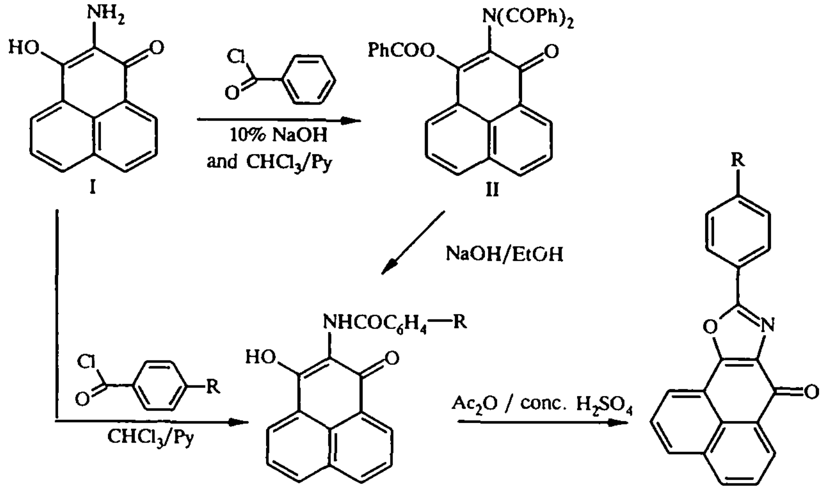
Chemistry of Heterocyclic Compounds, Vol. 34, No. 8, 1998

OXAZOLES BASED ON 2-AMINO-3-HYDROXYPHENALENONE

K. A. Balodis, I. A. Meirovits, and M. V. Petrova

2-Phenyl- and 2-(p-nitrophenyl)-4H-phenaleno[1,2-d]oxazol-4-ones were synthesized from 2-amino-3-hydroxyphenalenone.

A series of the derivatives of 2,5-diaryloxazoles and also naphthalic acid are effective luminophores [1]. In the present work we investigated the possibility of synthesizing compounds containing both these structures (oxazole and naphthalic acid) in one molecule. From published data it is known that benzoxazoles are obtained more from *o*-aminophenols than by any other method [2]. It was shown that the corresponding N,O-diacetyl or N,O-dibenzoyl derivatives are formed when *o*-aminophenol is boiled with acetic anhydride [3] or 8-hydroxy-9-aminofluoranthene is boiled with acetic anhydride or benzoyl chloride in the presence of a 10% solution of sodium hydroxide [4]. In order to achieve our aim we used 2-amino-3-hydroxyphenalenone (I) as starting compound [5]. During the benzoylation of compound (I) in the form of a suspension in benzoyl chloride in the presence of a 10% solution of sodium hydroxide, in contrast to the benzoylation of *o*-aminophenol or 8-hydroxy-9-aminofluoranthene, the tribenzoyl derivative 2-(N,N-dibenzoylamino)-3-benzoylhydroxyphenalenone (II) (73%) is formed, as demonstrated by the absence of the absorption band of the NH group in the IR spectrum in the region of 3300-3000 cm^{-1} and by the absence of the signals of the OH and NH protons in the PMR spectrum of compound (II). When we used *p*-nitrobenzoyl chloride under analogous conditions we were unable to obtain the corresponding tri-*p*-nitrobenzoyl derivative. The benzoylation of compound (I) by *p*-nitrobenzoyl chloride (and also by unsubstituted benzoyl chloride) in a molar ratio of 1:1.14 (1:2.4) was therefore conducted in chloroform in the presence of dry pyridine. In the present case the main products are compounds (IIIa) (40%) and (IIIb) (53%). When the molar ratio of 2-amino-3-hydroxyphenalenone to benzoyl chloride was increased to 1:7.4, compound (II) was isolated from the reaction mixture with a yield of 30%. Compound (IIIa) was also obtained with a 92% yield by the alkaline hydrolysis of the tribenzoyl derivative (II). In acetic anhydride with a catalytic addition of concentrated sulfuric acid compounds (IIIa, b) under cyclization to the oxazoles (IVa, b).



III a, b
.a R = H; b R = p-NO_2

IV a, b
a R = H; b R = p-NO_2

Riga Technical University, Riga LV-1048, Latvia. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1065-1067, August, 1998. Original article submitted November 28, 1997; revision submitted March 30, 1998.

