

PHOTOPHYSICS AND PHOTOCHEMISTRY OF 4-DIHYDROPYRIDINONES

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Abstract—Dihydropyridinones (DHP) react photochemically with olefins to form cycloaddition products. The reactions proceed through the lowest excited state T_1 of the DHPs, with rate constants which depend on the olefin and can approach the diffusional limit in the most favourable cases. Intra- and inter-molecular sensitization and quenching have been investigated, as well as spectroscopic properties such as absorption and luminescence spectra, and in particular electron energy loss spectra which have established the energy of the reactive T_1 state as 295 kJ mol⁻¹ (3.07 eV).

INTRODUCTION

The light-induced cycloaddition of many carbonyl derivatives to olefins is a reaction of considerable synthetic interest. It results in the formation of oxetanes and/or cyclobutanes which are useful intermediates in further thermal processes. The photochemical addition of enones to olefins has been thoroughly investigated (de Mayo *et al.*, 1971), whereas the photochemistry of the pyridinones has been studied only recently. Some general rules have been established concerning the conditions for efficient reaction, and the regio- and stereoselectivities of the cycloaddition have been described (Guerry and Neier, 1987).

In order to gain a better understanding of the primary photochemical process in the cycloaddition of pyridinones to olefins, we have undertaken a detailed study of the photophysics and photoreactivity of a series of substituted dihydro-4-pyridinones, the chemical structures of which are given in Scheme 1.

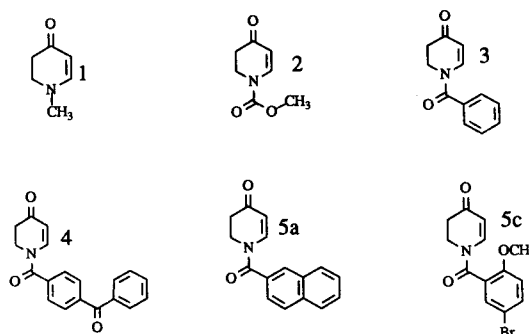
It is shown that the reactive state in all these molecules is the lowest triplet state T_1 ; in this respect the dihydropyridinones are similar to the enones. In the dihydropyridinones the lowest excited singlet and triplet states have a substantial charge-transfer character which explains the high reactivity and regioselectivity towards reaction with substituted olefins.

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§Abbreviations: CHO, 2-cyclohexen-1-one; DHP, 5,6-dihydro-4-pyridinone; EI, electron impact; E_T , triplet state energy; MS, mass spectrum; NMR, nuclear magnetic resonance; THF, tetrahydrofuran; TLC, thin layer chromatography; TMS, tetramethylsilane.



Scheme 1

MATERIALS AND METHODS

General procedures. Steady-state irradiations: silica cells with solutions degassed by freeze-pump-thaw cycles were used, and irradiations with a high pressure mercury lamp (100 W), using a high-aperture grating monochromator. Absorption spectra were measured with a Perkin-Elmer Lambda 3 spectrophotometer. Laser flash photolysis experiments have been performed with an N₂-laser (Oxford Lasers), producing a light output of 0.4 mJ per flash at 337 nm. The analysis light, set perpendicular to the laser beam, was produced by a high pressure xenon lamp (150 W). Solutions were degassed in the same manner as indicated above, and had an optical density of 1 at the irradiation wavelength. Luminescence measurements were performed on a conventional apparatus, which has been described previously (Butty, 1987), using a 200 W xenon/mercury lamp as excitation source at 313 nm for each luminescence spectrum.

Proton magnetic resonance (¹H-NMR)§ spectra were recorded with Bruker WP 80 CW and AM 360 spectrometers with tetramethylsilane (TMS) as internal standard; the chemical shifts are indicated in ppm and the coupling constants are in hertz. Carbon magnetic resonance spectra (¹³C-NMR) were recorded with a Bruker AM 360 spectrometer at 90.55 MHz with TMS as internal standard. Ultraviolet (UV) spectra were measured on a Perkin-Elmer 320 spectrophotometer, and infrared (IR) spectra on a Perkin-Elmer IR 599 spectrophotometer.

Mass spectra (MS), using EI conditions, were obtained with a VG instruments 7070 E mass spectrometer. Melting points (F) were determined with a Reichert Thermovar (Austria) apparatus and are uncorrected.

Samples and solvents for irradiations. 5,6-Dihydro-4-pyridinones were synthesized according to the methods described below. Olefins used for the cycloaddition reactions were used as received: acrylonitrile and methyl acrylate (puriss.), tetramethylethylene, cyclohexane and methylvinylketone (purum), fumarodinitrile and 1-hexene (pract.), and tetracyanoethylene [purum, being further purified by sublimation (90°C, 5.33 Pa)] were all purchased from Fluka (Buchs, Switzerland); diethyl maleate was obtained from Schuchart (Munich, W. Germany) and maleic anhydride from Merck (Zürich, Switzerland). Solvents for spectroscopic measurements and irradiations were of spectroscopic grade (Fluka) and used as received.

Materials. The starting materials were used as received: 4-piperidinone-ethyleneacetate was purchased from EGA-Chemie (Steinheim, W. Germany), *o*-methoxybenzoyl chloride was obtained from the reaction between *o*-methoxybenzoic acid and thionyl chloride and purified by distillation (Organikum 1974), all others from Fluka (Buchs, Switzerland): β -naphthoyl chloride (purum), triethylamine (puriss.), bromine (purum), potassium *tert*-butylate (pract.), perchloric acid (60%) (puriss.). The reaction-solvents were freshly distilled and in some cases dried as indicated in the text, and the solvents for extraction were of purum quality (Fluka).

Synthesis of *N*-(β -naphthoyl)-5,6-dihydro-4-pyridinone (**5a**)

N-(β -naphthoyl)-4-piperidinone-ethyleneacetate (**9a**). A solution of 6.84 g (36 mmol) of β -naphthoyl chloride (**8a**) in 20 ml methylene chloride (dried over LiAlH₄) was added drop by drop over a period of 1.5 h to a solution of 4.5 ml (5 g, 35 mmol) of 4-piperidinone-ethyleneacetate (**7**) and 5 ml (3.64 g, 36 mmol) of triethylamine in 120 ml of diethylether (dried over NaH), at room temperature. After stirring for 2.5 h at this temperature, the triethylammonium chloride was then filtered and washed with ether. After the solvent had been removed on the rotavap, 10.2 g of crude white product were obtained, which were purified by recrystallization in ether to give 8.6 g (80%) of white crystals. F = 104–106°C; ¹H-NMR (360 MHz, CDCl₃): δ = 7.90 [d, J = 1.5 Hz, 1H, H-C(9)], 7.89–7.83 [m, 3H, H-C(11), H-C(14), H-C(16)], 7.55–7.47 [m, 3H, H-C(12), H-C(13), H-C(17)], 3.98 (s, 4H, OCH₂CH₂O), 4.1–3.7, 3.7–3.4 [2m, 2 \times 2H, H₂C(6) and H₂C(2)], 2.0–1.5 [2m, 2 \times 2H, H₂C(5) and H₂C(3)]; ¹³C-NMR (90 MHz, CDCl₃): δ = 170.2 [s, C(7)], 133.5, 133.2, 132.5 [3s, C(8), C(10), C(15)], 128.2, 128.2, 127.6, 126.9, 126.5, 126.5, 125.0 [7d, C-H (naphthyl)], 106.8 [s, C(4)], 64.3 (t, OCH₂CH₂O), 48.3–47.5, 41.0–39.5 [2m wide, C(2) and C(6)], 35.5, 34.8 [2m wide, C(3) and C(5)]; IR (KBr, cm⁻¹): 3060w, 2970m, 2930w, 2890m, 1630vs, 1470m, 1433s, 1360m, 1235m, 1150m, 1125m, 1090s; MS (*m/z*; intensity in %): 297(M⁺, 47), 195(11), 172(21), 155(100), 127(85), 99(71).

