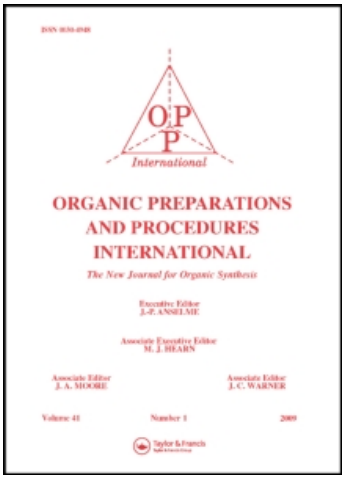

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

A NEW SYNTHESIS OF 6,7-DICHLORO-DIBENZO[c,f][2,7]-NAPHTHYRIDINES *via* PHOTOCYCLIZATION

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To cite this Article Vijayalakshmi, S. and Rajendran, S. P.(1998) 'A NEW SYNTHESIS OF 6,7-DICHLORO-DIBENZO[c,f][2,7]-NAPHTHYRIDINES *via* PHOTOCYCLIZATION', Organic Preparations and Procedures International, 30: 3, 356 — 359
To link to this Article: DOI: 10.1080/00304949809355297
URL: http://dx.doi.org/10.1080/00304949809355297

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A NEW SYNTHESIS OF 6,7-DICHLORO-DIBENZO[c,f][2,7]-NAPHTHYRIDINES *via* PHOTOCYCLIZATION

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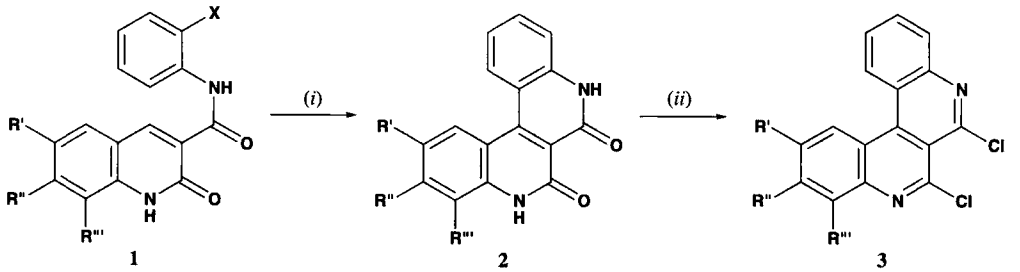
Substituted naphthyridines are of importance because of their bactericidal and fungicidal properties.[1-3] Many of the benzo and dibenzonaphthyridines exhibit chemotherapeutic behavior.[4] Earlier reports[5,6] showed that dibenzo[c,f][2,7]naphthyridines were synthesized from *N*-phenylcarbamoyl coumarins by the action of Grignard reagents and ketones followed by the annulation with cyclohexanone. We now report a new photochemical method which can be extended to the synthesis of derivatives of this system.

Our synthesis starts from *o*-halo-3-carboxanilidoquinolin-2(1H)ones (**1a-g**),[7] which were obtained from 2-oxoquinoline-3-carboxylic acids. The carboxanilides (**1a-g**), on eliminative photocyclization afforded dibenzo[c,f][2,7]naphthyridin-6,7-(5H,8H)diones (**2a-g**), which on treatment with $POCl_3$ in presence of N,N-dimethylaniline,gave 6,7-dichlorodibenzo[c,f][2,7]naphthyridines (**3a-g**).



1 2 3

i) hv, MeOH, Et_3N, 35h *ii*) $POCl_3$, $PhNMe_2$

a) R' = R" = R"' = H b) R' = OCH_3; R" = R"' = H c) R' = CH_3; R" = R"' = H d) R' = R"' = H; R" = OCH_3
e) R' = R"' = H; R" = CH_3 f) R' = R" = H; R"' = CH_3 g) R' = H; R" = R"' = -CH=CH-CH=CH-

Table 1. Physical and Spectroscopic Data of Compounds **2a-g**[a]

