

SHORT
COMMUNICATIONS

Cyclization of 1-Aryl-3-[4-aryl(cyclohexyl)amino-9,10-dioxo-1-anthryl]triazenes to 3-Aryl-5-aryl(cyclohexyl)-aminoanthra[1,2-*d*][1,2,3]triazole-6,11-diones

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There are almost no published data on chemical properties of triazenoanthraquinones. Taking into account the ability of deprotonated forms of various triazenes to act as nucleophiles (e.g., in alkylation reactions [1]), as well as the ability of anthraquinone derivatives to undergo nucleophilic substitution, we examined the behavior of 1-aryl-3-[4-aryl(cyclohexyl)aminoanthraquinon-1-yl]triazenes in the presence of bases. We have found that triazenoanthraquinones **Ia–Ic**, prepared by the procedure described in [2], are readily deprotonated by the action of potassium carbonate in dimethyl sulfoxide due to acceptor effect of the carbonyl group on the NH moiety. Anions **IIa–IIc** thus formed undergo further cyclization to 3-aryl-5-aryl(cyclohexyl)aminoanthra[1,2-*d*][1,2,3]triazole-6,11-diones **IIIa–IIIc** (Scheme 1).

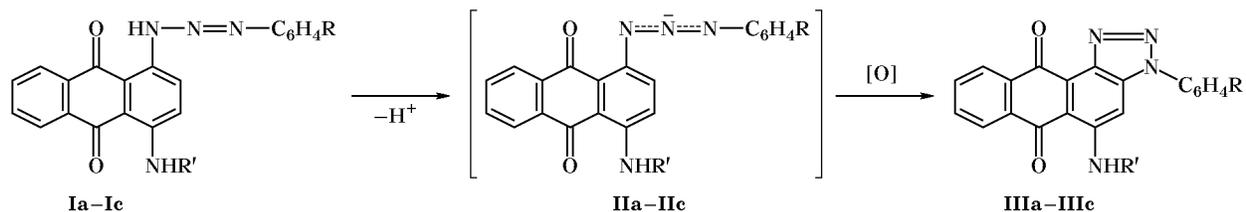
Some heterocyclizations have been reported, where nucleophilic fragment in position 1 of anthraquinone attacks position 2, resulting in nucleophilic substitution of the hydrogen atom. For example, the reaction of 1-chloroanthraquinone with 1,2-diaminoethane leads to formation of 1,2,3,4-tetrahydronaphtho[2,3-*f*]-

quinoxaline-7,12-dione [3], and treatment of *N*-(9,10-dioxo-1-anthryl)-*N'*-phenylurea with alkali in dimethyl sulfoxide yields anthra[1,2-*d*]imidazole derivatives [4]. Presumably, the revealed heterocyclization **I** → **III** also involves nucleophilic substitution of hydrogen.

The structure of compounds **Ia–Ic** and **IIIa–IIIc** was confirmed by the electron absorption and ¹H NMR spectra.

1-Phenyl-3-(4-cyclohexylamino-9,10-dioxo-1-anthryl)triazene (Ia). A mixture of 0.4 mmol of 1-amino-4-(cyclohexylamino)anthraquinone and 3 ml of acetic acid was treated with 0.6 mmol of isopentyl nitrite. The resulting solution of diazonium salt was gradually added with stirring to a solution of 4 mmol of aniline and 1 g of sodium acetate in 3 ml of dimethylformamide, cooled to 0°C. The mixture was stirred for 1 h, 1 ml of water was added, and the dark blue–green precipitate was filtered off, washed with water and ethanol, dried in air, and recrystallized from benzene or ethanol. Yield 0.14 g (83%), mp 180–183°C. IR spectrum, ν , cm⁻¹: 1618 (C=O), 3142 br (NH). ¹H NMR spectrum, δ , ppm: 1.35–2.09 m,

Scheme 1.



R = H, R' = cyclohexyl (a); R = 4-CH₃, R' = cyclohexyl (b); R = 4-CH₃, R' = 4-CH₃C₆H₄ (c).

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3.8 m (11H, CH₂, CH, cyclohexyl), 7.22–8.35 m (11H, H_{arom}), 10.69 s (1H, NHC), 13.9 (1H, NHN). Electron absorption spectrum, λ_{\max} , nm (log ϵ): 416 (4.23), 588 (4.14), 630 (4.13). Found, %: C 73.82; H 5.96; N 12.66. C₂₆H₂₄N₄O₂. Calculated, %: C 73.58; H 5.66; N 13.21.

Compounds **Ib** and **Ic** were synthesized in a similar way.