N-(β -naphthoyl)-3-bromo-4-piperidinone-ethyleneacetate (**10a**). To a solution of 20 g (18 mmol) of product (**9a**) in 240 ml ethyleneglycol (dried over CaH₂) at 50°C under nitrogen atmosphere, 4.95 ml (15.35 g, 96 mmol) of bromine were added in three portions in a period of 2 h. After 2 h stirring at this temperature, the reaction was complete (TLC control), and the solution was then poured in a suspension of 13.11 g K₂CO₃ (Fluka purum, 96 mmol) in 240 ml methylene chloride and stirred for 1 h. The two phases were separated and the ethyleneglycol phase extracted three times with 150 ml CH₂Cl₂. The CH₂Cl₂ phases were treated with 200 ml of a half-saturated aqueous solution of NaCl, and dried over K₂CO₃/MgSO₄. The solvent was removed by distillation on the rotavap and

the oily rest dried under high vacuum to obtain 25.2 g (98%) of product, which could be recrystallized in benzene to give a white powder. F = 134–137°C; ¹H-NMR (360 MHz, DMSO-d₆, 100°C): δ = 7.97 [d, J = 1.6 Hz, 1H, H-C(9)], 7.96–7.91 [m, 3H, H-C(11), H-C(14), H-C(16)], 7.59–7.50 [m, 3H, H-C(12), H-C(13), H-C(17)], 4.31 [ddd, J = 7.64 Hz, J = 3.7 Hz, J = 1.09 Hz, 1H, H-C(3)], 4.31–3.94 [m, 5H, OCH₂CH₂O, H-C(2) ax or eq], 3.76 [dd, J = 13.73 Hz, 1H, H-C(2) ax or eq], 3.62 [t, J = 6.1 Hz, 2H, H₂C(6)], 2.11 [ddd, J = 13.5 Hz, J = 5.7 Hz, J = 5.7 Hz, 1H, H-C(5) ax], 1.70 [dddd, J = 13.4 Hz, J = 12.2 Hz, J = 7.09 Hz, J = 1.09 Hz, 1H, H-C(5) eq]; ¹³C-NMR (90 MHz, CDCl₃): δ = 170.6 [s, C(7)], 133.6, 132.5 [2s, C(8), C(10), C(15)], 128.2, 127.7, 127.0, 126.9, 126.6, 124.2 [6d, C(9), C(11), C(12), C(13), C(14), C(16), C(17)], 106.2 [s, C(4)], 65.7 (t, OCH₂CH₂O), 52.1 [d, C(3)], 49.4 (*m* wide, C(2)), 42.4 [*m* wide, C(6)], 36.3 [*m* wide, C(5)]; IR (KBr, cm⁻¹): 3060w, 2970w, 2890w, 1640s, 1475w, 1430m, 1165w, 1120w, 1085w; MS (*m/z*, intensity in %): 377(M⁺, 12), 375 (M⁺, 12), 296(9), 155(59), 99(100).

N-(β -naphthoyl)-5,6-dihydro-4-pyridinone-ethyleneacetate (**11a**). A solution of 5.13 g (46 mmol) of potassium *tert*-butylate in 14 ml of THF (dried over K) was added drop by drop over 30 min at room temperature to a solution of 12 g of product (**10a**) in 110 ml dry THF under nitrogen atmosphere. After being stirred for 30 min, the solution was then chilled to 0°C, diluted with 220 ml water at 0°C and extracted three times with 100 ml CH₂Cl₂. The organic phases were dried over K₂CO₃ and the solvent removed by distillation on the rotavap. The oily residue was dried under high vacuum to give 3.81 g (40%) of crude product. It was recrystallized with CH₂Cl₂/hexane to give 3.5 g (37%) of white powder. F = 133–136°C; ¹H-NMR (360 MHz, CDCl₃): δ = 7.99 [d, J = 1.5 Hz, 1H, H-C(9)], 7.91–7.85 [m, 3H, H-C(11), H-C(14), H-C(16)], 7.60–7.52 [m, 3H, H-C(12), H-C(13), H-C(17)], 6.9–6.6 [*m* wide, 1H, H-C(2)], 5.0–4.7 [*m* wide, 1H, H-C(3)], 4.1–3.8 [m, 5H, OCH₂CH₂O, H₂C(6)], 2.3–1.9 [*m* wide, 2H, H₂C(5)]; ¹³C-NMR (90 MHz, CDCl₃): δ = 169.8 [s, C(4)], 134.0, 132.3, 131.4 [3s, C(8), C(10), C(15)], 130.9 [d wide C(2)], 128.5, 128.3, 127.7, 127.5, 126.8, 124.8 [6d, C(9), C(11), C(12), C(13), C(14), C(16), C(17)], 107.1 [d wide, C(3)], 103.4 [s, C(4)], 64.5 (t, OCH₂CH₂O), 40.3 [*m* wide, C(6)], 32.6 [t, C(3)]; IR (KBr, cm⁻¹): 3060w, 3030w, 2980w, 2900w, 1640vs, 1420m, 1360s, 1350s, 1300m, 1250m, 1120s, 1078s, 948m, 938m, 928m, 830m, 770m; MS (*m/z*; intensity in %): 295(M⁺, 24), 215(5), 155(100), 127(52), 99(7), 53(8).

N-(β -naphthoyl)-5,6-dihydro-4-pyridinone (**5a**). To a solution of 3 g of product (**11a**) in 88 ml CH₂Cl₂ and 26 ml THF chilled to 0°C was added to 9 ml of perchloric acid (60%) drop by drop over a period of 30 min, and the solution was stirred for 2.5 h at room temperature. The mixture was then neutralized with 88 ml of an aqueous solution 1N of NaHCO₃. After separation of the organic phase, the water solution was extracted three times with 50 ml CH₂Cl₂ and the combined organic phases were dried over K₂CO₃/Na₂SO₄. The solvent was removed on the rotavap and the rest dried under high vacuum to give, after recrystallization in CH₂Cl₂/hexane, 1.62 g (63%) of white crystalline product. F = 94–97°C; UV (MeOH): λ_{max} = 291 nm (ϵ = 20 120), 301 nm (*sh*, 17 900), 225 nm (41 200); ¹H-NMR (360 MHz, CDCl₃): δ = 8.09 [s, 1H, H-C(9)], 7.97–7.88 [m, 3H, H-C(11), H-C(14), H-C(16)], 7.67 [d, J = 8.24 Hz, 1H, H-C(2)], 7.65–7.55 [m, 3H, H-C(12), H-C(13), H-C(17)], 5.34 [d, J = 8.24 Hz, 1H, H-C(3)], 4.22 [t, J = 7.1 Hz, 2H, H-C(6)], 2.71 [t, J = 7.4 Hz, 2H, H-C(5)]. ¹³C-NMR (90 MHz, CDCl₃): δ = 193.2 [s, C(4)], 170.2 [s, C(7)], 144.8 [d, C(2)], 134.4, 132.2, 129.8 [3s, C(8), C(10), C(15)], 129.3, 128.7, 128.1, 127.8, 127.2, 124.7 [6d, C(9), C(11), C(12), C(13), C(14), C(16), C(17)], 107.7 [d, C(3)], 43.0 [t, C(6)], 36.0 [t, C(5)];

IR (KBr, cm^{-1}): 3080w, 1665vs, 1592vs, 1395m, 1230m, 1200m, 1185, 1145m, 980w, 840w, 820w, 780w; MS (m/z , intensity in %): 251 (M^+ , 12), 155(100), 127(67), 69(13), 57(20), 45(13).

