[2 + 2] Photocycloaddition of 2-Morpholinoprop-2-enenitrile to Perinaphthenone

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Dedicated to Prof. *André M. Braun* on the occasion of his 60th birthday

Perinaphthenone (=1*H*-phenalen-1-one), known for efficient population of its T_1 (π,π^*) state and suggested as a standard sensitizer for singlet oxygen ($^1\Delta g$) formation, forms a single stereoisomer of a head-to-tail [2 + 2] photoadduct across its C(2)=C(3) bond with 2-morpholinoprop-2-enenitrile in benzene by broad band UV excitation ($\lambda \geq 280$ nm). The reaction is advantageously run to low conversion of starting materials only. The structure of the adduct, especially the relative configuration at C(9), has been derived from ^{1}H-NMR data including NOE signal enhancement studies.

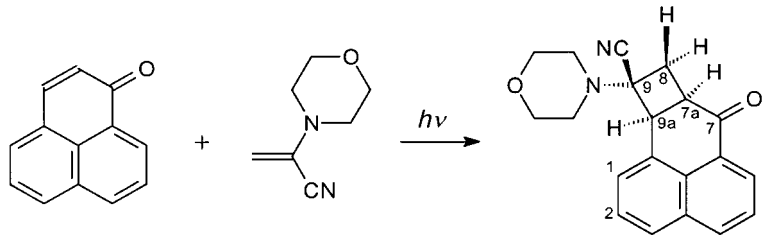
Introduction. – The photophysics and triplet-state quenching by oxygen of photoexcited perinaphthenone (=1*H*-phenalen-1-one, **1**) have been extensively investigated [1–7]. Special emphasis has been laid on the efficiency of **1** as a sensitizer in singlet-oxygen [$O_2(^1\Delta g)$] formation, and use of **1** as a reference sensitizer for singlet-oxygen formation has been recommended [1][5]. The quantum yield of $O_2(^1\Delta g)$ formation varies only in a narrow range ($0.94 \leq \phi\Delta < 1.00$) [5] for a series of common solvents, still there is concern about the stability of photoexcited **1** in hydrogen donating solvents (*N*,*N*-dimethylacetamide, 1,4-dioxane, and propan-2-ol) [8][9]. The 2,3-dihydro compound, phenalanone, has been identified as the first stable reduction product formed [9]. H-Atom abstraction out of deaerated EtOH has been reported earlier [10], and the photolysis of **1** in aerated EtOH is reported to produce various positional isomers of (1-hydroxyethyl)- and hydroxy-phenalenones [11].

To the best of our knowledge, light-induced cycloadditions of **1** have not been reported so far. Our previous experience in the highly regio- and stereoselective [2 + 2] photocycloadditions of α-cyano enamines to various aromatic and heteroaromatic carbonyl compounds [12] including coumarins [13] led us to try the photocycloaddition of 2-morpholinoprop-2-enenitrile (**2**) to **1** (*Scheme*).

Results and Discussion. – Since a H-donating solvent seemed to be impractical in the light of the aforementioned reduction reactions, and chlorinated solvents would not be compatible with the enamine nature of **2**, benzene was chosen for its low H-donating property. It should be noted, though, that α-H-atom abstraction from the morpholino group, as verified for triplet-excited benzophenone [14], remains a problem. After a series of trials, a threefold molar ratio of **2** in benzene and irradiation to low conversion only with filtered ($\lambda \geq 280$ nm) UV light seemed to be satisfactory.

Under these conditions, a highly regio- and stereoselective [2 + 2] photoaddition of **2** across the C(2)=C(3) bond was observed with formation of only one main reaction

Scheme



1 **2** **3**

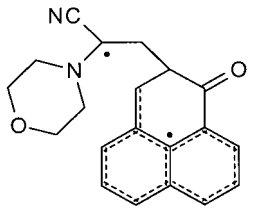
product **3** accompanied by minute amounts of an isomer, which, due to lack of availability of material, could not be investigated further. Reduction products of **1** could not be found, but some intractable material not originating from **1** was formed and separated off.

