

Bromination-Dehydrobromination of Long Chain α,β -Unsaturated Acid

M.U. AHMAD, M.S. AHMAD, JR., and S.M. OSMAN, Department of Chemistry, Aligarh Muslim University, Aligarh-202001, India

ABSTRACT

The bromination-dehydrobromination of *trans*-2-octadecenoic acid (*1a*) gave a mixture of rearranged products, (*3a*, 34.5%) and (*5a*, 49.2%). A vicinal diol (*4a*, 8.7%) was obtained as a minor side product. It is proposed that in the formation of *3a* and *5a*, the allenic intermediate *7a* is involved which is derived from the expected acetylenic intermediate *6a* by the usual base-catalyzed acetylene-allene rearrangement. The structures of individual reaction products were established by elemental analyses as well as by spectral studies.

INTRODUCTION

Many advances have been made in recent years in the methods for the synthesis of acetylenes, and many of these compounds are now rather readily available in pure state. Alcoholic, usually ethanolic, potassium hydroxide has been the most widely used reagent for the synthesis of acetylenes. Dehydrohalogenation reactions of fatty acids containing halogen substituents have been extensively studied (1-3) to synthesize the corresponding acetylenic acids. Literature scanning revealed that this reaction so far has not been carried out with long chain α,β -unsaturated fatty acids, probably because of the nonoccurrence of these acids in natural fats.

In continuation of earlier papers on the reactions of long chain α,β -unsaturated acids (4-7) and in view of the aforesaid objective, the present paper describes the results of bromination of *trans*-2-octadecenoic acid (*1a*) and dehydrobromination of the corresponding dibromo acid (*2a*). The present work revealed that dehydrobromination of *2a* did not give rise to the expected α,β -acetylenic acid (*6a*) apparently due to the proximity of unsaturation to the carboxyl function. An explanation has been advanced with respect to the instability of the α,β -acetylenic acid (*6a*).

EXPERIMENTAL PROCEDURES

All melting points were observed on a Kofler apparatus and are uncorrected. Infrared (IR) spectra were obtained with a Perkin-Elmer 621 spectrophotometer in CCl_4 . Nuclear magnetic resonance (NMR) spectra were obtained on a Varian A60 spectrometer. Chemical shifts are reported as δ (ppm) relative to tetramethylsilane (TMS). The samples were run as 10% solution in chloroform-*d*. The abbreviations "s, d, m, q, br, and t" denote "singlet, doublet, multiplet, quartet, broad, and triplet," respectively. Mass spectrum was obtained with AEI MS-9 mass spectrometer. Thin layer chromatographic (TLC) plates were coated with Silica Gel G, and a mixture of petroleum ether-ether-acetic acid (80:20:1, v/v/v) was used as developing solvent. The spots were visualized by charring after spraying with a 20% aqueous solution of perchloric acid. Light petroleum refers to a fraction of bp 40-60 C.

MATERIALS AND METHODS

α,β -Unsaturated acid, *1a* (mp 58-59 C), was prepared from stearic acid by the procedure of Palameta and Prostenik (8). The 2-enoic structure of this acid and its

geometry were established in the manner similar to that reported previously (4).

Bromination of *1a* (9)

Pure *trans*-2-octadecenoic acid, *1a* (5.0 g, 0.017 mole), was treated with cold solution of bromine (8.0 g, 0.05 mole) in dry, alcohol-free chloroform (40 ml) for 2 hr with continuous shaking at room temperature for 6 hr, and then warmed to 50 C for 12 hr. The reaction mixture was dissolved in ether, and the excess bromine was destroyed with aqueous sodium sulfite, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the ether gave a solid (~7.5 g) which on crystallization from petroleum ether at low temperature yielded 2,3-dibromostearic acid (positive Beilstein test), *2a* (6.86 g, ca. 88%), mp 71-72 C. *Analysis*: Calc. for $\text{C}_{18}\text{H}_{34}\text{O}_2\text{Br}_2$: C, 48.86; H, 7.69; Br, 36.19. Found: C, 48.58; H, 7.31; Br, 36.50%.

Its methyl ester, *2b*, was prepared with ethereal diazomethane, mp 40-42 C. *Analysis*: Calc. for $\text{C}_{19}\text{H}_{36}\text{O}_2\text{Br}_2$: C, 56.00; H, 7.89; Br, 35.08. Found: C, 55.72; H, 8.05; Br, 35.29%. (Spectral values are recorded in the discussion part of the paper.)

