239. Photolysis of the Azo-Precursors of 2,3- and 1,8-Naphtoquinodimethane[1])

Preliminary communication

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(9. VI. 76)

Summary. A novel oxidation method for the synthesis of labile azo-alkanes is reported. Matrix-isolated 2,3-naphthoquinodimethane is obtained by photolysis of 1,4-dihydrobenzo[*g*]-phthalazine in a rigid matrix (EPA glass) at 77 K and the electronic structure of its ground and lowest excited states is discussed. Nitrogen elimination from 1,4-dihydronaphtho[1,8-*de*][1,2]-diazepine to yield acenaphthene occurs exclusively upon π-π^* excitation while irradiation in the n-π^* absorption region induces *cis/trans* isomerization of the azo-moiety. Neither ns flash nor low-temperature photolysis provide evidence for the occurrence of 1,8-naphthoquinodi-methane as an intermediate in the formation of acenaphthene.

Quinone methides and dimethides occur as intermediates in numerous reactions of synthetic and biochemical interest. The direct investigation of the ground and excited state properties of such biradicaloid species should provide useful information for the understanding of photochemical and thermal reactions proceeding *via* these and related intermediates. Spectroscopic studies of matrix-isolated *o*-, *m*-, and *p*-benzo-quinodimethane [1] and of a bridged derivative of 1,8-naphthoquinodimethane [2] have been reported.

Results and Discussion. – A major problem with the synthesis of azo-com-pounds having enolizable hydrogen atoms is their facile irreversible tautomerization to hydrazones. Furthermore, from the experience of *Michl* [1] with 1,4-dihydro-phthalazine, spontaneous nitrogen elimination was expected to occur below room temperature with 1,4-dihydrobenzo[*g*]phthalazine (**1**). Searching for an oxidizing

Scheme 1
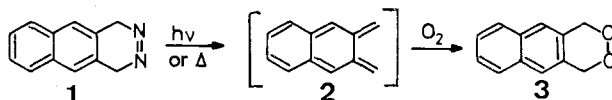
[1]) Presented at the VIth IUPAC Symposium on Photochemistry, Aix-en-Provence, July 20, 1976.
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agent suitable for low-temperature work under aprotic conditions we found that 4-phenyl-4H-1,2,4-triazoline-3,5-dione instantaneously oxidizes hydrazines at −60°.

The azo-compound **1** eliminated nitrogen above −40° yielding an intractable mixture of products in deaerated solution. In the presence of air, 1,4-dihydronaphtho-[2,3-d][1,2]dioxin (**3**) was formed in high yield. *Sondheimer* [3] has previously obtained **3** in a reaction where 2,3-naphthoquinodimethane (**2**) was postulated as an intermediate. A ruby colour rapidly developed upon 365 or 313 nm irradiation of **1** in a rigid EPA matrix (5 parts ether, 5 parts *iso*-pentane, 2 parts alcohol). The coloured species, identified with **2**, was stable at 77 K but rapidly disappeared when the matrix softened upon warming.
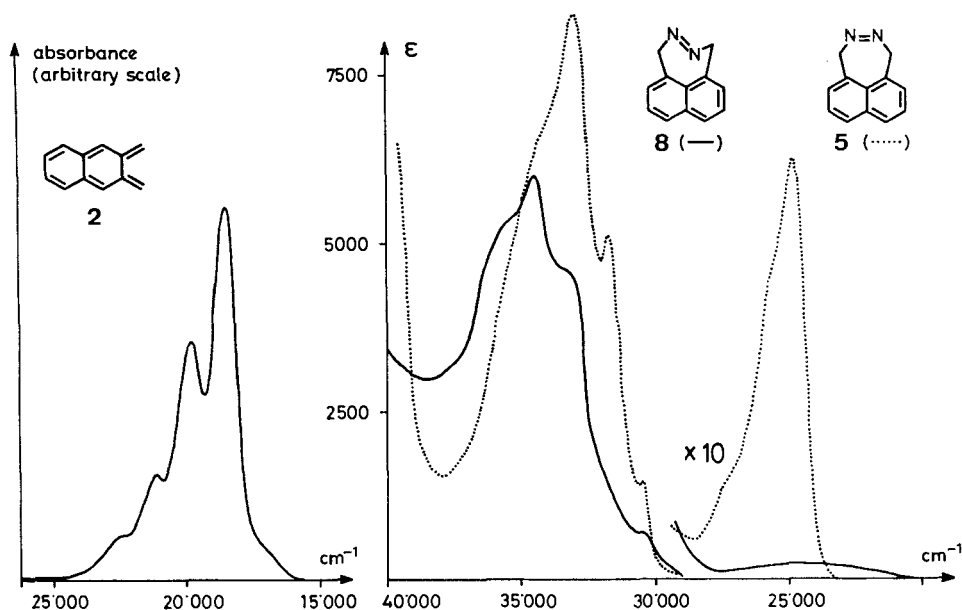

