

Reaction of *N,N,N',N'*-Tetramethyloxamide with Bromine

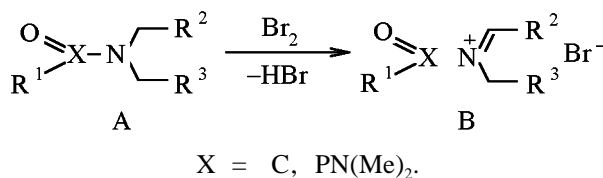
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Received April 30, 1999

Abstract—Reaction of bromine with *N,N,N',N'*-tetramethyloxamide results in dibromobromate of 3-methyl-5-dimethylimmoniooxazolidin-4-one (in an open system) and in dibromobromate of 4,5-dibromo-1,3-dimethylimidazolium (in a closed system).

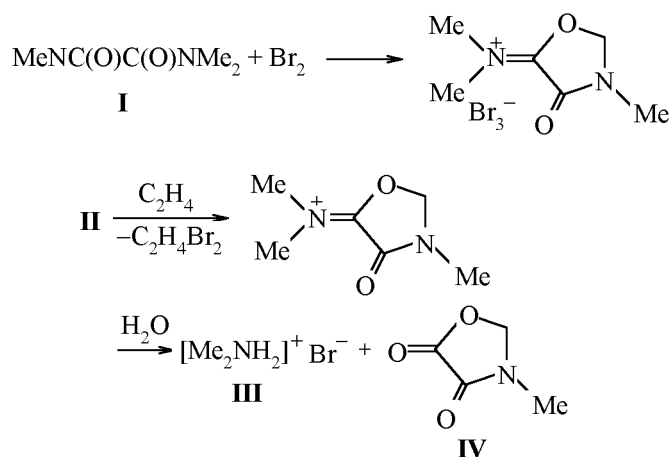
In the reaction of bromine and tertiary amides (A) the corresponding immonium salt (B) is assumed to be one among the first intermediates [1-3].



The high reactivity of the immonium cation due to the presence of a strong electrophilic center in compounds **B** arising in particular from dialkylacetamide [1], hexamethylphosphoramide [2], and dimethylcarbamoyl chloride [3] precludes the isolation of the immonium salt (B) from the reaction mixture and its characterization as an individual compound. At most only the products of immonium cation transformations are obtained [1-3].

We found an unusual stabilization mode of the above immonium salt. It consists in a cyclization of the immonium cation by an intramolecular nucleophilic attack of the amide carbonyl at the carbenium carbon.

Reaction of *N,N,N',N'*-tetramethyloxamide (**I**) with bromine in an open system (boiling of a mixture amide *I*-bromine at reflux with gradual addition of bromine throughout the process) afforded 3-methyl-5-*N,N*-dimethylimmoniooxazolidin-4-one (**II**). The latter was isolated and characterized by elemental analysis, ¹H and ¹³C NMR spectra. In the ¹H NMR spectrum of the reaction mixture appeared only signals of the reaction product **II** and the initial amide (Fig. 1). The attempt to obtain from salt **II** the corresponding bromide by halogen elimination with ethylene in methanol afforded hydrolysis products that were characterized as dimethylammonium bromide (**III**) and 3-methyloxazolidine-4,5-dione (**IV**).



Due to high electrophilicity of the carbon atom in position 5 the hydrolysis of salt **II** occurs even at its dissolution in dimethyl sulfoxide. In the ¹H and ¹³C NMR spectra of compound **II** in this solvent are observed signals of the hydrolysis products. As an example an ¹H NMR spectrum in DMSO-*d*₆ is shown on Fig. 2. In the more thoroughly dried dimethyl sulfoxide and at reducing time between the sample preparation and the spectrum recording the corresponding signals were less intensive but we failed to eliminate them completely.

The detected stabilization mode of the immonium salt by intramolecular attack on electrophilic center of the adjacent nucleophilic atom opens up wide opportunities for new synthesis of heterocyclic compounds.

In a sealed ampule at long heating the reaction takes a more complicated course and affords 4,5-dibromo-1,3-dimethylimidazolium dibromobromate (**V**).

The different outcome of the process in an open system and in sealed ampule may be understood as more severe halogenation conditions in the closed

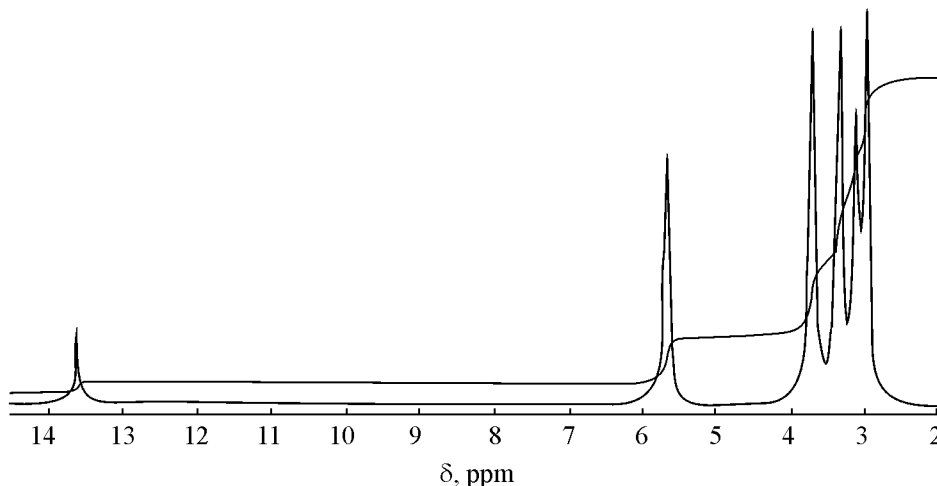


Fig. 1. ^1H NMR spectrum of the reaction mixture *N,N,N',N'*-tetramethyloxamide–bromine for an experiment carried out in an open system.

