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Reaction of Aliphatic Amines with 49% Formic Acid. [1] 1-Hexylamine, Di-1-hexylamine, *N,N*-Dimethyl-1-hexylamine, 1-Dodecylamine, *N,N*-Dimethyl-1-dodecylamine and *N,N*-Dimethyl-1-butylamine

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Abstract. Two primary amines, 1-hexylamine **2**, 1-dodecylamine **19**, one secondary amine, di-1-hexylamine **18**, and three tertiary amines, *N,N*-dimethyl-1-hexylamine **6**, *N,N*-dimethyl-1-butylamine **3**, and *N,N*-dimethyl-1-dodecylamine **22** were each heated at 150 °C, 250 °C or 350 °C with 49% aqueous formic acid for varying periods of time. The aliphatic primary amines underwent easy *N*-formylation and subsequent reduction to give *N*-methyl- and *N,N*-dimethylalkylamines. Especially at higher temperatures, other reactions intervened including elimination of NH_3 to the corresponding alkenes followed by partial double bond isomerization. Tertiary amines were more reactive at higher temperatures undergoing hydrolysis and reductive cleavages to secondary and primary amines, which subsequently followed the reaction sequences seen for primary amines.

This series of saturated amines showed none of the cleavage into smaller fragments that was observed in the reductive alkylation of pyridine and 4-methylpyridine to a series of *N*-alkylpiperdines. This result reinforces the bis-aza-retro-Aldol-fragmentation mechanism postulated for the formation of the *N*-alkylpiperidines.

Introduction

Formic acid readily reduces pyridine rings at 100–200 °C. Thus, pyridine, quinoline, isoquinoline and acridine give piperidine, 1,2,3,4-tetrahydroquinoline, 1,2,3,4-tetrahydroisoquinoline and 9,10-dihydroacridine, respectively; the analogous quaternary salts yield the corresponding *N*-substituted compounds, *e.g.* *N*-methylpyridinium cation gives *N*-methylpiperidine[1–4].

Recently, we demonstrated [5] that in 49% aqueous formic acid at 350 °C pyridine was converted into 1-formylpiperidine together with several *N*-alkylpiperidines and further that the *N*-ethyl and *N*-propyl groups of the latter originated by unprecedented C–C bond cleavages of the pyridine ring. Our postulated mechanism [5b] for these C–C bond cleavages should not apply to straight chain aliphatic amines. To test this, and thus to support the postulated mechanisms [5b], we have now studied the effect of 49% aqueous formic acid at 350 °C on two primary amines (1-hexylamine **2**, 1-dodecylamine **19**), a secondary amine (di-1-hexylamine **18**) and three tertiary amines (*N,N*-dimethylbutylamine **3**, *N,N*-dimethyl-1-hexylamine **6** and *N,N*-dimethyl-1-dodecylamine **22**) as representative examples.

Experimental

The gas chromatographic (GC) behavior (retention times) of all the compounds employed for this study (starting materials and products) is summarized in Table 1. The results from the aquathermolysis of each amine are collected in Tables 5–9. All product yields (molar %) are represented in the same fashion as described in detail previously [6].

Structures and proposed mechanistic pathways for the formation of these products (which are justified later in this paper) are given in Schemes 1–4. In these reaction schemes, numbers **>100** are used for postulated intermediates not detected by the GC-MS analyses.

General Procedure. The purities of all the starting materials were checked by GC prior to use. Aqueous 49% formic acid was deoxygenated with argon for 1 h prior to use. The model compound (0.45 g) and the acid (3.16 ml) were charged into a nitrogen blanketed stainless steel bomb which was then sealed. The reactor was then kept, without agitation, in a TECHNI fluidized sand bath (model SBS-4) set at 150 °C,

[1]) Part 24 in the series of aqueous high-temperature chemistry of carbo- and heterocycles

