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Synthesis of Dyes from Aromatic *C*-Nitroso-*N*-hydroxytriazenes

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Abstract—Aromatic *C*-nitroso-*N*-hydroxytriazenes can be used as stable forms of diazo compounds for preparation of azo dyes.

It is known [1] that acid hydrolysis of triazenes leads to formation of diazo compounds. Therefore, triazenes can be used as stable forms of diazonium salts for synthesis of azo dyes [2, 3].

In the preceding communications [4–7] we showed for the first time that arenediazonium salts react with *p*- and *o*-benzoquinone dioximes, yielding a new type of triazenes, namely nitrosoaryltriazenes, which exhibit some specific properties different from those inherent to classical triazenes. In particular, they give rise to nitroso–quinone oxime tautomerism [5]. In continuation of our studies on triazenes, we examined the behavior of *C*-nitrosotriazenes in acid medium. We found that nitrosoaryltriazenes readily generate diazo compounds which can be brought into azo coupling with various substrates, yielding azo dyes. Analysis of the products revealed formation of *o*- and *p*-benzoquinone dioximes. As azo component we used 2-hydroxynaphthalene, *N*-phenyl-3-hydroxynaphthalene-2-carboxamide, and *N*-(*o*-methoxyphenyl)-3-hydroxynaphthalene-2-carboxamide (Scheme 1).

The proposed scheme is supported by the fact that *o*- and *p*-benzoquinone dioximes **VIII** and **IX** were isolated from the reaction mixture. Azo dyes **X**–**XVII** showed in the electron absorption spectra a band at λ 420–550 nm, which is typical of conjugated bond system containing an N=N chromophore [8] (see table). The physical constants of the isolated products were in agreement with published data [9, 10].

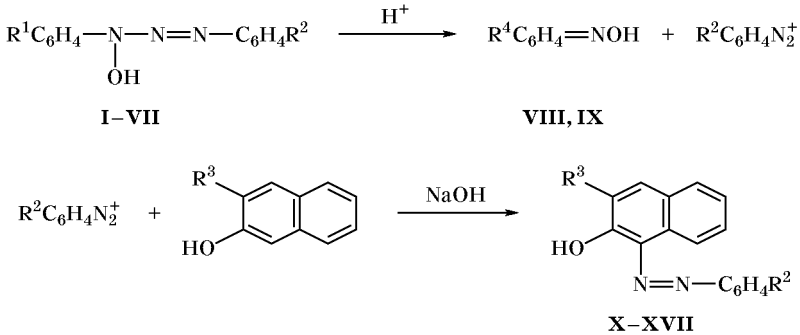
Thus our study of the behavior of aromatic *C*-nitroso-*N*-hydroxytriazenes in acid medium showed that these compounds decompose into benzoquinone dioximes and arenediazonium salts and that they can be used as stable forms of diazo components for preparation of azo dyes.

EXPERIMENTAL

The electron absorption spectra were measured on a Specord M40 spectrophotometer.

***o*-(2-Hydroxy-1-naphthylazo)nitrobenzene (X).** 3-Hydroxy-3-(*o*-nitrosophenyl)-1-(*o*-nitrophenyl)tri-

Scheme 1.



VIII, R^4 = *o*-NOH; **IX**, R^4 = *p*-NOH; for R^1–R^3, see table.

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Azo dyes $R^2C_6H_4N{=}NC_{10}H_5(2\text{-}OH)(3\text{-}R^3)$

Compound no.	R^2	R^3	Decomp. point, °C	UV spectrum, λ_{max}, nm ($\log\varepsilon$)	Triazene no.	R^1	R^2
X	*o*-NO_2	H	208	545 (3.92, H_2SO_4)	**I**	*o*-NO	*o*-NO_2
XI	*m*-NO_2	H	194	530 (4.07, H_2SO_4)	**II**	*o*-NO	*m*-NO_2
XII	*p*-NO_2	H	244	550 (4.28, H_2SO_4)	**III**	*o*-NO	*p*-NO_2
XIII	*o*-COOH	H	272	510 (3.87, EtOH)	**IV**	*p*–NO	*o*-COOH
XIV	*m*-COOH	H	243	508 (3.76, EtOH)	**V**	*p*-NO	*m*-COOH
XV	*p*-COOH	H	301	537 (4.01, EtOH)	**VI**	*p*-NO	*p*-COOH
XVI	*p*-NO_2	CONHPh	296	420 (3.94, EtOH)	**VII**	*p*-NO	*p*-NO_2
XVII	*p*-NO_2	$CONHC_6H_4OCH_3$-*o*	147	427 (3.82, EtOH)	**VII**	*p*-NO	*p*-NO_2

azene (**I**), 1.44 g, was dissolved in 200 ml of acetic acid (d = 1.07 g/cm^3), 3 ml of concentrated sulfuric acid (d = 1.83 g/cm^3) was added, and the mixture was kept for 5–7 min at 10°C. To the resulting solution of diazonium salt we added 0.72 g of 2-hydroxynaphthalene in 200 ml of 50% aqueous NaOH, and the mixture was kept for 10 min. The product was filtered off and thoroughly washed with water and ethanol. Yield 1.28 g (87%), orange–red substance, decomposition point 208°C.

