

SHORT
COMMUNICATIONS

Synthesis and Photoarylotropic Rearrangement of 10-Phenoxynaphthacenokeramidone

N. T. Sokolyuk¹ and L. P. Pisulina²

¹Research Institute of Fine Organic Synthesis at TOS Stock Company, Ivanovo, Russia

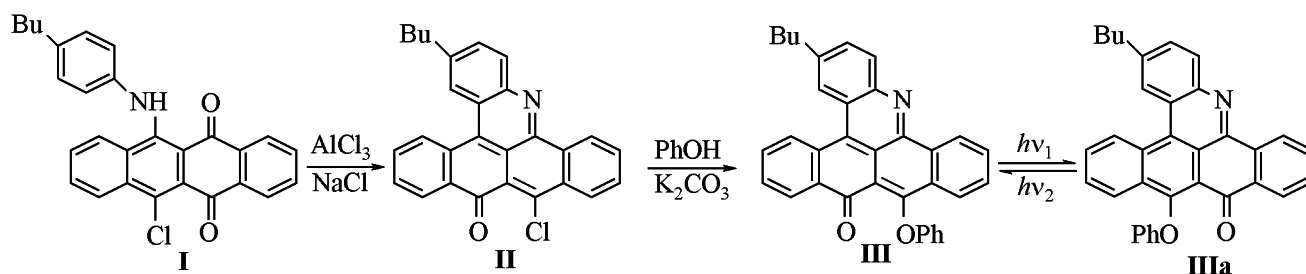
²Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, 153045 Russia

Received July 4, 2000

We showed formerly that photoarylotropic rearrangements [1] occurred also with compounds of *para*-quinone imine structure: pyrazolanthrones [2, 3], pyrazolenaphthocenes [4]. Phenoxy derivatives of these compounds in the light undergo reversible transformation into *ana*-quinone imine isomers.

In extension of the study on structural factors effect on the photoarylotropy we synthesized a photoarylotropic compound with the *ana*-quinone imine

distribution of bonds in a molecule, 10-phenoxynaphthacenokeramidone (**III**) (2-butyl-10-phenoxy-11*H*-naphtho[3,2,1-*kl*]benzo[*h*]acridin-11-one). Naphthacenokeramidone **III** was synthesized by the nucleophilic substitution with phenoxy group of a chlorine in naphthacenokeramidone **II** prepared by cyclization of naphthacenequinone **I** in the melt of aluminum chloride-sodium chloride mixture along procedure [5].



The structural similarity, the resemblance of spectral characteristics of naphthacenokeramidones **II**, **III** and keramidones [6] which possess *ana*-quinone imine bond distribution in the molecule suggest that naphthacenokeramidones **II** and **III** also have the *ana*-quinone imine structure.

Naphthacenokeramidone **III** possesses photochromic properties.

At irradiation of a benzene solution of compound **III** with visible light ($\lambda_{\text{act}} \geq 450$ nm) in the electron absorption spectra of compound **III** the optical density of the longwave band decreases and simultaneously appears an absorption band in the shortwave region at λ_{max} 340 nm. The subsequent irradiation of this solution with shortwave UV light (λ_{act} 300–380 nm) result in the restoration of the initial spectral curve.

The presence of an isobestic point in the group of the spectral curves originating from photochromic transitions of naphthacenokeramidone **III** evidences the presence of two photoforms. Naphthacenokeramidone **II** with no phenoxy group in the *peri*-position with respect to a carbonyl is photostable. The above data suggest that the photochromism of phenoxy-naphthacenokeramidone **III** is due to a photoarylotropic rearrangement consisting in the reverse migration of the phenyl ring to the *peri*-located oxygen of the carbonyl group. The rearrangement produces a reversible transformation of *ana*-quinone imine structure **III** into *para*-quinone imine structure **IIIa**.

6-(4-Butylphenylamino)-11-chloro-5,12-naphthacenequinone (I) was prepared by boiling for 6 h 3 g (9.17 mmol) of 6,11-dichloro-5,12-naphthacene-

quinone [7] with 15 ml of butylaniline in 150 ml of toluene. Under these conditions alongside product **I** formed also disubstituted compound 6,11-di(4-butyl-phenylamino)-5,12-naphthacenequinone (**IV**).