Table 1. Structure and Identification of Starting Materials and Products

no.	t_R(min)	compound	MW [a]	identification basis
1	1.24	1-butanol	56	Table 2
2	2.82	1-hexylamine	101	Table 2
3	3.68	*N,N*-dimethyl-1-butylamine	101	Table 2
4	3.74	hexanal	100	Table 3
5	4.86	1-hexanol	102	Table 2
6	5.31	*N,N*-dimethyl-1-hexylamine	129	Table 2
7	6.39	*N*-methyl-di-1-butylamine	143	Table 3
8	8.01	*N*-methyl-*N*-1-butylformamide	115	Table 4
9	8.40	*N*-hexylformamide	129	Table 2
10	9.94	tri-1-butylamine	185	Table 3
11	10.73	1-dodecene	168	Table 3
12	10.87	dodecane	170	Table 2
13	10.93	2-dodecene	168	Table 3
14	11.03	*N*-methyl-*N*-1-hexylformamide	143	Table 4
15	11.10	3-dodecene	168	Table 3
16	11.57	*N,N*-dibutylformamide	157	Table 3
17	12.06	*N*-methyl-di-1-hexylamine	199	Table 4
18	12.12	di-1-hexylamine	185	Table 2
19	14.64	1-dodecylamine	185	Table 2
20	15.06	1-dodecanol	186	Table 2
21	15.18	*N*-methyl-1-dodecylamine	199	Table 4
22	15.37	*N,N*-dimethyl-1-dodecylamine	213	Table 2
23	16.23	*N,N*-di-1-hexylformamide	213	Table 4
24	16.57	tri-1-hexylamine	269	Table 3
25	19.54	*N*-1-dodecylformamide	213	Table 2
26	19.99	*N*-methyl-*N*-1-dodecylformamide	227	Tabel 4
27	20.56	*N*-methyl-*N*-1-dodecylacetamide	241	Table 4
28	21.43	*N*-acetyl-*N*-1-dodecylformamide	255	Table 4
29	28.91	*N*-methyl-di-1-dodecylamine	367 [a]	Table 4
30	29.26	di-1-dodecylamine	353 [a]	Table 3

[a] Eq Wt = MW except for compounds **29** and **30** where Eq Wt = 0.5 MW.

250 °C or 350 °C. After the reaction period, the reactor was immediately quenched in a stream of cold air and then dry ice. The reaction mixture was then worked up as previously described [6], and subjected to GC/MS analyses on a Hewlett Packard 5890 Series II Gas Chromatograph fitted with a 15 m capillary co- lumn (SPB-1) and an oven temperature program of 10 °C/min from 50–250 °C and connected to a HP 5972A Mass Selective Dectector (MSD).

Product Identification: Within the reaction mixtures, the identities of all the starting materials, and some of the products (**1**, **2**, **3**, **5**, **6**, **12**, **18**, **19**, **20**, **22** and **25**) were confirmed by comparison of their retention times and mass spectral fragmentation patterns with those of authentic, commercially available or independently prepared compounds. Table 2 records the source and mass spectral fragmentation patterns of the authentic compounds used, either as starting materials or for the identification of products. Table 3 includes products for which authentic samples were not available, identification was by comparison of their MS fragmentation patterns with published mass spectra. The structures of the remaining products were assigned by consideration of their mass spectral fragmentation patterns together with the starting materials, reaction conditions and reasonable mechanistic pathways for their formation from the starting materials. These remaining products (**8**, **9**, **14**, **17**, **21**, **23** and **26–29**) are included in Table 4, together with a rationale for their fragmentation and identification.

NMR Data: ^{1}H NMR spectra were recorded either on a Varian VXR 300 (300 MHz) or a General Electric QE (300 MHz) spectrometer. ^{13}C NMR spectra were recorded at 75 MHz on the same spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) used as an internal standard. Coupling constants (*J* values) are reported in hertz (Hz). Analytical thin layer chromatography (TLC) was performed using precoated silica gel 60 F254 plastic plates (0.2 mm thick) using iodine as an indicator to visualize the product compounds.

