ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 11, pp. 1725–1726. © Pleiades Publishing, Inc. 2006.
Original Russian Text © A.P. Stankevicius, L.N. Janushene, P. B. Terentiev, K.T. Vitkevicius, 2006, published in Zhurnal Organicheskoi Khimii, 2006, Vol. 42, No. 11, pp. 1736–1737.

SHORT COMMUNICATIONS

Cleavage of 9,10-Phenanthrenequinone Monooxime *O*-Arenesulfonates in the Presence of Amines

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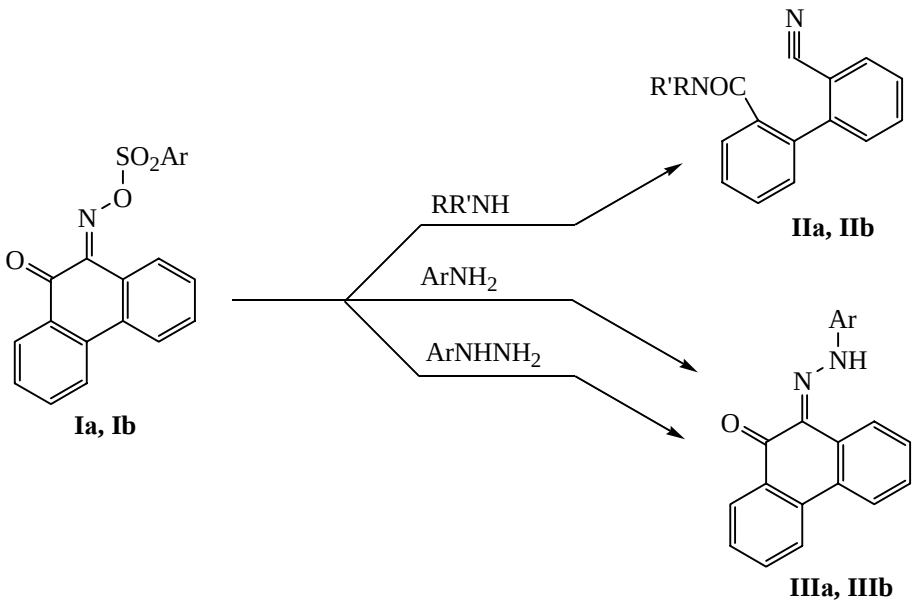
Received June 28, 2006

DOI: 10.1134/S1070428006110212

In extension of our research in the series of *o*-quinones monooximes acyl derivatives [1–3] we found that synthesized by us 9,10-phenanthrenequinone monoxime *O*-arenesulfonates **Ia** and **Ib** readily reacted with aliphatic and heterocyclic amines already at room temperature undergoing a cleavage of the intercarbonyl bond leading to the formation of the corresponding amides of 2-(2-cyanophenyl)benzoic acid: 2-hydroxyethylamide **IIa** and morpholide **IIb**. However the reaction of the same 9,10-phenanthrenequinone monoxime *O*-arenesulfonates with aromatic amines and also with arylhydrazine required short boiling of the components solution in acetonitrile or prolonged keeping at room temperature. Therewith instead of the expected arylide or hydrazide we suddenly obtained in good yields phenanthrenequinone-9,10 monophenylhydrazone (**IIIa**) [4] and phenanthrenequinone-9,10 mono-4-methylphenylhydrazone (**IIIb**) [5].

9,10-phenanthrenequinone monooxime was prepared by procedure [6].

***O*-Benzenesulfonate of 9,10-phenanthrenequinone monoxime (Ia).** To a solution of 22.3 g (100 mmol) of 9,10-phenanthrenequinone monoxime and 17.66 g (100 mmol)of benzenesulfonyl chloride in 50 ml of acetone cooled to 0–5°C was added a solution of 4.8 g



Ia, Ib — **IIa, IIb** — **IIIa, IIIb**

I, III, Ar = C_6H_5 (**a**), 4-$CH_3C_6H_4$ (**b**); **II**, R = H, R' = CH_2CH_2OH (**a**), R = R' = N⌒O (**b**).

(120 mmol) of NaOH in 50 ml of water. The mixture was stirred for 10 min, then diluted with ice water (50 ml), the precipitate was filtered off, washed with ice water, and dried at room pemperature. Yield 21 g (78%), yellowish-orange substance, mp 140–141°C (from 2-butanone), R_f 0.58. Mass spectrum, *m/z* (I_{rel}, %): 363 (6) $[M]^+$, 299 (4) $[M - SO_2]^+$, 222 (7) $[M - PhSO_2]^+$, 206 (100) $[M - PhSO_3]^+$, 179 (11) $[M - PhSO_3–HCN]^+$, 178 (24) $[M - PhSO_3–CO]^+$, 177 (21), 163 (6), 151 (20), 141 (9), 77 (43). Found, %: C 66.27; H 3.41; N 3.92; S 8.54. $C_{20}H_{13}NO_4S$. Calculated, %: C 66.11; H 3.61; N 3.85; S 8.82.

