Chlorinated Alcohols: III. 9,10-Dichlorostearylamine

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Abstract

9,10-Dichlorostearylamine was prepared by the hydrogenation of 9,10-dichlorostearonitrile, catalyzed by Rh/C, and by the chlorination of oleylamine hydrochloride. The dichloro amine was surprisingly heat-stable and could be purified by molecular distillation at 170 C (0.1 mm). Also described are the preparations of 9,10-dichlorostearoyl chloride, 9,10-dichlorostearamide and 9,10-dichlorostearonitrile. The chlorination of oleonitrile is not a simple reaction and the 9,10-dichlorostearonitrile was best prepared by dehydration of the amide.

Introduction

THE PREPARATION of 9,10-dichlorostearylamine was undertaken as part of a project on the study of 9,10-dichlorostearyl alcohol. Since the internal chlorine atoms are sufficiently hindered to be stable toward bases and to dechlorinating agents like silver nitrate (7,8), 9,10-dichlorostearylamine may be expected to be a stable compound. By analogy with the corresponding alcohols, its melting point should be lower than the melting point of stearylamine and it should have a higher density. Stable, chlorine-containing, primary aliphatic amines have not previously been reported.

Chlorine-containing amines, other than chloroamines, usually known only as intermediates in nucleophilic substitution reactions. Aziridines, for example, may be prepared by the alkali treatment of a β-chloroamine salt (2,4). Komori et al. (5,6) prepared various chlorinated fatty amine hydrochlorides by the free radical chlorination of saturated amine hydrochlorides. The chlorination products contained from 1 to 4 chlorine atoms per fatty chain, but the free, chlorine-containing amines were not described.

Two routes to 9,10-dichlorostearylamine were explored; the reduction of 9,10-dichlorostearonitrile and the additive chlorination of oleylamine hydrochloride.

Experimental Procedures

The 9,10-dichlorostearic acid used in this work was prepared by the additive chlorination of oleic acid followed by two crystallizations from Skellysolve B. Oleonitrile (purity greather than 95%18 C monounsaturated was prepared by distillation of a commercial sample on a 40-plate spinning band column. Oleylamine was a commercial sample containing 84% 18 C monounsaturated and 5%, 10% and 1% of the saturated 14, 16 and 18 C straight chain primary amines, respectively, and was used without further purification. The 5% rhodium on carbon catalyst was purchased from Englehard Industries.

Molecular distillations were carried out in a Kontes (Bantamware) falling film molecular still heated by 1-decene (bp 170 C) at reflux temperature. Preparative TLC was performed on 20 cm × 20 cm × 2 mm silica gel plates (Brinkmann) with ethanol containing a trace of ammonium hydroxide as the eluant.

9,10-Dichlorostearoyl Chloride

Recrystallized 9,10-dichlorostearic acid (42 g, 0.12 moles) was dissolved in Skellysolve B (500 ml), redistilled thionyl chloride (15 g, 0.13 moles) was added, and the mixture was heated at reflux temperature for 16 hr. After cooling, the solvent was removed to have a very pale yellow oil. The infrared spectrum showed it to be free of carboxyl absorptions and the main absorption at 1800 cm^{-1} indicated an acid chloride. Since a shoulder at 1750 cm^{-1} was also observed, the crude acid chloride was purified by molecular distillation at 170 C to have a color-less oil with a single carbonyl absorption at 1800 cm^{-1}.

Analysis. Calculated for $C_{18}H_{33}Cl_3O$: % C, 58.14; H, 8.95; Cl, 28.61. Found: C, 58.26; H, 8.70; Cl, 28.36.

9,10-Dichlorostearamide

A solution of ammonia in ethanol (550 ml, 2.6N, 500% excess) was cooled in a methanol-ice bath at −30 C. 9,10-Dichlorostearoyl chloride (100 g, 0.27 mole) was added dropwise to the stirred solution and after addition was complete the solution was stirred for another hour while warming to room temperature. Ethanol was partially removed under vacuum, the mixture was extracted into ether and the ether extracts were washed, dried, filtered and evaporated. Recrystallization of the residue from ether at −30 C produced a white solid amide, yield 63%, mp 85–87 C.