N-1-Dodecylformamide (**25**)

1-Dodecylamine (10.0 g, 54 mmol) was suspended in an excess of aqueous formic acid (88%) (2.48 g, 108 mmol). The mixture was refluxed in benzene (150 ml) under Dean-Stark conditions for the azeotropic removal of water. The reaction was refluxed for 18 h; cooled to room temperature and the solvent removed in vacuo. The pale yellow solid was recrystallized from petroleum ether to give the title compound as white flakes (9.70 g, 84%) (*m.p.* 33.5–35 °C) (Lit. [7] *m.p.* 35–36 °C). –

Table 2. Properties of Authentic Compounds Used as Starting Materials and for the Identification of Products

no.	compound	MW	S [a]	purity (%)	*m/z* (% relative intensity)	ref. spectra # [b]
1	1-butanol	56	F*	99	56(100); 43(51); 42(28); 41(56); 31(64)	116 552
2	1-hexylamine	101	A	100	101(3); 45(6); 44(7); 41(10); 30(100)	118 147
3	*N,N*-dimethyl-1-butylamine	101	A	99	101(7); 58(100); 44(5); 30(5)	122 789
5	1-hexanol	102	F*	98	102(1); 84(9); 69(24); 56(100); 55(58)	118 286
6	*N,N*-dimethyl-1-hexylamine	129	A	100	129(6); 58(100); 56(2); 42(8); 41(4)	6 209
12	dodecane	170	A	99	170(8); 85(46); 71(64); 57(100); 56(22)	126 002
18	di-1-hexylamine	185	A	98	185(5); 114(100); 84(4); 44(48); 43(21)	127 287
19	1-dodecylamine	185	F	99	185(2); 184(1); 55(9); 44(10); 30(100)	28 046
20	1-dodecanol	186	A	98	186(1); 140(8); 97(43); 83(65); 55(100)	127 402
22	*N,N*-dimethyl-1-dodecylamine	213	A	97	213(4); 212(1); 84(2); 59(4); 58(100)	40 885
25	*N*-1-dodecylformamide	213	S	100	213(18); 184(15); 72(39); 59(100); 58(68)	34 318

[a]) Source: A = Aldrich, F = Fluka, F* = Fisher, S = synthesized authentic compound (see experimental section). [b]) Spectral numbers of the mass spectral data for the compounds found from a search of the Wiley.L138 / MSP.

Table 3. Identification of Products by Comparison of Mass Spectral Fragmentation with Literature Data

no.	compound	MW	fragmentation found *m/z* (% relative intensity) {fragmentation reported}	ref. [a]) spectra #
4	hexanal	100	100(2); 82(20); 72(27); 57(67); 56(88); 44(100) {100(1); 82(14); 72(20); 57(44); 56(82); 44(100)}	117 973
7	*N*-methyl-di-1-butylamine	143	143(11); 100(100); 58(80); 44(31); 42(17) {143(13); 100(100); 58(35); 44(33); 42(10)}	122 289
10	tri-1-butylamine	185	185(5); 142(100); 100(44); 58(10); 44(12) {185(6); 142(100); 100(51); 58(15); 44(19)}	127 292
11	1-dodecene	168	168(33); 83(66); 70(71); 69(84); 55(100) {168(9); 83(32); 70(50); 69(67); 55(100)}	20 662
13	2-dodecene	168	168(47); 83(53); 70(95); 56(63); 55(100) {168(7); 83(36); 70(57); 56(75); 55(100)}	20 664
15	3-dodecene	168	168(7); 70(81); 69(87); 56(82); 55(100) {168(11); 70(68); 69(96); 56(87); 55(100)}	20 666
16	*N,N*-di-1-butylformamide	157	157(3); 114(59); 72(100); 58(13); 44(21) {157(2); 114(55); 72(100); 58(13); 44(17)}	15 804
24	tri-1-hexylamine	269	269(2); 198(100); 128(22); 44(6); 43(15) {269(2); 226(8); 198(100); 128(15); 44(5)}	13 230
30	di-1-dodecylamine	353	353(1); 199(15); 198(100); 44(14) {353(5); 199(17); 198(100); 44(32)}	88 747

[a]) Spectral numbers of the mass spectral data for the compounds from a search of the Wiley.138L/MSP.

