Preparation and Thermolysis of *N*-Ammonioamidates Containing Hydroxyl Group in Acyl Moiety

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The title *N*-ammonioamidates (aminimides) were prepared in satisfactory yields from lactones or α-hydroxy carboxylates. By the thermolysis of these aminimides in mesitylene, some types of urethane compounds were formed, depending on the structure of the aminimide and on the concentration of the solutions.

N-Ammonioamidates (aminimides) have been studied on the application to surfactants,[1,2] phase transfer catalysts,[3] and ion carriers in membrane transport systems.[4] As it is well known that they readily rearrange to isocyanates upon heating,[5] aminimides are considered as precursors of urethane or urea derivatives since isocyanates are convertible into urethane or urea compounds through a reaction with alcohols or amines.

On the other hand, the segmented-polyether-urethane polymer has recently been utilized as a "biomedical polymer material" for artificial hearts and artificial blood vessels.[6,7] Investigations of a new precursor of this type of urethane have been developed. As one of them, the preparation of a so-called "AB type" urethane-precursor which contains both a hydroxyl- and a functional group convertible into isocyanate in the same molecule have been reported.[8,9] But these are only a few studies regarding aminimide as an "AB type" precursor.[10,11]

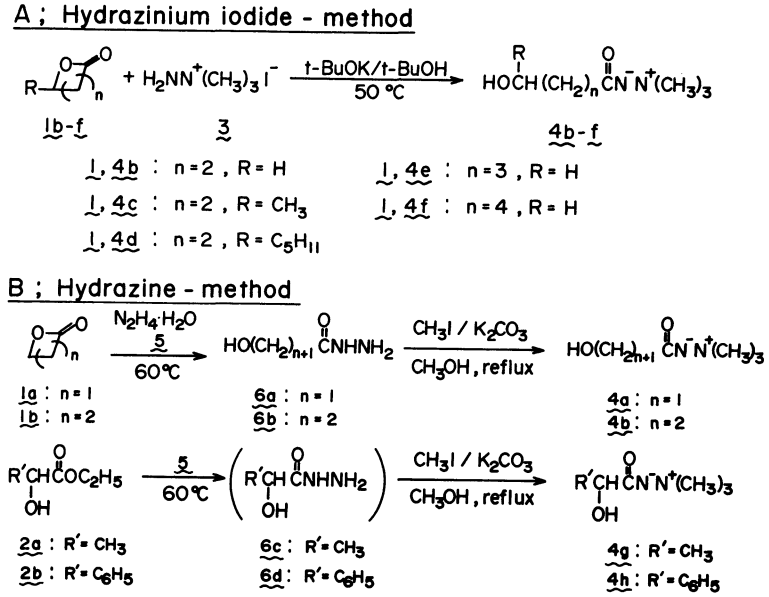
We have previously reported the synthesis of urethane-type crown ethers by a thermolytic reaction of aminimides containing an α-hydroxyoligo(ethylenoxy) group.[12] In the present paper, the preparations and properties of aminimides with a hydroxyl group in an acyl moiety from commercially available lactones or α-hydroxy carboxylates are described. Futhermore, the effects of the structure of aminimide and the solution concentration on the types of urethane compounds that were formed by thermolyses of aminimides in mesitylene are discussed.

Results and Discussion

Aminimides (**4**) were prepared from lactones (**1**) or α-hydroxy carboxylates (**2**) by the following two methods (Scheme 1).

(A) Hydrazinium Iodide Method. Aminimides were obtained by a one-step reaction between **1** and *N,N,N*-trimethylhydrazinium iodide (**3**), which was formed in quantitative yield from *N,N*-dimethylhydrazine and methyl iodide, in *t*-butyl alcohol in the presence of potassium *t*-butoxide.[13]

(B) Hydrazine Method. This method consisted of two-steps reactions. The preparation of acylhydrazines (**6**) from **1** or **2** and excess hydrazine hydrate (80%) (**5**) followed by a reaction with a large excess of methyl iodide (more than six folds to **1**) in methanol in the presence of potassium carbonate yielded aminimides.



Scheme 1.