Synthesis of *N*-(12-bromo-9-methoxybenzoyl)-5,6-dihydro-4-pyridinone (5c)

N-(9-Methoxybenzoyl)-4-piperidinone-ethyleneacetal (**9b**). The same method was used as for the synthesis of (**9a**), with 4.5 ml (5 g, 35 mmol) of 4-piperidinone-ethyleneacetal, 6.1 g (36 mmol) of *o*-anisoyl chloride (**8b**) and in the presence of 5.01 ml (3.64 g, 36 mmol) of triethylamine, producing 7.3 g (75%) of white crystals. $F = 90\text{--}93^\circ\text{C}$; $^1\text{H-NMR}$ (360 MHz, CDCl_3): $\delta = 7.34$ [ddd, $J = 8.3$ Hz, $J = 7.7$ Hz, $J = 1.7$ Hz, 1H, H-C(11)], 7.23 [dd, $J = 7.5$ Hz, $J = 1.7$ Hz, 1H, H-C(13)], 6.91 [d, $J = 8.3$ Hz, 1H, H-C(10)], 6.87 [ddd, $J = 7.5$ Hz, $J = 1.7$ Hz, $J = 0.9$ Hz, 1H, H-C(12)], 4.0–3.9, 3.85–3.75, 3.4–3.25 [4m, 5H, 1H, 2H, $\text{OCH}_2\text{CH}_2\text{O}$, H-C(6), H-C(2)], 3.82 (s, 3H, OCH_3), 1.85–1.75, 1.75–1.55 [2m, 2 \times 2H, $\text{H}_2\text{C}(5)$, $\text{H}_2\text{C}(3)$]; $^{13}\text{C-NMR}$ (90 MHz, CDCl_3): $\delta = 167.4$ [s, C(7)], 155.2 [s, C(9)], 130.2 [d, C(11)], 127.6 [d, C(13)], 125.9 [s, C(8)], 120.7 [d, C(12)], 110.8 [d, C(10)], 106.8 [s, C(4)], 64.3 (t, $\text{OCH}_2\text{CH}_2\text{O}$), 55.4 (q, OCH_3), 44.8, 39.4 [2t, C(6), C(2)], 35.4, 34.7 [2t, C(5), C(3)]; IR (KBr, cm^{-1}): 3000w, 2960w, 2930w, 2880w, 1625s, 1470m, 1440m, 1245m, 1120m, 1090m, 1030w, 950m, 770m; MS (m/z , intensity in %): 277(M^+ , 50), 276(61), 246(8), 135(100), 99(62), 77(48), 55(13), 42(12).

N-(12-bromo-9-methoxybenzoyl)-4-piperidinone-ethyleneacetal (**9c**). To a solution of 6.2 g (22.4 mmol) of product (**9b**) in 80 ml ethyleneglycol (dried over CaH_2) at 50°C under N_2 atmosphere 1.4 ml (4.35 g, 32 mmol) of Br_2 was added in three portions over 1 h. After stirring for 1 h at the same temperature, the solution was poured on a suspension of 4.4 g (32 mmol) of K_2CO_3 in 80 ml methylene chloride, and stirred further for 1 h. After separation of the CH_2Cl_2 phase, the solution of ethyleneglycol was extracted three times with 100 ml of CH_2Cl_2 . The gathered methylene chloride phases were extracted once with a half-saturated aqueous solution of NaCl. The organic phase was then dried over $\text{K}_2\text{CO}_3/\text{MgSO}_4$ and the solvent removed by distillation on the rotavap. This produced 6.9 g of (85%) of pure white powder ($^1\text{H-NMR}$), dried under high vacuum. $F = 130\text{--}134^\circ\text{C}$; $^1\text{H-NMR}$ (360 MHz, CDCl_3): $\delta = 7.41$ [dd, $J = 8.8$ Hz, $J = 2.5$ Hz, 1H, H-C(11)], 7.32 [d, $J = 2.5$ Hz, 1H, H-C(13)], 6.76 [d, $J = 8.8$ Hz, 1H, H-C(10)], 4.0–3.92 (m, 4H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.78 (s, 3H, OCH_3), 4.3–3.8 and 3.8–3.6, 3.4–3.2 [3m, 4H, H-C(6), $\text{H}_2\text{C}(2)$], 1.9–1.7, 1.8–1.5 [2m, 2 \times 2H, $\text{H}_2\text{C}(5)$, $\text{H}_2\text{C}(3)$]; $^{13}\text{C-NMR}$ (90 MHz, CDCl_3): $\delta = 165.7$ [s, C(7)], 154.3 [s, C(9)], 132.8 [d, C(11)], 130.4 [d, C(13)], 127.8 [s, C(8)], 112.9 [s, C(12)], 112.7 [d, C(10)], 106.7 [s, C(4)], 64.4 (t, $\text{OCH}_2\text{CH}_2\text{O}$), 55.8 (q, OCH_3), 44.9, 39.6 [2t, C(6), C(2)], 35.4, 34.7 [2t, C(5), C(3)]; IR [KBr, cm^{-1}]: 3000w, 2950w, 2930w, 2880w, 1630s, 1490w, 1470w, 1440w, 1260m, 1125w, 1090s, 1020w, 950w, 930w, 820w; MS (m/z , intensity in %): 357 (M^+ , 19), 355(M^+ , 26), 276(13), 213(42), 170(7), 135(27), 99(100), 78(42), 55(12), 42(10).

