

A Comprehensive Study on The Reaction of Nitrosyl Bromide on Methyl Docos-Trans-2-Enoate

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ABSTRACT

The present work gives a comprehensive study on the reaction between nitrosyl bromide with Methyl docos-trans-2-enoate (I). The products were isolated and analyzed and their structures were established through IR, and NMR spectroscopy.

Keywords : NMR spectroscopy, Methyl docos-trans-2-enoate

I. INTRODUCTION

Nitrosyl halides (NOCl and NOBr) addition represents one of the simplest ways of elaborating a carbon-nitrogen bond directly from unsaturated compounds and has been known for more than 100 years. Comprehensive literature review¹⁻¹⁰ have summarized the present state of knowledge. The addition of nitrosyl chloride to olefinic compounds and nitrochlorination of unsaturated fatty acids and their derivatives have been carried out. Nitrosyl chloride reacts with an extremely wide range of compounds¹¹⁻¹⁶ but no work has been done upon the nitrosobromination of unsaturated fatty acids. As a part of our own study of fatty acids, the nitrobromination of unsaturated fatty acid has taken up for the present work.

II. EXPERIMENTAL PROCEDURE

Material and Method

All melting points were observed on a kofler apparatus and are uncorrected. Infrared (IR) spectra were obtained with Perkin Elmer 621

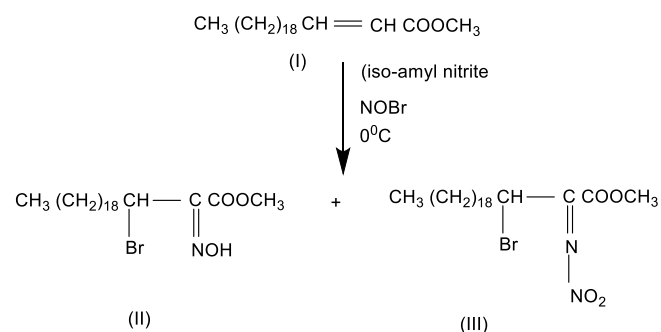
spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded with a varian A60 NMR spectrometer. Chemical Shifts are reported as delta (ppm) relative to tetramethyl silane (TMS). The sample were run as 10% solution in CDCl₃. The abbreviations s, d, t, q, m, um, mc, and br denote singlet, doublet, triplet, quartet, multiplet, unresolved multiplet, multiplet centred and broad respectively.

III. RESULT AND DISCUSSION

Nitrosobromination of Methyl docos-trans-2-enoate (I)

Ethanol solution of Methyl docos-trans-2-enoate was treated with NOBr (*in situ*) in a stoppered flask at 0-5°C by keeping it in a refrigerator for about a month. Monitoring the reaction by TLC showed that the reaction is extremely slow and that the sample from the reaction mixture after the work-up revealed the presence of three components, which were subjected to column chromatographic technique separation. The major component was found to be the starting material. Only about 10% of the compound (I) has

reacted. The products were characterized on the basis of elemental analysis, IR and NMR.



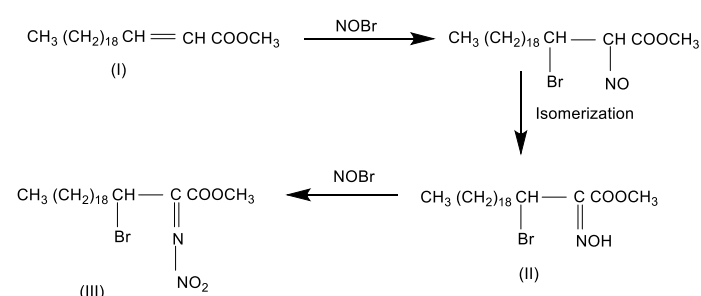
Characterization of the Compound (II)

The compound (II) gave satisfactory elemental analysis for $\text{C}_{22}\text{H}_{44}\text{O}_3\text{NBr}$ (positive Beilstein test). Compound (II) gave informative IR spectrum with a band at 3300 and 1640 cm^{-1} indicative of the oximino group. NMR spectroscopy was useful in confirming the structure of compound (II) as methyl 2-oximino-3-bromodocosanoate. A signal was obtained for a single proton at τ 2.76 (signal disappeared on addition of D_2O) attributed to the oximino group proton ($=\text{N}-\text{OH}$). A triplet was observed at τ 6.16 for the methine proton adjacent to the bromine atom. The chemical shift and multiplicity of $-\text{CHBr}-$ signal confirms the attachment of bromine atom to C-3 instead of C-2. Other proton signals were exhibited at τ 6.34 (s, 3H, $-\text{CO}-\text{OCH}_3$), 8.75 (br s, chain methylene protons) and 9.12 (distorted t, 3H, terminal group).

Characterization of the Compound (III)

The compound (III) was analyzed for $\text{C}_{23}\text{H}_{43}\text{O}_4\text{N}_2\text{Br}$. It responded to the Beilstein test. Aside from the elemental analysis, proof of structure for compound (III) was also obtained from spectroscopic evidence. The IR spectrum gave bands at 1640 ($\text{C}=\text{N}$), 1550 and 1360 cm^{-1} (NO_2) characteristic of the nitrimino group. The NMR data were also consistent with the structure methyl 2-nitroimino-3-bromo docosanoate for the compound (III). It exhibited a triplet at τ 5.98 for methine proton adjacent to bromine atom ($-\text{CHBr}-$). Usually fatty

ester signals were also observed at τ 6.36 (s, 3H, $-\text{CO}-\text{OCH}_3$), 8.65 (br s, chain methylene protons) and 9.1 (distorted t, 3H, terminal methyl). The chemical shift and multiplicity of methine proton signal adjacent to bromine atom confirms the attachment of bromine atom to carbon-3 as in the case of oximino compound (II). The formation of compound (II) and (III) can be well explained through the nitrosobromination of compound (I) as the primary reaction. The isomerization of nitroso compound will give an oxime (II) which on subsequent oxidation by NOBr will provide a nitrimine(III).



In the case of terminal unsaturated acid (I) only one isomer resulted during nitroso bromination. The presence of electron withdrawing group ($-\text{CO}-\text{OCH}_3$) adjacent to the double bond is involved in opening of nitrosonium ion intermediates. The electron withdrawing group will destabilize the transition state D relative to B and hence NO-carbonyl regioselective NOBr adduct E will be formed.

IV. CONCLUSION

The comprehensive study on the reaction between nitrosyl bromide with Methyl docos-trans-2-enoate reveals that the considerable slow rate of reaction is attributed to the proximity of the double bond to the electron withdrawing ester carbonyl function. Thus, the decrease in the nucleophilic character of terminal unsaturation slows down the electrophilic reaction of NOBr addition.

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