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Preparation of Pure Anhydrous Solutions of Hydrogen Iodide in Acetic Acid

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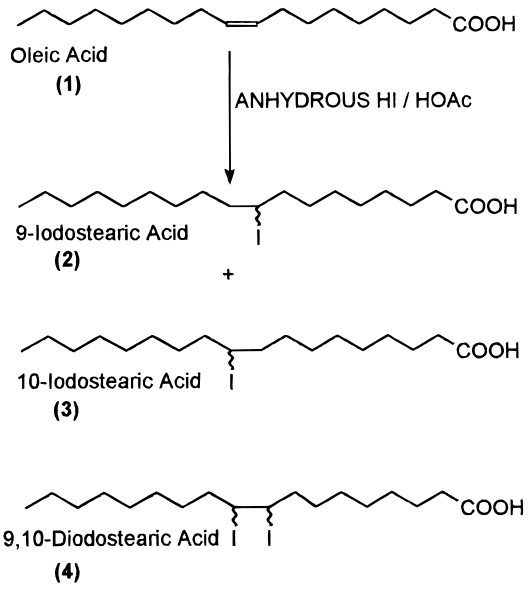
Abstract:

The presence of molecular iodine in anhydrous solutions of hydrogen iodide in acetic acid gives rise to unstable impurities during the hydriodination of isolated double bonds. This can be overcome by using aqueous hydriodic acid, as the source of hydrogen iodide, from which the iodine has been removed by washing with a solution of an organic soluble ion exchange resin.

In order to develop a practicable synthesis of mixtures of 9- and 10-iodostearic acids (**2** and **3**), prepared by the hydriodination of oleic acid (**1**), a procedure for generating anhydrous hydrogen iodide in acetic acid was required. Procedures using molecular iodine (iodine/tetralin at reflux, iodine, and red phosphorus) or compressed hydrogen iodide all proved to be unacceptable. This was because the procedure either was time-consuming or presented safety, handling, or waste management concerns.



All these procedures had one additional and important shortcoming in the context of the proposed chemistry, namely, that traces of iodine, residual during the preparation of the hydrogen iodide, were not readily removable from the resulting solutions produced by passing the gas stream into glacial acetic acid. The presence of the iodine resulted in the formation of varying quantities of 9,10-diiodostearic acid (**4**) as a byproduct. The instability of **4** resulted in the final product having poor colour stability, even at concentrations below 0.1%, due to the generation of iodine by oxidation of the eliminated hydrogen iodide.

The answer was to use analytical grade aqueous hydriodic acid as a readily available and cost effective source of hydrogen iodide. Hydriodic acid of accurately determined concentration was utilised, and all operations were carried out under an argon atmosphere. Traces of molecular iodine were removed by washing with a toluene solution of LA-2 ion exchange resin to produce a colourless and stable aqueous solution. The concentration of hydriodic acid was not affected by the washing process nor was its specific gravity, both of which needed to be accurately determined for the calculation of stoichiometric quantities. The anhydrous acetic acid solutions were prepared by adding the aqueous hydriodic acid to the appropriate quantity of degassed acetic anhydride, with control of the exotherm to below 55 °C. The clear and colourless solution was then cooled to 20 °C prior to the addition of a solution of oleic acid in glacial acetic acid. After completion of the required reaction period, the colourless reaction mixture was worked up by vacuum codistillation removal, using toluene, of the majority of the organic and inorganic acids, the product finally being extracted into toluene. This procedure gave a mixture of 9- and 10-iodostearic acids (ISA) as a colourless to very pale yellow oil with good colour stability without the need for further purification, by distillation or crystallisation.

Waste management was reduced to a minimum, and the only organic solvent used could readily be recycled after washing with aqueous base to remove acidic materials.

Conclusion

This procedure represents a simple and practical method for the generation of anhydrous hydrogen iodide in acetic acid that met all our requirements of process, handling, waste management, and above all, product quality.

Experimental Section

General. All materials, except for 67% hydriodic acid, were obtained from Sigma Aldrich Chemical Co. (Poole, England) and were of either ACS or analytical reagent grade. Hydriodic acid was obtained from Merck Ltd. (Poole, England).

9- and 10-Iodostearic Acids (ISA, 2 and 3). Into an argon-purged separation vessel fitted with a mechanical stirrer is placed hydriodic acid (2.165 L, specific gravity 1.91, 65.0% w/w). A solution of Amberlite LA-2 (0.395 kg) in toluene (5.0 L) is then added to the vessel, and the agitator is used to mix the layers for 2 min. After the layers are allowed to separate, the colourless hydriodic acid layer is run into an argon-purged holding vessel prior to returning to the separator for a single wash with a quantity of degassed toluene. For solutions heavily contaminated with molecular iodine, a second wash with the LA-2 resin solution is required.

Into an argon-purged reaction vessel is then placed acetic anhydride (6.94 L, 99.7%, 73.33 mol) which is vacuum

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degassed. Washed hydriodic acid (1.973 L, 19.15 mol of HI, 73.33 mol of H_2O) is added to the mechanically stirred solution at such a rate that the temperature is maintained below 55 °C by the use of external water cooling. If the temperature is allowed to rise above this limit, there is some loss of water vapour by entrainment, and this results in incomplete hydrolysis of the acetic anhydride.

The mixture is stirred for a further 60 min after completion of the addition of the aqueous acid and is then cooled to 20 °C prior to the addition of a vacuum-degassed solution of oleic acid (1.362 kg, 4.822 mol) in glacial acetic acid (2.0 L) over a period of 10 min.

After completion of the addition, the mixture is stirred for a further 16 h prior to removal of the majority of the acetic acid by vacuum codistillation with 10 volumes of toluene (50 mmHg, <50 °C). The dark residue is dissolved in toluene (14.0 L) and then transferred to a separating vessel followed by washing with a 5% solution of sodium thiosulphate (2.0 L) and then deionised water. The thiosulphate wash is first back-washed with a small quantity of toluene, which is combined with the main solution of product.

The organic solution is dried over magnesium sulphate and filtered through a short bed of 100−200 mesh Florisil prior to removal of the toluene under reduced pressure, to leave the product as a colourless to very pale yellow oil (1.8728 kg, 4.564 mol, 94.6%). Yield range: 90−97%. ^{1}H NMR ($CDCl_3$/TMS, 100 MHz): δ 11.6 (br s, COO*H*, 1), 4.1 (br, C*H*I, 1), 2.35 (br, CH_2OOH, 2), 1.0−2.1 (m, CH_2, 28), 0.9 (t, CH_3, 3). IR (neat): ν = 480 w (C−I). Microanal. Calcd for $C_{18}H_{35}O_2I$: C, 52.78; H, 8.60; I, 30.92. Found: C, 52.57; H, 8.81; I, 30.29. HPLC (analysed as methyl ester after derivatisation using diazomethane as all attempts to resolve the free carboxylic acids proved unsuccessful). Column: Vydac C-18, 4.6 mm × 250 mm. Isocratic @ 1.0 cm^3/min, 100% MeOH. Detection by refractive index and UV at both 215 and 254 nm. Purity: >99% mean of all three traces. Retention time = 8.67 min (ISA), 7.88 min (oleic acid <0.1%).

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