PHOTOINDUCED REACTION OF 2-DIAZO-3-OXO-5,10,15,20-TETRAPHENYLCHLORINS WITH ALCOHOLS

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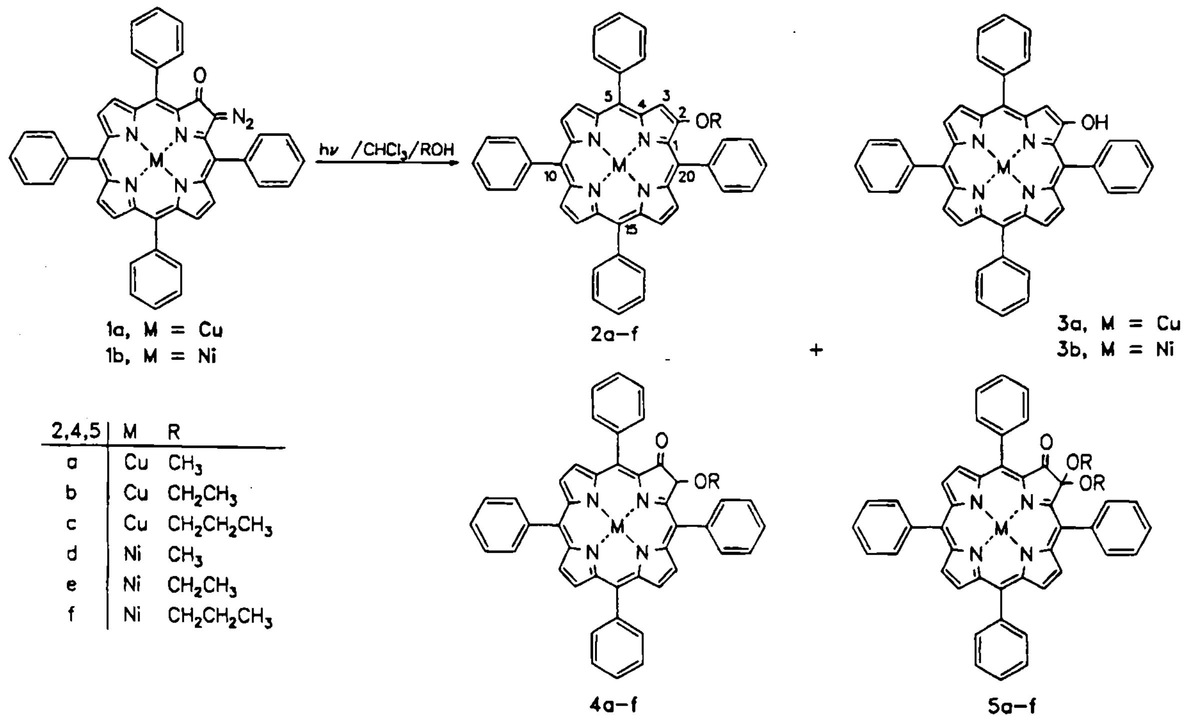
Abstract: The photochemical induced reaction of metallo 2-diazo-3-oxo-5,10,15,20-tetraphenylchlorins 1a and 1b with alcohols is described. Photochemical dediazoniation in presence of simple alcohols leads to the formation of 2-alkyloxy-5,10,15,20-tetraphenylporphyrins 2a - 2f, 2-hydroxy-5,10,15,20-tetraphenylporphyrins 3a - 3b, 2-alkyloxy-3-oxo-5,10,15,20-tetraphenylchlorins 4a - 4f and 2,2-dialkyloxy-3-oxo-5,10,15,20-tetraphenylchlorins 5a - 5f. The product distribution strongly depends upon the central metal ion of the irradiated diazoketones 1a and 1b.