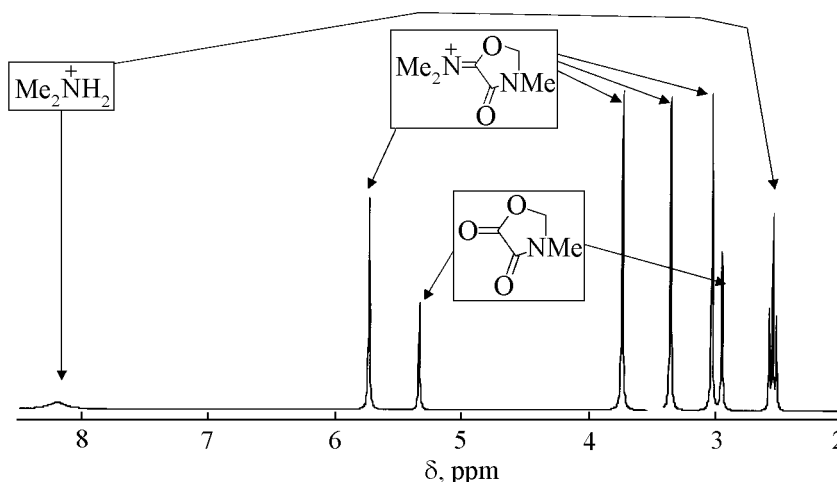


Fig. 2. ^1H NMR spectrum of dibromobromate of 3-methyl-5-*N,N*-dimethylimmoniooxazolidin-4-one (**II**) in $\text{DMSO-}d_6$ [in the spectrum appear the signals from hydrolysis products: dimethylammonium bromide (**III**) and 3-methyloxazolidine-4,5-dione (**IV**)].

system. The transformations resulting in compound **V** may occur as follows: The excess bromine at high temperature favors dication **VI** formation; the latter suffers nucleophilic attack by bromide ion with rupture of C(O)-C(O) bond to yield immonium cation **VII** and ylide **VIII**. The possibility of imidazole cycle formation is due to the interaction between the above intermediates. The further transformations are similar to the known reaction between *N,N*-dimethylcarbonyl chloride with bromine [3]. The composition and structure of salt **V** was confirmed by elemental analysis, ^1H and ^{13}C NMR spectra.

The overall stoichiometry of the process corresponds to the following equation:



The maximum yield of compound **V** was obtained just at the ratio amide (**I**) : halogen equal to 1 : 5.

EXPERIMENTAL

^1H NMR spectra were registered on spectrometers Gemini-200 (operating frequency 200 MHz) and Tesla BS-467 (60 MHz); ^{13}C NMR spectra were recorded on Gemini-200 instrument at 50.3 MHz, internal reference TMS. UV spectra were measured on a spectrophotometer Specord UV-Vis. The content of the active halogen was determined by iodometric

(NMe); 37.195 ($=N^+Me$), 40.882 (3H, $=N^+Me$), 151.400 (C=O), 161.179 (C=N⁺). In the ¹³C NMR spectrum as well as in the ¹H NMR spectrum appear the signals of hydrolysis products: dimethylammonium cation (34.52 ppm) and compound **IV**. UV spectrum **II** in acetonitrile: λ_{max} 270 nm (ϵ 55000, absorption of anion Br₃⁻ [5, 6]). Found, %: C 19.09; H 2.73; Br 62.30; Br_{2act} 41.80; N 7.29. C₆H₁₁Br₃N₂O₂. Calculated, %: C 18.82; H 2.90; Br 62.61; Br_{2act} 41.74; N 7.32.

The ¹H NMR spectrum of the reaction mixture obtained by bromine addition at ~120°C for 205 min and keeping it at the same temperature for 320 min is presented on Fig. 1 (the reaction mixture contains 53.83% of bromine and 5.78% of HBr).

Debromination of 3-methyl-5-*N,N*-dimethyl-immoniooxazolidin-4-one dibromobromate (II). Through a mixture of 1.35 g of compound **II** and 3 ml of methanol was passed a flow of ethylene till the particular color from tribromide ion disappeared. On distilling off the solvent we obtained 0.9 g of oily residue that slowly crystallized. The recrystallization from methanol afforded colorless crystalline compound, mp 106°C. ¹H NMR spectrum (DMSO-*d*₆, δ , ppm): 2.95 s (3H, NMe), 5.34 (2H, CH₂). ¹³C NMR spectrum (DMSO-*d*₆, δ_C , ppm): 28.059 (NMe), 77.612 (CH₂), 152.288 (C=O), 160.260 [C(O)O⁻]. Found, %: C 41.49; H 4.26; N 11.97. C₄H₅NO₃. Calculated, %: C 41.75; H 4.38; N 12.17.

Reaction between bromine and *N,N,N',N'*-tetramethyloxamide in a closed system. A sealed ampule containing 0.55 g of amide (**I**) and 0.98 ml of bromine was heated to 120°C for 280 h. Then the ampule was cooled in liquid nitrogen and opened, the volatiles were distilled off in a vacuum of water-jet pump. The weight of volatiles was 0.7 g. To the residue was added 1.5 ml of methanol, and the separated yellow precipitate was filtered off, washed with methanol (1 ml), and dried on the filter. Yield 0.46 g (27% according to the presumed stoichiometry). Characteristics of the compound are in agreement with the previously reported ones [3].

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