9,10-Dichlorostearonitrile

Redistilled phosphorus oxychloride (10.9 g, 0.07 mole) was added to a solution of 50 g (0.14 mole) of 9,10-dichlorostearamide in 37 ml of 1,2-dichloroethane. The mixture was refluxed 6 hr, cooled, washed with 10% K_2CO_3 and then with water, dried, filtered and evaporated. Since TLC (benzene-ether-acetic acid, 74:25:1) at this point showed the presence of a small amount of amide the entire product was applied to a column of silica gel and eluted with 75 benzene:25 ether. The first fractions (37 g) were pure and were collected and concentrated to a colorless liquid.

Analysis. Calculated for $C_{18}H_{33}Cl_2N$: % C, 64.65; H, 9.95; Cl, 21.21; N, 4.19. Found: C, 64.62; H, 10.15; Cl, 20.98; N, 4.16.

Chlorination of Oleonitrile

Oleonitrile (200 g, 0.755 moles) and 600 ml of methylene chloride were mixed in a 1 liter 3-neck flask equipped with a stirrer, thermometer and gas dispersion tube. The flask was cooled to −25 C and the chlorine flow started, regulated so that the temperature of the reaction mixture was nearly constant at −12 C. The chlorine flow was stopped when the exothermic reaction ceased and the product was concentrated under vacuum to give a yellow oil (262 g, 103% of theory). Thin-layer chromatography (benzene) showed only one spot for the starting oleonitrile but several for the chlorinated product at this point.

Analysis. Calculated for $C_{18}H_{33}Cl_2N$: % C, 64.65; H, 9.95; Cl, 21.21; N, 4.19. Found: C, 62.56; H, 9.49; Cl, 23.51; N, 4.09.

Molecular distillation at 170 C and 0.1 mm gave a purified 9,10-dichlorostearonitrile as a pale yellow oil.

Analysis. Found: C, 64.40; H, 9.72; Cl, 21.67; N, 4.08.

9,10-Dichlorostearylamine

Into a 300 ml magnetically stirred autoclave were placed 5% rhodium on carbon catalyst (3.5 g), a

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solution of ammonia in ethanol (6 N, 150 ml, 0.90 moles) and pure 9,10-dichlorostearonitrile (9 g, 0.027 moles). The autoclave was sealed, flushed with hydrogen and pressurized with hydrogen (300 psig) and allowed to stir at room temperature. When, after 6 hr, TLC showed nitrile no longer present, the autoclave was vented and emptied. The contents were filtered, concentrated, resuspended in ether and shaken with NH_4OH. The ether solution was dried and evaporated and the residue was crystallized from methanol at −30 C to give 1.2 g of a white solid further purified by preparative TLC to give a product mp 42–43 C.

Analysis. Calculated for the secondary amine $C_{36}H_{71}Cl_4N$: % C, 65.53; H, 10.85; Cl, 21.50; N, 2.12. Found: C, 66.81; H, 11.01; Cl, 19.82; N, 2.19.

The mother liquor was concentrated to a pale yellow oil and purified by TLC to give a colorless oil showing only one species.

Analysis. Calculated for $C_{18}H_{37}Cl_2N$: % C, 63.88; H, 11.02; Cl, 20.96; N, 4.14. Found: C, 64.84; H, 11.07; Cl, 19.77; N, 4.10.

Although values for C and Cl depart from theory and suggest impurities, infrared spectra showed absorption at 3375 and 3280 cm^{-1} (NH_2), 1620 cm^{-1}, and 650 cm^{-1} (–CHClCHCl–) consistent with the structure of 9,10-dichlorostearylamine. Nuclear magnetic resonance spectra also confirmed this.

A differential thermal analysis of dichlorostearylamine showed nothing significant below 225 C, but from 225 C to 285 C (peaking at 280 C) an exothermic process (2.5 C) occurred. From 300 C to 375 C (peak at 350 C) there occurred an endothermic process (3 C) and another (1 C) that peaked at 400 C.

