



Study of the Reaction of Nitrosyl bromide upon Methyl 10 – Undecenoate

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Abstract – We have carried out the reaction of Nitrosyl bromide upon methyl-10-undecenoate (I). The products II, III, IV and V were isolated, analysed and their structure were established by their IR and NMR spectra.

Introduction

A wide variety of reactions on fatty acids, especially with unsaturation have been carried out. Reactions of fatty acids in general are associated with a) the -COOH group and b) the aliphatic hydrocarbon chain. Among the reactions involving the hydrocarbon chain of fatty acids those of oxidation, hydrogenation and halogenation are of fundamental importance in lipid chemistry.

The addition reaction of NOCl and NOBr with olefins has been known for more than 100 years. Comprehensive literature review¹⁻¹⁴ have summarized the present state of knowledge.

As a part of our study of fatty acids, the nitrosobromination of fatty acids having terminal unsaturation was taken up for the present work.

Experimental

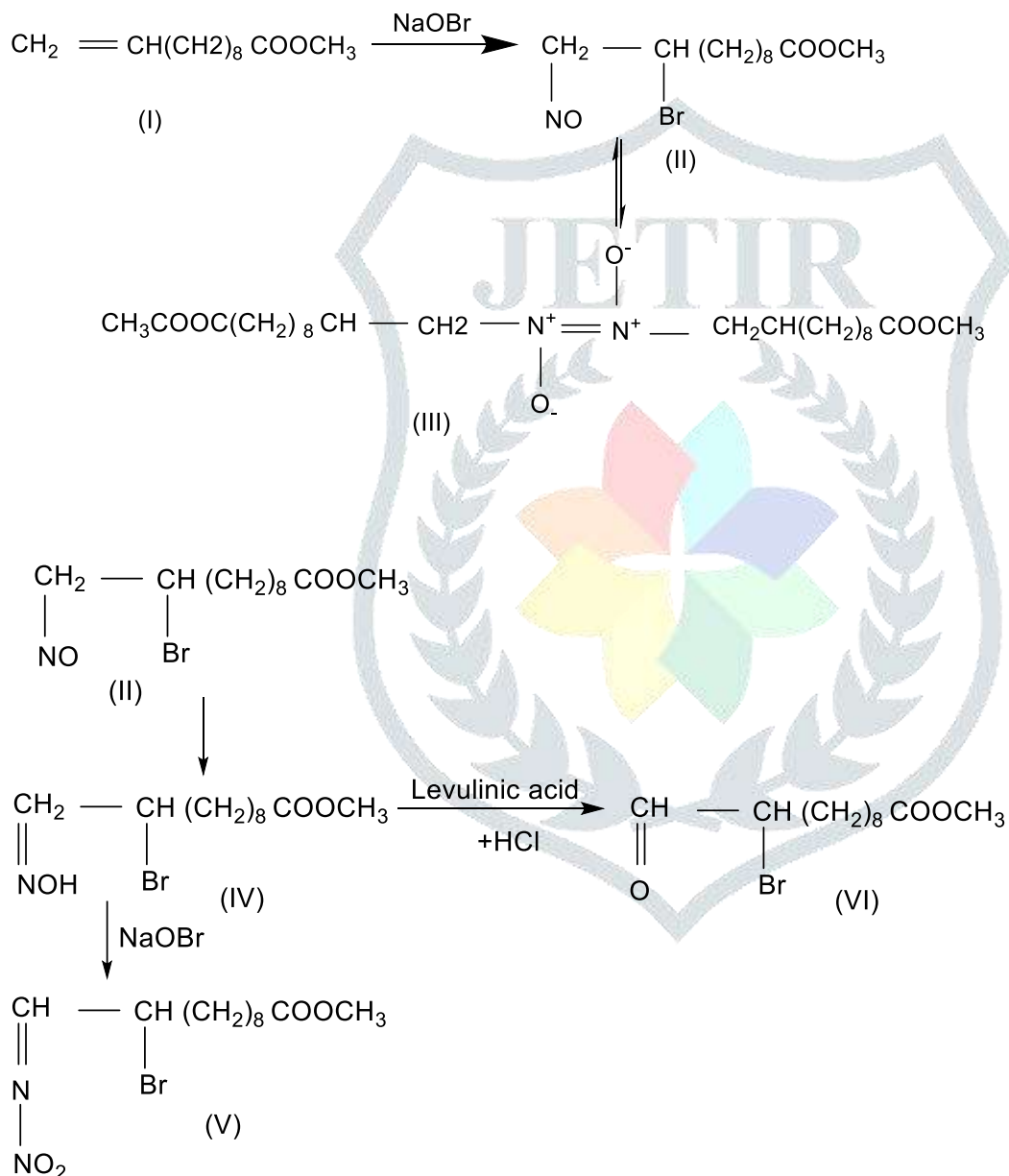
Method and Material

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.