INTRODUCTION

Synthesis of porphyrinic model systems for mimicking the function of photochemical reaction center chromophores recently became a topic in porphyrin chemistry (1). In these model systems light induced electron transfer from excited porphyrin to an appropriate electron acceptor takes place. For studying the electron transfer process it is often necessary to have well defined interchromophoric distances and orientations of the chromophores involved in the electron transfer process (2). Therefore a number of sophisticated porphyrin dimers were synthesised which differ in the interchromophoric distance and orientation of the two porphyrinic macrocycles (3). Further important applications of porphyrins are photodynamic therapy (PDT) of cancer (4) and the development of new porphyrinic oxidation catalysts (5). For all these applications the synthesis of porphyrins with a different, well defined substitution pattern at the *meso*- and β-positions of the porphyrinic system is of great importance. Especially for the synthesis of compounds used for mimicking the photochemical reaction center chromophores it is necessary to modify the electronic properties of the porphyrins. The electronic properties of a porphyrin or chlorin chromophore can be altered by substitution especially in the β-positions. Therefore it is of great importance to develop new synthetic procedures for introducing different substituents in these positions. We recently developed a new synthetic procedure for the synthesis of β-alkyloxy substituted porphyrins by a porphyrin diazonium ion (6). We now report here about the photochemical reactivity of porphyrinic diazoketones 1a and 1b which can be easily synthesized by reaction of metallo 2-amino-5,10,15,20-tetraphenylporphyrins with $NaNO_2$ in THF (7). These compounds exhibit very interesting chemical and photochemical properties.

RESULTS AND DISCUSSION

Diazoketones are known to be photoreactive compounds. We therefore investigated the photochemistry of the diazoketones 1a and 1b in alcoholic $CHCl_3$ solutions. Irradiations of compounds 1a and 1b, respectively, were performed under nitrogen with a halogen light source in a pyrex vessel. After 5 - 10 h the starting materials were totally reacted and in each case four new products were formed as shown by TLC analysis (8). The main products of the photochemical reaction of the copper complex 1a were the alkyloxy substituted compounds 2a - 2c (26 - 28%) and hydroxyporphyrin 3a (25 - 27%). Furthermore, compounds 4a - 4c (6 - 7%) and 5a - 5c (11 - 14%) were formed. Compound 3a was formed in 35% yield if 1a was irradiated in alcohol free $CHCl_3$. The photochemical reaction of the nickel derivative 1b leads to formation of the 2-alkyloxy-3-oxo-5,10,15,20-tetraphenylchlorins 4d - 4f (9 - 10%) and 2,2-dialkyloxy-3-oxo-5,10,15,20-tetraphenylchlorins 5d - 5f (13 - 14%) as the main reaction products. Interestingly, the hydroxyporphyrin 3b was only formed in very low yield (1 - 2%). Furthermore, compounds 2d - 2f were formed in 8 - 10% yield. The synthesised compounds were separated by column chromatography on silica gel using $CHCl_3$ as eluent. Attempts to remove the metal ion from compounds 4a - 4f and 5a - 5f by standard procedures only led to rapid decomposition of the products. Due to the acetal moiety of compounds 5a - 5f these compounds can be hydrolyzed to diketones. This reaction was performed for 5a - 5c in HCl / $CHCl_3$ in good yields (62 - 75%) leading to compound 6 (Scheme 2)



