LETTERS TO THE EDITOR

3-ARYLIDENE-6-NITRO-1,8-NAPHTHALIDES AND PHENALENE-1,3-DIONES BASED ON THEM

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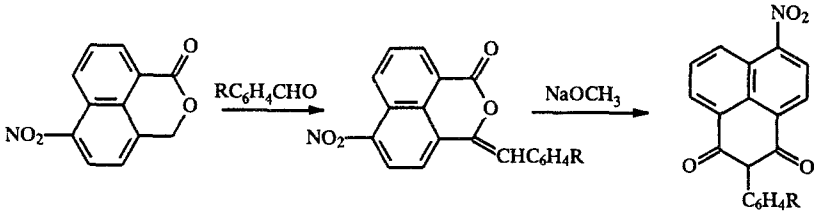
The 6-substituted 3-arylideneisobenzofuranones have been described as a new class of compounds that exhibit luminescence over a broad range of the visible and neighboring IR spectrum (400-850 nm) with a high quantum yield (up to 0.70%) [1, 2]. Their photostability is much greater than that of the corresponding trans-stilbene derivatives, whose fixed analogs they constitute. We obtained the 3-arylidene-6-nitro-1,8-naphthalide series (IIa-c) for the first time by condensing 6-nitronaphthalide I with aromatic aldehydes:



I IIa-c IIIa-c

II, III a) R = H, b) R = OCH_3, c) R = $N(CH_3)_2$

The reaction, which we performed by boiling the reagents in toluene with morpholine present as base, was accelerated to a significant extent by adding DMF. Arylidene derivative yields ranged from 32 to 42%. On treatment with sodium methylate compounds IIa-c regrouped quantitatively into the 2-aryl-6-nitrophenalene-1,3-diones (IIIa-c).

A feature of the luminescence exhibited by compounds IIa-c was the high Stokes shift (196 nm for IIc in DMF solution). The sensitivity of luminescence to variations in the polarity of the surroundings suggests that it may be possible to employ compounds IIa-c as luminescent probes for biological research.

3-Benzylidene-6-nitro-1,8-naphthalide (IIa, $C_{19}H_{11}NO_4$). mp 246-247°C (from toluene). IR spectrum, cm^{-1}: 1722 (C=O). PMR spectrum (DMSO-D_6): 7.29 (1H, s, =CH), 7.40-7.94 (5H, m, C_6H_5), 7.93-8.77 (5H, m, 4-H-9-H). UV spectrum (benzene), λ_{max} (log ε): 407.9 nm (4.15). Fluorescence, λ_{max}: 545 (benzene), 553 (chloroform), 569 nm (DMF).

3-(4-Methoxybenzylidene)-6-nitro-1,8-naphthalide (IIb, $C_{20}H_{13}NO_5$). mp 220-221°C (from acetone). IR spectrum, cm^{-1}: 1734 (C=O). PMR spectrum (DMSO-D_6): 3.78 (3H, s, CH_3), 7.22 (1H, s, =CH), 7.0-7.93 (4H, m, C_6H_4), 7.96-8.81 (5H, m, 4-H-9-H). UV spectrum (benzene), λ_{max} (log ε): 457.2 nm (4.29). Fluorescence, λ_{max}: 580 (benzene), 628 (chloroform), 649 nm (DMF).

3-(4-Methoxybenzylidene)-6-nitro-1,8-naphthalide (IIc, $C_{21}H_{16}N_2O_4$). mp 255-256°C (from hexane). IR spectrum, cm^{-1}: 1732 (C=O). PMR spectrum (DMSO-D_6): 2.97 [6H, s, $N(CH_3)_2$], 7.19 (1H, s, =CH), 6.8-7.98 (4H, m, C_6H_4), 8.33-8.8 (5H, m, 4-H-9-H). UV spectrum (benzene), λ_{max} (log ε): 535.5 nm (4.35). Fluorescence, λ_{max}: 689 nm (benzene).

8-Nitro-2-phenylphenalene-1,3-dione (IIIa, $C_{19}H_{11}NO_4$). IR spectrum, cm^{-1}: 1632 (C=O). PMR spectrum (DMSO-D_6): 7.33 (5H, m, Ch_6H_5), 7.09-8.56 (5H, m, 4-H-9-H), 10.16 (1H, broad, OH). UV spectrum (benzene), λ_{max} (log ε): 356.1 (3.92), 400 (bend) nm (3.79.

Riga Applied Science University, Chemical Engineering Faculty. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1288-1289, September, 1993. Original article submitted September 23, 1993.

0009-3122/93/2909-1104$12.50

2-(4-Methoxyphenyl)-6-nitrophenalene-1,3-dione (IIIb, $C_{20}H_{13}NO_5$). IR spectrum, cm^{-1}: 1632 (C=O). PMR spectrum (DMSO-D_6): 3.78 (3H, s, CH_3), 6.98-7.22 (4H, m, C_6H_4), 7.91-8.53 (5H, m, 4-H-9-H), 10.62 (1H, broad, OH). UV spectrum (benzene, λ_{max} (log ε): 358.6 (4.04), 419 nm (3.82).

2-(4-Dimethylaminophenyl)-6-nitrophenalene-1,3-dione (IIIc, $C_{21}H_{16}N_2O_4$). IR spectrum, cm^{-1}: 1632 (C=O). PMR spectrum (DMSO-D_6): 2.87 [6H, s, $N(CH_3)_2$], 6.73-7.16 (4H, m, C_6H_4), 7.89-8.53 (5H, m, 4-H-9-H), 10.36 (1H, broad, OH). UV spectrum (benzene), λ_{max} (log ε): 322 (4.16), 515.1 nm (3.49).

Elemental analysis data for C, H, and N were in line with calculated values.

REFERENCES

1. S. M. Stoyanov, F. D. Fratev, P. S. Nikolov, and A. A. Lyapova, Bulgarian Patent No. 36,432; RZhK, 22H241 (1986).
2. P. Nikolov, F. Fratev, O. E. Polansky, G. Olbrich, and S. Minchev, Bulg. Acad. Sci., Comm. Dep. Chem., **20**, No. 1, 73 (1987).