

Reactions of *N,N*-dibromo-*tert*-butylamine with ketoximes

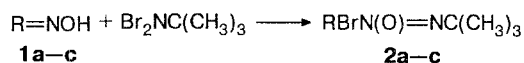
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Reactions of acetone, cyclohexanone, and adamantanone oximes with *N,N*-dibromo-*tert*-butylamine result in the corresponding C-bromo-diazeno-*N*-oxides. In the case of benzophenone oxime, *O,O'*-(diphenylmethylene)-bis-benzophenone oxime has been obtained.

Key words: oximes, diazeno-*N*-oxides, *N,N*-dibromo-*tert*-butylamine.

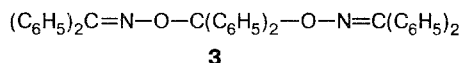
Reactions of *N,N*-dibromamines with nitroso compounds lead to diazeno-*N*-oxides (DO).¹ We have established that the interaction of a double excess of *N,N*-dibromo-*tert*-butylamine with acetone, cyclohexanone, and adamantanone oximes (**1a–c** respectively) also gives DO (**2a–c**).



- a:** R = CMe₂
b: R = *cyclo*-C₆H₁₀
c: R = C₉H₁₄ (adamantyl)

The reaction obviously proceeds through the intermediate formation of the corresponding α -bromonitroso compounds, which is confirmed by the blue-green coloring of the reaction mixture, as well as by the decrease in DO **2a–c** yields as the dibromoamine excess decreases.

In the case of benzophenone oxime, *O,O'*-(diphenylmethylene)-bis-benzophenone oxime (**3**) has unexpectedly proved to be the reaction product.



The structure of oxime **3** was established by a single-crystal X-ray study. The geometric parameters of the two symmetric moieties of molecule **3** coincide within experimental error. The planar, with accuracy not less than 0.04 Å, geminate C—O—N=C fragments form a dihedral angle of 80°. The Ph groups at the central carbon atom are rotated so that their planes form angles of 21.7° and 74.2° with the planes of the C—O—N=C fragments, while their orientation to one another is characterized by a dihedral angle of 76.8°. The planes of the terminal Ph groups make a dihedral angle of 72.4°. Molecule **3** has a synclinal conformation

relative to both the C—O bonds, which, in their turn, are in the antiperiplanar orientation to the N=C bonds. The acetal center can be represented as a distorted tetrahedron with bond angles from 104.7(3)° to 112.8(3)°. The O—C—O angle is 110.1(2)°. The mean value of the C—O bond lengths, 1.424(3) Å, appreciably exceeds the length of this bond (1.382 Å) in dimethoxymethane.² The N—O and C=N bonds (mean values 1.422(3) and 1.282(4) Å) have standard values.

The highest yield of **3** (87.5 %) is reached at an oxime : dibromoamine ratio of 1 : 3. The formation of compound **3** was previously observed in low yield³ in a reaction of a benzophenone oxime with various radical reagents.

Experimental

Crystals of **3** are monoclinic, at 20 °C $a = 16.258(5)$, $b = 11.877(2)$, $c = 17.385(7)$ Å, $\beta = 111.87(3)^\circ$, $V = 3115.3$ Å³, $Z = 4$, $d_c = 1.195$ g cm⁻³, sp. gr. $P2_1/c$. The unit cell dimensions and intensities of 1860 reflections with $F^2 \geq \sigma$ were measured on an «Enraf-Nonius CAD-4» automatic diffractometer (Mo-K α radiation, graphite monochromator, $\omega/2\theta$ scan technique, $2\theta < 50^\circ$).

The structure was solved by a direct method using the MULTAN program and refined in anisotropic approximation. The hydrogen atoms were placed in the calculated positions and refined in the final stages of refinement. The final $R = 0.049$ and $R_w = 0.064$. All the calculations were performed on a PDP-11/23 computer using the SDP program.⁴

The NMR spectra (in CCl₄) were recorded on a «Tesla-BS467» spectrometer.