Compd	mp. (°C)	Yield (%)	Elemental Analysis (Found) C	H	N	IR (cm^{-1})	^1H NMR (δ) ppm	MS m/z (M^+)
2a.	327-329	35	73.26 (73.26)	3.85 (3.79)	10.68 (10.63)	1680, 3100, 3200	7.2 (t, 2H, H_2&H_{11}); 7.25-7.6 (m, 2H, H_3 & H_{10}); 7.75-8.0 (m, 2H, H_4 & H_9); 8.6 (d, 2H, H_1&H_{12}; J = 8.9Hz); 12.65-12.75 (2H, 2NH two singlets merged)	262
2b	301	40	69.84 (69.88)	4.15 (4.12)	9.59 (9.54)	1670-1680, 3100-3300	3.7 (s, 3H, OCH_3), 7.2-7.9 (m, 5H, H_3,H_4, H_9, H_{10} & H_{11}); 8.1 (d, 1H, H_{12}; J = 9.12Hz); 9.1 (s, 1H, H_1); 12.2 (s, 2H, 2NH merged)	292
2c	280	38	73.88 (73.78)	4.39 (4.42)	10.14 (10.10)	1670, 1680, 3100-3200	2.5 (s, 3H, CH_3); 7.2-7.8 (m, 5H, H_3, H_4, H_9, H_{10} & H_{11}); 8.0 (d, 1H, H_{12}; J = 9.25Hz); 9.0 (s, 1H, H_9); 12.1 (s, NH); 12.75 (s, 1H, NH)	276
2d	310	37	69.84 (69.81)	4.15 (4.11)	9.59 (9.53)	1670 1690, 3100-3200	3.7 (s, 3H, OCH_3); 7.0-7.4 (m, 5H, H_2, H_3, H_9, H_{10} & H_{11}); 8.5 (d, 2H, H_1 & H_{12}; J = 9.2Hz); 9.0 (s, 1H, H_4); 12.7 (s, 1H, NH); 12.9 (s, 1H, NH)	292
2e	314-315	37	73.88 (73.85)	4.39 (4.42)	10.14 (10.19)	1670 1675, 3100-3200	2.3 (s, 3H, CH_3); 7.15 (t, 1H, H_{11}); 7.38 (d, 2H, H_2 & H_{10};J = 8.1Hz); 7.55 (d, 1H, H_9, J = 10.125Hz); 7.7-7.8 (m, 2H, H_1 & H_{12}); 8.9 (s, 1H, H_4); 12.25 (s, 1H, NH); 12.63 (s, 1H, NH)	276
2f	320-321	37	73.88 (73.78)	4.39 (4.42)	10.14 (10.10)	1670 1680, 3100-3200	2.5 (s, 3H, CH_3); 7.2-7.75 (m, 5H, H_2, H_3, H_9, H_{10} & H_{11}); 8.05 (d, 1H, H_{12}; J = 8.2Hz); 9.0 (s, 1H, H_1); 12.2 (s, NH); 12.75 (s, NH)	276
2g	330-332	25	76.90 (76.94)	3.87 (3.83)	8.97 (8.95)	1665 1680, 3300	6.75 (d, 1H, H_4; J = 8.6Hz); 6.97 (dd, 1H, H_3, J = 12.83Hz; J = 2.51Hz, 2.49Hz); 7.3-7.5 (m, 6H, H_2, H_5, H_6, H_{10}, H_{11} & H_{12}); 7.65 (d, 2H, H_1 & H_{13}; J = 11.3Hz); 12.25 (s,1H,NH);12.78(s,1H,NH)	312

a) Recrystallized from ethyl acetate.

EXPERIMENTAL SECTION

Melting points were determined on a Boetius microheating table, and are uncorrected. IR spectra were recorded on a Perkin-Elmer-597 Infrared Spectrophotometer as KBr pellets. ^{1}H NMR spectra were obtained on a Bruker WH-270 (270 MHz) NMR spectrometer or on an EM-390 (90MHz) NMR spectrometer in $CDCl_3$. Mass spectra were determined on a Jeol-D300 mass spectrometer or on Finnigan MAT 8230 GC/Mass spectrometer. Elemental analyses were performed by Cario-Elmer 1106 and Perkin-Elmer model 1240 CHN analyzer.