The ^{1}H-NMR spectrum (500 MHz) of **3** in $CDCl_3$ proved to be unsuitable for structure elucidation due to coincidential signal overlap and apparent simplicity of important signals (*e.g.*, for $CH_2(8)$). However, a 300-MHz ^{1}H-NMR spectrum in (D_6)benzene showed complete resolution of all *multiplets*, while most of the signals were markedly shifted upfield (*e.g.*, for H–C(9a): $\delta = 4.38$ ppm in $CDCl_3$ and 3.66 ppm in (D_6)benzene). Thus, all assignments have been made on the basis of the spectrum in (D_6)benzene. Structure **3**, thus, was delineated on the basis of the following findings:

Among the signals for the cyclobutane protons, that for H–C(9a) (3.63 ppm) should be at lowest field, showing coupling ($^3J = 9.2$ Hz) to primarily one proton only (H–C(7a)). The significant broadening of both lines of the apparent *doublet* points to weak long-range interactions. This supports a head-to-tail orientation of **3**, which is in full accord with the strict head-to-tail regioselectivity in the [2 + 2] photoadditions of α-cyano enamines to various coumarins [12][13] and in the analogous cyclobutane formations of aryl-carbonyl compounds with alkenes mentioned [12]. The signal at 3.04 ppm (*ddd*) was assigned to H–C(7a) on the basis of two vicinal couplings (^3J(7a,9a) = 9.2 Hz, ^3J(7a,8*exo*) = 10.5 Hz, typical in size for vicinal *cis*-couplings in cyclobutanes) and one *trans*-coupling (^3J(7a,8*endo*) = 4.6 Hz). For $CH_2(8)$, a geminal coupling $|^2J|$ of 12.1 Hz was found. The proton H_{endo}–C(8) (2.54 ppm, *ddd*) showed $^3J = 4.63$ and $^4J = 0.9$ Hz, while H_{exo}–C(8) (2.15 ppm, *ddd*) was split by $^3J = 10.5$ and $^4J = 1.1$ Hz.

The donor-*exo* geometry of **3** is established by applying the $\Delta_{eq,ax}$ criterion [15], here on the basis of the low chemical-shift difference (0.17 ppm) of the signals for equatorial and axial *N*-CH_2 protons (in $CDCl_3$: $\delta = 2.71$ for NCH_{eq} and 2.54 for NCH_{ax}) in line with similar shift values for analogous cyclobutane-type adducts of fused arenes or coumarins [12][16][17]. For an *endo*-oriented morpholino group residing above a benzoid ring, usually shift values of *ca.* 2.5 (NCH_{eq}) and 2.0 (NCH_{ax}) are found [16].

Further support of the structural assignment of **3** comes from NOE intensity-enhancement measurements in $CDCl_3$ solution. Irradiation into the unresolved 2.71 ppm resonance (NCH_{eq}) effects an enhancement of both the *doublet* at 4.38 ppm (H–C(9a)) and the 7.48-ppm *multiplet* for one aryl-H (probably H–C(1)),



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while a negative enhancement is observed for the 7.58 ppm signal (probably H–C(2)). This finding may be regarded as a case of a 'three-spin effect' [18], since inspection of a molecular model shows that, in the morpholino *exo* orientation, one NCH_{eq}, H–C(1), and H–C(2) are close and nearly colinear. Reversely, saturation of the H–C(1) resonance enhances the intensities of the H–C(9a) and NCH_{eq} signals. Irradiation into the NCH_{ax} resonance at 2.54 ppm has a significant effect on the 2.85-ppm signal (CH_2(8)). All these effects are in accord with the morpholino *exo* geometry only.

The course of [2+2] photocycloadditions of alkenes to cyclohexenones has been amply discussed (see, *e.g.* [19]), and a triplet biradical **4**, being resonance-stabilized at one terminus and captodatively (see, *e.g.*, [20]) stabilized at the other, may be regarded as a most logical intermediate.

Conclusion. – Using the proper conditions, especially low conversion and absence of oxygen, a highly regio- and stereoselective [2+2] photocycloaddition of an α-cyano enamine to perinaphthenone (**1**) could be achieved. Since the aminonitrile function in the adduct may, as in other examples [12], be hydrolyzed to an oxo group, α-cyano enamines function as ketene equivalents. The use of chirally labeled α-cyano enamines [12] would allow diastereoselective conduct of such cycloadditions. Further work along these lines is in progress.

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Experimental Part

General. M.p.: not corrected. IR Spectra: *Perkin-Elmer 983* spectrometer. ^{1}H-NMR Spectra: *Bruker DRX-500* (500 MHz) and *Bruker WM-300* (300 MHz), with TMS as internal standard. Assignments are supported by homonuclear correlation. MS: *AMD 604*.