Preparation of diazeneoxides 2a–c. A solution of 2 mmol of **1a–c** in 10 mL anhydrous CH₂Cl₂ was added dropwise under an Ar atmosphere to a solution of 0.924 g (4 mmol) of *N,N*-dibromo-*tert*-butylamine in 10 mL anhydrous CCl₄ with stirring at a temperature of -5 °C. The resulting solution was stirred for 1 h at -5 ± 0 °C, allowed to stand for 1 to 2 days at 20 °C, poured into water, extracted with ether, the extract was washed with a Na₂CO₃ solution and then with water, and

dried over MgSO_4 . After ether evaporation the product was purified by thin-layer chromatography (Silperl, eluent — benzene/hexane, 1 : 1).

The following DO were obtained:

1-(2-Bromopropyl)-2-*tert*-butyldiazene-1-oxide (2a), yield 35 %, NMR spectrum (δ_{H}): 1.23 (s, 9 H, CMe_3); 2.12 (s, 6 H, MeCBr) (cf. Ref. 1). **1-(1-Bromocyclohexyl)-2-*tert*-butyldiazene-1-oxide (2b)**, yield 52 %, NMR spectrum (δ_{H}): 1.26 (s, 9 H, CMe_3); 2.35 (m, 4 H, 2 CH_2CBr). IR spectrum (ν/cm^{-1}): 1450 (NO); 1500 (N=N). Found (%): C, 45.44; H, 7.50; Br, 30.49; N, 10.75. $\text{C}_{10}\text{H}_{19}\text{BrN}_2\text{O}$. Calculated (%): C, 45.62; H, 7.22; Br, 30.41; N, 10.64. **1-(1-Bromo-*adamantan-1-yl*)-2-*tert*-butyldiazene-1-oxide (2c)**, yield 60.5 %, m.p. 35–37 °C, NMR spectrum (δ_{H}): 1.26 (s, 9 H, CMe_3); 2.87 (m, 2 H, 2 CHCBr). IR spectrum (ν/cm^{-1}): 1455 (NO); 1500 (N=N). Found (%): C, 53.13; H, 7.48; Br, 25.30; N, 8.90. $\text{C}_{14}\text{H}_{23}\text{BrN}_2\text{O}$. Calculated (%): C, 53.33; H, 7.30; Br, 25.39; N, 8.88.

Preparation of compound 3. A solution of benzophenone oxime (0.4 g in 10 mL anhydrous CH_2Cl_2) was added dropwise, with stirring, to a solution of *N,N*-dibromo-*tert*-butylamine

(0.47 g in 10 mL anhydrous CH_2Cl_2) at –5 °C under an Ar atmosphere, stirred for 2 h at –5±0 °C, and the precipitate was filtered off. After evaporation of the filtrate, hexane (2 mL) was added to the remaining oil-like residue, the precipitated crystals were filtered off, and 0.33 g (87.5 %) of compound 3, m.p. 170–171 °C (hexane–benzene, 10 : 1) was obtained.

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Synthesis of potassium salts of *O*-substituted *N*-nitrohydroxylamines

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Potassium salts of *O*-substituted *N*-nitrohydroxylamines were synthesized by nitration of *O*-substituted *N*-acetylhydroxylamines followed by treatment of the reaction products with potassium methoxide.

Key words: *N*-nitrohydroxylamines; *O*-substituted *N*-hydroxylamines; potassium salts; nitration.

Disubstituted salts of *N*-nitrohydroxylamine, Angeli salts,¹ are known, whereas no salts of *O*-substituted *N*-nitrohydroxylamines (NHA) have been reported to date. The present communication is devoted to the preparation of compounds of this class.

Hydroxylamines (HA) **1a–d** were studied as model compounds.



R = C_4H_9 (**a**), CH_3 (**b**), $\text{CH}_3\text{N}(\text{NO}_2)\text{CH}_2$ (**c**), $\text{NH}_2\text{OCH}_2\text{CH}_2$ (**d**)

It was found that the method used for synthesizing Angeli salts¹ and nitramine salts,² consisting of treatment of the respective substrates with alcohol nitrates in the presence of alkaline metal ethoxides, is not suitable for obtaining NHA salts since the HA studied do not undergo this reaction. However, nitration of compound **1a** with ethyl nitrate in the presence of potassium *tert*-butoxide in THF affords the respective potassium salt of NHA (**2a**) in a yield of up to 40 %. This is not a general procedure. For example, it is not applicable to compound **1c**, which is rapidly decomposed by potassium *tert*-butoxide under the reaction conditions.