Table 1. Yield and Melting Point of Aminimides (**4**)

Aminimide	Method[a)]	Yield[b,c)] %	Mp θ_m/°C
4a	B	75 (53)	125—126
4b	A	80 (62)	107—108
4b	B	82	
4c	A	93 (69)	92—94
4d	A	85 (63)	86—88
4e	A	94 (61)	95—96
4f	A	85 (68)	116—117
4g	B	86 (55)	108—109
4h	B	81 (59)	140(dec)

a) A; Hydrazinium iodide method, B; Hydrazine method. b) Crude yields based on **1** or **2**. c) Values in parentheses are yields after recrystallization.

After reactions involving both methods, crude products of aminimides were separated by extraction with dichloromethane and pure compounds were obtained by recrystallization from acetone or ethyl acetate. The isolated products were characterized by spectral and elemental analyses (Tables 4 and 5). The yields and melting points of **4** are listed on Table 1. Differences in the yields of *N*-trimethylammonio-4-hydroxybutanamidate (**4b**) from 4-butanolide (**1b**) were not observed between both methods, and **4b** was obtained in good yield (above 80%) by each method. However, in the hydrazinium iodide-method, aminimides were hardly obtained from 3-propanolide (**1a**) and α-hydroxy carboxylates (**2**). The hydrazine-method has some advantages: Using an inexpensive hydrazine hydrate (**5**) instead of *N,N,N*-trimethylhydrazinium iodide and being applicable to both lactones and α-hydroxy carboxylates. Intermediates, 3-hydroxypropanohydrazide (**6a**) and 4-hydroxybutanohydrazide (**6b**), obtained from **1a** and **1b**, respectively, were isolated by recrystallization from ethanol and identified by spectral analyses (Table 4). However, there was no difference in yield when crude acylhydrazine was used in a following reaction without further purification.

The thermolysis of prepared aminimides (**4a—h**) was carried out in mesitylene as an inert and high-boiling-point solvent. The aminimide was stirred at 160°C in mesitylene under a nitrogen atmosphere until the carbonyl absorption in the IR spectrum shifted to about 1700 cm^{-1} due to the formation of a urethane bond. The solvent was evaporated off and the residue (solid or semisolid) was extracted with chloroform to separate the soluble and insoluble portions (insoluble one; Fraction 3). The chloroform-soluble portion was further separated into the distillate (Fraction 1) and the residue (Fraction 2) by distillation at 120°C/2.7 Pa using a Kugelrohr apparatus.

The thermolysis was carried out in both dilute (1.00 g of aminimide/100 ml of mesitylene) and concentrated (1.00 g of aminimide/10 ml of mesitylene) conditions. The yields of reaction products and the weight percentage of each fraction are shown in Table 2.

In the thermolyses of **4a—f**, the distillates (Fraction 1) were white solids which showed one peak in GLC. Also, needle-like crystals were obtained by recrystallization from ethyl acetate. From their spectral data and elemental analyses, these fractions were identified as cyclic urethanes (**7a—f**). These compounds may be formed by the intramolecular addition of a hydroxyl group to an isocyanato group which was introduced by a thermolytic rearrangement of the aminimides. The properties and an elemental analysis of **7a—f** are shown in Tables 3 and 5.

The residual compounds in the distillation (Frac-

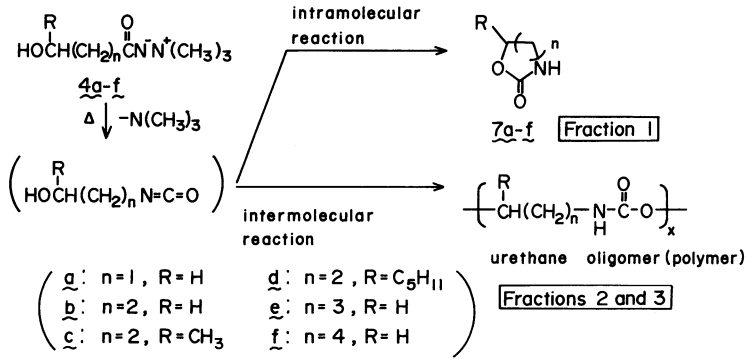
Table 2. Thermolysis of Aminimides (**4a—h**)

