Sequential Nature of the Thermal Reaction of Stearic Acid with Some 1,2-Diamines

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The thermal reactions of stearic acid with ethane-1,2-diamine, bis-(2-aminoethyl)amine, and 2-(2-aminoethylamino)ethanol with a heavy hydrocarbon oil as solvent were investigated. The reactions proved general and followed a sequential pattern of (i) salt formation, (ii) acylation of the amine, and (iii) cyclisation of the amide, each successive step taking place at a higher temperature. The amounts of water formed during the reaction were consistent with the foregoing scheme. The structures of the products were determined from i.r. and ^{1}H and ^{13}C n.m.r. data

THE thermal reactions of 1,2-diamines with carboxylic acids provide routes to Δ^2-imidazolines.[1] However, a wide variety of yields of imidazolines and the formation of complexes of imidazolines with carboxylic acids in these reactions have been reported.[1,2] In many cases the yields of imidazolines are low and other products have not been described.[2-6] In some cases imidazolines derived from high molecular weight alkanoic acids have been obtained from reactions carried out at 200—300 °C

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[1] For a review see R. J. Ferm and J. L. Riebsomer, *Chem. Rev.*, 1954, **54**, 593.

[2] J. L. Riebsomer, *J. Amer. Chem. Soc.*, 1948, **70**, 1629.

[3] H. C. Chitwood and E. E. Reid, *J. Amer. Chem. Soc.*, 1935, **57**, 2424.

[4] G. Bauman, *Ber.*, 1895, **28**, 1176.

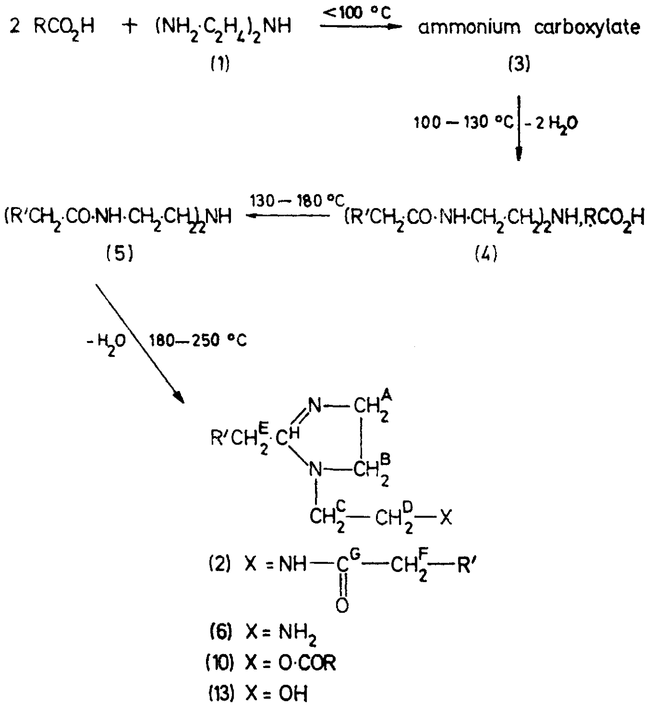
[5] E. Klingenstein, *Ber.*, 1895, **28**, 1173.

[6] A. Landenburg, *Ber.*, 1894, **27**, 2952.

with a catalyst such as hydrochloric acid,[7] a metal chloride,[8,9] or phosphorus pentaoxide.[8-10] Recently the formation of the imidazoline (6) in the reaction of equimolar quantities of stearic acid and bis-(2-aminoethyl)-amine (1) at 250 °C, has been reported although no structural evidence was given.[11] In general, although attention has been paid to catalytic effects on yields of imidazolines, little information is available concerning the stoicheiometry and overall course of the reaction. We report here a study of the thermal reactions of stearic acid with some 1,2-diamines in the heavy hydrocarbon solvent, tractor vaporising oil (TVO). The compound (6) previously reported was not encountered by us, but its stearamido-derivative was isolated.

