semiempirical calculations (Sect. 1.1. and 1.5.) implies a relatively low reactivity of T_1 (**3**) towards hydrogen abstraction although the calculations predict a considerable degree of radical character at the carbonyl oxygen in the ${}^3L_a$ state. The rate of hydrogen abstraction from 2-propanol by benzophenone in its $\mathrm{n}\pi^*$ excited triplet state [20] is about five orders of magnitude higher than that of T_1 (**3**). Nevertheless, the long lifetime of T_1 (**3**) in degassed solutions enables photoreduction to take place with fair efficiency in 2-propanol ($\phi_R = 0.05$ at



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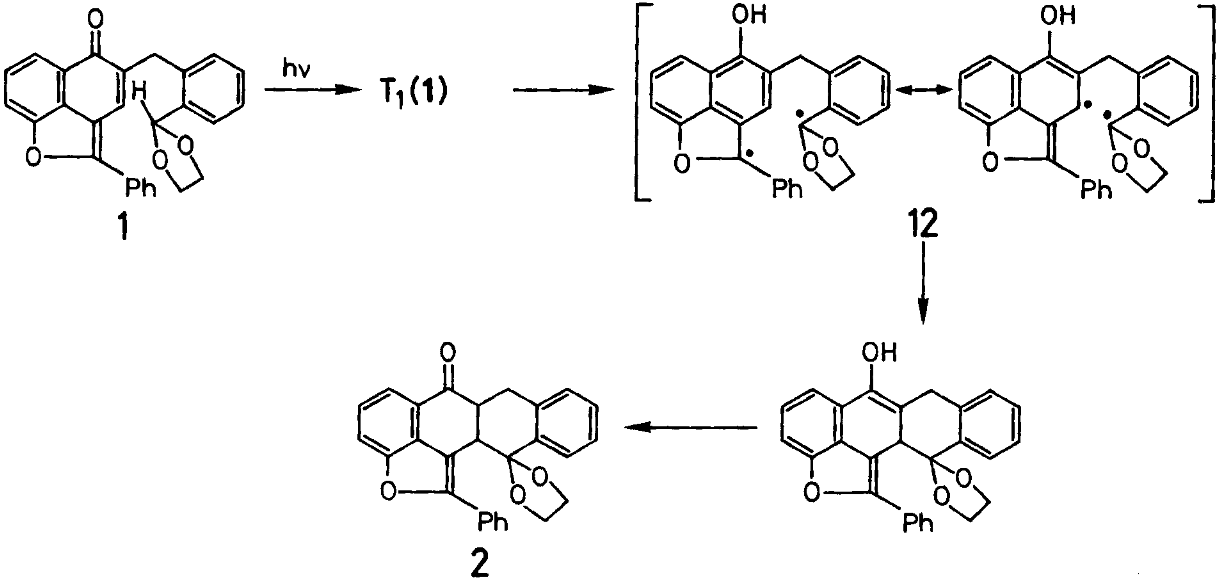
Scheme 4



25°). Even in this solvent the lifetime of T_1 (**3**) and concomitantly the quantum yield ϕ_R appear to be limited essentially by diffusion controlled impurity quenching. Presumably, the C(1)–O(2) single bond connecting the *peri* positions of **3** is essential for the long intrinsic lifetime of T_1 (**3**). The related naphthoquinone methide derivative **11**, for example, is expected to be rapidly deactivated in its lowest triplet state by isomerisation of the exocyclic double bond.

The product formed from T_1 (**3**) by hydrogen abstraction was detected as a transient intermediate by kinetic flash photolysis and specified as the semiquinone methide radical **5**. The radical **5** disappears by a second order reaction yielding its dimer **6** as a major product. The photoreduction of **3** by 2-propanol thus conforms to the general D–R mechanism of dye photobleaching as proposed by *Koizumi et al.* [21].