N-(12-bromo-9-methoxybenzoyl)-3-bromo-4-piperidinone-ethyleneacetal (**10c**). 2.2 ml (6.85 g, 43 mmol) of bromine were added in four portions and in 2 h to a solution of 6.6 g (18.5 mmol) of product (**9c**) in 90 ml ethyleneglycol (dried over CaH_2) at 50°C under N_2 atmosphere. The solution was stirred for 15 h, then poured on a suspension of 5.91 g (42.8 mmol) of K_2CO_3 in 70 ml methylene chloride and stirred for 1 h. After separation of the sol-

*For a certain number of protons (in $^1\text{H-NMR}$ spectra) and carbons (in $^{13}\text{C-NMR}$ spectra), the signals due to the two rotamers around the amide bond could be observed.

ution of methylene chloride, the phase of ethyleneglycol was extracted three times with 50 ml of CH_2Cl_2 . The gathered methylene chloride phases were extracted once with 100 ml of a half-saturated aqueous solution of NaCl and dried over Na_2SO_4 . After the solvent was removed on the rotavap, 7.8 g (97%) of powder could be recrystallized in ethyl acetate to give white crystals. $F = 183\text{--}187^\circ\text{C}$; $^1\text{H-NMR}$ (360 MHz, DMSO-d_6 , hot temperature: 150°C): $\delta = 7.52$ [dd, $J = 8.8$ Hz, $J = 2.6$ Hz, 1H, H-C(11)], 7.36 [d, $J = 2.5$ Hz, 1H, H-C(13)], 6.40 [d, $J = 8.8$ Hz, 1H, H-C(10)], 4.20 [ddd, $J = 8.2$ Hz, $J = 3.9$ Hz, $J = 0.9$ Hz, 1H, H-C(3)], 4.1–3.9 [m, 5H, $\text{OCH}_2\text{CH}_2\text{O}$, H-C(2)], 3.82 [s, 3H, OCH_3], 3.8–3.3 [m, 3H, H-C(2) and H-C(6)], 2.07 [ddd, $J = 13.5$ Hz, $J = 6.9$ Hz, $J = 3.9$ Hz, 1H, H-C(5) ax or eq], 1.66 [dddd, $J = 13.5$ Hz, $J = 8.4$ Hz, $J = 4.3$ Hz, $J = 0.9$ Hz, 1H, H-C(5) ax or eq]; $^{13}\text{C-NMR}$ (90 MHz, CDCl_3): $\delta = 166.0$ [s, C(7)], 154.3 [s, C(9)], 133.3, 131.6 [2d, C(11)], 130.4, 130.4 [2d, C(13)], 127.2, 126.8 [2s, C(8)], 113.0, 112.9, 112.7, 112.5 [4s, C(10), C(12)], 108.4, 108.2 [2s, C(4)], 77.4 [d, C(3)], 65.8 (t, $\text{OCH}_2\text{CH}_2\text{O}$), 55.9, 55.8 (2q, OCH_3), 51.8, 51.7 [2t, C(6)], 46.4, 44.6 [2t, C(2)], 39.3, 35 [2t, C(5)]; IR (KBr, cm^{-1}): 3000–2700w, 1630s, 1440m, 1270m, 1260m, 1240w, 1170m, 1140m, 1075w, 1030w, 950w, 825w, 750w; MS (m/z , intensity in %): 437(M^+ , 17), 435(M^+ , 37), 433(M^+ , 18), 354(35), 215(56), 157(7), 99(100).

N-(12-bromo-9-methoxybenzoyl)-5,6-dihydro-4-pyridinone-ethyleneacetal (**11c**). The same method was used as for the synthesis of (**11a**), with 7 g (16 mmol) of product (**10c**), 120 ml THF, 2.6 g (23 mmol) of potassium *tert*-butylate in 15 ml THF. This produced 4.8 g (84%) of white powder that could be re-crystallized in CH_2Cl_2 /hexane. $F = 102\text{--}105^\circ\text{C}$; $^1\text{H-NMR}$ (360 MHz, CDCl_3): $\delta = 7.5\text{--}7.3$ [m, 2H, H-C(11), H-C(13)], 6.81 [d, $J = 8.8$ Hz, 1H, H-C(10)], 6.33 [d, $J = 8.4$ Hz, 1H, H-C(2)], 5.13, 4.76 [2d, $J = 8.4$ Hz, 2 \times 1H, H-C(3)], 4.1–3.85 (m, 4H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.82, 3.79 (2s, 2 \times 3H, OCH_3), 4.2–3.2 [m, 2H, $\text{H}_2\text{C}(6)$], 2.1–1.55 [m, 2H, $\text{H}_2\text{C}(5)$]; $^{13}\text{C-NMR}$ (90 MHz, CDCl_3): $\delta = 165.7$ [s, C(7)], 154.7, 153.6 [2s, C(9)], 133.8, 132.9 [2s, C(11)], 131.1, 127.2 [2d, C(13)], 130.1 [d, C(2)], 126.0 [s, C(8)], 113.9, 112.9, 112.8, 112.7 [4s, C(10), C(12)], 110.0, 107.7 [2d, C(3)], 103.3 [s, C(4)], 64.5, 64.4 (2t, $\text{OCH}_2\text{CH}_2\text{O}$), 56.0, 55.8 (2q, OCH_3), 39.6, 39.2 [2t, C(6)], 32.9, 32.1 [2t, C(5)]; IR (KBr, cm^{-1}): 3000–2800w, 1630s, 1490–1450m, 1420–1390m, 1355m, 1255m, 1120m, 1080m, 950w, 925w, 915w, 655w, 625w; MS (m/z , intensity in %): 355(M^+ , 19), 353(M^+ , 16), 296(24), 294(24), 213(100), 155(10), 157(10), 126(34), 99(22).

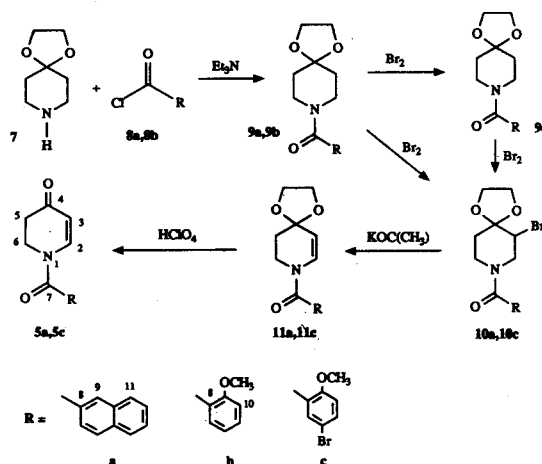
N-(12-bromo-9-methoxybenzoyl)-5,6-dihydro-4-pyridinone (**5c**). The same method was used as for the synthesis of (**5a**), with 10 ml of a solution of perchloric acid (60%), 4 g (11.3 mmol) of fourth step product in 30 ml of THF and 100 ml of CH_2Cl_2 . After recrystallization in diethylether, 2.73 g (80%) of crystals were obtained. $F = 111\text{--}115^\circ\text{C}$; UV (MeOH): $\lambda_{\text{max}} = 291.5$ nm ($\epsilon = 18$ 500); $^1\text{H-NMR}$ (360 MHz, CDCl_3): $\delta = 7.566$ [dd, $J = 8.8$ Hz, $J = 2.5$ Hz, 1H, H-C(11)], 7.477 [d, $J = 2.5$ Hz, 1H, H-C(13)], 7.25–7.1 [br, 1H, H-C(2)], 6.868 [d, $J = 8.8$ Hz, 1H, H-C(10)], 5.4–5.2 [br, 1H, H-C(3)], 4.4–3.5 [br, 2H, $\text{H}_2\text{C}(6)$], 3.83 (s, 3H, OCH_3), 2.75–2.45 [br, 2H, $\text{H}_2\text{C}(5)$]; $^{13}\text{C-NMR}$ (90 MHz, CDCl_3): $\delta = 193.2$ [s, C(4)], 166.2 [s, C(7)], 154.7 [s, C(9)], 144.4 [d, wide, C(2)], 134.8 [d wide, C(11)], 131.6 [d, C(13)], 124.5 [s, C(8)], 113.2, 113.1 [2s, C(10), C(12)], 107.9 [d wide, C(3)], 56.1 (q, OCH_3), 40.8 [t wide, C(6)], 35.7 [t wide, C(5)]; IR [KBr, cm^{-1}]: 3060w, 2980–2800w, 1660vs, 1590vs, 1485m, 1465m, 1410s, 1350s, 1305s, 1260m, 1225vs, 1190m, 1165m, 1130m, 1030m, 980m, 960m, 915w, 900w, 825m, 640m, 625m; MS (m/z , intensity in %): 311 (M^+ , 32), 309(M^+ , 32), 215(100), 213(100), 172(20), 170(20), 157(20), 155(20), 76(15).