RESULTS AND DISCUSSION

(a) *Bis-(2-aminoethyl)amine and Ethane-*1,2-*diamine*.—When equimolar quantities of bis-(2-aminoethyl)amine (1) and stearic acid were heated in TVO, initially at temperatures below 100 °C, amine salts (3) were formed (Scheme). Further heating at 100—130 °C resulted in the diamide–acid complexes (4). In the range 130—180° acid liberated from compound (4) reacted with available amine, and the free diamides (5) were formed in 85% yield. Continued heating in the range 180—250° resulted in cyclisation of the diamides (5) to 2-heptadecyl-1-(2-stearamidoethyl)-Δ^2-imidazoline (2) in 86% yield. In order to bring this step to completion, prolonged heating at the higher temperature was required. The stoicheiometry of the whole sequence (Scheme) requires that, irrespective of the molar ratio of reactants used, 1.5 mol of water is evolved for each mol of acid consumed, provided that an adequate quantity of amine is present. This was indeed observed. For example, for a reaction involving heating 0.2 mol of stearic acid with 0.1 mol of amine, expected to yield 0.3 mol of water, evolution of water was rapid in the early stages of the reaction, leading to the diamides (5) at temperatures below 200 °C. After this, the evolution was gradual, approaching the expected 0.3 mol value as the temperature was raised and held at 260 °C. With ethane-1,2-diamine a similar sequence was observed. In this case after heating for 3 h in the range 160—190 °C the diamide (7) was obtained in 89% yield. When heating was prolonged for 2—3 days at 240—260 °C, compound (7) was obtained in 76% yield along with 17% of the imidazoline (8).



SCHEME $R = C_{17}H_{35}$; $R' = C_{16}H_{33}$

(b) 2-(2-*Aminoethylamino*)*ethanol*.—Similar treatment of 2-(2-aminoethylamino)ethanol with stearic acid also gave a sequence of reactions involving salt formation and acylation of the primary amino-group. After heating for 3 h, during which the temperature reached 170—180 °C, the amide (9) was obtained in 91% yield. On further heating at 200—220 °C cyclisation occurred to give the imidazoline (13). I.r. spectra of samples withdrawn from reaction mixtures which had reached 200—220 °C sometimes showed weak ester-type bands at 1 740 and 1 270 cm^{-1} and it is possible that a compound such as (10), comparable with (2), may be present as an intermediate or in low concentration; however such a compound was not isolated.

(c) *Structure Determinations*.—The presence of the ammonium salts in the early stages of the reaction was detected from i.r. spectra[12] of samples ($\nu_{max.}$ 2 100—2 220 cm^{-1}). The progress of the reaction could be followed from i.r. spectra of samples withdrawn periodically, which showed successive development and replacement of bands due to ammonium salts, amides, and the imidazoline ring. Stopping the reactions at the appropriate points allowed isolation of compounds (2), (4), (5), (7)—(9), and (13). Their structures were established from elemental analyses, i.r. and ^{1}H and ^{13}C n.m.r. spectra, and independent interconversions. The complex (4) was converted into the diamide (5) and sodium stearate by cold dilute sodium hydroxide, and the diamide (5) was easily converted back into the complex (4) by treatment with stearic acid. Compound (5) was readily cyclised to the substituted imidazoline (2) in high yield on heating independently at 250—260 °C for 48 h.

[7] E. Waldmann and A. Chwala, *Ber.*, 1941, **74**, 1763.

[8] E. Waldmann and A. Chwala, Fr. P. 811,423/1937 (*Chem. Abs.*, 1937, **31**, 8550); B.P. 479,491/1938 (*Chem. Abs.*, 1938, **32**, 5002); U.S.P., 221,5861/1940 (*Chem. Abs.*, 1942, **36**, 2735).

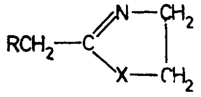
[9] A. L. Wilson, U.S.P., 226,795/1941 (*Chem. Abs.*, 1942, **36**, 2735).