EXPERIMENTAL

The PMR spectra were recorded on a Bruker WH-90/DS instrument in deuterochloroform and DMSO-d_6. The chemical shifts of the protons are given in parts per million with reference to TMS as internal standard. Some of the signals of the protons in the naphthalene ring were assigned with the use of data from [6]. However, a full analysis of the more strongly coupled spin systems of the naphthalene and benzene fragments in the obtained compounds was not made on account of the uncertainty in the assignment of the overlapping resonance signals. The IR spectra were recorded on a Specord M-80 spectrometer for suspensions in Vaseline oil. The UV spectra were recorded on a Specord M-40 spectrometer.

2-Dibenzoylamino-3-benzoylhydroxyphenalenone (II). A. To a suspension of 0.8 g (3.8 mmole) of compound (I) in 7.7 g (54.8 mmole) of benzoyl chloride we added dropwise with stirring 80 ml of a 10% solution of sodium hydroxide over 30 min. After 15 min the resinous mass was treated with ethanol. The finely crystalline light-yellow substance that separated was filtered off and washed with water. The yield of compound (II) was 1.45 g (73%); mp 210-212°C (from toluene). IR spectrum, cm^{-1} (thin layer): 1754 (C=O, ester), 1704 (C=O, amide), 1684 (C=O, amide), 1640 (C=O), 1600 (C=C), 1578 (C=C). UV spectrum (in chloroform), λ_{max} (log ε): 330 (3.84), 365 (4.06), 402 (4.04). PMR spectrum, deuterochloroform (δ, ppm): 8.68 (1H, dd, ^3J = 8.0, ^4J = 1.5 Hz, H-9); 8.27 (1H, dd, ^3J = 8.0, ^4J = 1.5 Hz, H-4); 8.11-7.13 (19H, m, $3C_6H_5$ and $C_{10}H_6$). Found %: C 78.12; H 4.00; N 2.75. $C_{34}H_{21}NO_5$. Calculated %: C 78.00; H 4.04; N 2.68.

B. To a mixture of 0.5 g (2.4 mmole) of the ketone (I) and 2.5 g (17.8 mmole) of benzoyl chloride in 15 ml of chloroform we added 2 ml of dry pyridine. The reaction mixture was kept at room temperature for 24 h and evaporated. To the dry residue we added 50 ml of ether. The precipitate was filtered off and washed with ether and with water. After drying (80°C) the substance was recrystallized from toluene. The yield was 0.37 g (30%); mp 209-210°C.

2-Benzoylamino-3-hydroxyphenalenone (IIIa). A. To a solution of 0.32 g (8.0 mmole) of sodium hydroxide in 35 ml of ethanol at 40°C we added 0.42 g (0.8 mmole) of compound (II). The mixture was stirred for 30 min, the precipitate was filtered off and dissolved in water, and the solution was filtered. The filtrate was acidified with acetic acid. The finely crystalline orange substance was filtered off and washed with water. The yield of compound (IIIa) was 0.29 g (92%); mp 188-190°C (from toluene). IR spectrum, thin layer, cm^{-1}: 3450 (O–H), 3304 (N–H), 3076 (C–H), 1644 (C=O and C=O, amide), 1588 (C=C), 1568 (C=C), 1539 (amide 2), 1492 (C=C), 1282 (amide 3). UV spectrum (in chloroform), λ_{max} (log ε), nm: 340 (4.22), ~356 sh, 436 (3.61). PMR spectrum, deuterochloroform (δ, ppm): 13.8 (1H, s, OH); 9.75 (1H, bs, NH); 8.64 (1H, dd, ^3J = 7.2, ^4J = 1.3 Hz, H-9.4); 8.5 (1H, dd, ^3J = 1.3 Hz, H-9.4); 8.25-7.53 (9H, m, C_6H_5 and $C_{10}H_6$). Found %: C 76.35; H 4.28; N 4.41. $C_{20}H_{13}NO_3$. Calculated %: C 76.43; H 3.85; N 4.45.

B. To a mixture of 0.5 g (2.4 mmole) of the ketone (I) and 0.82 g (5.8 mmole) of benzoyl chloride in 15 ml of chloroform we added 2 ml of dry pyridine. The reaction mixture was heated until the precipitate had completely dissolved. After 1 h the solvent was distilled on a rotary evaporator. The remaining mixture was separated by adsorption column chromatography (2.5 × 25 cm). The stationary phase was silica gel, and the eluant was benzene. The main orange fraction was collected. The yield of compound (IIIa) was 0.3 g (40%); mp 185-187°C, R_f 0.69 (Silufol UV-254, benzene).