Synthesis

The synthesis of most products used in this work has been already published (Guerry and Neier, 1987; Guerry, 1983). Nevertheless further different substituted DHPs were needed for photochemical investigations, and products **5a** and **5c** were synthesized according to the methods described in the references mentioned above.

As shown in Scheme 2, the starting molecule was in most cases the piperidinone-ethyleneacetal **7**, which was acylated to give the *N*-arylcarbonyl-derivatives **9a** and **9b**. The following steps involved bromination in α -position of the carbonyl group, elimination of HBr and finally deprotection in acidic conditions to give the product molecules, *N*-arylcarbonyl-5,6-dihydro-4-pyridinones **5a** and **5c**.

In the case of **9b**, the bromination occurred first in the aromatic ring at the position *para* to the methoxy group, followed by bromination at the desired place. This transformation could be effected in a one pot procedure or in two separated steps.



Scheme 2

Absorption and luminescence spectra, energy level diagrams

Compound **1** is the only dihydropyridinone (DHP) in this series with an electron donor substituent on the nitrogen atom; it differs from the others in showing a red-shifted absorption spectrum with the first absorption band near 310 nm of extinction coefficient $1.8 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. Dihydropyridinones **2-5** (**a** and **c**) have an electron acceptor group linked to the nitrogen and show a first absorption band near 290 nm.

These absorption bands are solvent sensitive, both for the wavelength and for the extinction coefficients. A comparison of the six solutes in alcohol solvents is given in Table 1.

Table 1. Comparison of the first absorption band of the different solutes

	1	2	3	4	5a	5c
Solvent	EtOH	EtOH	EtOH	EtOH	MeOH	MeOH
ϵ ($\text{l mol}^{-1} \text{ cm}^{-1}$)	15 300	16 700	18 000	25 300	20 100	18 500
λ_{max} (nm)	324	286	292	280	291	291.5

Figure 1 shows a plot of the transition energy (at λ_{max}) for the first observable absorption band of **1** as a function of solvent polarity defined by the Onsager function $f(D) = 2(D-1)/(2D+1)$ of the static dielectric constant D (Onsager, 1936). While the values of extinction coefficients clearly show that this band corresponds to a $\pi-\pi^*$ transition, it must be borne in mind that the much weaker $n-\pi^*$ band may be hidden under it.

The dipole moment μ_e of the excited molecule can then be calculated if the ground state dipole moment μ_g is known, according to the usual solvatochromic shift equation (Suppan, 1968):

$$\Delta h\nu_{i-j} = -\frac{\mu_e(\mu_e - \mu_g)}{a^3} \Delta f(D)_{i-j} \quad (1)$$

where a is the molecular radius ($(4/3)\pi a^3$ is the molecular volume $V = \rho M/L$ for a molecule of density ρ and molecular weight M , L being Loschmidt's number). This simple equation of solvatochromic shifts applies only to a series of solvents (i, j) of similar refractive index, as it is restricted to the dipole-dipole orientation interaction between the solute and the solvent molecules. It yields for **1** an excited state dipole moment $\mu_e = 9.5 \text{ D}$, the ground state dipole moment being estimated as $\mu_g = 4.5 \text{ D}$ (from the vector addition of the CO and NMe bond dipoles) and the molecular radius being $a = 3.5 \times 10^{-10} \text{ m}$.

The anomalous red shift in ethanol is in keeping with the spectroscopic properties of other carbonyl derivatives, e.g. benzophenone (Suppan, 1974). It has been explained as the result of an increased

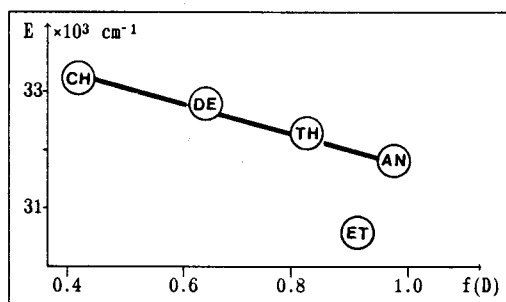


Figure 1. Solvatochromic shift of DHP **1**, where CH is cyclohexane, DE diisopropylether, TH tetrahydrofuran, AN acetonitrile, and ET ethanol.

charge-transfer character of the $\pi-\pi^*$ state when the carbonyl π^* orbital is lowered through hydrogen bonding by the protic solvent to the oxygen atom.

No fluorescence has been detected from these molecules in solution so that an upper limit of lifetime of 10^{-11} s can be given for the $\pi-\pi^*/\text{CT}$ singlet excited state according to the natural radiative lifetime calculated from the integrated absorption (Parker, 1968) and the sensitivity of our fluorimeter according to the following considerations. The natural radiative decay rate constant k_{rn} can be calculated from the extinction coefficient at the absorption maxima:

$$k_{rn} = 10^4 \times \epsilon_{\max} \quad (2)$$

With

$$\Phi_f = k_{fn}/(k_{fn} + k_d) \quad (3)$$

provided that

$$k_d = k_{f, \text{obs}} \quad (4)$$

yields

$$k_d = \frac{k_{fn}}{\Phi_f} = \frac{10^4 \times \epsilon_{\max}}{\Phi_f} \geq \frac{10^4 \times \epsilon_{\max}}{\Phi'} \quad (5)$$

where Φ_f is the fluorescence quantum yield, Φ' the minimal fluorescence quantum yield, which can be measured with our fluorimeter, taken as 10^{-4} , k_{fn} the natural fluorescence decay rate constant, k_d the deactivation rate constant, $k_{f, \text{obs}}$ the observed fluorescence decay rate constant. Thus, with $\epsilon_{\max} = 1.5 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $\Phi_f = 10^{-3}$, we obtain $k_d \geq 1.5 \times 10^{11} \text{ s}^{-1}$.

For **1**, this state is the first singlet excited state in EtOH; in non-protic solvents the first singlet excited state is probably of $n-\pi^*$ type, and this would have a much longer natural radiative lifetime, so that fluorescence would not be expected.

A weak phosphorescence is observed in rigid low temperature glasses from the carbonyl substituted species **2**, **3**, **4** and **5c** with an onset near 425 nm; the β -naphthoyl substituted molecule **5a** shows a more intense phosphorescence characteristic of the aromatic moiety, with an onset at 485 nm (Fig. 2).