1a, M = Cu
1b, M = Ni

2a–f

3a, M = Cu
3b, M = Ni

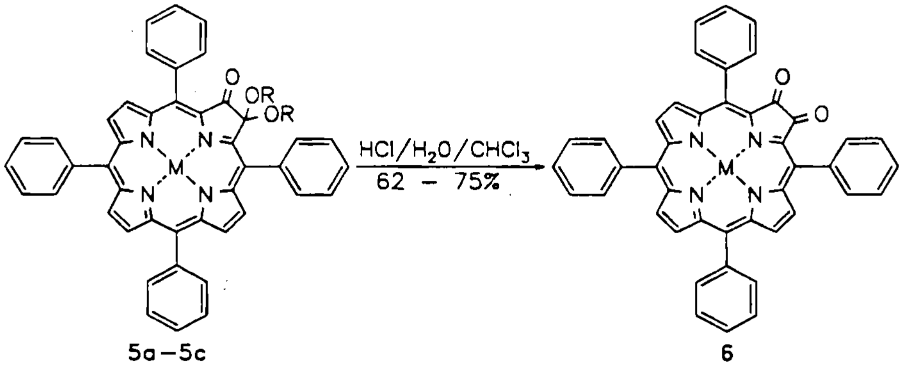
4a–f

5a–f

2,4,5	M	R
a	Cu	CH_3
b	Cu	CH_2CH_3
c	Cu	$CH_2CH_2CH_3$
d	Ni	CH_3
e	Ni	CH_2CH_3
f	Ni	$CH_2CH_2CH_3$

Scheme 1

which is a versatile starting compound for the synthesis of different porphyrinoquinoxalines (9). Formation of 6 clearly proves the structure of the dialkyloxy compounds. Furthermore, strong absorptions of an oxo chlorin type chromophore were observed at 606 nm for the copper complexes 4a - 4c and at 598 nm for the nickel complexes 4d - 4f. The 2,2-dialkyloxy-3-oxo-5,10,15,20-tetraphenylchlorins 5a - 5f exhibit strong absorptions at 631 - 633 nm and a shifted Soret absorption at 432 - 435 nm. The NMR data of the nickel complexes are also in accordance with the proposed structures.



Scheme 2

It is interesting to notice the difference in product distribution between the copper and the nickel complexes. Compounds of type 2 and 3 are the main reaction products of the photochemical reaction of the copper complex 1a, whereas equivalent products were only formed in low yield by irradiation of the nickel complex 1b. This finding indicates the existence of different reaction pathways for the formation of the observed reaction products. It is well known that diazoketones undergo photoinduced dediazoniation with formation of ketocarbenes. Furthermore it is commonly assumed that insertion of carbenes or ketocarbenes into O-H bonds occurs *via* singlet states (10) and that triplet carbenes often undergo H-abstraction reactions (11). Therefore it is most likely, that compounds 4a - 4f were formed by insertion of singlet ketocarbenes into O-H bonds of alcohols. In contrast to this the formation of 3a and 3b, respectively, is likely to occur *via* triplet ketocarbenes formed by intersystem crossing from singlet carbenes and subsequent H-abstraction. Therefore formation of triplet ketocarbenes seems to be more important for the copper complex 1a. Formation of alkyloxy compounds 2a - 2f can be explained by reaction of 3a or 3b, respectively, with alcohol in acidic solution. The extremely low yield of 3b is partly due to the increasead sensitivity of this compound compared to 3a. Therefore this compound shows slight decomposition during the purification procedure.

As a conclusion we have shown that the porphyrinic diazoketones are versatile intermediates for the synthesis of several new compounds. Along this way new studies are beeing carried out in our laboratories.

EXPERIMENTAL

NMR spectra were obtained in $CDCl_3$ and recorded with a Varian XL 200 spectrometer. Chemical shift values were given in ppm relative to TMS. Mass spectra were measured with a VG-Analytical VG70:250 E instrument. Electronic spectra were recorded on a Kontron Uvikon 860 instrument. IR spectra were recorded on a Shimadzu IR 435 spectrometer. Melting points were measured on a Büchi 510 apparatus and are uncorrected. Column chromatography was carried out with Merck silica gel mesh size 0.060 - 0.2 mm.

Irradiation of 2-Diazo-3-oxo-5,10,15,20-tetraphenylchlorins 1a and 1b

General Procedure: A solution of 30 mg (0.042 mmol) of 1a in a mixture of 10 ml of the appropriate alcohol and 10 ml $CHCl_3$ with a small amount (100 µl) of conc. H_2SO_4 was irradiated with a halogen lamp (30 W) for 5 h in a pyrex vessel. The irradiation was performed under nitrogen (12). The reaction mixture was poured into water (20 ml), the organic layer was separated and washed with water and dried (Na_2SO_4). The solvent was removed and the residue chromatographed on a silica gel column (4 x 20 cm) with $CHCl_3$ as eluent. Analytical pure compounds were obtained by chromatography on a silica gel plate using $CHCl_3$ / hexane (3:1) as eluent.