Irradiation of the naphthofuranone derivative **1** is known to give high yields of the desired cyclisation product **2** (*Scheme 1*) only if the solution (i) is carefully deoxygenated [1b], (ii) contains catalytic amounts of acid (*e.g.* benzoic acid) [1b], and (iii) is heated to about 70° [22]. The author has confirmed by spectrophotometric monitoring of the photoreaction of **1** that the above statements hold for very dilute solutions of **1** ($5 \cdot 10^{-5}$ M) and that both heat and acid must be present *during the irradiation period* to obtain high yields of **2**. In view of these facts, the effect of acid and heat on the photochemistry of **3** has been examined. The pK_a values of the acid **4** in its lowest excited singlet and triplet state are estimated as +6 and +1, respectively (Sect. 1.4. and 1.6.). Despite the high basicity of S_1 (**3**), protonation to form S_1 (**4**) is ineffective even in glacial acetic acid, presumably due to the short lifetime of S_1 (**3**). Hence, protonation of **3** by benzoic acid in benzene solution is not expected³) to occur to any significant extent in either the lowest singlet or triplet state. Experimentally, addition of benzoic acid has no appreciable effect on the fluorescence, the triplet-triplet absorption, or the photoreduction of **3**. The photoreduction does, however, depend on the temperature. The rate of hydrogen abstraction by T_1 (**3**) from 2-propanol increases by a factor of about twenty in going from 5 to 65°.

Are the results of the present investigation relevant to the photocyclisation reaction of **1**? Preliminary experiments have shown [23] that the photochemical reaction can be promoted either by direct irradiation of **1** or by sensitisation with ethyl 1-thionaphthoate. In both cases the dependence of the photoreaction on temperature and the presence of acid appears to be the same. The lifetime and absorption spectrum of T_1 (**1**) are very similar to that of T_1 (**3**). The acetal group on ring A of **1** offers a highly activated C–H bond to the triplet excited chromophore. Intramolecular hydrogen abstraction to form the biradical **12** thus appears as an obvious suggestion for a primary photochemical process from T_1 (**1**). It is seen by inspection of molecular models that the constraints imposed on the rotational freedom of **1** make this process quite feasible although it involves an eight-membered transition state (*cf.* [24] for related examples).

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³) For comparison, 10^{-4} M quinoline ($pK_a = 4.9$) in benzene is protonated to an extent of $\leq 5\%$, $\sim 20\%$, and $\geq 90\%$ by addition of excess benzoic ($pK_a = 4.2$), chloroacetic ($pK_a = 2.9$), and dichloroacetic ($pK_a = 1.5$) acid, respectively.

The hypothetical reaction mechanism shown in *Scheme 4* is consistent with the observation [23] that the quantum yield of disappearance of **1** ($\phi_D \cong 0.1$ at 25°) does not depend on the presence of acid but increases with increasing temperature. It can obviously not account for the effect of heat and acid on the chemical yield of **2**. Clearly, a more complex scheme, allowing for the formation of photoproducts other than **2**, is needed.

Experimental Part

In cooperation with Mr. *E. Notegen*, M. *E. Rommel* and Mr. *J. P. Walliser*.

A one-step synthesis of 2-phenylnaphtho[1,8-*bc*]furan-5-one **3** has been described by *Barton et al.* [1c]. The product was purified by recrystallisation from ethanol followed by vacuum sublimation at 120°. Quinine sulfate (*Fluka*, purum) and N,N-dimethyl-3-nitroaniline (*BDH*) were purified by repeated recrystallisation from water and diethyl ether, respectively, fluorescein (*Fluka*, fluorescence standard) by the method of *Lindqvist* [25]. Spectroscopic grade (*Merck, Uvasol*) solvents were used except for preparative work. The removal of oxidisable impurities from benzene was attempted by a number of methods [26] including partial chromate oxidation and column crystallisation [27]. The best results were obtained when a solution of **3** (500 mg) in spectroscopic grade benzene (300 ml) was irradiated for 100 hours through *Pyrex* with a 200 W high pressure mercury arc (*Osram HBO 200*) and distilled before use.

Solutions were degassed by the freeze-pump-thaw technique until the pressure remained below 10^{-3} Torr upon thawing and refreezing.

UV./Vis. absorption spectra were recorded at least three times on a *Cary 14* spectrophotometer, NMR. spectra on a *Varian* HA-100 D instrument, IR. spectra on a *Perkin-Elmer* 457 grating spectrophotometer, and phosphorescence spectra on a *Perkin-Elmer* MPF-2 A fluorescence spectrophotometer equipped with a rotating can attachment and an *RCA* 1P28 photomultiplier. Phosphorescence decay signals were taken from the latter instrument and displayed on an oscilloscope except for the PMMA sample containing **3** which was excited by flash photolysis. Molecular weights were measured by the isopiestic method on a *Hitachi Perkin-Elmer* 115 instrument.