2-Butyl-10-chloro-11H-naphtho[3,2,1-kl]benzo[h]acridin-11-one (II) was obtained by treating 0.14 g (0.318 mmol) of compound **I** with molten mixture of 1.11 g (8.32 mmol) of anhydrous aluminum chloride and 0.12 g (1.98 mmol) of sodium chloride at 130–140°C for 10 min. On completion of the reaction the melt was treated with saturated water solution of oxalic acid in keeping with [8].

2-Butyl-10-phenoxy-11H-naphtho[3,2,1-kl]benzo[h]acridin-11-one (III) was synthesized by treating 0.048 g (0.115 mmol) of naphthacenokeramidone **II** at 130–140°C for 20 min with phenol-phenolate melt prepared from 1 g of phenol and 0.05 g (0.545 mmol) of potassium carbonate. Compounds **I–IV** were isolated in the individual state by chromatography on silica gel 40 × 100 μ, eluent benzene. Further purification was carried out by recrystallization from hexane–benzene mixture, 2:1. Below are given: compound number; its yield, %; melting point, °C; IR spectrum taken in KBr pellets, ν , cm^{-1} , ($\text{C}=\text{O}$); electron absorption spectrum in benzene, λ_{max} , nm ($\log \epsilon$). (**I**): 66.1; 125–126 (from benzene–ethanol, 2:1); 1670; 408 (3.91), 504 (3.99). (**II**): 57.5; –; 1652; 347 sh (4.10), 408 sh (4.20), 427 (4.34), 452 sh (4.05) (in toluene). (**III**): 52.9; 229–230; 1648; 346 sh (4.02), 405 sh (4.17), 426 (4.32), 451 sh (4.07). (**IV**): 6.5; 176–177; 1625; 477 (3.99), 584 (4.13), 613 sh (4.11). The elemental analyses are consistent with the calculated data. The molecular weight of naphthaceno-

keramidone **III** estimated from its mass spectrum was 479. calculated M 479.55.

Electron absorption spectra were measured on spectrophotometer Specord M-40, IR spectra on spectrophotometer Specord M-80. Mass spectra were registered on Varian Match-6 instrument. The melting points were measured on PTP device (production standard TU 25-11-1144-76). The solutions of the compounds under study were irradiated in airtight quartz cells ($l = 1$ cm) with a lamp DRK-120. The necessary spectral range was obtained with the use of standard light filters (State standard GOST 9411-66).

REFERENCES

1. *Organicheskie fotokhromy* (Organic Photochroms), El'tsov, A.M., Ed., Leningrad: Khimiya, 1982, pp. 224–233.
2. Sokolyuk, N.T., Pisulina, L.P., and Kozhevnikova, E.I., *Zh. Org. Khim.*, 1992, vol. 28, no. 10, pp. 2193–2200.
3. Sokolyuk, N.T. and Pisulina, L.P., *Izv. Vuz. Khim. i Khim. Tekhn.*, 1993, vol. 36, no. 12, pp. 12–15.
4. Sokolyuk, N.T. and Pisulina, L.P., *Zh. Org. Khim.*, 1994, vol. 30, no. 3, pp. 447–452.
5. Waldman, H. and Hindenburg, K.G., *J. Pr. Chem.*, 1940, vol. 156, pp. 157–168.
6. Ektova, L.V., Shishkina, Z.P., and Fokin, E.P., *Izv. SO Akad. Nauk SSSR, Ser. Khim. Nauk*, 1977, no. 3, no. 7, pp. 158–161.
7. Gerasimenko, Yu.E., Poteleshchenko, N.T., and Romanov, V.V., *Zh. Org. Khim.*, 1980, vol. 16, no. 9, pp. 1938–1945.
8. Sokolyuk, N.T. and Pisulina, L.P., *Zhurn. Nauchn. i Prikl. Fotograf.*, 1998, vol. 43, no. 5, pp. 59–65.