Run	Aminimide	Reaction system[a)]	Reaction time/h	Yield[b)] g	Fraction ratio/wt % Fr.1[c)]	Fr.2[d,e)]	Fr.3[f)]
1	**4a**	Dilute	6	0.57	≃100	Trace	0
2	**4a**	Concd	3	0.55	40	55 (157)	5
3	**4b**	Dilute	2	0.55	≃100	Trace	0
4	**4b**	Concd	3	0.52	30	65 (255)	5
5	**4c**	Dilute	3	0.65	≃100	Trace	0
6	**4c**	Concd	3	0.60	70	27 (270)	3
7	**4d**	Dilute	3	0.68	≃100	Trace	0
8	**4d**	Concd	3	0.69	55	45 (242)	0
9	**4e**	Dilute	3	0.56	32	38 (416)	30
10	**4e**	Concd	3	0.51	0	15 (425)	85
11	**4f**	Dilute	3	0.57	10	65 (555)	25
12	**4f**	Concd	3	0.54	0	10 (520)	90
13	**4g**	Dilute	5	0.61	37	18 (271)	45
14	**4g**	Concd	5	0.59	0	21 (285)	79
15	**4h**	Dilute	5	0.70	31	28 (354)	41
16	**4h**	Concd	5	0.68	0	17 (339)	83

a) Dilute system: 1.00 g (**4**)/100 ml (mesitylene); concd system: 1.00 g (**4**)/10 ml (mesitylene). b) Yield of the residue after removal of mesitylene. c) The distillate of chloroform-soluble portion using a Kugelrohr apparatus (120°C/2.7 Pa). d) The residue of chloroform-soluble portion by Kugelrohr-distillation. e) Values in parentheses are number-averaged molecular weights ($\overline{Mn}$) measured by a VPO in a chloroform at 25°C. f) The chloroform-insoluble portion.

Table 3. Characterization of cyclic urethanes (**7a—f**)

Compound	Starting aminimide	Mp θ_m/°C	IR (KBr pellet) ν/cm^{-1}	^{1}H NMR ($CDCl_3$) δ	MS (70 eV) *m*/*z*(rel. intensity)
7a	**4a**	88—89	3370, 1730	3.62(t, 2H), 4.44(t, 2H), 6.55(s, 1H)	87(M^+, 100), 59(49), 42(23), 28(43)
7b	**4b**	83—84	3275, 1690	1.96(q, 2H), 3.35(t, 2H), 4.30(t, 2H), 6.6—7.2(br, 1H)	101(M^+, 100), 56(39), 33(16), 29(23), 28(77)
7c	**4c**	98—99	3260, 1720	1.38(d, 3H), 1.75(m, 2H), 3.35(q, 2H), 4.41(m, 1H), 6.88(s, 1H)	115(M^+, 40), 71(21), 56(45), 43(66), 42(70), 30(100), 28(99)
7d	**4d**	102—103	3265, 1700	0.88(t, 3H), 1.1—2.1(m, 10H), 3.35(m, 2H), 4.25(m, 1H), 6.75(s, 1H)	171(M^+, 1), 100(88), 82(23), 74(41), 55(69), 43(30), 30(100)
7e	**4e**	61—62	3345, 1710	1.6—2.0(m, 4H), 3.15(q, 2H), 4.16(t, 2H), 6.47(s, 1H)	115(M^+, 77), 70(11), 56(21), 42(100), 30(60)
7f	**4f**	75—76	3350, 1700	1.5—2.0(m, 6H), 3.30(m, 2H), 4.20(t, 2H), 6.05(s, 1H)	129(M^+, 11), 68(40), 56(99), 43(82), 30(100)



Scheme 2.

tion 2) were semisolids which showed some peaks for longer retention times than that of the corresponding Fraction 1 in GLC. But their IR spectra and both the chemical shifts and integral ratios in their ^{1}H NMR were similar to those of the corresponding Fraction 1. Their molecular weights were determined by a VPO method (Table 2) and they were considered as the urethane oligomers with low molecular weights which might be formed by the intermolecular reaction between hydroxyl and isocyanato groups. It is probable that Fraction 2 was for the most part cyclic oligomers since their molecular weights were not so large and the existence of expected terminal groups in linear structures were not observed in the ^{1}H NMR spectra.