Irradiation of (2-Diazo-3-oxo-5,10,15,20-tetraphenylchlorinato)copper(II) 1a in methanol/ $CHCl_3$

Compounds 2a (6), 3a, 4a and 5a were obtained.

(2-Methoxy-5,10,15,20-tetraphenylporphyrinato)-copper(II) 2a : Yield: 8.2 mg (28%).- UV-vis ($CHCl_3$): λ (lg ε) = 415 (5.25), 537 (3.89), 578 (3.25) nm.- MS (FAB): m/z (%) = 706 (M^+, 75, peak-cluster centered at 706).- IR (KBr): ν = 3386, 2911,1579 cm^{-1}.

(2-Hydroxy-5,10,15,20-tetraphenylporphyrinato)copper(II) 3a (9c, 13): Yield: 7.0 mg (25%).- UV-vis ($CHCl_3$): λ (lg ε) = 414 (5.50), 537 (4.22), 578 (3.75) nm.- MS (FAB): *m/z* (%) = 691 (M^+ , 100).- IR (KBr): ν = 1604 cm^{-1}.

(2-Methoxy-3-oxo-5,10,15,20-tetraphenylchlorinato)copper(II) 4a: Yield: 1.5 mg (5%).- UV-vis ($CHCl_3$): λ (lg ε) = 412 (5.16), 570 (4.07), 606 (4.43) nm.- MS (FAB): *m/z* = 722 (M^+).- IR (KBr): ν = 1738 cm^{-1}.- Anal. Calc. for $C_{45}H_{30}N_4O_2Cu$ (722.30): C 74.83 H 4.19 N 7.77. Found: C 74.95 H 4.19 N 7.67.

(2,2-Dimethoxy-3-oxo-5,10,15,20-tetraphenylchlorinato)copper(II) 5a: Yield: 3.4 mg (11%).- UV-vis (CH_2Cl_2): λ (lg ε) = 432 (5.13), 593 (4.10), 632 (4.35) nm.- MS (FAB): *m/z* = 752 (M^+).- IR (KBr): ν = 1728 cm^{-1}.- Anal. Calc. for $C_{46}H_{32}N_4O_3Cu$ (752.23): C 73.44 H 4.29 N 7.45. Found: C 72.95 H 4.63 N 7.06.

Irradiation of (2-Diazo-3-oxo-5,10,15,20-tetraphenylchlorinato)copper(II) 1a in ethanol/ $CHCl_3$

Compounds 2b (6), 3a (6.6 mg, 28%), 4b and 5b were obtained.

(2-Ethoxy-5,10,15,20-tetraphenylporphyrinato)copper(II) 2b: Yield: 8.4 mg (28%).- UV-vis ($CHCl_3$): λ (lg ε) = 415 (5.19), 537 (3.89), 578 (3.17) nm.- MS (FAB): m/z (%) = 721 (M^+ + 1, 100).- IR (KBr): ν = 3396, 2911, 1578 cm^{-1}.

(2-Ethoxy-3-oxo-5,10,15,20-tetraphenylchlorinato)copper(II) 4b: Yield: 1.8 mg (6%).- UV-vis ($CHCl_3$): λ (lg ε) = 412 (5.12), 570 (4.05), 606 (4.32) nm.- MS (FAB): *m/z* = 737 (M^+ + 1).- IR (KBr): ν = 1735 cm^{-1}.- Anal. Calc. for $C_{46}H_{32}N_4O_2Cu$ (736.33): C 75.04 H 4.38 N 7.62. Found: C 75.70 H 4.75 N 6.89.

