

Reaction of Nitrosyl Bromide Upon Mono Unsaturated Fatty ACID

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ABSTRACT

Nitrosyl bromide, is the chemical compound, with a condensing point just below room temperature whereas Methyl oleate is a fatty acid methyl ester resulting from the formal condensation of the carboxy group of oleic acid with methanol. In the present work attempts has been made to synthesize nitrosyl bromide in situ and chemical reaction has been carried out between nitrosyl bromide with methyl oleate. The products obtained by the chemical reaction were analysed and their structures were established through spectroscopic analysis.

Keywords: Nitrosyl Bromide, Chemical Reaction

INTRODUCTION

Although addition of nitrosyl chloride to olefinic compounds¹⁻⁴ and nitroso chlorination of unsaturated fatty acids and their derivatives have been carried out. The addition of nitrosyl chloride on oleic acid was first carried out by Tilden et al in 1894⁵. Reexamination by Miller et al ⁶ and Hasan et al¹³ has demonstrated that the addition of NOCl is essentially quantitative, but no work has been done upon the nitroso bromination of unsaturated fatty acids and their derivatives. The reported addition of nitrosylbromide upon olefins and norbornene has highlighted the application of this reaction to fatty acid chemistry. Nitrosyl halides (NOCl and NOBr) addition represents one of the simplest ways of elaborating a C-N bond directly from unsaturated compounds. The reaction of nitrosyl chloride with olefins has been known for more than one century and an extensive wealth of literature has been accumulated on this subject. Nitrosyl chloride reacts with an extremely wide range of compounds. Comprehensive literature reviews⁸⁻¹⁸ have summarized the present state of knowledge and it is necessary here to highlight some of the salient features of the nitrosyl chloride reaction upon organic compounds. As a part of our study of fatty acids, the nitrosobromination of aliphatic fatty acids was taken up for the present work.

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MATERIALS AND METHODS

Preparation of nitrosyl bromide *in situ* – The nitrosyl bromide was generated *in situ* by the action of HBr on iso-amyl nitrite. All melting points were observed on a koflers apparatus and are uncorrected. Infrared (IR) spectra were obtained with Perkin Elsemer 621 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded with a varian A60 NMR spectrometer. Chemical Shifts are reported as delta (ppm) relative to tetramethyl silane (TMS). The sample were run as 10% solution in CDCl₃. The abbreviations s, d, t, q, m,

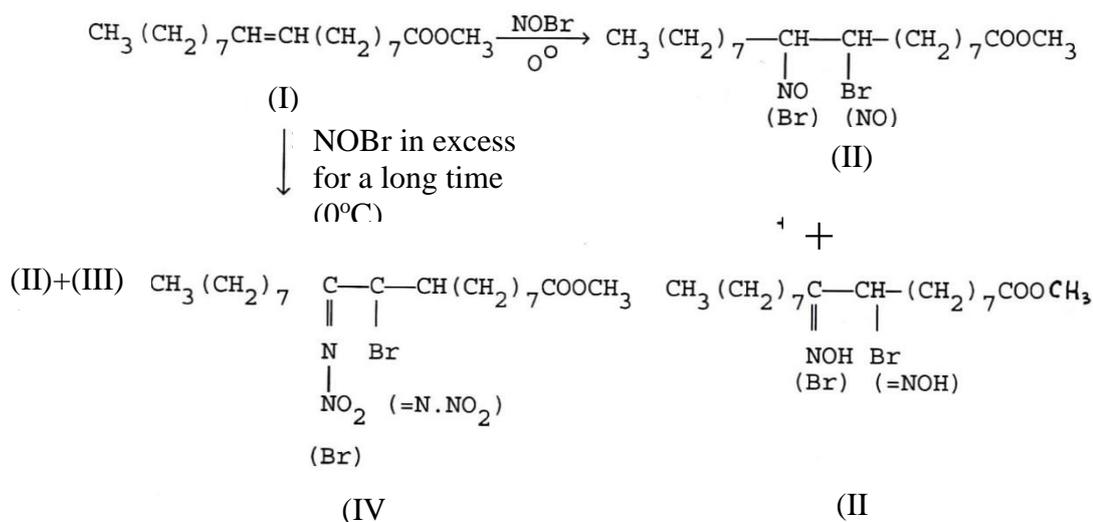
um, mc and br denote singlet, doublet, triplet, quartet, multiplet, unresolved multiplet, multiplet centred and broad, respectively.

RESULT AND DISCUSSION

Nitrosobromination of methyl oleate (I)

Methyl oleate (I) on treatment with approximately stoichiometric quantities of nitrosyl bromide *in situ* (isoamyl nitrite+HBr) at 0° in ethanol for 3-4 hrs. gave essentially quantitative yield of (II) in admixture with a little of its isomeric oximino form (IV). After usual workup of the reaction mixture, there was obtained a green liquid.

Scheme



Reaction

products were separated into two fractions (1 and 2) by column chromatography over silica gel. A major fraction 1, eluted first as a green colour liquid contained chiefly a nitrosyl bromide adduct (II) in admixture with a little oximino form (III). With respect to the positions of the nitroso and the bromine, product (II) is probable a mixture of isomers [methyl-9 (10)-bromo-10(9)- nitrosostearate, (II)]. That both isomers were indeed formed was evident from the TLC of the reaction product which showed two closely associated spots (R_f 0.8 and 0.85).