A sample of chlorinated oleonitrile (very impure 9,10-dichlorostearonitrile) was hydrogenated in the manner described above. The product was a yellow-orange oil that formed a slush after standing in a stoppered bottle for several weeks (per cent amino N = 3.4). The slush was filtered and the main product was an oil that on molecular distillation at 170 C (0.1 mm) gave equal amounts of a viscous residue and a colorless, oily, distillate (per cent amino N = 4.23). The colorless oil had an infrared spectrum identical with that of 9,10-dichlorostearylamine and a density at 25 C of 0.96.

N-(9,10-dichlorostearyl) benzamide

This derivative, formed by the reaction of dichlorostearylamine in benzene with a benzene solution of benzoyl chloride and triethylamine was obtained as a white powder, mp 71–72 C.

Analysis. Calculated for $C_{25}H_{41}Cl_2NO$: % C, 67.85; H, 9.34; Cl, 16.03; N, 3.17. Found: C, 68.00; H, 9.39; Cl, 16.11; N, 3.23.

Chlorination of Oleylamine Hydrochloride

Hydrogen chloride was bubbled through a solution of 100 g oleylamine in 300 ml of methylene chloride until a drop of the solution was acid to indicator paper, solvent and excess HCl were removed in a rotary evaporator and the residue was redissolved in 250 ml of methylene chloride.

The solution was cooled in a methanol-dry ice bath (−30 C) to −14 C and chlorine was bubbled into the stirred solution. The exothermic process eventually raised the temperature to +1 C, then subsided, a precipitate formed and the chlorine flow was discontinued. The reaction mixture was concentrated to a solid, then mixed with ether and concentrated NH_4OH and extracted with ether. The ether extract was washed, dried, decolorized and evaporated to give a yellow oil. Molecular distillation at 170 C gave a yellow oily distillate with an infrared spectrum identical to that of 9,10-dichlorostearylamine prepared from the nitrile. This spectrum differs from that of oleylamine in that the band at 975 cm^{-1} (–CH=CH–) is missing and there is a new band at 650 cm^{-1} (–CHClCHCl–).

Analysis. Theoretical, corrected for the composition of commercial oleylamine: % N, 4.36; Amino N, 4.36. Found: N, 4.43; Amino N, 4.02. The product is one species by TLC. Partial crystallization occurred on standing.

Discussion

9,10-Dichlorostearylamine is a fairly stable compound. Differential thermal analysis showed it to be stable below 225 C. The exothermic process which occurred from 225 to 280 C was probably dehydrohalogenation since experience with the DTA and TGA curves of related dichlorostearyl compounds had shown no process occurring in this range. The endothermic process occurring from 300 to 375 C (350 C peak) correlates with related compounds and corresponds to volatilization. The endothermic process at 400 C is unexplained. The results from differential thermal analysis prompted the molecular distillation of hydrogenated chlorinated oleonitrile. The amine distilled smoothly, though in low yield, as a colorless oil. Assuming additive chlorination to occur in a *trans* manner, the isomer prepared is *threo*-9,10-dichlorostearylamine and as anticipated, it is a liquid at room temperature and has nearly the same density as water.

Both routes to 9,10-dichlorostearylamine are usable but have limitations. The nitrile reduction is best for preparing pure samples because chlorination occurs on an all *cis* double bond (oleic acid) and stereochemistry at the 9,10-positions is more certain. However, losses incurred in the purification of the 9,10-dichlorostearic acid and during the reduction lower the yield. Loss during the reduction step is due to the formation of the solid, mp 42–43 C, that is probably the secondary amine. Rhodium on carbon was the catalyst selected because it is a good catalyst for nitrile reduction (1) and has little tendency to cause carbon-chlorine hydrogenolysis (3). Conditions for catalytic hydrogenation were not optimized.

The chlorination of oleylamine hydrochloride has the advantage that the yields are better but in the preparation of oleylamine the double bond is often isomerized to an unknown extent. As a result, the stereochemistry and location of the vicinal dichloro-groups is less certain. Nevertheless, this chlorination appears to proceed smoothly to give the desired product with a minimum of side reactions.

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