(2,2-Diethoxy-3-oxo-5,10,15,20-tetraphenylchlorinato)copper(II) 5b: Yield: 4.4 mg (14%).- UV-vis ($CHCl_3$): λ (lg ε) = 432 (5.09), 592 (4.08), 632 (4.29) nm.- MS (FAB): *m/z* = 779 (M^+).- IR (KBr): ν = 1728 cm^{-1}.- Anal. Calc. for $C_{48}H_{38}N_4O_3Cu$ (780.38): C 73.88 H 4.65 N 7.18. Found: C 73.63 H 4.66 N 6.99.

Irradiation of (2-Diazo-3-oxo-5,10,15,20-tetraphenylchlorinato)copper(II) 1a in 1-propanol/ $CHCl_3$

Compounds 2c (6), 3a (7 mg, 25%), 4c and 5c were obtained.

(2-Propyloxy-5,10,15,20-tetraphenylporphyrinato)copper(II) 2c: Yield: 8.0 mg (26%).- UV-vis ($CHCl_3$): λ (lg ε) = 415 (5.19), 538 (3.79), 579 (3.05) nm.- MS (FAB): *m/z* (%) = 734 (M^+, 60).- IR (KBr): ν = 3396, 2910, 1578 cm^{-1}.

(2-Propyloxy-3-oxo-5,10,15,20-tetraphenylchlorinato)copper(II) 4c: Yield: 2.0 mg (6.5%).- UV-vis (CH_2Cl_2): λ (lg ε) = 412 (5.12), 579 (4.06), 606 (4.40) nm.- MS (FAB): *m/z* = 750 (M^+).- IR (KBr): ν = 1735 cm^{-1}. Anal. Calc. for $C_{47}H_{34}N_4O_2Cu$ (750.36): C 75.23 H 4.57 N 7.47. Found: C 74.93 H 4.47 N 6.85.

(2,2-Dipropyloxy-3-oxo-5,10,15,20-tetraphenylchlorinato)copper(II) 5c: Yield: 4.1 mg (12%).- UV-vis (CH_2Cl_2): λ (lg ε) = 431 (5.08), 595 (4.10), 631 (4.25) nm.- MS (FAB): *m/z* = 808 (M^+).- IR (KBr): ν = 1729 cm^{-1}. Anal. Calc. for $C_{50}H_{40}N_4O_3Cu$ (808.44): C 74.29 H 4.99 N 6.93. Found: C 74.42 H 5.03 N 6.55.

Irradiation of (2-Diazo-3-oxo-5,10,15,20-tetraphenylchlorinato)copper(II) 1a in $CHCl_3$.

8.8 mg (0.013 mmol) 1a were irradiated in 15 ml $CHCl_3$. Yield: 3.0 mg (35%) 3a.

Irradiation of (2-Diazo-3-oxo-5,10,15,20-tetraphenylchlorinato)nickel(II) 1b in methanol/ $CHCl_3$

0.030 g (0.042 mmol) of 1b were irradiated. Compounds 2d, 3b, 4d and 5d were obtained.

(2-Methoxy-5,10,15,20-tetraphenylporphyrinato)nickel(II) 2d: Yield: 2.3 mg (8%).- UV-vis ($CHCl_3$): λ (lg ε) = 414 (5.13), 531 (3.96), 568 (3.59) nm.- ^{1}H NMR ($CDCl_3$): δ = 3.89 (s, 3 H, OCH_3), 7.55 - 7.70 (m, 13 H, H_m, H_p, H-3), 7.76 - 7.80 (m, 2 H, H_o henyl at C-20), 7.93 - 8.00 (m, 6 H, H_o), 8.58 (d, 1 H, *J* = 4.9 Hz, 17-H,18-H), 8.65 (d, 1 H, *J* = 5.4 Hz, 7-H, 8-H), 8.67 (d, 1 H, *J* = 4.9 Hz, 17-H, 18-H), 8.69 (d, 1 H, *J* = 5.4 Hz, 7-H, 8-H).

