The brightest CL is registered for $Na^{+}X^{+-}$, which are stronger electron donors.

The CL spectrum measured using an MZD-2M monochromator and corrected for self-absorption of the reaction solution has a maximum at 590 nm (Fig. 1) and correlates well with the FL spectrum of the phenoxide anion,³ which was obtained during the low-temperature (77 K) photoirradiation of a solution of 1 in an ether--isooctane mixture. From this it follows that the excited phenoxide anion (RO^-)* resulting from the electron transfer reaction

 $RO^{-} + e^{-} \longrightarrow (RO^{-})^{*} \longrightarrow RO^{-} + hv,$ (2)

is a CL emitter.

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Reactions of 1-aryl-2-bromodiazene 1-oxides with acids and bases

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The reactions of 1-aryl-2-bromodiazene 1-oxides with HCl in nonaqueous media give aryldiazonium chlorides, while 1,3.3-substituted triazenes-1 are formed in the reactions with secondary amines. Using $2-{^{15}N}$ label, it was shown that the aryl group does not migrate in these reactions.

Key words: 1-aryl-2-bromodiazene 1-oxides, diazonium salts, triazenes. ¹⁵N NMR spectroscopy.

Recently,¹ we obtained 1-aryl-2-bromodiazene 1-oxides (BDO) by the reactions of arylnitroso compounds with NH_4Br in the presence of N-bromosuccinimide. Their reactions with olefins were studied. In this work, the reactions of BDO with some acids and bases are studied.

1-Aryl-2-bromodiazene 1-oxides 1 react with HCl in Et_2O to form aryldiazonium chlorides 2 (Scheme 1). Their structure was confirmed by azo coupling with β -naphthol yielding the corresponding compounds. Due to high yields of products 2, the reaction of BDO with HCl can be used for preparing diazonium salts in nonaqueous media, including preparation from weakly basic amines.

Based on the result of this reaction with $2-{15N}-1a$ (synthesized by the reaction of nitrobenzene with

Scheme I

$$\begin{array}{ccc} 0 & & & \\ & & & \\ Ar - N = N - Br & - & \\ 1a.b & & 2a.b \end{array}$$

a: Ar = Ph (**2a**, including the sample labeled by ¹⁵N, yield 95%), **b:** Ar = 2,4,6-Br₃C₆H₂ (**2b**, 92%)

 15 NH₄Br), we can exclude the mechanisms associated with the migration of the aryl substituent. Phenyldiazonium chloride 15 N-2a obtained via Scheme 1 was

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transformed into stable diazonium tetrafluoroborate in which, according to the ${}^{15}N$ NMR data, the ${}^{15}N$ label is entirely retained on the terminal nitrogen atom.

The possible routes of formation of aryldiazonium cations from BDO are presented in Scheme 2. One of them includes the intermediate formation of diazenoxide A. There were unsuccessful attempts to synthesize A by alkaline hydrolysis of 1-aryl-2-carbomethoxydiazene 1-oxides as early as the 1940s.² However, this reaction resulted only in diazotates, and it still remains unclear whether compound A can exist.

Scheme 2



The reactions of 1-phenyl-2-bromodiazene 1-oxide (1a) with dimethylamine and morpholine give 3,3-disubstituted 1-phenyltriazenes-1 (3a,b) in high yields (Scheme 3).



At the first stage of the reaction, BDO acts evidently as the brominating agent with respect to amine. In any case, for the reaction of BDO 1a with an excess of morpholine, N-bromomorpholine formed in 90% yield was identified by ¹H NMR. N-Bromodimethylamine was not detected by this method, likely due to its instability under the reaction conditions.

In the reaction of dimethylamine with labeled diazenoxide $2-\{^{15}N\}-1a$, the formation of triazene $2-\{^{15}N\}-3$ only with the label at the central nitrogen atom was proved by ^{15}N NMR. We did not study the mechanism of this reaction in more detail. However, it cannot be ruled out that phenyldiazenoxide A is the intermediate in this transformation as well (Scheme 4), although the route of its transformation into triazene **3a** is still unclear.



Experimental

¹H and ¹⁵N NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13 and 30.42 MHz, respectively). Chemical shifts were measured relative to Me₄Si (¹H) and Me¹⁵NO₂ (¹⁵N, external standard). IR spectra were recorded on a UR-20 instrument (liquid compounds were prepared in a thin layer (NaCl glass) and solid substances were prepared in pellets with KBr). The following compounds were obtained by known procedures: N-bromomorpholine,³ 1-phenylazonaphthol-2,⁴ N-bromodimethylamine,⁵ 3,3-dimethyl-1-phenyltriazene,⁶ 1-phenylazomorpholine,⁷ phenyldiazonium chloride,⁸ and 1-(2,4,6-tribromophenyl)azonaphthol-2.⁹

Labeled 1-phenyl-2-bromodiazene 1-oxide $(2-{}^{15}N}-1a)$. Nitrosobenzene (268 mg, 2.5 mmol) and NBS (2.14 g, 12 mmol) were suspended in a mixture of CH₂Cl₂ (5 mL) and MeCN (5 mL). Finely powdered ¹⁵NH₄Br (295 mg, 3 mmol, degree of enrichment in ¹⁵N 98%) was added to the suspension with rigorous stirring and cooling to -10 °C. The mixture was stored for 1 h at -10-0 °C and concentrated *in vacuo* (the temperature of the bath was <40 °C). The product was extracted with pentane, and the solvent was distilled off *in vacuo*. The yield was 478 mg (95%), m.p. 46-47 °C (pentane).