Table 2. Physical and Spectroscopic Data of Compounds **3a-g**

Compd	mp.[a] (°C)	Yield (%)	Elemental Analysis (Found) C	H	N	IR (cm^{-1})	^{1}H NMR (δ) ppm	MS m/z (M^+)
3a	165-166	75	64.21 (64.25)	2.70 (2.66)	9.37 (9.32)	1590, 1605,	7.0-7.35 (m, 2H, H_3 & H_{10}); 7.7-7.9 (m, 2H, H_2 & H_{11}); 8.35 (m, 2H, H_4 & H_9); 8.7 (m, 2H, H_1 & H_{12})	298 300 302
3b	162-163	72	62.20 (62.23)	3.03 (3.01)	8.54 (8.50)	1590 1605	3.4 (s, 3H, OCH_3): 7.2 (s, 1H, H_{11}); 7.64-7.9 (m, 2H, H_4 & H_9); 7.96-8.0 (d, 1H, H_{12}; J = 8.12Hz); 8.9 (s, 1H, H_1)	328 330 332
3c	170	70	65.18 (65.19)	3.22 (3.26)	9.85 (9.80)	1590 1610	2.3 (s, 3H, CH_3); 7.25 (1H, H_9); 7.5-7.9 (m, 4H, H_3, H_4, H_{10} & H_{11});8.8 (s, 1H, H_1)	312 314 316
3d	148	75	62.20 (62.21)	3.03 (3.01)	8.54 (8.50)	1590 1605,	4.07 (s, 3H, OCH_3);7.4 (t, 1H & H_{11});7.6-7.7 (t, 1H, H_2); 7.8-7.95 (m, 3H, H_9, H_{10} & H_{12}); 8.1 (d, 1H, H_1, J = 12.1Hz); 8.96 (s, 1H, H_4)	328 330 332
3e	156-157	75	65.18 (65.15)	3.22 (3.24)	9.85 (9.81)	1590 1605	2.6 (s, 3H, CH_3);7.46 (m, 2H, H_2 & H_{11});7.68 (dd, 1H, H_{10}); J = 11.36Hz ,J = 2.13Hz, 1.7Hz); 7.9 (m, 3H, H_1, H_9 & H_{12});8.94 (s, 1H, H_4)	312 314 316
3f	178	70	65.18 (65.19)	3.22 (3.26)	8.95 (8.90)	1590 1610	2.65 (s, 3H, CH_3); 6.5-6.7 (d, 1H, H_9, J = 8.28Hz); 7.5-7.7 (m, 5H, H_2, H_3, H_{10}, H_{11} & H_{12}); 8.2 (s, 1H, H_1)	312 314 316
3g	181-182	70	68.78 (68.75)	2.88 (2.83)	8.02 (8.05)	1590 1605	7.4 (m, 4H, H_4, H_5, H_{11} & H_{12}); 7.6 (d, 4H, H_2, H_6, H_{10} & H_{12}); 7.97 (dd, 1H, H_{13}, J = 8.36Hz, J = 2.15, 1.93Hz); 8.15 (d, 1H, H_1, J = 10.8Hz)	348 350 352

a) Recrystallized from ethyl acetate.

Dibenzo[c,f][2,7]naphthyridin-6,7(5H,8H)diones (2a-g).- A solution of **1** (0.001 mole) in dry methanol (300 mL) in the presence of triethylamine (4-5 drops) was placed in a quartz tube, purged with oxygen-free nitrogen for 20 min. and then irradiated with 253.7 nm light for 30-35 h until TLC analysis showed the absence of the spot corresponding to **1**. The product, which had settled at the walls of the quartz tube, was collected and chromatographed over silica gel (60-120 mesh;50g) using benzene-ethyl acetate (60:40v/v). The product was then recrystallized from ethyl acetate (Table 1).

6,7-Dichlorodibenzo[c,f][2,7]naphthyridines (3a-g).- Compound **2** (0.001 mole) in phosphorus oxychloride (10 mL) and N,N-dimethylaniline (3-4 drops) was boiled under reflux for 4 h, cooled and poured onto crushed ice. The solid that separated was collected, dried and chromatographed over silica gel (60-120 mesh;50g) using pet.ether-ethyl acetate (9:5). The product was then recrystallized from ethyl acetate (Table 2).

Acknowledgement.- We thank the CSIR, New Delhi for the award of SRF to one of us (S.V). We also thank the services rendered by the "Sophisticated Instrumentation Facility" at IISc., Bangalore and the "Regional Sophisticated Instrumentation Centre' at IIT, Madras and CDRI (Lucknow) in recording ^{1}H NMR and Mass spectra.

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