(2-Hydroxy-5,10,15,20-tetraphenylporphyrinato)nickel(II) 3b (13): Yield: traces.- UV-Vis ($CHCl_3$): λ (lg ε) = 411 (5.30), 528 (4.10), 570 (3.76) nm. MS (FAB): *m/z* (%) = 687 (M^+ +1, 40).

(2-Methoxy-3-oxo-5,10,15,20-tetraphenylchlorinato)nickel(II) 4d: Yield: 3 mg (10%).- UV-vis ($CHCl_3$): λ (lg ε) = 406 (5.16), 565 (4.09), 597 (4.48) nm.- IR (KBr): ν = 1743, 1669 cm^{-1}.- ^{1}H NMR ($CDCl_3$): δ = 3.37 (s, 3 H, OCH_3), 5.94 (s, 1 H, 2-H), 7.57 - 7.67 (m, 14 H, H_m, H_p, H_o phenyl at C-5), 7.83 - 7.97 (m, 6 H, $H_o$phenyl at C-10, C-15 and C-20), 8.27 (s, 2 H, 12-H, 13-H), 8.43 - 8.49 (m, 4 H, 7-H, 8-H,17-H,18-H).

(2,2-Dimethoxy-3-oxo-5,10,15,20-tetraphenylchlorinato)nickel(II) 5d: Yield: 4.4 mg (14%).- UV-vis ($CHCl_3$): λ (lg ε) = 434 (5.13), 588 (4.10), 632 (4.35) nm.- IR (KBr): ν = 1722, 1595 cm^{-1}.- ^{1}H NMR ($CDCl_3$): δ = 3.31 (s, 6 H, OCH_3), 7.43 - 7.80 (m, 16 H, H_m, H_p, H_o phenyl at C-5, C-20), 7.81 - 7.87 (m, 4 H, H_o phenyl at C-10, C-15), 8.03 (d, 1 H, *J* = 4.9 Hz, 17-H, 18-H), 8.25 (s, 2 H, 12-H, 13-H), 8.35 (d, 1 H, *J* = 4.9 Hz, 17-H, 18-H), 8.38 (d, 1 H, *J* = 4.9 Hz, 7-H, 8-H), 8.41 (d, 1 H, *J* = 4.9 Hz, 7-H, 8-H).

Irradiation of (2-Diazo-3-oxo-5,10,15,20-tetraphenylchlorinato)nickel(II) 1b in ethanol/ $CHCl_3$

0.030 g (0.042 mmol) 1b were irradiated. Compounds 2e, 3b (traces), 4e and 5e were obtained.

(2-Ethoxy-5,10,15,20-tetraphenylporphyrinato)nickel(II) 2e: Yield: 2.1 mg (7%).- UV-vis ($CHCl_3$): λ (lg ε) = 414 (5.13), 530 (3.96), 570 (3.59) nm.- MS (FAB): *m/z* (%) = 714 (M$^+$, 100).- ^{1}H NMR ($CDCl_3$): δ = 1.03 (t, 3 H, *J* = 6.8 Hz, $C\underline{H}_3$), 4.09 (q, 2 H, *J* = 6.8 Hz, O-$C\underline{H}_2$), 7.53 - 7.67 (m, 13 H, H_m, H_p, 3-H), 7.76 - 7.80 (m, 2 H, H_o, phenyl at C-20), 7.92 - 8.00 (m, 6 H, H_o), 8.57 (d, 1 H, *J* = 4.9 Hz, 17-H, 18-H), 8.65 (d, 1 H, *J* = 5.4 Hz, 7-H, 8-H), 8.67 (d, 1 H, *J* = 4.9 Hz, 17-H, 18-H), 8.69 (d, 1 H, *J* = 5.4 Hz, 7-H, 8-H), 8.72 (s, 2 H, 12-H, 13-H).