Dehydrobromination of *2a* (3)

A mixture of *2a* (5.0 g, 0.011 mole), potassium hydroxide (10 g), water (3 ml), and ethanol (42 ml) was heated under reflux for 8 hr. Most of the alcohol was removed under reduced pressure, and the residue diluted with water, acidified with cold dil. sulfuric acid, and extracted with ether. The combined ether extracts were washed with water and dried over anhydrous sodium sulfate. The crude product (3.6 g) obtained after evaporation of the solvent showed three distinct spots on TLC.

A column of Silica Gel G (80 g), prepared in petroleum ether, was charged with total crude mixture (3.6 g), and the column was eluted with a mixture of petroleum ether-ether (96:4, v/v) (each fraction of 15 ml was collected). The TLC-monitored eluates were combined to give 4-ethoxy-*trans*-2-octadecenoic acid, *3a*, as a colorless solid (1.27 g, ca. 34.5%), mp 35-36 C. It resisted all attempts to crystallization. *Analysis*: Calc. for $\text{C}_{20}\text{H}_{38}\text{O}_3$: C, 73.57; H, 11.73. Found: C, 73.69; H, 11.95%.

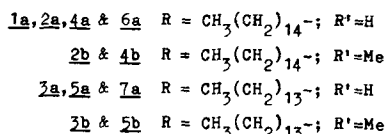
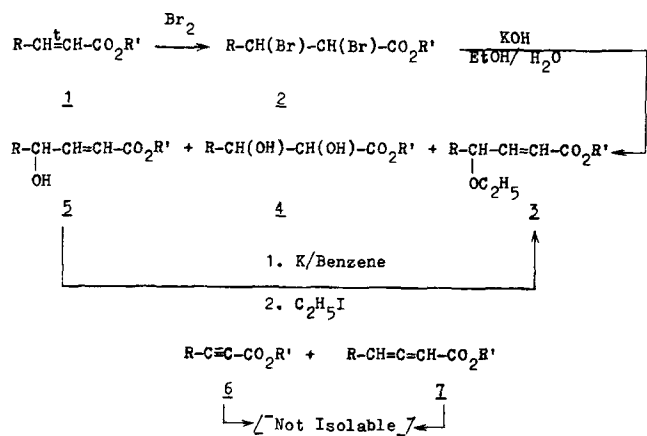
Its methyl ester, *3b* (semi-solid), was prepared with ethereal diazomethane. *Analysis*: Calc. for $\text{C}_{21}\text{H}_{40}\text{O}_3$: C, 74.06; H, 11.84. Found: C, 74.20; H, 11.61%.

Elution with a mixture of petroleum ether-ether (90:10, v/v), followed by crystallization from petroleum ether gave 2,3-dihydroxystearic acid, *4a* (~0.31 g, ca. 8.7%), mp 105-106 C. *Analysis*: Calc. for $\text{C}_{18}\text{H}_{36}\text{O}_4$: C, 68.31; H, 11.47. Found: C, 68.04; H, 11.36%.

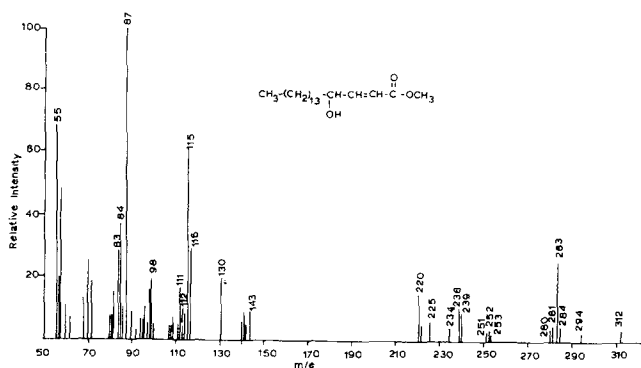
Its methyl ester, *4b*, was prepared with ethereal diazomethane, mp 80-82 C. *Analysis*: Calc. for $\text{C}_{19}\text{H}_{38}\text{O}_4$: C, 69.04; H, 11.59. Found: C, 68.82; H, 11.28%.