The *N*-methyl derivative **1** shows no phosphorescence, but its triplet state energy (E_T) could be

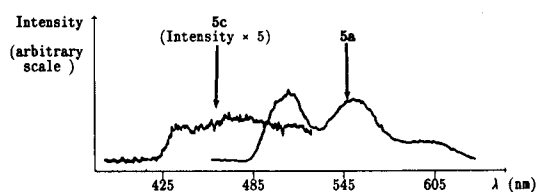


Figure 2. Phosphorescence of β -naphthoyl substituted DHP **5a** and DHP **5c** as an example.

obtained from electron energy loss spectroscopy (Allan, 1982; Labhart and Haselbach, 1984); the E_T value is 295 kJ mol^{-1} (3.07 eV) (Fig. 3). It must be borne in mind, however, that these are gas phase values which may need some correction for solvation effects when comparisons are made with condensed phase data. These corrections are, however, quite small in most cases, on the order of about 10 kJ mol^{-1} (tenths of an eV) except when the dipole moment of the excited molecule is very large (Suppan, 1968).

The energy level diagrams shown in Fig. 4 are established on the basis of the spectroscopic data, and when necessary, by comparison with 2-cyclohexen-1-one (CHO) (de Mayo *et al.*, 1970). In particular, it is assumed that the $n-\pi^*$ singlet and triplet states are the same in CHO, DHP **1** and the DHPs **2-5** (a and c) for which a common energy level diagram provides a sufficient approximation.

CHO: The $n-\pi^*$ (S_1) and $\pi-\pi^*$ (S_2) transitions are observed in the absorption spectrum, and it is noteworthy that the energy of the former remains unchanged in the 3,5-dimethyl derivative, whereas the energy of the $\pi-\pi^*$ state is lowered by about 2000 cm^{-1} . This is the main justification for the assumption of the invariance of the $n-\pi^*$ levels in the DHPs (*The Sadler Handbook of Ultraviolet Spectra*, 1979). The energy of the lowest triplet level T_1 of CHO is set at 2.9 eV following the indirect measurements of de Mayo *et al.* (1970); this is assigned as a $^3\pi-\pi^*$ state, similar to that observed through the phosphorescence of more rigid CHO derivatives (Jones and Kearns, 1977).

The energy of the $n-\pi^*$ triplet (T_2) of the CHO is not known experimentally; it is estimated according to the usually observed small singlet-triplet splitting of carbonyl $n-\pi^*$ states (Murrell, 1963), this splitting being around 2000 cm^{-1} . Indeed, phosphorescence polarization measurements have shown that there is little interaction between $\pi-\pi^*$ and $n-\pi^*$ triplets (Jones and Kearns, 1977) in molecules of this type.

DHP **1**: The $\pi-\pi^*/\text{CT}$ states are shown simply as "CT" in Fig. 4. The singlet state must be a little

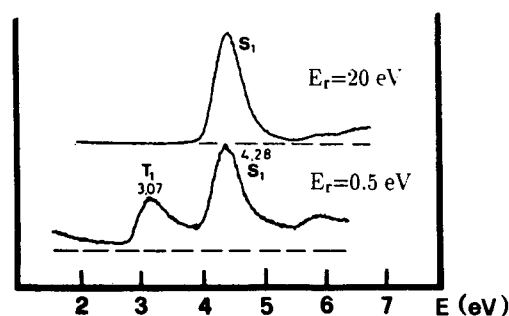


Figure 3. Electron energy loss spectra of DHP **1** (E_r is the residual energy of the scattered electron). (See Allan, 1982; Labhart and Haselbach, 1984 for details about this method.)

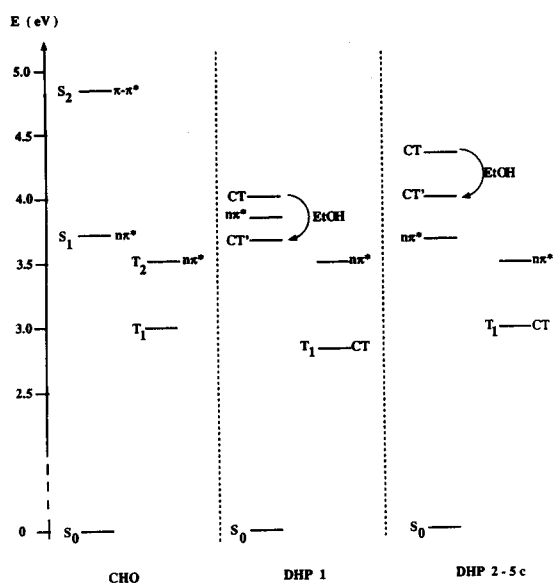


Figure 4. Energy level diagrams of 2-cyclohexen-2-one (CHO), DHP 1 and DHPs 2c-5c (see text).

higher in energy than the $^1(n-\pi^*)$ state in non-protic solvents, but reversal of the levels probably takes place in protic EtOH. This has consequences for the photophysics and for the photochemistry of **1** which are discussed later ("Photochemical reactivity"). Note that this reversal of CT and $n-\pi^*$ levels does not take place in the triplet manifold.

DHPS 2-5c: Because the N atom is substituted with an electron-acceptor carbonyl group instead of an electron-donor methyl group, the CT singlet and triplet states are substantially higher in energy than in **1**: reversal of the 1CT and $^1(n-\pi^*)$ levels does not take place in EtOH.

The lowest excited states are of $\pi-\pi^*/CT$ type in these molecules, the charge densities changes being given as follows by a simple Hückel calculation:

This agrees qualitatively with the dipole moment change derived from the solvatochromic shift of the absorption spectrum. It leads to the conclusion that the largest decrease of electron density takes place at C_3 and the largest increase at C_4 .

Table 2. Coefficients of the π - and π^* -MOs, and charge-density changes for the $\pi \rightarrow \pi^*$ transition of DHP 1

Atoms	HMO-coefficients		Charge-density changes $\pi \rightarrow \pi^*$ transition
	π -MO	π^* -MO	
N	0.40	-0.25	-0.098
C_2	-0.37	0.64	0.273
C_3	-0.62	-0.11	-0.372
C_4	-0.12	-0.59	0.334
O	0.53	0.40	-0.121

Triplet state absorption spectrum and decay kinetics, triplet yields

The transient absorption spectrum of **1** in CH_2Cl_2 has been measured by laser flash photolysis and is shown in Fig. 5. The extinction coefficients were determined by comparison with a benzophenone/naphthalene standard of the same absorbance at the excitation wavelength (337 nm). The triplet yield of benzophenone being unity, the naphthalene concentration ($5 \times 10^{-2} M$) is sufficiently high to ensure practically quantitative energy transfer.

The decay of the triplet state of **1** in CH_2Cl_2 follows first order kinetics, with a lifetime of 16 μs at a concentration $[1] = 1.6 \times 10^{-4} M$. Neglecting triplet-triplet annihilation in view of the absence of a second-order component in the decay kinetics, the apparent first order decay rate constant can be ascribed to concentration quenching,



The experimental pseudo first-order rate constants for the decay of the triplet states are given in Table 3, together with the triplet yields.

The triplet yields were determined by energy transfer to naphthalene. At high enough naphthalene concentrations to intercept practically all DHP triplets formed in laser flash photolysis (N_2 laser at 337 nm), the T-T absorption of naphthalene observed at 413 nm provides a direct measurement of the DHP triplet yield. A solution of benzophenone/naphthalene was used as a standard, the triplet yield of benzophenone being taken as unity. All solutions were degassed and prepared so as to have the same absorbance at the laser wavelength. Note in particular the very low triplet yield of **1** in ethanol, compared to other solvents.