[10] D. W. Hein, R. J. Alheim, and J. J. Leavitt, *J. Amer. Chem. Soc.*, 1957, **79**, 427.

[11] C. F. Huber and P. F. Thompson, U.S.P., 2,950,211/1960 (*Chem. Abs.*, 1960, **54**, 232,56b).

[12] R. M. Silverstein, C. G. Bassler, and T. C. Morrill, ' Spectrometric Identification of Organic Compounds,' Wiley, London, 1974, 3rd edn., pp. 101—110.

The amide groups in these compounds and in the model compound (11) showed N–H stretching bands at 3 300—3 320, N–H bending at 1 540—1 550, and amide C=O stretching consistently at 1 640 cm^{-1}. The imidazoline C=N stretching bands in the products and in the model compound (12) appeared at 1 600—1 610 cm^{-1}. ^{1}H N.m.r. spectra (Experimental section) were consistent with the structures proposed. ^{13}C N.m.r. data, few of which have been reported for imidazoline systems[13-15] or for long chain aliphatic amides, also confirmed the structures. Good agreement was observed (Figure) between the measured ^{13}C shifts for compound (5) and those predicted for replacement of a terminal Me group of n-decane by CO•NR$_2$.[13] The imidazoline shifts (Experimental section) were generally consistent with recently reported ^{13}C spectra of some 2-amino-imidazolines,[14,15] and the amide carbonyl and methylene shifts were in general agreement with shifts reported for simpler amides.[16] The amide carbonyl carbon resonance appeared at 172.2—174.5 p.p.m., and the imidazoline C=N signal appeared at higher field (168.2—168.8 p.p.m.).



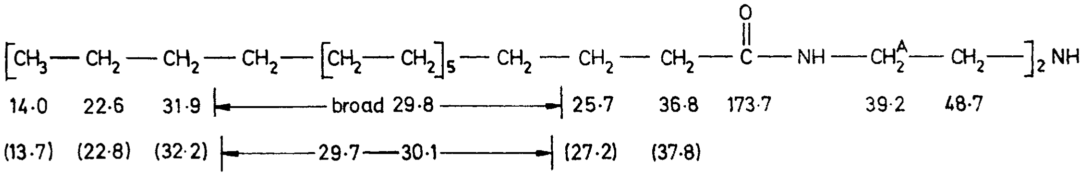
(8) R = $C_{16}H_{33}$.X = NH
(12) R = H, X = NH

$(RCH_2\cdot CO\cdot NH\cdot CH_2^A)_2$

(7) R = $C_{16}H_{33}$
(11) R = H

$C_{16}H_{33}\cdot CH_2^A—CO—NH—CH_2^B—CH_2^C—NH—CH_2^D—CH_2^E—OH$

(9)



Observed and calculated (in parentheses) ^{13}C n.m.r. chemical shifts (p.p.m. from Me$_4$Si) for compound (5)

EXPERIMENTAL

M.p.s were measured with an Electrothermal apparatus. I.r. spectra were measured for either films or mulls with a Perkin-Elmer 377 or 457 spectrophotometer. ^{1}H and ^{13}C n.m.r. spectra were measured for solutions in CDCl$_3$ at probe temperatures (Me$_4$Si as reference) with a JEOL JNM-100 or CFT-20 spectrometer. Commercial samples of stearic acid (Aldrich; 95%) and the amines were thoroughly purified by recrystallisation (stearic acid had m.p. 69—71°) and distillation before use. Reaction mixtures were heated under a condenser fitted with a calibrated Dean–Stark-type water trap, which was used to measure the evolution of water with accuracy to within ±0.1 ml. Temperature were measured directly with a thermometer embedded in the reaction mixture.

