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SHORT COMMUNICATIONS

Amination of 1-Arylazo-4-chloroanthraquinones*

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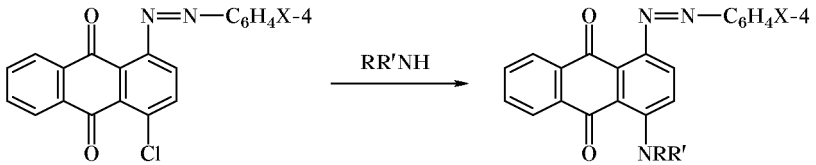
The simplest 1-arylazoanthraquinones have been known for a long time [1]. (4-Hydroxyphenylazo)-anthraquinones typically give rise to azo–quinone-hydrazone tautomerism [2], while the other chemical properties of these compounds were poorly studied. Taking into account high reactivity of various halogen-substituted anthraquinones in nucleophilic amination [3], we have examined the reactions of 4-chloro-1-(4-hydroxyphenylazo)anthraquinone (**Ia**) and 4-chloro-1-(4-dimethylaminophenylazo)anthraquinone (**Ib**) with cyclohexylamine, morpholine, and piperidine. Compounds **Ia** and **Ib** reacted with highly nucleophilic amines in dimethylformamide at 60–80°C and in dimethylacetamide at 50–60°C within several hours (Scheme 1). The reactions with weakly nucleophilic amines required more severe conditions and were not selective.

We failed to synthesize 4-amino-1-arylazoanthraquinones by the other method, namely by reaction of diazotized 1-amino-4-RNH-anthraquinones with phenol or dimethylaniline. In all cases, products of other transformations were isolated instead of the expected azo coupling products. For instance, from diazotized 1-amino-4-cyclohexylaminoanthraquinone and phenol in dimethylformamide we obtained 1,1-dimethyl-3-(9,10-dioxoanthracen-1-yl)triazene. When dimethylformamide was replaced by water, the product was 1-cyclohexylaminoanthraquinone. The latter was also obtained by attempted azo coupling of the same diazonium salt with *N*,*N*-dimethylaniline in dimethylformamide.

The structure of compounds **IIa**–**IIc** and **III** was confirmed by elemental analyses and IR, ^{1}H NMR, and mass spectra.

1-Cyclohexylamino-4-(4-hydroxyphenylazo)-anthraquinone (IIa). A mixture of 1.1 mmol of anthraquinone **Ia** [4], 11 mmol of cyclohexylamine, and 5 ml of dimethylacetamide was stirred at 50–60°C for 4 h (until initial anthraquinone **Ia** disappeared according to the TLC data). The mixture was cooled to room temperature and diluted with water. The dark brown tar-like precipitate was filtered off, washed with water and aqueous ethanol, dried, and subjected to column chromatography on silica gel (40/100 μm)

Scheme 1.



Ia, Ib **IIa–IIc, III**

Ia, **IIa**–**IIc**, X = OH; **Ib**, **III**, X = $N(CH_3)_2$; **IIa**, R = H, R′ = cyclohexyl; **IIb**, RR′N = morpholino; **IIc**, **III**, RR′N = piperidino.

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using methylene chloride as eluent. Yield of **IIa** 37%, mp 224–226°C. IR spectrum, ν, cm^{-1}: 1618, 1645 (C=O); 3180 (OH); 3250 (NH). ^1H NMR spectrum, δ, ppm: 1.43–3.8 m (11H, cyclohexyl), 6.95–8.22 (10H, H_{arom}), 10.15 br.s (1H, OH), 10.27 d (1H, NH). Electron absorption spectrum, λ_{max}, nm (log ε): 336 (4.22), 382 (4.29), 544 (3.99). Found, %: C 73.61; H 5.46; N 9.35. $C_{26}H_{23}N_3O_3$. Calculated, %: C 73.41; H 5.41; N 9.88.

Compounds **IIb**, **IIc**, and **III** were synthesized in a similar way.

1-(4-Hydroxyphenylazo)-4-morpholinoanthraquinone (IIb). Yield 40%, mp 153–154°C. IR spectrum, ν, cm^{-1}: 1660 (C=O), 3180 (OH). ^1H NMR spectrum, δ, ppm: 3.28 m and 3.89 m (8H, CH_2N and CH_2O in morpholine), 6.95–8.16 m (10H, H_{arom}), 10.06 s (1H, OH). Electron absorption spectrum, λ_{max}, nm (log ε): 337 (4.16), 402 (4.15), 515 sh (3.68). Found, %: C 69.53; H 4.46; N 10.00. $C_{24}H_{19}N_3O_4$. Calculated, %: C 69.73; H 4.60; N 10.17.

1-(4-Hydroxyphenylazo)-4-piperidinoanthraquinone (IIc). Yield 38%; the product has no sharp melting point: it begins to melt at 180°C. IR spectrum, ν, cm^{-1}: 1660 (C=O), 3180 (OH). ^1H NMR spectrum, δ, ppm: 1.69–1.80 m, 3.28 m (10H, piperidine), 6.94–8.15 m (10H, H_{arom}), 10.03 s (1H, OH). Electron absorption spectrum, λ_{max}, nm (log ε): 338 (4.23), 416 (4.25), 526 (3.75). Found, %: C 72.70; H 4.96; N 9.70. $C_{25}H_{21}N_3O_3$. Calculated, %: C 72.99; H 5.11; N 10.20.

1-(4-Dimethylaminophenylazo)-4-piperidinoanthraquinone (III). Yield 38%, mp 196–200°C. IR spectrum, ν, cm^{-1}: 1645 (C=O), 3180 (OH). ^1H NMR spectrum, δ, ppm: 1.69–1.80 and 3.29 m (10H, CH_2, piperidine), 3.09 m (6H, $2CH_3$), 6.83–8.15 m (10H, H_{arom}). Electron absorption spectrum, λ_{max}, nm (log ε): 320 (3.99), 457 (4.34). Found, %: C 73.72; H 5.93; N 12.55.$C_{27}H_{26}N_4O_2$. Calculated, %: C 73.97; H 5.94; N 12.78.

The ^1H NMR spectra were recorded on a Bruker DRX-500 spectrometer (500.13 MHz) in DMSO-d_6 using TMS as internal reference. The electron absorption spectra were measured on a Specord UV-Vis spectrophotometer in DMSO. The IR spectra were obtained on a Specord 75IR instrument in mineral oil. The mass spectra (70 eV) were run on an MS-902 instrument at 26°C.

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