Photochemical reactivity with and without olefins in various solvents

The photochemical cycloaddition of the DHPs **1-5** (a and c) is observed by the change in the absorption spectrum and from this the quantum yield can be determined. These are listed in Tables

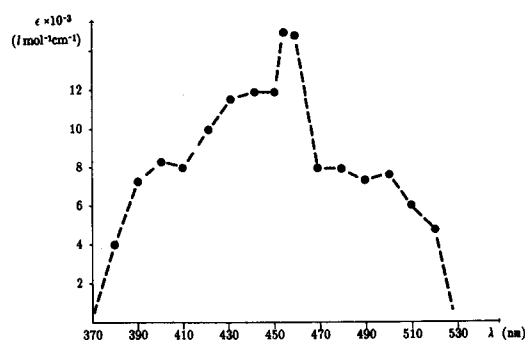
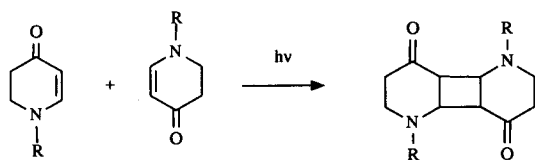


Figure 5. Triplet absorption spectrum of DHP 1.

4a and b for various olefins in different solvents, for DHPs **1** and **5c**.

The following observations can be made from these results:

- The quantum yield Φ_r of pyridinone-olefin cycloaddition is sensitive to quenching by oxygen only when the olefin concentration is low, typically $\leq 10^{-3}M$;
- The quantum yield Φ_r depends on the olefin concentration (Table 4a); it reaches a maximum value as the olefin concentration is increased. This limiting value corresponds closely to the triplet yield;
- In the absence of olefins, the reaction quantum yield is very low and is due to the photodimerization reaction:



Scheme 3

- The solvent has little influence on Φ_r , except when **1** is irradiated in a protic solvent such as EtOH. The very low quantum yield is related to the equally low triplet yield, as shown in Table 3; clearly the protic solvent quenches the singlet excited state of **1** in competition with intersystem crossing.

Coming back to the energy level diagrams of Fig. 4, this quenching may be related to the reversal of the $^1(n-\pi^*)$ and 1CT levels in a protic solvent. The red-shift anomaly of the absorption spectrum of **1** (Fig. 1) is evidence for hydrogen bonding of the carbonyl oxygen atom to hydroxylic solvent molecules already in the ground-state; in the excited 1CT state protonation at the carbonyl group may then take place, and this results in its deactivation. There are indeed many examples of such deactivations of $\pi-\pi^*$ states when protonation takes place in the π -system (Ireland and Wyatt, 1976).

There is no such quenching effect of EtOH on the N-carbonyl substituted DHPs because the 1CT state remains in all cases well above the $^1(n-\pi^*)$ level from which intersystem-crossing takes place to the reactive 3CT state, T_1 .

Quenching by oxygen and by naphthalene

The quenching effect of dissolved molecular oxygen on the pyridinone-olefin cycloaddition reaction has already been mentioned above. Naphthalene shows a similar quenching effect, the reaction quantum yield going to zero as the naphthalene concentration is increased. This observation is conclusive proof that the photochemical process originates

exclusively from the triplet excited state T_1 of the DHPs.

In the case of compound **5c**, the reaction quantum yield is 0.25 in the presence of $10^{-4}M$ tetramethylethylene in degassed acetonitrile; it drops to zero ($\leq 10^{-2}$) when $5 \times 10^{-3}M$ naphthalene is added. Assuming a diffusion-controlled quenching rate constant of $10^{10}M^{-1}s^{-1}$, the pseudo first-order quenching rate constant is then $\approx 5 \times 10^7s^{-1}$ against a pseudo first-order cycloaddition rate constant of $\approx 10^5s^{-1}$.

The β -naphthoyl substituted pyridinone **5a** shows a naphthalene-like phosphorescence and is totally unreactive towards cycloaddition even at high olefin concentrations ($10^{-2}M$), being deactivated intramolecularly.

Table 3. Quantum yields (Φ_T), lifetimes (τ), decay rate constants (k_r) and wavelengths of T_1-T_n absorption maxima of DHP **1**, **2**, **3**, and **5c** in different solvents

	1	1*	2	3	5c
Solvent	CH ₂ Cl ₂	EtOH	EtOH	EtOH	MeOH
Φ_T	0.2	0.03	1	1	1
τ (μ s)	16	—	0.5–1.0	1.5	1.5
k_r (s ⁻¹)	2×10^9	—	10^9	1.6×10^9	10^9
$\lambda_{\max T-T_n}$ (nm)	455	—	385	370	390

*In case of DHP **1** in ethanol, only the quantum yield could be measured.

Table 4.(a) Quantum yield Φ_r of photocycloaddition of $5 \times 10^{-5}M$ DHP **5c** with acrylonitrile in a degassed solution of acetonitrile at an excitation wavelength of 313 nm, as a function of olefin concentration

Concentration of olefin (M)	10^{-4}	2×10^{-4}	5×10^{-4}	10^{-3}	2×10^{-3}	5×10^{-3}
Φ_r	0.25	0.39	0.45	0.64	0.70	0.78

Table 4.(b) Quantum yield Φ_r of photocycloaddition of $5 \times 10^{-5}M$ DHP **1** with methyl acrylate at an excitation wavelength of 313 nm as a function of olefin concentration

Concentration of olefin (M)	Solvent	Degassed	Φ_r
Observation a:			
6.4×10^{-4}	MeCN	No	0.015
8.2×10^{-3}	MeCN	No	0.058
8.8×10^{-5}	MeCN	Yes	0.14
7.0×10^{-4}	MeCN	Yes	0.18
Observation c:			
No olefin	MeCN	Yes	0.0014
Observation d:			
2×10^{-1}	EtOH	Yes	0.023
2.7×10^{-4}	CH ₂ Cl ₂	Yes	0.13
2.8×10^{-4}	C ₆ H ₆	Yes	0.15

Intramolecular sensitization

The *p*-substituted molecule **4** provides an example of intramolecular sensitization such that the cycloaddition takes place for irradiation at 365 nm where the pyridinone chromophore does not absorb. As mentioned above, the phosphorescence spectrum of **4** is characteristic of the pyridinones and shows that the lowest triplet level is localized on that chromophore.

When **4** is irradiated at 365 nm in the presence of olefins the absorption spectrum changes towards that of the saturated pyridinone, while the absorption of the benzophenone-type chromophore ($n-\pi^*$ band near 360 nm, $\pi-\pi^*$ band near 250 nm) remains unchanged (Fig. 6).

If reaction of the triplet state of the benzophenone chromophore could take place, the 360 and 250 nm absorption bands should gradually disappear as the carbonyl group is saturated through oxetane formation and/or hydrogen abstraction.

Kinetic scheme and rate constants

Since the photoreactivity can be traced entirely to the triplet state of the DHPs, the reaction quantum yield can be expressed as follows:

$$\Phi_r = \left[\frac{k_r[L]}{k_r[L] + k_d + \sum k_q[Q]} \right] \Phi_T \quad (6)$$

where Φ_T is the triplet yield, k_r the second-order rate constant for pyridinone-olefin addition, $[L]$ the olefin concentration, k_d the pseudo-first order rate constant for triplet decay in the absence of reaction, k_q the second-order rate constant for any other bimolecular processes which deactivate the triplet state (with or without chemical reaction), and $[Q]$ the quencher concentration.