Subsequent elution with a mixture of petroleum ether-ether (80:20, v/v), followed by crystallization from petroleum ether gave 4-hydroxy-*trans*-2-octadecenoic acid, *5a* (1.66 g, ca. 49.2%), mp 75-76 C. *Analysis*: Calc. for $\text{C}_{18}\text{H}_{34}\text{O}_3$: C, 72.43; H, 11.48. Found: C, 72.27; H, 11.32%.

Its methyl ester, *5b*, was prepared with ethereal diazomethane, mp 58-59 C. M^+ 312 ($\text{C}_{19}\text{H}_{36}\text{O}_3$). *Analysis*:



SCHEME I.

FIG. 1. Mass spectrum of methyl 4-hydroxy-*trans*-2-octadecenoate.

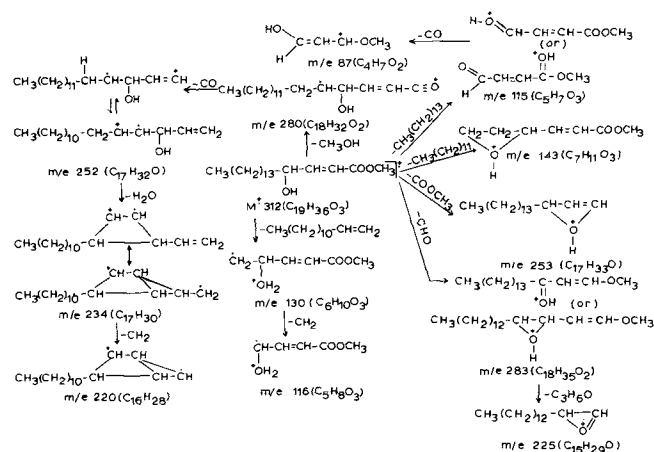
Calc. for C₁₉H₃₆O₃: C, 73.03; H, 11.61. Found: C, 72.80; H, 11.32%.

Conversion of 5b to 3b

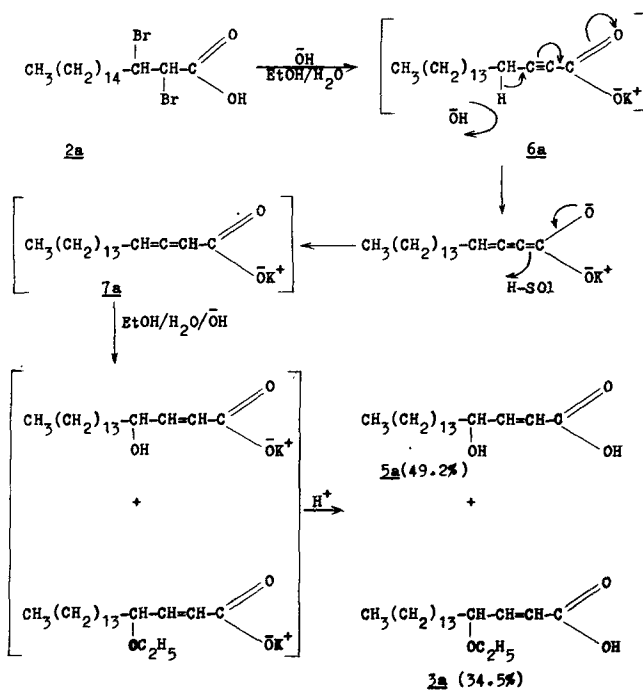
To a solution of 5b (0.5 g, 0.0016 mole) in sodium-dried benzene (40 ml), potassium metal (0.45 g) was added, and the mixture was refluxed for 1 hr with vigorous shaking at intervals to disperse the molten potassium into small globules. Freshly distilled ethyl iodide (25 ml) was added, and the heating was continued for 4 hr, during which time potassium iodide gradually separated out. The reaction mixture was cooled to room temperature, and ethanol (100 ml) was added to destroy the excess of potassium metal. The bulk of the solvents was removed under reduced pressure. The residue was poured into water, extracted with ether, and the combined ether extracts were washed, and dried over anhydrous sodium sulfate. The ethereal solution was filtered through a short column of neutral alumina (40 g). Evaporation of the solvent gave the compound 3b. Co-chromatography on TLC gave a single spot. *Analysis*: Calc. for C₂₁H₄₀O₃: C, 74.06; H, 11.84. Found: C, 73.98; H, 11.70%.