A minor fraction 2, of lower (R_f 0.23), was characterized as the oximino form (III) of compound (II). This fraction was also believed to be an isomeric mixture of oximes [methyl-9-(10)-bromo-10(9)-oximinostearate (III)]. The characterization of different fractions was made on the basis of microanalysis, IR and NMR.

Characterization of Fraction 1

The product was tested quantitatively for the presence of halogen by the Beilstein Test. It gave satisfactory microchemical analysis for $\text{C}_{19}\text{H}_{36}\text{NO}_3\text{Br}$ (compound II/III). The IR spectrum of fraction 1 showed, besides the bands usually found in long chain fatty esters, absorption at 1570 (N=O), 1110 (C-N) and 540 (C-Br) cm^{-1} indicative of the nitrosobromide functions. The presence of weak bands at 1640 (C=N) and 3440 (OH) cm^{-1} indicated the presence of ketoxime, a rearranged product of II in minor amount.

The NMR spectrum was decisive in arriving at a more firm conclusion regarding the composition of fraction 1 as an isomeric mixture of methyl 9 (10)-bromo-10(9) nitrosostearate II and methyl 9-(10)-bromo-10-(9)-oximinostearate (III), former being in a major amount. NMR spectrum displayed a signal at τ 2.52 (D_2O

exchangeable) ascribed to the oximino group proton (=N-OH), an unresolved multiple at τ 6.14 for methine proton adjacent to the bromine atom and an unresolved multiplet centered at τ 6.65 assigned to the methine proton adjacent to the nitroso group. A signal at τ 8.40 was also observed due to methylene protons α to the -CHBr- (-CH.Br-CH₂-). Other proton signals usually present in fatty acid ester at τ 6.34 (s, 3H, -CO.OCH₃), 7.76 (2H, protons α to the ester group), 8.65 (brs, chain methylene protons), and 9.12 (distorted t, 3H, terminal methyl protons) were also observed.

Characterization of Fraction 2

Microanalysis of Fraction 2 (compound III) supported the formula C₁₉H₃₆NO₃Br (positive Bleistein test). IR spectrum of the compound (III) displayed band at 3450 (OH), and 1640 (C=N) cm⁻¹ indicative of the oximino group. NMR spectrum showed an apparent multiplet centered at τ 2.65 for one proton which is D₂O exchangeable and assigned to the hydroxyl proton of oximino group (=N-OH). Another signal at τ 6.18 is attributed to the methine proton adjacent to the bromine atom (-CHBr-). Other signals characteristic for long-chain fatty esters were also exhibited: the esters methyl protons (-CO.OCH₃) gave rise to the singlet at τ 6.35, protons α to the ester carbonyl gave rise to a triplet at τ 7.76, the methylene protons appeared as a large broad signal centered at τ 8.65. A distorted triplet appeared at τ 9.12 for the terminal methyl group. Both IR and NMR substantiated the assigned structure (III).

Presence of hydrogen on the carbon carrying the nitrosyl group permits rearrangement to the oximes. For most of the examples cited in the literature this rearrangement is spontaneous or is promoted under the mildest conditions. The product bromooxime is usually solid, more stable than the nitroso isomer. But in this case isomerization seems to be very slow. About 0.5-1.0% of oxime was already present in the freshly prepared compound (II) as evidenced by the TLC, IR and NMR. Oxime content increased at room temperature to a maximum of about 20% after two weeks. As regards the formation of oxime our observations conform to those reported by Miller et al⁷.

Many nitrosochloro compounds dimerize to white solids². We have found no evidence for appreciable dimerization. The persistent green color at 0-5° and the presence of the strong IR nitrosyl band as well as non-formation of any solid adduct, all indicate little, if any, dimer formation. Miller et al⁷ also did not report the formation of dimer during nitrosochlorination of methyl oleate. Precedents exist for the suggestion that dimer formation is inhibited due to steric hindrance.

By treating with an excess of NOBr for a long-time methyl oleate gave a product (IV, 10%) in addition to products (II) and (III). The product (IV), having R_f value greater than the R_f of the oxime (III) was characterized as methyl 9 (10) Bromo-10- (9) -nitriminostearate on the basis of microanalysis, IR and NMR.

Characterization of Product IV

Strong IR band at 1550 and 1360 (NO₂) cm⁻¹ and a medium band at 1640 (C=N) cm⁻¹ characteristic of nitrimines were observed. NMR spectroscopy was useful in confirming the structure of product (IV). In addition to expected signals for remainder of the molecule (τ 6.34, 7.76, 8.76 and 9.12), diagnostically useful signals were observed at τ 5.90 (mc) due to the methine proton adjacent to Br atom (-CHBr-) and at τ 7.38 (t) for methylene group α to the nitrimino group [-CH₂-C(=N.NO₂)-].

The nitrimine (IV) is formed by the oxidizing action of NOBr upon oxime (III). The oxidizing action of NOX to convert an oxime into nitrimine was first reported by Shiue et al⁸ and later confirmed by other workers⁹. The mechanism of nitrimine formation suggested by Freeman¹⁰⁻¹¹ and supported by Boswell¹² seems adequate to account for the results obtained in this reaction. Although the formation of nitrimine was not

reported by Miller et al⁷. However, they observed that when methylene chloride solution of compound II was treated with NOCl for a long time, IR showed the presence of nitro group in the product.

CONCLUSION.

In the present work the products obtained by the chemical reaction between nitrosyl bromide with methyl oleate were analysed and their structures were established through spectroscopic analysis. From the foregoing results it is summarised that the nitro band is due to the formation of nitrimine which has been isolated and characterized in the present work.

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