(2-Ethoxy-3-oxo-5,10,15,20-tetraphenylchlorinato)nickel(II) 4e: Yield: 3.1 mg (10%).- UV-vis ($CHCl_3$): λ (lg ε) = 407 (5.01), 565 (3.89), 598 (4.32) nm.- MS (FAB): *m/z* (%) = 729 (M$^+$ - 1, 20).- IR (KBr): ν = 1729.7, 1595.4, 1540.0, 1437.2 cm^{-1}.- ^{1}H NMR ($CDCl_3$): δ = 0.80 - 0.87 (t, 3 H, *J* = 7.3 Hz, $C\underline{H}_3$), 3.79 - 3.90 (q, 2 H, *J* = 7.3 Hz, $OC\underline{H}_2$), 5.97 (s, 1 H, 2-H), 7.57 - 7.65 (m, 14 H, H_m, H_p, H_o phenyl at C-5), 7.86 - 8.00 (m, 6 H, $H_o$phenyl at C-10, C-15 and C-20), 8.27 (s, 2 H, 12-H, 13-H), 8.47 (s, 4 H, 7-H, 8-H, 17-H, 18-H).

(2,2-Diethoxy-3-oxo-5,10,15,20-tetraphenylchlorinato)nickel(II) 5e: Yield: 4.3 mg (13%).- UV-vis ($CHCl_3$): λ (lg ε) = 435 (5.07), 589 (4.02), 632 (4.34) nm.- MS (FAB): *m/z* (%) = 775 (M$^+$ + 1, 100).- IR (KBr): ν = 1729.7, 1595.5, 1540.0 cm^{-1}.- ^{1}H NMR ($CDCl_3$): δ = 1.06 (t, 6 H, *J* = 7.0 Hz, $C\underline{H}_3$), 3.60 (q, 2 H, *J* = 7.0 Hz, $OC\underline{H}_2$), 3.62 (q, 2 H, *J* = 7.0 Hz, OCH_2), 7.47 - 7.49 (m, 2 H, H_o phenyl at C-5), 7.51 - 7.67 (m, 12 H, H_p, H_m), 7.71 - 7.73 (m, 2 H, H_o phenyl at C-20), 7.86 - 7.88 (m, 4 H, H_o phenyl at C-10, C-15), 8.07 (d, 1 H, *J* = 4.86 Hz, 18-H), 8.28 (s, 2 H, 12-H, 13-H), 8.37 (d, 1 H, *J* = 4.86 Hz, 17-H), 8.42 (d, 1 H, *J* = 5.03 Hz, 7-H), 8.44 (d, 1 H, *J* = 4.86 Hz, 8-H).

Irradiation of (2-Diazo-3-oxo-5,10,15,20-tetraphenylchlorinato)nickel(II) 1b in 1-propanol/ $CHCl_3$

0.030 g (0.042 mmol) 1b were irradiated. Compounds 2f, 3b (traces), 4f and 5f were obtained.

(2-Propyloxy-5,10,15,20-tetraphenylporphyrinato)nickel(II) 2f: Yield: 2.4 mg (8%).- UV-Vis ($CHCl_3$): λ (lg ε) = 414 (5.13), 531 (3.96), 568 (3.59) nm.- MS (FAB): *m/z* (%) = 728 (M$^+$ - 1, 100).- ^{1}H NMR ($CDCl_3$): δ = 0.74 (t, 3 H, *J* = 7.8 Hz, $C\underline{H}_3$), 1.46 (tq, 2 H, *J* = 7.3 Hz, *J* = 7.8 Hz, $C\underline{H}_2$-CH_3), 4.04 (t, 2 H, *J* = 7.3 Hz, $OC\underline{H}_2$-CH_2), 7.53 - 7.67 (m, 13 H, H_m, H_p, 3-H), 7.77 - 7.82 (m, 2 H, H_o phenyl at C-20), 7.92 - 8.00 (m, 6 H, H_o), 8.57 (d, 1 H, *J* = 4.9 Hz, 17-H, 18-H), 8.65 (d, 1 H, *J* = 5.5 Hz, 7-H, 8-H), 8.66 (d, 1 H, *J* = 4.9 Hz, 17-H, 18-H), 8.68 (s, 2 H, 12-H, 13-H), 8.71 (d, 1 H, *J* = 5.5 Hz, 7-H, 8-H).