RESULTS AND DISCUSSION

The present work describes the results (Scheme I) of bromination of *trans*-2-octadecenoic acid (1a), and dehydrobromination of 2a. The structures of the reaction



SCHEME II.



SCHEME III.

products were determined by combustion and spectroscopic data.

Compound 2a analyzed correctly for C₁₈H₃₄O₂Br₂. In the IR spectrum of its methyl ester, 2b, bands at 1740 (COOCH₃) and 720 cm⁻¹ (C-Br) were observed. There was no evidence for the presence of an olefinic bond. The NMR spectrum likewise was devoid of any signal for vinylic proton. It gave signals at δ 4.25m (2H, C₂-C₃-), 3.7s (3H, COOCH₃), 1.2br,s (chain-CH₂), and 0.85t like (3H, terminal-CH₃). From these data, 2b was formulated as methyl 2,3-dibromo-octadecanoate.

Compound 5a (mp 75-76 C) analyzed for C₁₈H₃₄O₃. Its methyl ester, 5b (C₁₉H₃₆O₃) had IR bands at 3620 (OH), 1730 (C=C-COOCH₃), 1660 (C=C), 1170, 1050 (C-O), and 980 cm⁻¹ (*trans* olefin). The NMR spectrum of 5b gave a doublet of doublet centered at δ 6.9 (1H, J=15 and 5 Hz) ascribable to a proton β to ester carbonyl, a doublet at 6.0 (1H, J=15 Hz with a small long range coupling, *trans* olefinic proton) ascribable to a proton α to

ester carbonyl, 4.3br (1H, CH-OH), 3.7s (3H, COOCH₃), 2.35br (1H, CH-OH, disappeared on addition of D₂O), 1.3br,s (chain-CH₂), and 0.9t like (3H, terminal-CH₃). The J values of vinylic protons strongly suggest *trans* configuration of the double bond. After deuterium exchange, the signal at δ 2.35 disappeared with a small change in the signal at δ 4.3.

The above structure of *5b* was further substantiated by its mass spectrum. It (Fig. 1) gave the molecular ion peak at *m/e* 312 (C₁₉H₃₆O₃) along with other salient ion peaks at *m/e* 294 (M-H₂O), 283 (M-CHO), 281 (M-CH₃O), 280 (M-CH₃OH), 253 (M-COOCH₃), 252 (283-CH₃O), 251 (283-CH₃OH), 239, 238, 234, 225, 220, 143, 130, 116, 115, 112 (130-H₂O), 111 (143-CH₃OH), 98 (130-CH₃OH), 87 (base peak), 84 (115-CH₃O), 83 (115-CH₃OH), and other low mass ion peaks. The genesis of important fragment ions (Scheme II) supports the structure of methyl 4-hydroxy-*trans*-2-octadecenoate, *5b*, assigned on the basis of elemental analysis, IR, and NMR studies.

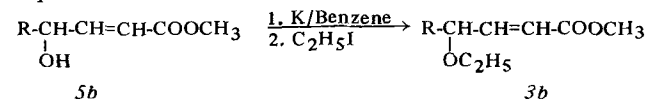
Elemental analysis of the minor product (*4a*, mp 105-106 C) corresponded to formula C₁₈H₃₆O₄. The ester, *4b* analyzed for C₁₉H₃₈O₄. Its IR spectrum gave bands at 3450 (OH), 1740 (COOCH₃), 1140, 1100, and 1080 cm⁻¹ (C-O). The NMR spectrum gave conclusive support in favor

of *4b*. It gave signals at δ 4.5br,m (1H, $\begin{array}{c} \text{OH} \\ | \\ \text{CH}-\text{CH}-\text{COOCH}_3 \\ | \quad | \\ \text{OH} \quad \text{OH} \end{array}$), 3.9m (1H, $\begin{array}{c} \text{OH} \\ | \\ \text{CH}-\text{CH}-\text{COOCH}_3 \\ | \\ \text{OH} \end{array}$), 3.7s (3H, COOCH₃), 1.3br,s (chain-CH₂), and 0.9t like (terminal-CH₃). A broad signal at δ 2.3 integrating for two protons (2 x C-OH) disappeared on addition of D₂O. After deuterium exchange, the spectrum was simplified at δ 4.5d (J=7 Hz) and 3.9, which further supports the structure of *4b*.