Fluorescence spectra were determined at room temperature on a *Zeiss* PMQII/ZFM 4 spectrophotometer equipped with a *Hamamatsu* R213 photomultiplier tube. The samples were irradiated in a direction at right angle to the detection system with 436, 405, or 365 nm light which was isolated with *Zeiss* glass filters from a medium pressure mercury lamp *Hanau* St. 41. Highly dilute solutions ($\leq 10^{-5}$ M, optical density $D \leq 0.02$) were used to avoid reabsorption effects. The relative spectral sensitivity of the instrument in the range of 14000 to 25000 cm^{-1} was calibrated with standard fluorescent solutions (quinine sulfate and N,N-dimethyl-3-nitroaniline) of known spectral distribution [28]. The resulting spectral sensitivity curve was in reasonable agreement with that derived from characteristic data provided by the manufacturers of the instrument parts and was used for correction of the apparent fluorescence spectra. The luminescence from reference solvent blanks never exceeded 1% of the maximum sample fluorescence intensity and was typically much lower. Comparative fluorescence intensity measurements for quantum yield determinations (Eq. 1, Sect. 1.3.) were carried out repeatedly within short time periods and with identical instrument settings on a minimum of three reference and sample solutions prepared independently. The quantum yields of fluorescein ($1 \cdot 10^{-6}$ M in 0.1 N sodium hydroxide) and of 5-dimethylaminonaphthalene-1-sulfonate (DANS, $4 \cdot 10^{-6}$ M in 0.1 M sodium hydrogen-carbonate) were determined by reference to quinine sulfate ($1 \cdot 10^{-5}$ M in 1 N sulfuric acid) with excitation at 313 nm as a test for satisfactory performance of the experimental set up. With $\phi_{Fl} = 0.55$ as a reference value for quinine sulfate [5] quantum yields of $0.8_5 \pm 0.1$ and $0.3_9 \pm 0.05$ were obtained for fluorescein and DANS, respectively, in good agreement with available literature values [5]. Fluorescence lifetimes were measured on an apparatus constructed by *Beddard* [29].

Kinetic flash photolysis experiments on the sub-microsecond time scale were performed using the second harmonic of a Q-switched ruby laser as an excitation source ($\lambda = 347$ nm, $E \cong 50$ mJ, $\tau \cong 2 \cdot 10^{-8}$ s). A pulsed xenon arc provided the monitoring beam for the photoelectric detection of transients. Details of the apparatus have been described [30]. The instruments for kinetic and spectrographic registration of longer-lived intermediates were of standard design [31]. Energies of 250 to 1000 J could be dissipated per flash. The lower limit was usually sufficient to produce suitable transient concentrations. The oscillograph traces from kinetic measurements (transmission *vs.* time) were transformed point by point to first order ($\log|D(t) - D(\infty)|$ *vs.* time) and/or second order plots ($[D(t) - D(\infty)]^{-1}$ *vs.* time). If the decay of a transient followed complex kinetics of mixed order it was attempted to approach the limiting cases of 'pure' first and second order, respectively, by variation of sample parameters such as solute concentration, cell dimensions, and flash intensity.

For the preparative photoreduction of the naphthofuranone **3** a solution of 500 mg **3** in 150 ml 2-propanol was degassed in a *Pyrex* vessel equipped with a magnetic stirrer and irradiated during 48 h with a high pressure mercury arc (*Osram* HBO 200 W). The yellow colour of the solution did not disappear completely but the end of the reaction was indicated by the appearance of a strong blue fluorescence and confirmed by taking the UV. spectrum of a diluted aliquot. The solution was condensed to *ca.* 20 ml by solvent evaporation on the vacuum line until the product **6** was precipitated in the cold. The solid was filtered off and chromatographed on a silica column with benzene as eluent. All manipulations had to be performed under a nitrogen atmosphere since the product **6** is quickly reoxidised to **3** even as a solid. The UV. spectrum of **6** was nearly identical with that of the photolysed solution of **3** (Fig. 4) as well as with that of compounds **7** and **9**. **7** was prepared by anaerobic reduction of **3** with zinc and acetic acid while **9** was obtained by treatment of **3** with sodium hydroxide in ethanol [1d] and rapid neutralisation shortly before taking the spectrum. It must be noted that no attempt was made to properly characterise the alleged products **7** and **9**. Addition of base to solutions of **6**, **7**, and **9** resulted in an immediate change of the UV. spectrum (broad structureless band, λ_{max} 345 nm) due to ionisation of the phenolic OH group. As expected, the UV. spectra of **6**, **7**, and **9** in neutral and basic media closely resemble those of 1,5-naphthalenediol and its hemi-ionic form [32], respectively. The essential features of the IR. and NMR. spectra of **6** were the absence of a carbonyl group and of protons on saturated carbon, respectively. **6** was decomposed when sublimation *in vacuo* was attempted, presumably by disproportionation, as small amounts of **3** were detected in the sublimate. Disproportionation of **6** also occurred slowly upon heating in degassed solution. In aerated solutions **6** was quantitatively reoxidised to **3** within a few hours at room temperature. This process was monitored by UV. and on the molecular weight apparatus. The apparent molecular weight of **6**

