

Ring-opening reactions of 9,10-epimino-octadecane with acids

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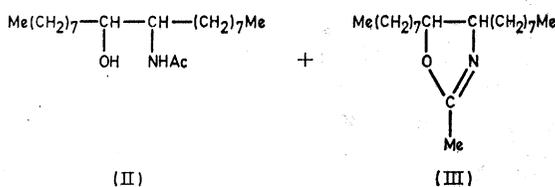
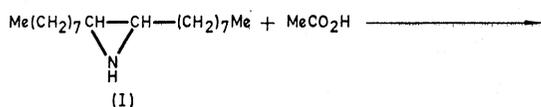
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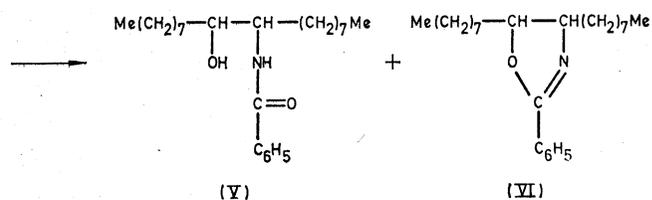
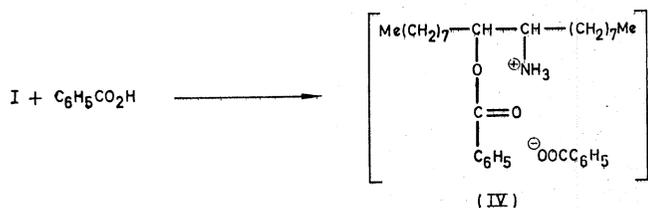
In view of a recent communication by McGhie and Warren¹ concerning the ring fission of *cis*- and *trans*-epiminoalkan-1-ols with acetic acid, we report our work of a related nature.

As part of a more extensive study of heterocyclic derivatives of long-chain aliphatic compounds we have prepared *cis*-9,10-epimino-octadecane (I) (mp 64.5–65.1°C, purity by HI titration: >99 per cent) and have caused it to react with acetic acid. Contrary to the results obtained by McGhie with epimino-alkan-1-ols, the principal product isolated in our experiments was 9-acetamido-10-hydroxy-octadecane (II) (mp 88.2–88.7°C). Compound (II) was identified by elemental analysis, and infrared, r.m.r. and mass spectral measurements. The chemical properties exhibited by compound (II) further supported the β-hydroxyalkyl-amide structure. Exhaustive analysis by column and thin layer chromatography did not reveal the presence of any β-hydroxyalkylamine.

In a search for identifiable by-products examination of the crude reaction mixture led to the isolation and purification of a new minor component. This compound had the empirical formula C₂₀H₃₉NO, was a nitrogen base titratable with standard perchloric acid, showed no amine or hydroxyl bands in the infrared region, and was identified as 4,5-di-n-octyl-2-methyl-Δ²-oxazoline (III) liquid, n_D²⁰: 1.4502; picrate, mp 33.5–35.0°C.



The formation of Δ²-oxazolines in the reaction of carboxylic acids with aziridines has not been reported previously, although their synthesis by dehydration of β-hydroxyalkylamides is well known.² The by-product obtained in this instance was identical with the compound obtained by thermal or acid-catalysed dehydration of the



corresponding β-hydroxyalkylamide. Amounts of oxazoline formed varied between 1 and 20 per cent of theory and depended on the particular reaction conditions employed.

It has been pointed out by Clapp³ that the initial product formed in the reaction of aryl carboxylic acids with 2,2'-dialkylaziridines is the β-aminoalkyl ester, which he isolated as the amine salt. In neutral or alkaline medium the amino-ester then rearranges to the β-hydroxyalkylamide. Using Clapp's procedure we were unable to isolate the analogous benzoate salt of 10-(9-amino-octadecyl) benzoate (IV). Neutralisation of the reaction mixture gave 9-hydroxy-10-benzamido-octadecane (V) mp 86.2–86.9°C and 4,5-di-n-octyl-2-phenyl-Δ²-oxazoline (VI) liquid, n_D: 1.4943; picrate: liquid. Undoubtedly, the β-aminoalkyl ester derived from internal aziridines is even less stable with respect to the hydroxyamide than the ester derived from terminal aziridines.

It seems likely that the oxazolines formed in the reaction of carboxylic acids with internal long-chain aziridines have as their precursors intermediates which also lead to the formation of the hydroxyamides, and do not stem from a secondary dehydration of the latter. This hypothesis is supported by the experimental finding that reaction time does not influence the hydroxyamide to oxazoline ratio and that exposure of pure hydroxyamide to the same reaction conditions produces no demonstrable amounts of oxazoline. Furthermore, isomerisation of pure hydroxyamide to the amino-ester salt with anhydrous hydrogen chloride in dioxan followed by neutralisation of the salt with weak base gave both hydroxyamide and oxazoline.

Further investigations into the acid-catalysed ring fission reactions of long-chain aliphatic internal aziridines are in progress. These studies include other carboxylic acids as well as acids of the type HX where X are anions of varying nucleophilicity.

Received 20 May 1968

References

- McGhie, J. F. & Warren, B. T., *Chem. & Ind.*, 1968, 253
- Wiley, R. H. & Bennett, L. L., Jr, *Chem. Rev.*, 1949, **44**, 447
- Powers, D. H., Jr, Schatz, V. B. & Clapp, L. B., *J. Am. chem. Soc.*, 1956, **78**, 907