Compound *3a* (mp 35-36 C) analyzed correctly for C₂₀H₃₈O₃. Its ester, *3b* corresponded to formula C₂₁H₄₀O₃. From the composition, it appears that this is the corresponding ethyl ether of *5b*. Its IR spectrum gave bands at 1730 (C=C-COOCH₃), 1690 (C=C), and 980 cm⁻¹ (*trans* olefin). The other weak bands were observed at 1190, 1160, 1100, 1090 cm⁻¹ (C-O). The NMR spectrum was found to be more informative in the elucidation of the structure of *3b*. It gave signals at δ 6.9d,d (J=15 and 5Hz, 1H, β to ester carbonyl), 6.0d (J=15 Hz with small long range coupling, *trans* olefinic proton, 1H, α to ester carbonyl), 4.1m (1H, $\begin{array}{c} \text{OC}_2\text{H}_5 \\ | \\ \text{CH}_2-\text{C}-\text{CH}=\text{CH}- \\ | \\ \text{H} \end{array}$), 3.71s (3H, COOCH₃), 3.5q (2H, -CH-OCH₂-CH₃), 1.32br,s (chain-CH₂), 1.2 (merging triplet, 3H, -OCH₂-CH₃), and 0.9t like (3H, terminal-CH₃). The presence of a double bond conjugated with ester carbonyl is fully justified by the presence of signals at δ 6.9 and 6.0, as mentioned above. The magnitude of splitting suggested the *trans* configuration of olefinic bond. From these data, *3b* was formulated as methyl 4-ethoxy-*trans*-2-octadecenoate.

The relationship between *3b* and *5b* was established by conversion of the latter into the former by the following

sequence of reaction,



The spectral and elemental analysis gave conclusive support of *3b*.

The nonisolation of the corresponding α,β -acetylenic acid, *6a*, can be rationalized in terms of the mechanistic sequence in Scheme III.

From the above mechanism it appears reasonable to suggest that since the center of unsaturation in *6a* is adjacent to the carboxyl group, an inductive effect of the latter isomerizes *6a* into *7a*, an allene as a reaction intermediate. Allenes are not as stable as dienes with conjugated or isolated double bonds. The order of stability is conjugated dienes > isolated dienes > cumulated dienes. The intermediate, *7a*, is not indefinitely stable, and therefore undergoes addition of water and alcohol (present in the reaction medium) which give rise to *5a* (49.2%) and *3a* (34.5%) as major reaction products; the mode of addition is

governed by conjugation with $\begin{array}{c} \text{O} \\ || \\ \text{C} \end{array}$ group. Simple substitution of one nucleophile (2 x Br⁻) in *2a* by other nucleophile (2 x OH⁻) gave *vic*-diol, *4a* as a minor side product (8.7%) of the reaction.

From the above discussion it is obvious that fatty acids with a triple bond adjacent to the carboxyl group apparently cannot be prepared by dehydrobromination of 2,3-dibromo acids. In conclusion, it may be added that the formation of acetylenic and/or allenic acids from the appropriate vicinal dihalogen derivatives depend upon the relative position of the halogen atoms and the structure of the chain.

ACKNOWLEDGMENTS

We thank W. Rahman for providing necessary facilities and M.S. Ahmad for helpful discussion. One of us (MUA) thanks the Council of Scientific and Industrial Research, New Delhi, for a Senior Research Fellowship.

REFERENCES

- Myddleton, W.W., R.G. Bercham, and A.W. Barrett, *J. Am. Chem. Soc.* 49:2264 (1927).
- Gunstone, F.D., and G.M. Hornby, *Chem. Phys. Lipids* 3:91 (1969).
- Kannan, R., M.W. Roomi, M.R. Subbaram, and K.T. Achaya, *Fette Seifen Anstrichm.* 69:644 (1967).
- Ansari, A.A., and S.M. Osman, *JAOCS* 53:118 (1976).
- Ansari, A.A., F. Ahmad, and S.M. Osman, *Ibid.* 53:541 (1976).
- Ansari, A.A., F. Ahmad, and S.M. Osman, *Fette Seifen Anstrichm.* 79:328 (1977).
- Ahmad, M.U., M.S. Ahmad, and S.M. Osman, *JAOCS* 55:491 (1978).
- Palameta, B., and M. Prostenik, *Tetrahedron* 19:1463 (1963).
- Myers, G.S., *J. Am. Chem. Soc.* 73:2100 (1951).

[Received April 4, 1978]