Result and Discussion

Nitrosobromination of Methyl-10-Undecenoate

Reaction of methyl 10-undecenoate (I) with NOBR *in situ*, resulted in the formation of four distinct products (II-V) as evidenced by analytical TLC. These components were separated by silica gel column chromatography. Formation of a bromonitroso product (II) was indicated by the appearance of bluish green colour in the reaction mixture. IR spectrum of the product also revealed the formation of nitrosylbromide adduct. Work-up of the reaction mixture yielded no appreciable amount of the adduct in the pure form as it easily dimerizes or rearranges to an oxime.



Characterization of the Compound (III)

The product (III) separated as white solid (m.p.97⁰C) gave satisfactory microanalysis for (C₁₂H₂₂O₃NBr)₂. The molecular mass determination by Rast method¹⁴ in camphor supported the molecular formula (C₁₂H₂₂O₃NBr)₂ for compound (III). It gave positive Beilstein test. The IR spectrum (*in nujol*) showed, besides the bands usually found in long-chain fatty acid absorption at 1270 cm⁻¹ indicative of dimer

formation. The absence of nitrosyl band in the region $1520\text{-}1570\text{ cm}^{-1}$ further supported the dimer formation. The NMR spectrum also supported the structure of compound (III) as dimer of methyl-10-bromo-11-nitrosoundecanoate. The NMR spectrum exhibited the significant signal at τ 5.46 for six protons due to the

methine protons adjacent to bromine atom and methylene groups adjacent to nitrogen ($^-\text{CH}_2\text{-N}^+=\text{O}$). Other usual fatty ester signals were observed at τ 6.34 (s, 6H ester methyl), τ 7.76 (protons α to the ester $-\overset{\text{O}}{\parallel}{\text{C}}-$ group) and 8.68 (br s, shielded chain methylenes). The dimer (III) appears to have a *trans* structure as suggested by Gowenlock and Luttker¹⁵ in their IR spectral studies on dimers of nitroso compounds.

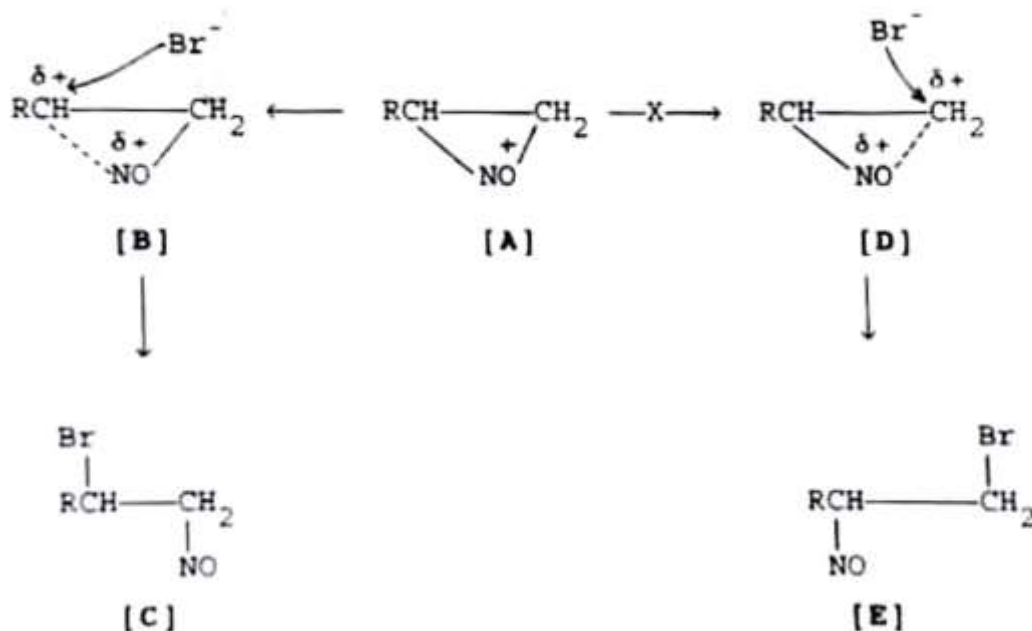
Characterisation of the Compound (IV)