2-(*p*-Nitrobenzoylamino)-3-hydroxyphenalenone (IIIb). To a suspension of 0.5 g (2.5 mmole) of the ketone (I) in 20 ml of chloroform we added 0.5 g (2.7 mmole) of *p*-nitrobenzoyl chloride and 2 ml of dry pyridine. The reaction mixture was stirred for 2 h. The yellow precipitate was filtered off, washed with ethanol, and recrystallized from 120 ml of xylene. The yield of compound (IIIb) was 0.45 g (53%); mp 296-298°C. IR spectrum, thin layer, cm^{-1}: 3450 (O–H), 3280 (N–H), 3112 (C–H), 1640 (C=O and C=O, amide), 1590 (C=C), 1562 (C=C), 1540 sh (amide 2), 1528 (NO_2, as), 1346 (NO_2, sym), 1322 (amide 3). UV spectrum, chloroform, λ_{max}, nm (log ε): 348 (4.31), ~365 sh, 430 sh (3.87). PMR spectrum, DMSO-d_6 (δ, ppm): 11.48 (1H, bs, OH); 9.77 (1H, bs, NH); 8.34 (8H, bm, C_6H_4 and $C_{10}H_6$); 7.79 (2H, m, ^3J = 8 Hz, C_6H_4). Found %: C 66.88; H 3.32; N 7.65. $C_{20}H_{12}N_2O_5$. Calculated %: C 66.67; H 3.38; N 7.78.

2-Phenyl-4H-phenaleno[1,2-*d*]oxazol-4-one (IVa). To 0.18 g (0.57 mmole) of the ketone (IIIa) in 6 ml of acetic anhydride we added a few drops of concentrated sulfuric acid. The mixture was left for 24 h with stirring, the precipitate was filtered off and washed with water, and after drying it was recrystallized from xylene. The yield of compound (IVa) was 0.09 g (53%); mp 206-208°C (from xylene). IR spectrum, thin layer, cm^{-1}: 1660 (C=O), 1590 (C=C), 1578 (C=C), 1558 (C=N). UV spectrum, chloroform, λ_{max} (log ε), nm: 313 (4.36), 334 (4.23), 355 (4.01), 414 (3.86). PMR spectrum, DMSO-d_6 (δ, ppm): 8.66 (1H, dd, ^3J = 7.5, ^4J = 1.3 Hz, H-9.4), 8.51 (1H, dd, ^3J = 7.5, ^4J = 1.3 Hz, H-9.4); 8.44-7.69 (9H, m, C_6H_5 and $C_{10}H_6$). Found %: C 80.73; H 3.77; N 4.53. $C_{20}H_{11}NO_2$. Calculated %: C 80.80; H 3.73; N 4.71.

1-(*p*-Nitrophenyl)-4H-phenaleno[1,2-*d*]oxazol-4-one (IVb). To a suspension of 0.18 g (0.5 mmole) of the ketone (IIIb) in 6 ml of acetic anhydride we added a few drops of concentrated sulfuric acid. The reaction mixture was heated gently until the precipitate had dissolved, and left at room temperature for 24 h. The precipitate was filtered off and recrystallized from xylene. The yield was 0.1 g (58%). The analytically pure product was obtained by chromatography on silica gel (ethyl acetate), and the second main fraction was collected; mp 326-328°C. IR spectrum, thin layer, cm^{-1}: 1656 (C=O), 1606 (C=C), 1598 (C=C), 1558 (C=N), 1512 (NO_2, as), 1348 (NO_2, sym). UV spectrum, chloroform, λ_{max} (log ε), nm: 354 (4.43), ~405 sh, ~420 sh. PMR spectrum, DMSO-d_6 (δ, ppm): 8.66-7.90 (10H, m, C_6H_4 and $C_{10}H_6$). Found %: C 69.62; H 2.96; N 7.98. $C_{20}H_{10}N_2O_4$. Calculated %: C 70.18; H 2.96; N 8.18.

REFERENCES

1. B. M. Krasovitskii and B. M. Bolotin, Organic Luminophores [in Russian], Khimiya, Moscow (1984).
2. J. Cornforth, in: Heterocyclic Compounds, R. Elderfield (ed.) [Russian translation], Vol. 5, IL, Moscow (1961).
3. W. Theilacker, J. Prakt. Chem., **153**, 54 (1939).
4. M. I. Shenbor and V. N. Tikhonov, Khim. Geterotsikl. Soedin., No. 5, 608 (1973).
5. B. Eistert, W. Eifler, and H. Goth, Chem. Ber., **101**, 2162 (1968).
6. Kh. A. Kazhoka, M. V. Petrova, E. E. Liepin'sh, and I. A. Meirovits, Izv. Akad. Nauk Latv. SSR. Ser. Khim., No. 1, 93 (1989).