^{1}H NMR ($CDCl_3$): δ 0.90 (t, 3H, J = 7.0), 1.21–1.46 (m, 18H), 1.48–1.58 (m, 2H), 3.24 (q, 2H, J = 7.3), 5.70 (br. s, 1H), 8.18 (s, 1H). – ^{13}C NMR ($CDCl_3$): δ 14.06, 22.62, 26.79, 29.18, 29.29, 29.46, 29.51 (2C), 29.56, 29.57, 31.85, 38.15, 161.13.

Results and Discussion

1-Hexylamine (**2**). 1-Hexylamine **2** was moderately reactive at 150 °C for 1 h in 49% aqueous formic acid. A 59.2% conversion was observed to yield mainly *N*-1-hexylformamide (**9**, 59.0%) and *N*-methyl-*N*-1-hexylformamide (**14**, 0.2%). On increasing the reaction temperature to 250 °C for 1 h, an increased conversion of 96.2% was noted to give the same product distribution but with increased yields: *N*-1-hexylformamide (**9**, 93.8%) and *N*-methyl-*N*-1-hexylformamide (**14**, 2.4%). The initial reaction step is obviously formylation followed by reduction to give probably *N*-methyl-1-hexylamine (**101**) as an intermediate which by formylation yields **14**.

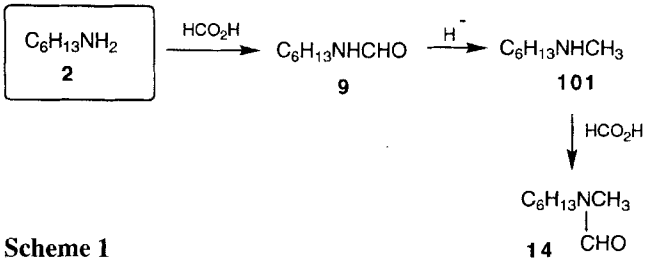
Di-1-hexylamine (**18**). After 1 h at 150 °C in 49% aqueous formic acid, a 40.1% conversion was observed with *N,N*-di-1-hexylformamide (**23**) as the major product

Table 4. Identification of Products from Mass Spectral Fragmentation Patterns

no.	compound	MW	fragmentation pattern *m/z* (% relative intensity, structure of fragment ion)
8	*N*-methyl-*N*-1-butylformamide	115	115(14, M^+); 114(22, M–H); 86(7, M–H-CO); 72(82, M–C_3H_7); 44(100, M–C_3H_7-CO); 42(23)
9	*N*-hexylformamide	129	129(2, M^+); 101(11, M–CO); 100(32M–CO-H); 86(12, M–C_3H_7); 72(23); 58(99); 44(14); 30(100)
14	*N*-methyl-1-hexylformamide	143	143(11, M^+); 142(16, M–H); 73(35, M–C_5H_{10}); 72(100, M–C_5H_{11}); 44(87); 42(19)
17	*N*-methyl-di-1-hexylamine	199	199(4, M^+); 129(10, M–C_5H_{10}); 128(100, M–C_5H_{11}); 58(57); 44(17); 42(10)
21	*N*-methyl-1-dodecylamine	199	199(5, M^+); 198(1, M–H); 184(1, M–CH_3); 170(1, M–C_2H_5); 58(91, M–$C_{10}H_{21}$); 44(100); 30(8)
23	*N,N*-di-1-hexylformamide	213	213 (1, M^+); 143(11, M–C_5H_{10}); 142(100, M–C_5H_{11}); 114(7, M–C_5H_{11}-CO); 72(92, M–C_5H_{10}-C_5H_{11}); 44(15)
26	*N*-methyl-*N*-1-dodecylformamide	227	227 (7, M^+); 226(13, M–H); 212(11, M–CH_3); 198(3, M–H-CO); 184(3, M–CH_3-CO); 170(4); 156(5); 142(6); 128(9); 114(13); 110(10); 86(13); 72(100); 58(4); 44(35)
27	*N*-methyl-*N*-1-dodecylacetamide	241	241 (6, M^+); 240(8, M–H); 213(13, M–CO), 212(13, M–CO-H); 185(1); 184(3); 157(1); 156(5); 129(3); 128(6); 101(4); 100(14); 86(100,); 73(28); 72(14); 58(37); 44(7)
28	*N*-acetyl-*N*-1-dodecylformamide	255	255(2, M^+); 254(2, M–H); 240(2, M–CH_3); 226(100, M–H-CO); 198(3); 184(3); 156(3); 100(71); 72(38); 44(6)
29	*N*-methyl-di-1-dodecylamine	367	367(2, M^+); 366(3, M–H); 213(16, M–$C_{11}H_{22}$); 212(100, M–$C_{11}H_{23}$); 198(1)