The chloroform-insoluble matter (Fraction 3) was a white or pale-brown solid and showed the same IR spectra as the corresponding Fraction 2. Thus, Fraction 3 could be considered as a linear or cyclic urethane polymer with a higher molecular weight than Fraction 2. However, their molecular weights and ^{1}H NMR spectra were not measured since they were only slightly soluble in water, alcohols, tetrachloromethane or other organic solvents.

The mechanism of the formation of the urethane compounds mentioned above is shown in Scheme 2.

In the thermolyses of α-hydroxyl type aminimides (**4g,h**), Fraction 1 was obtained as a pale-yellow liquid which showed some peaks in GLC and absorption peaks at 1830 and 1760 cm^{-1}, besides 1710 cm^{-1} in IR spectra. But the formation of compound **7**- type cyclic urethane was not detected by mass spectra. Additionally, their ^{1}H NMR spectra were complicated, so that their ingredients could not be identified. The IR spectra of Fraction 2 was similar to that of Fraction 1. Fraction 3 was a white solid which showed a strong absorption peak at 1740 cm^{-1}.

As shown in Table 2, the formation ratios of cyclic urethanes (**7**), urethane oligomers with low molecular weights, and urethane polymers was considerably affected by both the chain length (defined as the number of carbons between carbonyl and hydroxyl group of **4**) and the concentration of the solution. In the case of dilute conditions, five-membered (**7a**) and six-membered rings (**7b—d**) of cyclic urethanes were quantitatively formed from **4a** (chain length=2) and **4b—d** (chain length=3), respectively, and the formation of oligomer and polymer was not observed

(Table 2. Runs 1, 3, 5, and 7). On the other hand, oligomers were mainly obtained in the thermolysis of **4e** and **4f**. It seems reasonable that an intermolecular reaction took place prior to an intramolecular reaction in which a seven- (**7e**) or eight-membered ring (**7f**) compound was formed (Runs 9 and 11). In concentrated conditions, oligomer was also formed in a reaction of **4a—d** (Runs 2, 4, 6, and 8) and a polymer was obtained (for the most part) in the case of **4e** and **4f** (Runs 10 and 12).

Experimental

The ^{1}H NMR and IR spectra were taken on a JEOL JNM-PS-100 spectrometer and a Hitachi 260 spectrometer, respectively. The mass spectra were measured with a Hitachi RMU-6E mass spectrometer at an ionization potential of 70 eV. The GLC analyses were performed on a Shimadzu gas chromatograph GC-4CPT using a 1 m×3 mm column packed with 10% Silicone OV-1 on Uniport KS. The number-averaged molecular weight was measured with a Hitachi Perkin Elemer 115-type vapor-pressure osmometer in a chloroform solution at 25 °C. The starting materials were the commercial products of analytical reagent grade. Their purities were checked by GLC and IR, and they were purified by distillation when necessary. *N,N,N*-Trimethylhydrazinium iodide (**3**) was obtained as a white solid by the interaction of equivalent *N,N*-dimethylhydrazine and methyl iodide in diethyl ether at 20 °C and used without further purification. Mesitylene was distilled under a reduced pressure before use.

Preparation of N-*Trimethylammonio-4-hydroxybutanamidate (4b) by the Hydrazinium Iodide Method.* Potassium metal (4.7 g, 0.12 mol) was dissolved in 300 ml of *t*-butyl alcohol, and then **3** (20.2 g, 0.10 mol) and 4-butanolide (**1b**, 8.6 g, 0.10 mol) were slowly added, in turn, to the solution. After 5 h of stirring at 50 °C and subsequent neutralization by hydrochloric acid (to pH 8.0), the reaction mixture was filtered. The precipitate was washed with dichloromethane, and the solvent was removed from a combined solution of filterate and washings. The solid-liquid extraction of the residue with dichloromethane several times was followed by the filteration and evaporation of the extracts. This afforded 12.8 g of crude aminimide, as white solids (80%). The pure **4b** was obtained by recrystallization from acetone as fine white needles (9.9 g, 62%). Crude aminimide showed a similar IR spectrum as the corresponding pure one. Using a similar procedure, *N*-(trimethylammonio)hydroxyalkanamidates (**4c—5**) were also obtained (Table 1).