(i) *Ethane*-1,2-*diamine*.—(*a*) A mixture of stearic acid (2.84 g), ethane-1,2-diamine (0.6 g) and TVO (5 ml) was heated to 100 °C over 90 min followed by 2 h at 170—180 °C and then cooled. The resulting solid on crystallisation from aqueous alcohol yielded NN′-*ethylenedistearamide* (7) (2.55 g, 89%), m.p. 140—141° (Found: C, 77.45; H, 13.05; N, 5.1. $C_{38}H_{76}N_2O_2$ requires C, 77.1; H, 12.8; N, 4.7%); τ 7.76 (t, *J* 8 Hz, CH$_2$•CO) and 6.56 (d, *J* 5 Hz, NH•CH$_2$); $\nu_{max.}$ 1 640 (C=O) and 3 300 cm^{-1} (N–H) [similar spectra were observed for compound (11)]; δ_C 174.5 (C=O), 40.4 (NH•CH$_2$), and 36.8 (*C*H$_2$•C=O).

(*b*) When the reaction mixture was treated as above followed by 3 days at 240—260 °C, fractional crystallisation of the products gave a 76% yield of compound (7), along with the imidazoline (8) (17%) (from the late fractions), m.p. 87—89° (from aqueous ethanol) (lit.,[7] 94—95°) (Found: C, 78.2; H, 12.8; N, 8.9. Calc. for $C_{20}H_{40}N_2$: C, 77.9; H, 13.0; N, 9.1%); τ 7.80 (t, *J* 8 Hz, CH$_2$•C=N) and 6.46 (s, =N•C$_2$*H*$_4$•NH); δ_C 168.5 [C(NH)=N] and 49.9 (=N•C$_2$H$_4$•NH); $\nu_{max.}$ 1 600 cm^{-1} (C=N).

(ii) *Bis*-(2-*aminoethyl*)*amine*.—(*a*) A mixture of stearic acid (2.84 g), bis-(2-aminoethyl)amine (1.03 g), and TVO (5 ml) was heated to 170—180° for 3 h, then cooled. The solid mixture crystallised from aqueous ethanol to yield NN′-(*iminodiethylene*)*distearamide* (5) (2.71 g, 85%), m.p. 110—112° (Found: C, 75.8; H, 12.55; N, 6.8. $C_{40}H_{81}N_3O_2$ requires C, 75.55; H, 12.75; N, 6.6%); τ 7.80 (t, *J* 8 Hz, CH$_2$•CO), 7.24 (t, *J* 6 Hz, C*H*$_2$•NH•C*H*$_2$), 6.64 (q, *J* 5 Hz, CO•NH•C*H*$_2$), and 4.16br (s, NH); δ_C see Figure; $\nu_{max.}$ 1 640 (C=O), 3 300 (amide NH), and 3 200w cm^{-1} (amine NH).

(*b*) Treatment of the reaction mixture as in (*a*) followed by further heating at 240—260 °C for 48 h yielded 2-*heptadecyl*-1-(2-*stearamidoethyl*)-Δ^2-*imidazoline* (2) (2.6 g, 86%), m.p. 82—84° (from ethanol) (Found: C, 77.2; H, 12.8; N, 6.8. $C_{40}H_{79}N_3O$ requires C, 77.8; H, 12.8; N, 6.8%); τ 7.78—8.0 (overlapping triplets, CH$_2^E$ and CH$_2^F$), 6.60—6.88 (6 H, overlapping m, CH$_2^B$, CH$_2^C$, and CH$_2^D$), 6.36 (t, *J* 8 Hz, CH$_2^A$), and 4.28br (NH); $\nu_{max.}$ 1 605 (C=N), 1 640 (C=O), and 3 320 cm^{-1} (N–H); δ_C 49.65 (C^A), 51.3 (C^B), 46.2 (C^C), 38.5 (C^D), 36.4 (C^F), 27.4 (C^E), 173.8 (C^G), and 168.2 (C^H). When a mixture of compound (5) (3.0 g) and TVO (5 ml) was heated at 240—260 °C for 48 h, then cooled, and the residue was crystallised from ethyl alcohol (35 ml) containing a few drops of water, compound (2) (89%), identical (mixed m.p., i.r. and n.m.r. spectra) with the sample described above, was obtained.