***m*-(2-Hydroxy-1-naphthylazo)nitrobenzene (XI).** 3-Hydroxy-3-(*o*-nitrosophenyl)-1-(*m*-nitrophenyl)triazene (**II**), 1.44 g, was dissolved in 200 ml of acetic acid (d = 1.07 g/cm^3), 50 ml of 1.5% hydrochloric acid (d = 1.19 g/cm^3) was added, and the mixture was kept for 5–10 min at 10°C. A solution of 0.72 g of 2-hydroxynaphthalene in 200 ml of 50% aqueous NaOH was added. The resulting dye was filtered off and washed with water and ethanol. Yield 1.31 g (89%), orange substance, decomposition point 194°C.

***p*-(2-Hydroxy-1-naphthylazo)nitrobenzene (XII)** was synthesized as described above for compound **XI** from 1.44 g of 3-hydroxy-3-(*o*-nitrosophenyl)-1-(*p*-nitrophenyl)triazene (**III**). Yield of **XII** 1.33 g (90%), red substance, decomposition point 244°C.

***o*-(2-Hydroxy-1-naphthylazo)benzoic acid (XIII).** 3-Hydroxy-1-(*o*-carboxyphenyl)-3-(*p*-nitrosophenyl)triazene (**IV**), 1.43 g, was dissolved in 30 ml of acetic acid (d = 1.07 g/cm^3), 20 ml of 1.5% hydrochloric acid (d = 1.19 g/cm^3) was added, and the mixture was kept for 5 min at 5°C. A solution of 0.72 g of 2-hydroxynaphthalene in 60 ml of 30% aqueous sodium hydroxide was then added, and the product was filtered off and washed with water. Recrystallization from ethanol gave 1.38 g (96%) of azo dye **XIII** as a red substance with decomposition point 272°C [9].

***m*-(2-Hydroxy-1-naphthylazo)benzoic acid (XIV)** was synthesized as described above for compound **XIII** from 1.43 g of 3-hydroxy-3-(*p*-nitrosophenyl)-1-(*m*-carboxyphenyl)triazene (**V**). Recrystallization from ethanol gave 1.29 g (88%) of reddish–yellow azo dye **XIV**, decomposition point 243°C.

***p*-(2-Hydroxy-1-naphthylazo)benzoic acid (XV)** was synthesized as described above for compound **XIII** from 1.43 g of 3-hydroxy-1-(*p*-carboxyphenyl)-3-(*p*-nitrosophenyl)triazene (**VI**). Yield 1.34 g (91%), red substance, decomposition point 301°C.

1-(4-Nitrophenylazo)-2-hydroxynaphthalene-3-carboxanilide (XVI). 3-Hydroxy-3-(*p*-nitrosophenyl)-1-(*p*-nitrophenyl)triazene (**VII**), 1.44 g, was dissolved in 200 ml of acetic acid (d = 1.07 g/cm^3), 50 ml of 1.5% hydrochloric acid (d = 1.19 g/cm^3) was added, and the mixture was kept for 7 min at 10°C. A solution of 1.32 g of 3-hydroxynaphthalene-2-carboxanilide in 200 ml of 50% aqueous sodium hydroxide was added, and the product was filtered off and washed with water. Yield 1.92 g (92%), claret substance, decomposition point 296°C [10].

2-Hydroxy-1-(4-nitrophenylazo)-*N*-(*o*-methoxyphenyl)naphthalene-3-carboxamide (XVII) was synthesized as described above for compound **XVI** from 1.44 g of 3-hydroxy-3-(*p*-nitrosophenyl)-1-(*p*-nitrophenyl)triazene (**VII**). Coupling with 1.47 g of 3-hydroxy-*N*-(*o*-methoxyphenyl)naphthalene-2-carboxamide gave 1.86 g (84%) of orange–red azo dye **XVII**, decomposition point 147°C.

In all experiments, acidification of the filtrates resulted in precipitation of crystals of *o*- or *p*-benzoquinone dioxime. The precipitate was filtered off, washed with water, and recrystallized from ethanol. *p*-Benzoquinone dioxime, mp 243°C; published data [10]: mp 243°C; *o*-benzoquinone dioxime, mp 143°C; published data [11]: mp 143°C.

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