Photocycloaddition of 2-Morpholinoprop-2-enenitrile (**2**) *to Perinaphthenone* (**1**). A benzene soln. (75 ml) containing **1** (180 mg, 1.0 mmol) and **2** (415 mg, 3.0 mmol) was purged with a stream of Ar for 15 min and thereafter irradiated for 3 h with a 125-W *Philipps HPK* high-pressure Hg burner through a water-cooled *Duran* jacket ($\lambda \geq 280$ nm) with continuous Ar purging. The brown photolysate was concentrated under reduced pressure. From the partly crystalline residue (582 mg), 236 mg of colorless crystals were sublimed off at 2.6×10^{-2} mbar and 50° bath temp. and shown to be almost pure **2** by IR spectroscopy. The residue (338 mg) was separated by prep. TLC with two plates 48 cm wide and 20 cm high covered with a 1-mm thick air-dry layer of silica gel *Merck* PF_{254} and toluene/AcOEt 1:1 (*v*/*v*) to give five zones (R_f given). *Zone 1* (0.83), orange colored, gave 58 mg of a reddish material, which did not crystallize and showed only neglible ^{1}H-aryl signals and was, therefore, discarded. *Zone 2* (0.67) contained 25 mg of **2**, thus a total of 261 mg (63%) of this material was

recovered. *Zone 3* (0.53), yellow, gave 148 mg (82%) of crystalline **1**, identified by its IR spectrum. Thus, the maximum conversion of **1** was 18%. *Zone 4* (0.40) gave 5 mg of a crystalline residue, m.p. 174–176° (from AcOEt/hexane), IR (KBr): 2950, 2849 (CH); 2219 (CN), 1678 (C=O), 1113 cm^{-1}, numerous medium-intense bands in the 1600–700-cm^{-1} range, general appearance like the IR spectrum of **3**; probably representing an isomer of the latter. *Zone 5* (0.13), colorless, 55 mg, containing **3**. *Start:* Dark brown residue.

*(7a*R*,9*S*,9a*S*)-7a,8,9,9a-Tetrahydro-9-morpholino-7-oxocyclobuta[*b*]phenalene-9-carbonitrile* (**3**). Crystallization of the residue of *Zone 5* from AcOEt/hexane gave 43 mg (0.135 mmol, 76% referred to nonrecovered **1**) of colorless crystals. M.p. 188°. IR: 3057 (aryl−CH); 2853, 2817 (CH_2); 2225 (CN), 1670 (C=O); 1338, 1255, 1115, 771. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.38 (*dd*, 1 arom. H); 8.16 (*d*, 1 arom. H); 7.91 (*d*, 1 arom. H); 7.66 (*dd*, 1 arom. H); 7.58 (*dd*, 1 arom. H); 7.48 (*d*, 1 arom. H); 4.38 (*d*, $^3J = 9.5$, H−C(9a)), 3.82 (*m*, 2 CH_2O) 3.61–3.56 (7-lines *m*, H−C(7a)); 2.85 (unresolved *m*, CH_2(8)); 2.71 (unresolved *m*, NCH_{eq}); 2.54 (unresolved *m*, 2 NCH_{ax}). ^{1}H-NMR (300 MHz, C_6D_6): 8.53 (*dd*, $J = 7.25$, 1.3, 1 arom. H); 7.61 (*dd*, $J = 8.2$, 1.3, 1 arom. H); 7.50 (*d*, $J = 8.2$, 1 arom. H); 7.30–7.00 (several *m*, 3 arom. H); 3.63 (*d*, $^3J = 9.2$, both lines broadened due to long-range couplings, H−C(9a)); 3.04 (*ddd*, $^3J = 9.3$, 10.5, 4.6, H−C(7a)); 2.54 (*ddd*, $|^2J| = 12.1$, $^3J = 4.6$, $^4J = 0.9$, H_{endo}−C(8)); 2.15 (*ddd*, $|^2J| = 12.1$, $^3J = 10.5$, $^4J = 1.1$, H_{exo}−C(8)); 2.30 (*m*, 2 NCH_{eq}); 2.06 (*m*, 2 NCH_{ax}). MS (70 eV, 160°): 318 (1, $M^{+\bullet}$), 291 (41, $[M - HCN]^+$?), 246 (6), 232 (8), 206 (16), 205 (34), 181 (22), 180 (47, $\mathbf{1}^+$), 176 (13), 166 (10), 152 (50, $[I - CO]^+$), 138 (44, $\mathbf{2}^+$), 137 (100), 125 (7), 110 (12), 88 (12), 86 (14), 80 (22), 69 (40). Anal. calc. for $C_{20}H_{18}N_2O_2$ (318.36): C 75.45, H 5.70, N 8.80; found: C 75.30, H 5.76, N 8.76.

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