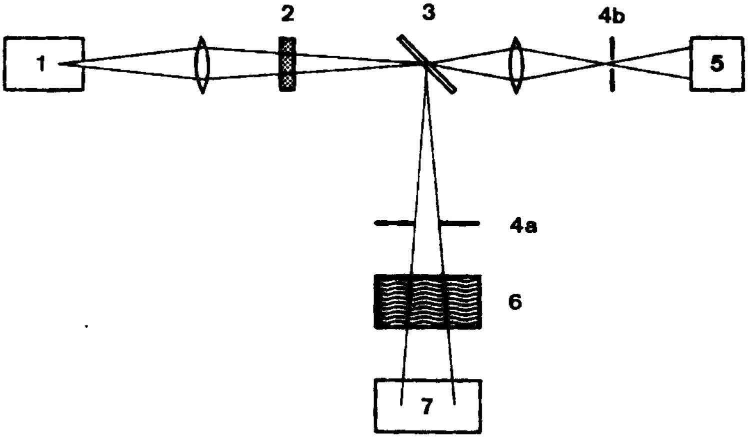

Fig. 5. *Apparatus for photochemical quantum yield determinations.* (1) Medium pressure mercury arc (*Hanau* St. 41), (2) Glass and solution filters, (3) Quartz plate, (4) Shutters, (5) Thermostatted sample cuvette, (6) Thermostatted water bath with quartz windows (heat shield), (7) Compensated thermopile (*Kipp* + *Zonen*, CA1)

continuously decreased during the oxidation from 500 ± 100 (by extrapolation to zero conversion) to 240 ± 20 after complete conversion to **3**.

Quantum yields of photoreduction were measured spectrophotometrically with degassed $5 \cdot 10^{-5}$ M solutions for conversions of less than 10% on a split beam apparatus (Fig. 5). The photolysis light intensity was measured during the irradiations with a thermopile calibrated by ferrioxalate actinometry [18].

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144. An Investigation of the Tea Aroma Part I. New Volatile Black Tea Constituents

by **Walter Renold, Regula Näf-Müller, Urs Keller, Bruno Willhalm** and **Günther Ohloff**

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(15. V. 74)

Summary. A total of 68 constituents, mainly aldehydes, ketones and esters, have been identified for the first time in a black tea aroma concentrate using coupled gas-chromatography/mass spectrometry.

Introduction. – Tea is one of the world's most widely consumed beverages [1] [2]. The volatile substances that are present in the tea leaves play an important role in determining the overall flavor impression received [2]. Despite the identification of many constituents of green and black tea leaves¹), a satisfactory reconstitution of black tea aroma proved to be impossible. We therefore undertook a detailed analysis of this aroma and would like to report here on the occurrence of 68 newly identified constituents. Using the direct coupling technique of a mass spectrometer with a glass capillary column, we were able to identify these new components by their mass spectra and their respective retention times. The reference samples were either commercially available or were synthesized.

Results. – New substances are listed in the Table, including the *m/e* values of substances whose mass spectra have not been reported.

The first group in the Table consists of 21 aldehydes, the majority being straight chain alkenals and alkadienals. These represent an expected extension of the few that were already known to exist in tea aroma, since they can be considered as degradation products from lipid precursors [7–11]. *β*-Cyclocitral and safranal have probably carotenoids as their precursors [12], whereas 2-methylbenzaldehyde and 4-methoxybenzaldehyde might be regarded as degradation products from polyphenolic substances, the largest chemical class found in the young tea shoot [3]. The two 2-phenyl-2-alkenals identified might be derived from the amino acid pairs leucine/phenylalanine and valine/phenylalanine, all known to occur in green tea leaves [13].

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¹) Two recent reviews by *Sanderson & Graham* [2] and *Sanderson* [3] are a good introduction to the tea literature. For the most recent work on black tea aroma since the latest review [2], see [4] [5] [6].