

SHORT
COMMUNICATIONS

Reactions of Anthra[1,2-*c*]isoxazole-6,11-dione
with Alkylamines*

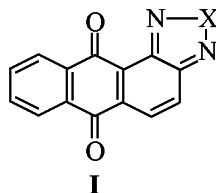
L. M. Gornostaev¹, R. V. Mitrokhin¹, and S. I. Firgang²

¹Krasnoyarsk State Pedagogical University, Krasnoyarsk, 660049 Russia

²Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow

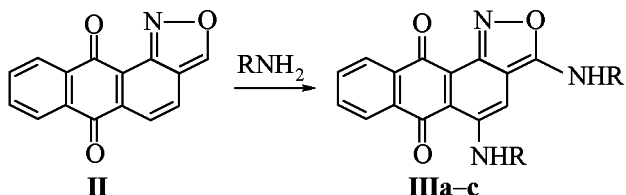
Received December 20, 2000

Anthra[1,2-*c*][1,3]diazoles (**I**) are known to react with amines at 4-position due to strong electron-withdrawing effect of a carbonyl in 1-position and of diazole ring [1].



X = O, Se, NAr.

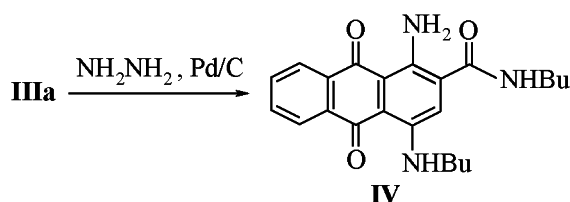
We found that anthra[1,2-*c*]isoxazole-6,11-dione (**II**), isoelectronic analog of diazoles **I**, is aminated in alkylamine medium at 10–15°C into another position, 3.



R = Bu (a), *i*-Bu (b), *i*-Pr (c).

3,5-Di(alkylamino)-6,11-dihydroanthra[1,2-*c*]isoxazole-6,11-diones **IIIa-c** spontaneously crystallized in the course of formation.

The composition and structure of reaction products were confirmed by the data of ¹H NMR and mass spectra, and also by reduction of compound **IIIa** into 1-amino-*N*-butyl-4-butylamino-9,10-dioxo-9,10-dihydro-2-anthracenecarboxamide (**IV**).



3,5-Di(butylamino)anthra[1,2-*c*]isoxazole-6,11-dione (IIIa). A mixture of 0.2 g (0.8 mmol) of anthra[1,2-*c*]isoxazole-6,11-dione and 1.46 g (0.02 mol) of butylamine was stirred for 1 h at 20°C. The separated precipitate was filtered off and washed with alcohol and ether. Yield 60%, mp 110–112°C.

¹H NMR spectrum, δ , ppm: 1.0 m (6H, 2CH₂CH₂CH₂CH₃), 1.45 m (4H, 2CH₂CH₂CH₂CH₃), 1.65 m, 1.75 m (4H, 2CH₂CH₂CH₂CH₃), 3.45 m, 3.70 m (4H, 2CH₂CH₂CH₂CH₃), 7.70–8.40 (4H, arom), 7.97 s (1H, H⁴), 9.98 s (2H, 2NH). Found, %: C 69.95; H 6.46; N 10.42. C₂₃H₂₅N₃O₃. Calculated, %: C 70.59; H 6.39; N 10.74.

3,5-Di(isobutylamino)anthra[1,2-*c*]isoxazole-6,11-dione (IIIb) was prepared similarly to compound **IIIa** from isoxazole **I** and isobutylamine. Yield 63%, mp 166–167°C. ¹H NMR spectrum, δ , ppm: 1.03 t, 1.08 t [12H, 2CH₂CH(CH₃)₂], 1.95 m, 2.05 m [2H, 2CH₂CH(CH₃)₂], 3.30 t, 3.55 t [4H, 2CH₂CH(CH₃)₂], 7.70–8.40 (4H, arom.), 7.98 s (1H, H⁴), 10.10 s (2H, 2NH). Found, %: C 70.03; H 6.09; N 10.49. C₂₃H₂₅N₃O₃. Calculated, %: C 70.59; H 6.39; N 10.74.

3,5-Di(isopropylamino)anthra[1,2-*c*]isoxazole-6,11-dione (IIIc) was prepared similarly to compound **IIIa** from isoxazole **I** and isopropylamine. Yield 50%, mp 219–229°C. ¹H NMR spectrum, δ , ppm: 1.3 d, 1.45 d [12H, 2CH(CH₃)₂], 4.2 q, 4.4 q (2H, 2CH(CH₃)₂), 7.5–8.45 m (4H, arom), 8.0 s

* The study was carried out under financial support of (Krasnoyarsk Regional Science Foundation (grants 9F0158, 10F141c).

(1H, H⁴), 9.99 d (2H, 2NH). Found, %: C 68.67; H 5.53; N 11.25. C₂₁H₂₁N₃O₃. Calculated, %: C 69.42; H 5.79; N 11.57.

1-Amino-N-butyl-4-butylamino-9,10-dioxo-9,10-dihydro-2-anthracenecarboxamide (IV). A mixture of 0.2 g (0.5 mmol) of compound **IIIa**, 1 ml (0.02 mol) of hydrazine hydrate, 0.1 g of Pd/C and 10 ml of ethanol was boiled for 30 min, the hot solution was filtered, the filtrate was diluted with water, and the separated precipitate was filtered off and dried. Yield 60%, mp 145–147°C. ¹H NMR spectrum, δ, ppm: 0.95 t, 1.05 t (6H 2CH₂CH₂CH₂CH₃), 1.4 m, 1.53 m (4H, 2CH₂CH₂CH₂CH₃), 1.56 m, 1.75 m (4H, 2CH₂CH₂CH₂CH₃), 3.30 m, 3.50 m

(4H, 2CH₂CH₂CH₂CH₃), 7.5–8.25 m (4H, arom), 8.75 s (1H, H³), 8.80 s (2H, NH₂), 10.55 s (2H, 2NH). Found, %: C 69.81; H 6.70; N 10.68. C₂₃H₂₇N₃O₃. Calculated, %: C 70.23; H 6.87; N 10.69.

¹H NMR spectra were registered on spectrometer Bruker DRX500 (operating frequency 500.13 MHz) from solutions in DMSO-*d*₆, internal reference TMS.

REFERENCES

1. Gorelik, M.V., Dokunikhin, N.S., Korolev, A.I., Koptyuk, P.G., Maslennikova, E.V., and Fodiman, I.V., *Khimiya antrakhinona*, Moscow: Khimiya, 1969, pp. 45–52.