Table 5. Products from 1-Hexylamine (**2**), 49% HCOOH

temp. (°C)			150	250
time (h)			1	1
no.	compound	MW		
2	1-hexylamine	101	41	3.8
9	*N*-1-hexylformamide	129	59	94
14	*N*-methyl-1-hexylformamide	143	0.2	2.4



Scheme 1

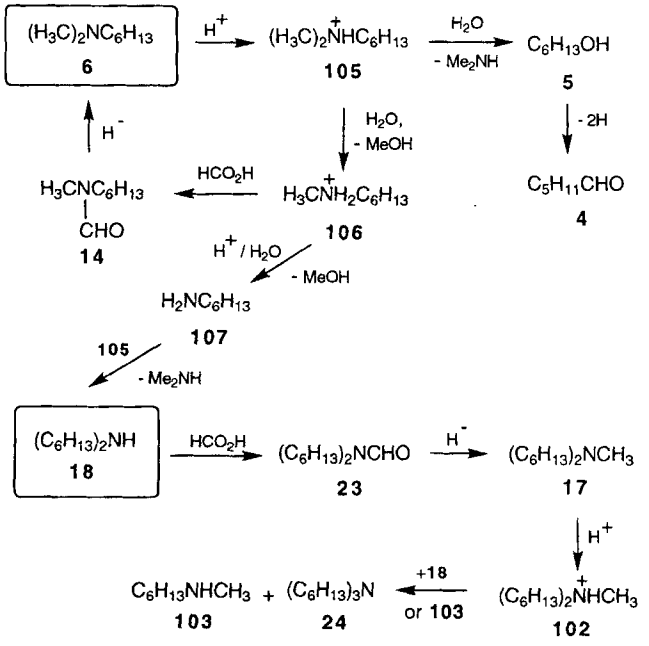
(38.3%) along with minor amounts of *N*-methyl-di-1-hexylamine (**17**, 1.0%) and tri-1-hexylamine (**24**, 0.8%). On increasing the reaction temperature to 250 °C, an identical product slate was observed with conversion increased to 93.8% to form **23** (88.9%), **17** (3.8%) and **24** (1.1%).

The reaction pathway proceeds initially *via* formylation of **18** to yield **23** which can undergo reduction to **17**. Protonation of **17** and subsequent attack by **18** yields the tertiary amine product **24** and *N*-methyl-1-hexylamine (**103**) as an intermediate. Compound **103** is not observed in the product slate and evidently undergoes further reaction by converting more of the protonated species **102** into *tri*-1-hexylamine **24**.

N,N-Dimethyl-1-hexylamine (**6**). After 2 h at 250 °C in 49% aqueous formic acid a 37.5% conversion was observed. Formation of *N*-methyl-*N*-1-hexylformamide (**14**) as the main product can be envisaged to arise through initial protonation of **6** to yield **105** as an intermediate which is readily attacked by water to furnish

Table 6. Products from *N,N*-Dimethyl-1-hexylamine (**6**) and Di-1-hexylamine (**18**), 49% HCOOH

temp. (°C)			250	350	150	250
time (h)				2	1	11
no.	compound	MW	**6**	**6**	**18**	**18**
4	hexanal	100	–	3.8	–	–
5	1-hexanol	102	2.8	6.5		–
6	*N,N*-dimethyl-1-hexylamine	129	63	26	–	–
14	*N*-methyl-*N*-1-hexylformamide	143	24	4.7	–	–
17	*N*-methyl-di-1-hexylamine	199	11	45	1.0	3.8
18	di-1-hexylamine	185	–	7.2	60	6.2
23	*N,N*-di-1-hexylformamide	213	–	1.3	38	89
24	tri-1-hexylamine	269	–	5.8	0.8	1.1