Phenyldiazonium chloride (2a). A 3 *M* ether solution of HCl (0.8 mL, 2.4 mmol HCl) was added to a solution of 1-phenyl-2-bromodiazene 1-oxide (1a) (220 mg, 1.1 mmol) in abs. ether (2 mL). The resulting precipitate was filtered off. The yield of the product was 147 mg (95%). The IR spectrum coincides with the IR spectrum of the authentic sample. 1-Phenylazonaphthol-2 (identical to the authentic sample in m.p. and IR spectrum) was obtained using a known procedure⁴ by the reaction of chloride **2a** with β -naphthol.

2,4,6-Tribromophenyldiazonium chloride (2b). A 3 M ether solution of HCl (0.4 mL, 1.2 mmol HCl) was added to a solution of 1-(2,4,6-tribromophenyl)-2-bromodiazene 1-oxide (1b) (0.2 g, 0.46 mmol) in anhydrous ether (5 mL) at 0 °C. Salt 2b (160 mg, 92%) was filtered off. The product decomposes above 70 °C. IR, v/cm⁻¹: 2240, 2260. 1-(2,4,6-Tribromophenyl)azanaphthol-2 (identical to the authentic sample by m.p. and IR spectrum) was obtained using a known procedure⁹ by the reaction of chloride 2b with β -naphthol.

3,3-Dimethyl-1-phenyltriazene (3a). A solution of BDO 1a (280 mg, 1.39 mmol) in CH_2Cl_2 (0.3 mL) was added to a solution of Me_2NH (184 mg, 4.1 mmol) in CH_2Cl_2 (0.7 mL) with stirring and cooling to -30 °C. The mixture was stored for 5 min at -20 °C. The solvent was evaporated *in vacuo*, and the product was purified by column chromatography (silica gel, CHCl₃ as cluent). The yield of triazene **3a** was 155 mg (75%). The product is identical to the authentic sample in its 1R spectrum.

Reaction of 2-{15N}-1a with HCL A 3 M ether solution of HCl (0.8 mL, 2.4 mmol HCl) was added to a solution of 2-{¹⁵N}-1a (220 mg, 1.1 mmol) in abs. ether (2 mL) at 0 °C. The precipitate that formed was filtered off. The yield of phenyldiazonium chloride 2-{15N}-2a was 147 mg (95%). The product was dissolved in 30% aqueous HBF_4 (2 mL), and ether (5 mL) was added. The residue was filtered off, washed with ether, and dried in vacuo. The yield of labeled phenyldiazonium tetrafluoroborate was 0.1 g (50%). ^{15}N NMR (DMSO-d_6), δ : -67.96 (see Ref. 10:

 $Ph \rightarrow N \equiv N BF_4$ (complex with 18-crown-6 in CHCl₃): -150.2 (N-1) and -57.2 (N-2).

Reaction of 2-{15N}-1a with dimethylamine. A solution of BDO 2-{¹⁵N}-1a (280 mg, 1.39 mmol) in CD₂Cl₂ (0.3 mL) was added to a solution of Me2NH (184 mg, 4.1 mmol) in CD_2Cl_2 (0.7 mL) with stirring and cooling to -30 °C. The mixture was stored for 5 min at -20 °C and analyzed by ¹H NMR using internal standard. The yield of 3,3-dimethyl-1-phenyltriazene 2-(15N)-3a was 80%. 15N NMR (CD2CI2),

S: 65.48 (see Ref. 11: Ph-N=N-NMe, in CDCl₃: -19.8 (N-1), 72.2 (N-2), -224.6 (N-3).

Reaction of BDO 1a with morpholine. Morpholine (254 mg, 2.9 mmol) was added to a solution of BDO 1a (201 mg, 1 mmol) in CCl₄ (2 mL) and stored for 2 h at 20 °C. The reaction mixture was analyzed by ¹H NMR using internal standard. The yields of 1-phenylazomorpholine and N-bromomorpholine were 95 and 90%, respectively (the products were identified by comparison with the authentic samples). The solvent was evaporated in vacuo, and the product was purified

by column chromatography (silica gel, CHCl₃ as eluent). The yield of triazene 3b was 172 mg (90%, identical to the authentic sample in its IR spectrum).

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Unexpected transformations of O-vinylacetophenone oxime in the system Bu^tOK-THF

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Transformation of O-vinylacetophenone oxime in the system Bu⁴OK-THF was studied. The reaction at 60-65 °C was shown to afford not the anticipated 2-phenylpyrrole, but, instead, 2,4-diphenylpyrrole (21% yield) and oligomer products (40% yield). The latter have the same elemental composition as the starting O-vinyl oxime but do not contain vinyloxy groups or pyrrole fragments.

Key words: O-vinyl oximes. O-vinylacetophenone oxime, 2-phenylpyrrole, 2,4-diphenylpyrrole.

O-Vinyl oximes are precursors of the pyrroles that are formed from ketoximes and acetylene in the system KOH-DMSO¹⁻⁴. In light of said data, we obtained an

unexpected result when heating acetophenone O-vinyloxime (1) with Bu^IOK in THF at 60-65 °C: instead of 2-phenylpyrrole⁴, we isolated 2,4-diphenylpyrrole (2) in

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