In the absence of olefins, the only photochemical reaction is the dimerisation ${}^3M^* + M \rightarrow M_2$ of rate constant k_r' and quantum yield:

$$\Phi_r = \left[\frac{k_r'[M]}{k_r'[M] + k_d + \sum k_q[Q]} \right] \Phi_T \quad (7)$$

Equation 6 can be rearranged to show explicitly the dependence of the reaction quantum yield on olefin concentration:

$$\frac{1}{\Phi_r} = \frac{1}{\Phi_T} + \frac{k_d}{k_r \Phi_T [L]} \quad (8)$$

from which the reaction rate constant is obtained as:

$$k_r = \frac{k_d}{[L] \left[\left(\frac{\Phi_T}{\Phi_r} \right) - 1 \right]} \quad (9)$$

Experimental plots of $1/\Phi_r$ vs $1/[L]$ are indeed linear, and yield Φ_T as the intercept; these values

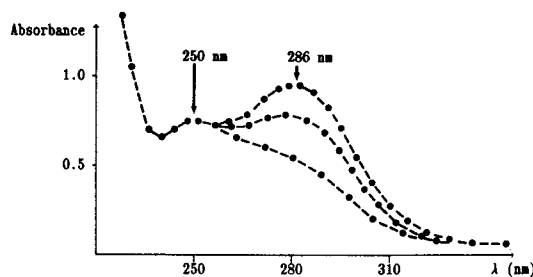


Figure 6. Decrease of absorption of DHP **4** in acetonitrile when irradiated at 365 nm in presence of $10^{-2} M$ tetramethylethylene.

are in satisfactory agreement with the triplet yields obtained from direct flash photolysis measurements, as shown in Fig. 7 and Table 5.

The reaction rate constants k_r are derived from the slope of the double-reciprocal plots, taking for k_d the experimental value of the triplet decay rate constant measured by flash photolysis in the absence of olefins.

In the absence of olefins the DHPs disappear slowly through the process of photodimerisation. The quantum yield is very low, e.g. 1.3×10^{-3} for $[1] = 5 \times 10^{-5} M$ in MeCN; the reaction rate constant is calculated as $k_r' = 10^6 M^{-1}s^{-1}$ from the triplet lifetime of 16 μs .

The effect of the temperature on the reaction rate constant has been investigated for the case of **1** with methyl acrylate in acetonitrile, in the temperature range 0–50°C. The effect is too small to show differences in the quantum yield within experimental error, and this confirms the fact that the activation barrier E_a in the Arrhenius equation $k_r = A \exp(-E_a/RT)$ must be very small.

Photoreactivity with substituted olefins

The influence of various electron-acceptor and donor substituents on the olefin has been investigated with the DHP **5c** in MeCN. The olefin concentration was kept low, $5 \times 10^{-4} M$, so as to stay in the linear region of the quantum yield vs olefin concentration plot. The observed quantum yields are shown in Table 6.

Electron acceptor substituents such as CN decrease the reactivity, while electron donors have the opposite effect.

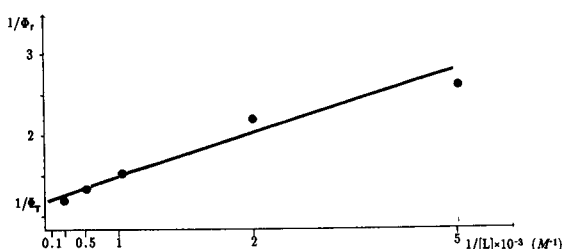


Figure 7. Plot of the reciprocal of reaction quantum yield vs reciprocal of olefin concentration.

Table 5. Triplet yields of DHP 1, 2, 3, and 5c obtained by laser flash photolysis and by reaction quantum yields for the photocycloaddition of the DHPs with acrylonitrile at high olefin concentration ($\geq 10^{-1} M$)

	1	2	3	5c
Solvent	CH ₂ Cl ₂	EtOH	EtOH	EtOH
Φ_T by flash	0.2	0.95	0.90	1.00
Solvent	CH ₂ Cl ₂	MeCN	MeCN	MeCN
Φ_T by reaction	0.18	0.95	0.80	0.82

In the case of tetracyanoethylene (Guerry and Neier, 1987) a non-photochemical reaction takes place which destroys the DHP in the absence of irradiation; this system was therefore not further investigated.

DISCUSSION

Nature of the reactive state—electron distribution and reactivity

The excited state responsible for the cycloaddition is the first excited triplet state T_1 . This is a $\pi-\pi^*$ state which corresponds to the first singlet state S_1 , the electron distribution resulting from a partial charge transfer towards the carbonyl group. Since electron-rich olefins react faster than electron-deficient ones, the primary process can be seen as a nucleophilic attack at C_3 , with the formation of a biradical intermediate, as shown in Scheme 4.

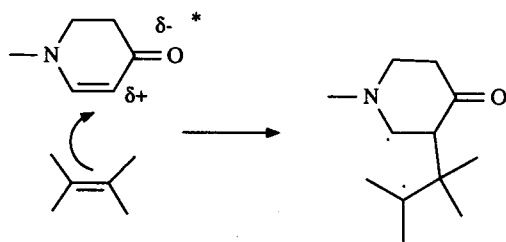


Table 6. Dependence of the reaction quantum yield on the substitution of the olefin

Φ_r	0.03	0.39	0.49
Φ_r	0.42	0.58	0.69

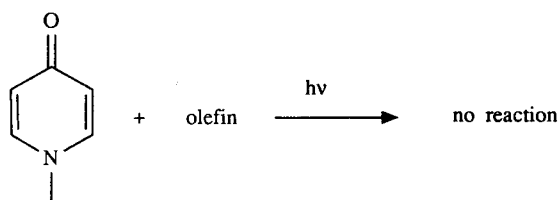
Intermediates in the photochemical reaction

Although there is no spectroscopic evidence for an exciplex intermediate between the DHP and the olefin, the intermediacy of a non-fluorescent exciplex could be postulated. This is not unreasonable since it would involve the triplet excited state to form a triplet exciplex. It has been noted, however, that the polarity of the solvent has little influence on the cycloaddition quantum yields, and this speaks against the involvement of a dipolar exciplex.

Electron transfer between the DHP and the olefin can also be excluded as the primary process. This would form a radical ion pair which would separate in highly polar solvents such as acetonitrile, but no such radical ions have been detected optically in the laser flash photolysis experiments, nor has a significant transient photocurrent been observed. The primary process is therefore most probably the formation of a single bond between the DHP and the olefin with production of a triplet biradical.

Unreactivity of pyridinones

The pyridinones, unlike DHP, show no photochemical reactivity with olefins, as shown in Scheme 5.



The UV absorption spectra of pyridinones are quite different from those of DHPs, being substantially blue-shifted and showing no solvent dependence. It is likely that their lowest triplet excited state is of $n-\pi^*$ type, which would not undergo this type of reaction. Phosphorescence measurements show that the energy of T_1 comes to 3.55 eV, with a short lifetime (< 1 ms).

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