Scheme 2

methanol and **106**. Intermediate **106** is formylated to give product **14**. Loss of another molecule of methanol from **106** forms the intermediate primary amine **107** which is alkylated through reaction with **105** (with subsequent loss of dimethylamine) to yield **18**. Formylation and reduction of **18** generates **17**. Attack of water on intermediate **105** also generates 1-hexanol **5** which, under more forcing conditions as described below, is oxidized to hexanal (**4**).

After 1 h at 350 °C in 49% aqueous formic acid a 74% conversion to a wide product slate was observed. Large amounts of *N*-methyl-di-1-hexylamine (**17**, 44.7%), 1-hexanol (**5**, 6.5%) and *N*-methyl-*N*-1-hexylformamide (**14**, 4.7%) were also formed. In addition, di-1-hexylamine (**18**, 7.2%), tri-1-hexylamine (**24**, 5.8%) *N,N*-di-1-hexylformamide (**23**, 1.3%) and hexanal (**4**, 3.8%) were obtained. Of these, **18**, **24** and **23** were also products from the reaction of di-1-hexylamine **18** and suggest the intermediacy of compound **18**.

1-Dodecylamine (**19**). 1-Dodecylamine **19** was very reactive in 49% aqueous formic acid showing 97.1% conversion after 0.5 h at 350 °C. Formation of the six major products is envisaged to occur by hydrolysis and loss of ammonia from **19** to yield 1-dodecanol **20** and by initial formylation of **19** to generate *N*-1-dodecylformamide **25** (Scheme 3). Compound **25** is reduced to the *N*-methyl derivative **21** which can undergo further formylation to form *N*-methyl-*N*-1-dodecylformamide **26**. Reduction of **26** leads to *N,N*-dimethyl-1-dodecylamine **22**. Compound **22** can undergo protonation to intermediate **110** which can act as an alkylating agent towards **19** yielding di-1-dodecylamine **30**. Compound **30** undergoes formylation and then reduction to *N*-methyl-di-1-dodecylamine **29**. Dodecane **12** arises through deamination of **19** or **22**.

Formation of the unsaturated derivatives **13** and **15** involves formation of the cationic intermediate **104** from **22**: **104** undergoes proton shifts to form **108** and then **109** which can each lose protons to form **11**, **13** and **15**.