Preparation of N-*Trimethylammonio-3-hydroxypropanamidate (4a) by the Hydrazine Method.* A mixture of 3-propanolide (**1a**, 7.2 g, 0.10 mol) and hydrazine hydrate (80%) (9.4 g, 0.15 mol) was stirred at 60 °C for 5 h. After evaporation of the unreacted hydrazine, methyl iodide (85.2 g, 0.60 mol) was dropped into the suspension of the crude 3-hydroxypropanohydrazide (**6a**, 10.9 g, about 0.1 mol) and potassium carbonate (27.6 g, 0.20 mol) in 300 ml of methanol at 20 °C. The reaction mixture was stirred for 8 h at reflux temperature, and then an insoluble solid was separated by filtration. Excess methyl iodide and the solvent of the

Table 4. Characterization of aminimides (**4**) and acylhydrazines (**6**)

Compound	IR (KBr pellet)	^{1}H NMR ($CDCl_3$)	MS (70 eV)
	ν/cm^{-1}	δ	*m/z* (rel. intensity)
4a	3200, 1580	2.21(t, 2H), 3.33(s, 9H), 3.72(t, 2H), 4.7(br, 1H)	146(M^+, 3), 101(14), 59(100), 58(47)
4b	3300, 1580	1.77(m, 2H), 2.25(t, 2H), 3.35(s, 9H), 3.65(t, 2H), 5.4—5.9(br, 1H)	160(M^+, 2), 116(27), 101(39), 59(100), 58(62)
4c	3350, 1580	1.16(d, 3H), 1.65(m, 2H), 2.25(m, 2H), 3.37(s, 9H), 3.80(m, 1H), 5.5(br, 1H)	174(M^+, 3), 116(18), 101(36), 59(100), 58(56)
4d	3350, 1580	0.87(t, 3H), 1.1—1.6(m, 8H), 1.70(m, 2H), 2.28(m, 2H), 3.36(s, 9H), 3.70(m, 1H), 4.6—5.8(br, 1H)	230(M^+, 2), 159(42), 116(24), 101(40), 59(100), 58(71)
4e	3350, 1580	1.4—1.9(m, 4H), 2.06(t, 2H), 3.38(s, 9H), 3.60(t, 2H), 4.3(s, 1H)	174(M^+, 1), 116(14), 101(39), 59(100), 58(61)
4f	3300, 1580	1.2—1.8(m, 6H), 2.05(t, 2H), 3.40(s, 9H), 3.62(t+s, 2H+1H)	188(M^+, 2), 116(28), 101(34), 59(100), 58(54)
4g	3300, 1600	1.29(d, 3H), 3.40(s, 9H), 3.7—4.1(br, 1H), 4.00(q, 1H)	146(M^+, 1), 101(42), 59(100), 58(74)
4h	3330, 1600	3.22(s, 9H), 4.63(s+s, 1H+1H), 7.1—7.6(m, 5H)	149(M^+—59, 3), 106(66), 101(16), 77(72), 59(58), 58(100)
6a[a]	3300, 1630	2.16(t, 2H), 3.58(t, 2H), 4.6(br, 3H), 8—10(br, 1H)	104(M^+, 1) 73(20), 43(28), 32(100)
6b[b]	3300, 1640	1.63(m, 2H), 2.02(m, 2H), 3.40(t, 2H), 4.15(s, 2H), 4.47(t, 1H), 8.9(s, 1H)	118(M^+, 3), 87(10), 43(14), 32(100)

a) Mp; 95—97 °C. b) Mp; 94—96 °C.

Table 5. Elemental analysis of aminimides (**4**) and cyclic urethanes (**7**)