***O*-Tosylate of 9,10-phenanthrenequinone monoxime (Ib)** was obtained in a similar fashion from 11.15 g (50 mmol) of 9,10-phenanthrenequinone monoxime, 10.48 g (55 mmol) of tosyl chloride in 80 ml of acetone, and solution of 2.4 g (60 mmol) of NaOH in 20 ml of water. Yield 17.5 g (93%), mp 147–148°C (from 2-butanone), R_f 0.36. Found, %: C 66.53; H 3.70; N 3.42; S 58.37. $C_{21}H_{15}NO_4S$. Calculated, %: C 66.83; H 4.01; N 3.71; S 8.49.

2-(2-Cyanophenyl)benzoic acid 2-hydroxyethylamide (IIa). Into 3 ml of 2-aminoethanol (excess) cooled to 10°C was added by portions 0.74 g (2 mmol) of compound **Ib**, the cooling was continued for 30 min more, and 2 days the mixture was kept at room temperature. Excess 2-aminoethanol was neutralized with dilute hydrochloric acid, the precipitate was filtered off, and washed with water. On recrystallization from ethyl acetate in the presence of activated carbon we obtained 0.17 g (31%) of amide **IIa**, mp 143–144°C (from benzene), R_f 0.82. Found, %: C 71.84; H 5.18; N 10.34. $C_{16}H_{14}N_2O_2$. Calculated, %: C 72.16; H 5.30; N 10.52.

2-(2-Cyanophenyl)benzoic acid morpholide (IIb) was obtained in a similar fashion as amide **IIa** from 5 ml of morpholine (excess) and 1.2 g (3 mmol) of compound **Ib**. The mixture was left overnight at room temperature. Yield 0.47 g (54%), mp 112–113°C, R_f 0.12. Found, %: C 73.68; H 5.29; N 9.30. $C_{18}H_{16}N_2O_2$. Calculated, %: C 73.95; H 5.52; N 9.58. On performing the reaction at 0°C and keeping the reaction mixture at 0°C for 4 days the yield of morpholide **IIb** increased to 74%.

Amides **IIa** and **IIb** were also prepared by reaction of 2-(2-cyanophenyl)benzoyl chloride with the same amines by procedure [7].

9,10-Phenanthrenequinone phenylhydrazone (IIIa). To 3 ml of aniline (excess) at cooling with running water was added 1.2 g (3 mmol) of tosylate **Ib**. The dark-red solution formed was kept at room temperature for 3 days and extracted with hot ethyl acetate (2 × 10 ml). Ethyl acetate was distilled off, the residue was washed with dilute hydrochloric acid (1:1), with water, and recrystallized from 2-propanol in the presence of activated carbon. Yield 0.42 g (49%), mp 164–165°C (166°C [4]), R_f 0.72.

9,10-Phenanthrenequinone 4-methylphenylhydrazone (IIIb). *a*. A solution of 1.13 g (3 mmol) of compound **Ia** and 0.73 g (6 mmol) of 4-methylphenylhydrazine in 10 ml of acetonitrile was boiled for 5 min, cooled to room temperature, diluted with 10 ml of water, acidified with dilute hydrochloric acid till pH 6–6.5, the precipitate was filtered off and washed with water On recrystallization from acetic acid yield was 0.57 g (61%), mp 169–170°C [5], R_f 0.22.

b. Similarly from 0.75 g (2 mmol) of compound **Ia** and 3 ml 4-of methylphenylamine in 10 ml of acetonitrile we obtained 0.48 g (77%) of compound **IIIb**, mp 169–170°C (from acetic acid with activated carbon), R_f 0.22.

The homogeneity of compounds obtained was checked by TLC on Silufol UV-254 plates, eluent systems: tetrachloromethane–ethyl acetate, 3:1 (**Ia, IIIa**), tetrachloromethane–ethyl acetate, 6:1 (**Ib**), benzene–dioxane, 3:1 (**IIa**), ethyl acetate–benzene, 1:4 (**IIb**), benzene–heptane, 1:2 (**IIIb**), development in iodine vapor. Mass spectra were measured on Varian MAT-111 instrument at ionizing electrons energy 70 eV, direct admission of the sample ino the ion source.

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