The compound (IV) was separated as a white solid (mp 45° in pure form having R_f , 0.2). It responded to Beilstein test. The compound (IV) was analyzed for $\text{C}_{12}\text{H}_{22}\text{O}_3\text{NBr}$. Its IR spectrum gave absorption at 3300 (OH) and 1680 ($\text{C}=\text{N}$) cm^{-1} attributed to the oximino group and at 540 cm^{-1} to C-Br linkage. Its NMR spectrum was more informative regarding the position of oximino group in the fatty acid chain. It exhibited an apparent singlet at τ 2.6 which can be assigned to the proton of oximino group ($=\text{N-OH}$). The proton was found to be exchangeable with deuterium. The proton at C-11 appeared at τ 3.6 ($-\text{CH}=\text{NOH}$), which conclusively proves the attachment of oximino group to the terminal carbon atom (C-11). Methine proton adjacent to bromine atom displayed a signal at τ 5.72. Other NMR signals were observed at τ 6.34 (s, 3H $-\text{CO-OCH}_3$), 7.76 (2H, α to the ester $-\overset{\text{O}}{\parallel}{\text{C}}-$ group). 8.65 (br s, chain methylene protons). Thus, the spectral data established the structure as methyl 10-bromo-11-oximino-undecanoate (IV). Further support to the structure was obtained from the analysis of the corresponding carbonyl compound (VI) obtained by the deoxygenation of the product (IV) with the help of levulinic and hydrochloric acid¹⁶. The deoxygenation formed a compound (VI) which was shown to have an aldehydic group. The presence of aldehydic group in product (VI) was confirmed with the help of chemical test and spectroscopy. It gave yellow colour on heating with NaOH and reduces Fehling's solution. It also gave a positive DNP test on TLC. IR spectrum showed the disappearance of bands at 3300 and 1680 cm^{-1} (shown by oxime) and new bands appeared at 1710 ($\text{C}=\text{O}$) and 2800 (aldehyde C-H str) cm^{-1} attributed to the aldehydic function.

Characterization of Compound (V)

The compound (V) which migrated ahead of oxime (IV) on TLC plate, analyzed for $\text{C}_{12}\text{H}_{21}\text{N}_2\text{O}_4\text{Br}$ (positive Beilstein test). The IR spectrum showed bands at 1630 ($\text{C}=\text{N}$) and 1550 (NO_2) cm^{-1} characteristic of nitrimino group. NMR showed significant signals at τ 3.84 for one proton at C-11 ($-\text{CH}=\text{N.NO}_2$) and a multiplet centered at τ 5.46 for methine proton adjacent to bromine atom ($-\text{CHBr}-$). Other NMR signals usually displayed by the fatty acid esters (τ 6.34, 7.76 and 8.68) were also present. The product was thus assigned the structure as methyl 10-Bromo-11-nitrimino-undecanoate.

The formation of only one isomer (II) in the nitrosobromination of 10-undecenoate indicated that the reaction is regiospecific and addition of NOBr is in accordance with the Markownikoff's rule. The exclusive formation of (II) as primary product in the NOBr addition to methyl 10-undecenoate is consistent with the intermediary of a three membered ring ion, A, opening of which proceeds via the lower energy transition state (B rather than D where R can stabilize an incipient positive charge).



Further the results showed that nitrosobromination is the only primary reaction and the secondary products were formed as a result of two simultaneous pathways. Dimerization leads to product (III) and isomerization followed by oxidation yields an oxime (III) and nitrimine (IV). Dimerization seems to be much more feasible in methyl 10-undecenoate than in methyl oleate probably due to steric reasons. Isomerization of nitroso compound to an oxime also seems to be faster than in the case of methyl oleate as evidenced by the yields, Brominitrimine formation was found to be $\approx 8\%$ in yield when excess of nitrosyl bromide was used. None of the remainder is oxidized to the bromonitro compound apparently because of isomerization to bromooxime and subsequent oxidation to bromonitrimine.

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