(2-Propyloxy-3-oxo-5,10,15,20-tetraphenylchlorinato)nickel(II) 4f: Yield: 2.8 mg (9%).- UV-vis ($CHCl_3$): λ (lg ε) = 406 (5.05), 564 (3.93), 597 (4.37) nm.- MS (FAB): *m/z* (%) = 744 (M^+ + 1, 100).- IR (KBr): ν = 1728.0, 1595.7, 1507.0 cm^{-1}.- ^1H NMR ($CDCl_3$): δ = 0.54 (t, 3 H, *J* = 7.3 Hz, CH_3), 1.20 (tq, 2 H, *J* = 6.8 Hz, *J* = 7.3 Hz, CH_2-CH_3), 4.04 (d, 2 H, *J* = 6.8 Hz, OCH_2-CH_2), 5.98 (s, 1 H, 2-H), 7.53 - 7.69 (m, 14 H, H_m, H_p, H_o phenyl at C-5), 7.86 - 7.97 (m, 6 H, $H_o$phenyl at C-10, C-15 and C-20), 8.27 (s, 2 H, 12-H, 13-H), 8.47 (s, 4 H, 7-H, 8-H, 17-H, 18-H).

(2,2-Propyloxy-3-oxo-5,10,15,20-tetraphenylchlorinato)nickel(II) 5f: Yield: 4.7 mg (14%).- UV-vis ($CHCl_3$): λ (lg ε) = 435 (5.14), 589 (4.10), 632 (4.36) nm.- MS (FAB): *m/z* (%) = 803 (M^+ + 1, 20).- IR (KBr): ν = 1730.2, 1595.4 cm^{-1}.- ^1H NMR ($CDCl_3$): δ = 0.72 (t, 6 H, *J* = 7.3 Hz, CH_3), 1.42 (tq, 2 H, *J* = 6.8 Hz, *J* = 7.3 Hz, CH_2-CH_3); 3.49 (t, 2 H, *J* = 6.8 Hz, OCH_2-CH_2), 7.43 - 7.50 (m, 2 H, H_o phenyl at C-5), 7.52 - 7.73 (m, 14 H, H_m, H_p, H_o phenyl at C-20), 7.77 - 7.85 (m, 4 H, H_o phenyl at C-10, C-15), 8.02 (d, 1 H, *J* = 4.9 Hz, 18-H), 8.25 (s, 2 H, 12-H, 13-H), 8.36 (d, 1 H, *J* = 4.9 Hz, H-17), 8.37 (d, 1 H, *J* = 4.9 Hz, 8-H), 8.42 (d, *J* = 4.9 Hz, 7-H).

Synthesis of (2,3-Dioxo-5,10,15,20-tetraphenylchlorinato)copper(II) 6 (9)

To a solution of 0.0062 mmol 5a, 5b or 5c, respectively, in 2 ml $CHCl_3$, 4 ml HCl (20%) were added. The reaction mixture was stirred for 20 min. at 65°C. Then the organic layer was separated and dried (Na_2SO_4). The solvent was evaporated and the residue chromatographed on a silica gel column using $CHCl_3$ as eluent.

6: Yield: 2.7 mg (62%) from 5a, 3.3 mg (75%) from 5b and 2.7 mg (62%) from 5c. UV-vis ($CHCl_3$): λ = 407, 484, 609, 631 nm.- MS (FAB): *m/z* = 705 (M^+).- IR (KBr): ν = 1720 cm^{-1}.

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