Fig. 1. *VIS. absorption spectrum of **2** in EPA glass at 77 K* (left) *and UV./VIS. spectra of **5** and **8** in ether at +25° and −50°, respectively* (right)

Standard PPP SCF CI calculations [4] for **2** (all bond lengths assumed 1.4 Å, $\beta = -2.318$ eV, $\gamma_{\mu\nu} = 14.395/[1.328 + R_{\mu\nu}]$ eV) using all 36 singly excited configurations predict a single electronic transition in the visible region which lies at 532 nm ($f = 0.36$) and corresponds essentially to the HOMO → LUMO excitation. On the basis of his extended CI calculations for o-benzoquinodimethane *Michl* [1] has predicted the presence of a weak transition to a 'doubly excited' state ('S_2') in the neighbourhood of the allowed HOMO → LUMO transition to 'S_1'. The strong fluorescence exhibited by o-benzoquinodimethane leaves little doubt that its lowest

excited singlet state corresponds to the 'S_1' state with essentially planar equilibrium geometry. Our calculation for **2** places the energy of the lowest doubly excited configuration (2.52 eV) just slightly above the lowest singly excited one (2.46 eV) and we may expect that extended CI would shift the 'S_2' state well below the allowed 'S_1' state. The experimental absorption band of **2** (first maximum at 541 nm, Fig. 1) is strikingly similar in vibrational fine structure and overall shape to the corresponding band in N-methyl benz[f]isoindole (**4**) [5]. However, we note two important differences between **2** and **4**: (i) The strong fluorescence emission of **4** ($\phi_{Fl} = 0.7$) is absent in **2**; (ii) While the 0–0 transition of **4** is the most intense vibronic band in both absorption and emission, the corresponding feature in the absorption spectrum of **2** at 541 nm is preceeded by a weak shoulder near 590 nm. Both observations are readily explained by assigning the long-wavelength shoulder to the forbidden $S_0 \rightarrow$ 'S_2' transition. It should be mentioned that the spectrum of **2** is incompatible with that predicted by PPP calculations for an assumed triplet ground state.

1,4-Dihydronaphtho[1,8-*de*][1,2]diazepine (**5**) was first synthesized in 1963 by *Carpino* [6] who noted the formation of acenaphthene (**6**) upon its thermal decomposition. We speculated that light-induced nitrogen elimination from **5** at low temperature might yield 1,8-naphthoquinodimethane (**7**) as a metastable triplet ground state molecule. Much to our surprise, direct irradiation of **5** in the region of its (n-π*)-absorption band (λ_{max} 403 nm) or sensitization with benzophenone both resulted in a smooth conversion of **5** to its highly strained *trans*-isomer **8** which could readily be purified by low-temperature chromatography and to our knowledge represents the first compound containing a *trans* double bond in a seven-membered ring which has been isolated in a pure state[3]). The UV./VIS. (Fig. 1) and NMR. spectra are fully compatible with structure **8**. On the NMR. time scale at up to room temperature the diazepine ring appears to be frozen in a conformation of C_2-symmetry since the methylene protons at the (equivalent) C(1) and C(4) atoms give rise to a quartet (δ_A 5.64, δ_B 6.04, geminal coupling constant $^2J_{AB}$ 12 Hz in CDCl$_3$). The coalescence of the same proton signals in the *cis*-isomer **5** (δ 5.64 and 6.04 ppm, $^2J_{AB} = 12$ Hz in CDCl$_3$ at −50°) due to conformational exchange was found to be in the temperature interval from −50° to 25°. At room temperature in the dark **8** was reconverted to **5** in a first-order reaction with a rate of $k_{tc} = 3 \cdot 10^{-4}$ s^{-1} which was essentially solvent independent. From the temperature dependence of k_{tc} in acetonitrile the following 90 percent confidence ranges were obtained for the activation parameters: $\Delta H^{\neq} = 22.0 \pm 0.4$ kcal/mol and $\Delta S^{\neq} = -0.6 \pm 1.3$ e.u. These findings clearly reflect the strain energy which must be present in **8** [7]. Reconversion of **8** to **5** was also observed upon n-π* excitation of **8**. From the wavelength-dependent photostationary state compositions **5/8** we derived a ratio of one to ten for the ratio of the *cis* → *trans* and *trans* → *cis* quantum yields. Further chemical evidence for the structure of **8** is shown in *Scheme 2*.

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[3])   The *cis*- and *trans*-isomers of 2,3,6,7-tetrahydro-3,3,6,6-tetramethyl-1,4,5-thiadiazepine-1,1-dioxide are under investigation at *Ciba-Geigy SA*, Basel (*H. Lind, G. Rist* and *G. Rihs*, personal communication). *trans*-2-Cycloheptenone has been detected by IR. at −160° [10] and the *trans*-isomers of 1-phenylcycloheptene and -hexene by flash photolysis [11].