(*c*) When a mixture of stearic acid and bis-(2-aminoethyl)amine was heated at 120—140 °C for 2 h and worked

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[13] G. C. Levy and G. L. Nelson, ' Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley, London, 1972, pp. 40, 47.

[14] K.-H. Pook, H. Stahle, and H. Daniel, *Chem. Ber.*, 1974, **107**, 2644.

[15] T. J. Batterham, ' NMR Spectra of Simple Heterocycles,' Wiley, London, 1973, p. 217.

[16] G. C. Levy and G. L. Nelson, *J. Amer. Chem. Soc.*, 1972, **94**, 4897.

up as before, the *complex* (4) (40%) was obtained; m.p. 91—94° (Found: C, 76.3; H, 12.7; N, 4.7. $C_{58}H_{117}N_3O_4$ requires C, 75.7; H, 12.75; N, 4.6%); $\nu_{max.}$ 1 640 (C=O) and 3 315 and 3 280 cm^{-1} (two NH); τ 7.84 (t, *J* 7 Hz, $CH_2{\cdot}CO$), 7.20br (unresolved) ($CH_2{\cdot}N{\cdot}CH_2$), and 6.60br (unresolved) ($CO{\cdot}NH{\cdot}CH_2$); δ_C 172.2 (C=O), 45.5 ($CH_2{\cdot}N{\cdot}CH_2$), 41.5 ($CH_2{\cdot}NH{\cdot}CO$), and 33.3, 31.8, 29.7 (strong), 25.1, 22.6, and 14.0 (stearyl chains). Compound (4) was also obtained (50%) when a mixture of stearic acid (0.28 g) and the diamide (5) (0.6 g) was stirred in ethanol (75 ml) for 3 h at room temperature. When a mixture of compound (4) (1.0 g) and sodium hydroxide (0.28 g) was stirred for 2 h at room temperature in ethanol (20 ml), the diamide (5) (85%) and stearic acid (75%; after acidification of sodium stearate) were obtained. Similar products were obtained when the same reaction was carried out under reflux for 2 h.

(iii) 2-(2-*Aminoethylamino*)*ethanol*.—(*a*) A mixture of stearic acid (14.2 g), 2-(2-aminoethylamino)ethanol (5.15 g), and TVO (15 ml), heated at 160—170 °C for 3 h, cooled, and crystallised from aqueous ethanol, yielded N-[2-(2-*hydroxyethylamino*)*ethyl*]*stearamide* (9) (16.1 g, 87%), m.p. 103—105° (Found: C, 71.45; H, 12.3; N, 7.2. $C_{22}H_{46}N_2O_2$ requires C, 71.35; H, 12.4; N, 7.55%); $\nu_{max.}$ 1 640 (C=O) and 3 310—3 280 cm^{-1} (NH and OH); τ 7.76 (2 H, t, *J* 8 Hz, CH_2^A), 7.08—7.24 (4 H, overlapping triplets, CH_2^C and CH_2^D), 6.55 (2 H, q, *J* 6 Hz, CH_2^B), 6.24 (2 H, t, *J* 5 Hz, CH_2^E), and 3.92br (OH or NH).

(*b*) This reaction, when carried out at 210—220 °C for 5 h, yielded 2-*heptadecyl*-1-(2-*hydroxyethyl*)-Δ^2-*imidazoline* (13) (89.0%), m.p. 63—65° [from toluene–petroleum (b.p. 60—80°)] (Found: C, 75.0; H, 12.4; N, 7.95. $C_{22}H_{44}N_2O$ requires C, 75.0; H, 12.5; N, 7.95%); $\nu_{max.}$ 1 600 cm^{-1} (C=N); τ 7.68 (2 H, t, *J* 7 Hz, CH_2^E), 6.92br (OH), 6.52—6.72 (4 H, overlapping triplets, CH_2^B and CH_2^C), and 6.08—6.32 (4 H, overlapping triplets, CH_2^A and CH_2^D).

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