3-(4-Cyclohexylamino-9,10-dioxo-1-anthryl)-1-p-tolyltriazene (Ib). Yield 81%, mp 171–175°C. IR spectrum, ν , cm⁻¹: 1610 (C=O), 3148 br (NH). ¹H NMR spectrum, δ , ppm: 1.35–2.09 m, 3.8 m (14H, H_{aliph}), 7.30–8.31 m (10H, H_{arom}), 10.65 s (1H, NHC), 13.9 s (1H, NHN). Electron absorption spectrum, λ_{\max} , nm (log ϵ): 423 (4.38), 588 (4.18). Found, %: C 73.49; H 6.23; N 12.29. C₂₇H₂₆N₄O₂. Calculated, %: C 73.97; H 5.94; N 12.78.

3-[9,10-Dioxo-4-(p-tolylamino)-1-anthryl]-1-p-tolyltriazene (Ic). Yield 83%, mp 187–189°C. IR spectrum, ν , cm⁻¹: 1622 (C=O), 3148 br (NH). ¹H NMR spectrum, δ , ppm: 2.35 m (6H, H_{aliph}), 6.6–8.6 m (14H, H_{arom}), 12.2 s (1H, NHC), 13.86 s (1H, NHN). Electron absorption spectrum, λ_{\max} , nm (log ϵ): 420 (4.39), 588 (4.21). Found, %: C 74.95; H 4.67; N 12.08. C₂₈H₂₂N₄O₂. Calculated, %: C 75.34; H 4.93; N 12.56.

5-Cyclohexylamino-3-phenylanthra[1,2-d][1,2,3]-triazole-6,11-dione (IIIa). A mixture of 0.17 mmol of compound **Ia**, 0.5 mmol of K₂CO₃, and 2 ml of dimethyl sulfoxide was vigorously stirred for several hours at 80°C (until initial compound **Ia** disappeared; TLC data), several drops of water were added, and the dark violet precipitate was filtered off, washed with water and ethanol, dried in air, and recrystallized from ethanol or benzene. Yield of **IIIa** 50 mg (73%), mp 197–210°C. IR spectrum, ν , cm⁻¹: 1618, 1670 (C=O); 3270 (NH). ¹H NMR spectrum, δ , ppm: 1.35–1.98 m and 3.4 m (11H, H_{aliph}), 6.9–8.2 m (10H, H_{arom}), 9.66 s (1H, NH). Electron absorption spectrum, λ_{\max} , nm (log ϵ): 400 (3.25), 538 (3.76). Found, %: C 73.69; H 4.94; N 13.46. C₂₆H₂₂N₄O₂. Calculated, %: C 73.93; H 5.21; N 13.27.

Compounds **IIIb** and **IIIc** were synthesized in a similar way.

5-Cyclohexylamino-3-p-tolylanthra[1,2-d][1,2,3]-triazole-6,11-dione (IIIb). Yield 72%, mp 225–227°C. IR spectrum, ν , cm⁻¹: 1630, 1660 (C=O); 3295 (NH). ¹H NMR spectrum, δ , ppm: 1.4–2.0 m and 3.67 m (14H, H_{aliph}), 7.0–8.2 m (9H, H_{arom}), 9.66 s (1H, NH). Electron absorption spectrum, λ_{\max} , nm (log ϵ): 400 (3.06), 540 (3.66). Found, %: C 73.92; H 5.66; N 12.34. C₂₇H₂₄N₄O₂. Calculated, %: C 74.31; H 5.50; N 12.84.

3-p-Tolyl-5-p-tolylaminoanthra[1,2-d][1,2,3]-triazole-6,11-dione (IIIc). Yield 86%, mp 240–243°C. IR spectrum, ν , cm⁻¹: 1632, 1670 (C=O); 3254 (NH). ¹H NMR spectrum, δ , ppm: 2.33 m (6H, H_{aliph}), 7.25–8.25 m (13H, H_{arom}), 11.05 s (1H, NH). Electron absorption spectrum, λ_{\max} , nm (log ϵ): 400 (3.23), 540 (3.78). Found, %: C 75.84; H 4.14; N 12.12. C₂₈H₂₀N₄O₂. Calculated, %: C 75.68; H 4.50; N 12.61.

The ¹H NMR spectra were obtained on a Bruker DRX-500 instrument at 500.13 MHz using DMSO-*d*₆ as solvent and TMS as internal reference. The electron absorption spectra were measured on a Specord UV-Vis spectrophotometer in chloroform. The IR spectra were recorded on a Specord 75IR spectrometer from samples dispersed in mineral oil.

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