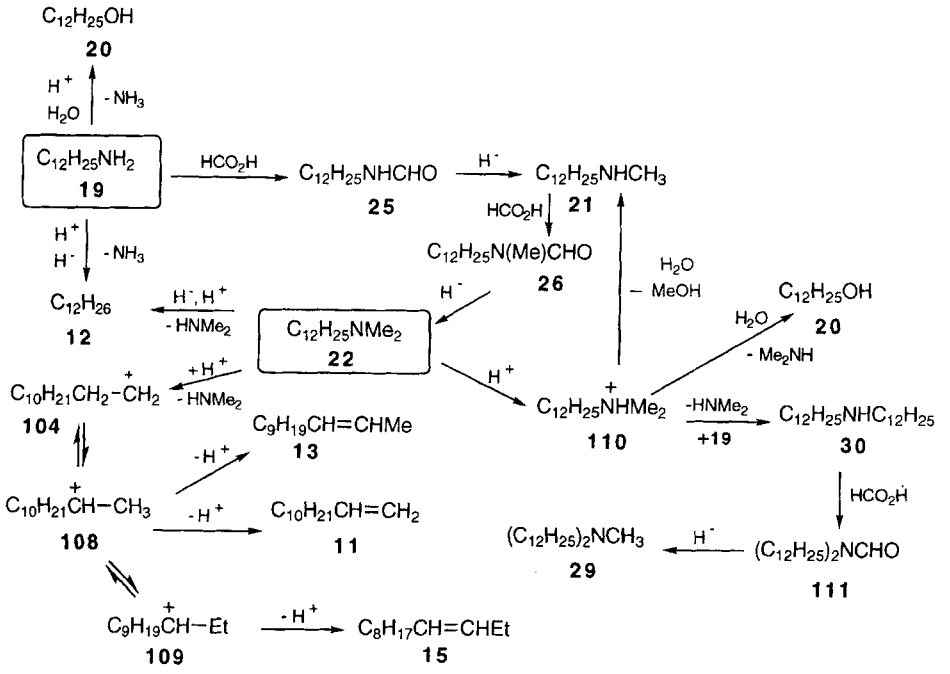
Lower temperature runs also showed moderate to high reactivity. After 1 h at 150 °C in 49% aqueous formic-acid, 1-dodecylamine **19** showed a 58.2% conversion to *N*-1-dodecylformamide **25**, 57.5%) and a trace of di-1-dodecylamine (**30**, 0.7%). After 0.5 h at 150 °C, an 88.7% conversion was observed with *N*-1-dodecylformamide **25**, 81.2%) and *N*-methyl-*N*-1-dodecylformamide (**26**, 7.5%) as the major products. A 99.3% conversion was observed after 10 h at 250 °C with *N*-1-dodecylformamide (**25**, 47.2%), *N*-methyl-*N*-1-dodecylformamide (**26**, 34.7%) and *N,N*-dimethyl-1-dodecylamine (**22**, 7.6%) as the major products.

Table 7. Products from 1-Dodecylamine (**19**), 49% HCOOH

temp. (°C)			150	250	250	350
time (h)			1	0.5	10	0.5
no.	compound	MW				
11	1-dodecene	168	–	–	–	–
12	dodecane	170	–	–	–	0.2
13	2-dodecene	168	–	–	–	0.3
15	3-dodecene	168	–	–	–	–
19	1-dodecylamine	185	42	11	0.7	2.9
20	1-dodecanol	186	–	–	–	6.1
21	*N*-methyl-1-dodecylamine	199	–	–	–	–
22	*N,N*-dimethyl-1-dodecylamine	213	–	–	7.6	8.6
25	*N*-1-dodecylformamide	213	58	81	47	19
26	*N*-methyl-*N*-1-dodecylformamide	227	–	7.5	35	12
27	*N*-methyl-*N*-1-dodecylacetamide	241	–	–	2.1	1.4
28	*N*-acetyl-*N*-1-dodecylformamide	255	–	–	1.6	0.4
29	*N*-methyldi-1-dodecylamine	367	–	–	3.3	20
30	di-1-dodecylamine	353	0.7	–	2.8	29

N,N-Dimethyl-1-dodecylamine (**22**). A 46.0% conversion was observed after reacting *N,N*-dimethyl-1-dodecylamine **22** with 49% aqueous formic acid for 2 h at 350 °C to give **29**, **20** as major, and **26**, **11** and **12** as minor products.

Compound **22** was much less reactive at 250 °C in 49% aqueous formic acid for 0.5 h. Only a 7.3% conversion was observed with 1-dodecanol (**20**, 4.2%) and *N*-methyl-*N*-1-dodecylformamide (**26**, 2.2%) as the



Scheme 3

major products. Extending the reaction time to 10 h showed a 28.2% conversion with *N*-methyl-di-1-dodecylamine (**29**, 17.2%), *N*-methyl-1-*N*-dodecylformamide (**26**, 5.8%) and 1-dodecanol (**20**, 5.2%) as the major products. All products can be envisaged to arise through similar pathways to those described for 1-dodecylamine **19** (see above). Indeed the substrate **22** is formed as a product of the reaction of **19** under identical reaction conditions. The main pathways of conversion of **22** progress as shown in Scheme 3 through the intermediacy of the protonated (activated) intermediate **110**. Further reaction of this intermediate allows formation of **21** from which products **11** and **26** arise; and also formation of **30** from which **29** is formed. Alcohol **20** is generated *via* hydrolysis of **110**.