Irradiation of either **5** or **8** in the region of the π-π^* naphthalene-absorption bands induced a clean conversion to acenaphthene (**6**). Several isosbestic points were observed with both starting materials upon spectrographic monitoring of the conversion at temperatures down to 77 K. Hence, no appreciable *cis/trans*-isomerization occurs with short wavelength light. The remarkable wavelength dependence of the photochemistry of **5** and **8** suggests that the azo group and the naphthalenic moiety may be regarded as two weakly interacting chromophores in these systems. *Steel* et al. have shown [8] that intermolecular singlet energy transfer between naphthalene and various azoalkanes is predominantly induced by exchange interactions since the rates calculated for *Förster*-type transfer are too slow. Exchange interactions require close

Scheme 2
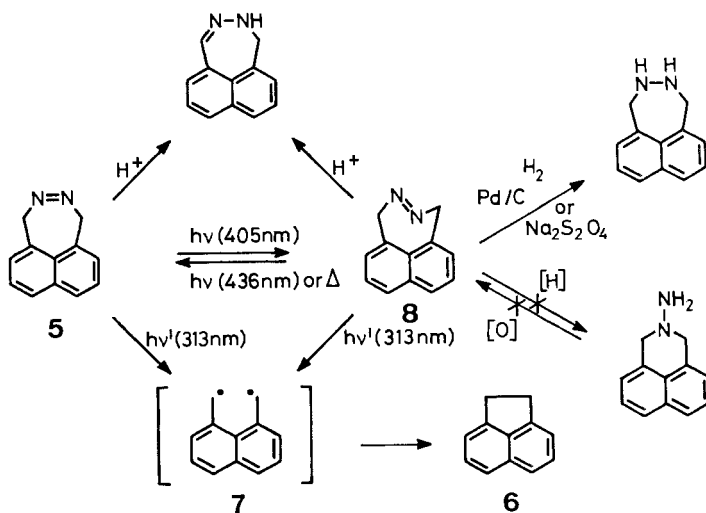
contact between the chromophores. Apparently, the methylene bridge in the bichromophoric systems **5** and **8** is sufficient as a spacer to allow for the independent photochemical reactivity of the two subunits.

Our low-temperature irradiations of **5** and **8** did not provide any evidence for the occurrence of 1,8-naphthoquinodimethane (**7**) as an intermediate in the formation of **6**. The same negative result was obtained by attempted trapping reactions and by ns flash photolysis experiments with a frequency-quadrupled Nd laser[4]) at temperatures down to $-80°$. We conclude that **7**, if at all a distinct species, is extremely unstable with respect to ring closure to **6**[5]).

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[5]) *Added in proof*: The triplet state of **7** has now been observed by EPR. at 77 K (footnote 42 of [2] and *R. M. Pagni*, personal communication).

Experimental Part. – *1,2,3,4-Tetrahydrobenzo*[g]*phthalazine* (**9**) was synthesized in 65 percent overall yield from 2,3-bis(bromomethyl)naphthalene [9] following the procedure of *Carpino* [6] for the synthesis of **5**. The neutral compound is sensitive to air oxidation. M.p. (hydrochloride) 287° (dec.). – ¹H-NMR. (hydrochloride in DMSO-d₆, internal CDCl₃/TMS): δ 4.47 (s, 4H); 7.42 to 7.90 ppm (m, 6H). – ¹H-NMR. (neutral compound in deaerated CDCl₃, internal TMS): δ 3.08 (br.s, 2H); 4.28 (s, 4H); 7.35 to 7.80 ppm (m, 6H). – MS. (neutral compound) (m/e): 184 (M^+), 154 (base peak).

1,4-Dihydrobenzo[g]*phthalazine* (**1**). A cooled solution of 80 mg 4-phenyl-4H-1,2,4-triazoline-3,5-dione (*Fluka*) in 3 ml methylene chloride is added dropwise to a solution of **9** (freshly prepared by extraction of a neutralized aqueous solution of 110 mg hydrochloride) in methylene chloride at – 60°. Complete conversion is indicated when the red colour of the oxidant is no longer discharged upon its addition to the reaction mixture. Pure **1** is a colourless solid which exhibits a transient red colour upon decomposition at room temperature. – ¹H-NMR. (CDCl₃, internal TMS, – 50°): δ 5.19 (s, 4H); 7.48 to 7.96 ppm (m, 6H). – UV. (λ_{max} (approximate ε)): 360 (280), 319 (600), 314 (700), 295 (4300), 285 (6300), 274 (6400), 265 nm (6000 M^{-1} cm^{-1}).

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