N,N-Dimethyl-1-butylamine (**3**). After 1 h at 250 °C in 49% formic acid, a 20.2% conversion of *N,N*-dimethyl-1-butylamine (**3**) was observed. The main product was *N*-methyl-*N*-1-butylformamide (**8**, 15.7%) formed *via* initial protonation of substrate **3** to yield the intermediate **112** which can undergo hydrolysis and loss of methanol to generate the intermediate secondary amine **113**. Formylation of **113** furnishes the observed product **8**. A smaller amounts of 1-butanol (**1**) is formed *via* hydrolysis of the intermediate **112**; and *N*-methyl-di-1-butylamine **7** *via* attack of the secondary amine **113** on the activated tertiary amine **112** (an alkylating agent) forming the desired product **7** and dimethylamine as a side product.

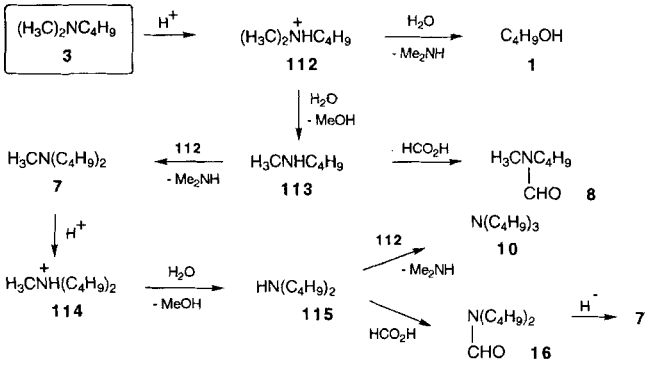
On increasing the reaction time to 2 h at 250 °C a wider product slate was observed with an increased conversion of 67.6%. The main product was *N*-methyl-di-1-butylamine (**7**, 28.3%) formed *via* the pathway described above, through intermediates **112** and **113**, but also *via* reduction of a minor product *N,N*-di-1-butylformamide (**16**, 1.3%). The other major products were *N*-methyl-*N*-1-butylformamide (**8**, 24.0%) and 1-butanol (**1**, 13.1%). A minor amount of tri-1-butylamine (**10**, 0.9%) was observed, formed probably *via* alkylation of the intermediate secondary amine **115** using the activated substrate **112** as the alkylating agent.

Table 8. Products from *N,N*-Dimethyl-1-dodecylamine (**22**), 49% HCOOH

temp.(°C)			250		350
time (h)			0.5	10	2
no.	compound	MW			
11	1-dodecene	170	0.4	–	1.2
12	dodecane	170	0.2	–	0.9
13	2-dodecene	170	0.2	–	–
15	3-dodecene	170	0.1	–	–
20	1-dodecanol	190	4.2	5.2	15
22	*N,N*-dimethyl-1-dodecylamine	210	93	72	54
26	*N*-methyl-*N*-1-dodecylformamide	230	2.2	5.8	1.3
27	*N*-methyl-*N*-1-dodecylacetamide	240	–	–	–
29	*N*-methyl-di-1-dodecylamine	370	–	17	28
30	di-1-dodecylamine	350	–	–	–

Table 9. Products from *N,N*-Dimethyl-1-Butylamine (**3**), 49% HCOOH

temp.(°C)			250	250
time(h)			1	2
no.	compound	MW		
1	1-butanol	56	2.0	13
3	*N,N*-dimethyl-1-butylamine	100	80	32
7	*N*-methyl-di-1-butylamine	140	2.5	28
8	*N*-methyl-*N*-1-butylformamide	120	16	24
10	tri-1-butylamine	190	–	0.9
16	*N,N*-di-1-butylformamide	160	–	1.3



Scheme 4

Conclusion

In conclusion, we have shown that the treatment of aliphatic primary, secondary and tertiary amines with formic acid at high temperatures effects a wide range of hydrolysis, cleavage, alkylation and elimination reactions, in addition to formylation. However, there is a notable absence of the C–C bond cleavages which were observed [5] in analogous treatments of *N*-alkylpyridines which supports the reaction mechanism postulated in our previous paper.

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