Compound	Molecular formula	Found (Calcd)/%		
		H	C	N
4a	$C_6H_{14}N_2O_2$	9.61 (9.65)	49.25 (49.30)	19.12 (19.16)
4b	$C_7H_{16}N_2O_2$	9.94 (10.07)	52.39 (52.48)	17.23 (17.48)
4c	$C_8H_{18}N_2O_2$	10.35 (10.41)	55.01 (55.15)	15.99 (16.08)
4d	$C_{12}H_{26}N_2O_2$	11.27 (11.38)	62.33 (62.57)	12.04 (12.16)
4e	$C_8H_{18}N_2O_2$	10.32 (10.41)	55.21 (55.15)	15.91 (16.08)
4f	$C_9H_{20}N_2O_2$	10.61 (10.71)	57.53 (57.42)	14.85 (14.88)
4g	$C_6H_{14}N_2O_2$	9.55 (9.65)	49.54 (49.30)	19.32 (19.16)
4h	$C_{11}H_{16}N_2O_2$	7.75 (7.74)	63.42 (63.44)	13.37 (13.45)
7a	$C_3H_5NO_2$	5.85 (5.79)	41.51 (41.38)	16.08 (16.09)
7b	$C_4H_7NO_2$	6.96 (6.98)	47.23 (47.52)	13.80 (13.85)
7c	$C_5H_9NO_2$	7.88 (7.88)	52.10 (52.16)	12.10 (12.17)
7d	$C_9H_{17}NO_2$	9.97 (10.01)	63.00 (63.13)	8.20 (8.18)
7e	$C_5H_9NO_2$	7.95 (7.88)	52.22 (52.16)	12.14 (12.17)
7f	$C_6H_{11}NO_2$	8.59 (8.58)	55.62 (55.80)	10.85 (10.84)

filtrate were evaporated off. The residue was extracted with acetone several times followed by filtration and evaporation of the extracts. This afforded 11.0 g of crude aminimide as white solids (75%). The pure **4a** was obtained by recrystallization from acetone as fine white needles (7.7 g, 53%). Using a similar procedure, aminimides (**4b**, **4g**, and **4h**) were also obtained (Table 1). A characterization of the aminimides (**4a—h**) and the isolated acylhydrazines (**6a** and **6b**) (recrystallization from ethanol) was accomplished by a standard method (Table 4). The elemental analysis of **4a—h** is shown in Table 5.

Thermolysis of 4a under Dilute Conditions. Dry mesitylene (100 ml) was heated at 160 °C in a 200-ml separable reaction flask under a nitrogen atmosphere. After the addition of **4a** (1.00 g, 6.84 mmol) to hot mesitylene, the solution was stirred until the absorption peak (based on the carbonyl group in the IR spectrum of aliquot) completely shifted to about 1700 cm^{-1} (6 h). Then, the solvent was evaporated off and the residue (0.57 g, solid), which was entirely dissolved in chloroform and showed one main peak in GLC, was distilled using a Kugelrohr apparatus (120 °C/2.7 Pa) to give 0.55 g of 2-oxazolidinone (**7a**) as fine white needles (92% yield based on **4a**). A very small amount of residue was observed. The thermolysis and work-up of the thermolytic products of **4b—d** under dilute conditions were undertaken in the same way as above since the crude product in each case was also wholly dissolved in chloroform. Perhydro-1,3-oxazin-2-one (**7b**, 86%), 6-methylperhydro-1,3-oxazin-2-one (**7c**, 95%), and 6-pentylperhydro-1,3-oxazin-2-one (**7d**, 90%) were obtained from **4b**, **4c**, and **4d**, respectively.

Thermolysis of 4e under Dilute Conditions. A solution of **4e** (1.00 g, 5.74 mmol) in dry mesitylene (100 ml) was heated as described above. The solvent was evaporated off and the residue (0.56 g, semisolid) was extracted with chloroform (100 ml) and filtered. The insoluble solid was washed with chloroform and dried *in vacuo* (pale brown; 0.17 g after drying). The chloroform extracts were combined, the solvent was evaporated off, and the residue (0.39 g) was distilled using the Kugelrohr apparatus at 120 °C/2.7 Pa to separate a distillate (0.18 g) as fine white needles and a residue (0.21 g) as a pale-brown solid. The distillate was identified as perhydro-1,3-oxazepin-2-one (**7e**, 27% yield based on **4e**). Perhydro-1,3-oxazocin-2-one (**7f**, 0.06 g, 8% yield based on **4f**) as a distillate, 0.37 g of a residue, and a 0.14 g of chloroform-insoluble solid were obtained from **4f** using a similar procedure.

The elemental analysis of **7a—f** is shown in Table 5.

Thermolysis of 4a under Concentrated Conditions. A solution of **4a** (1.00 g, 6.84 mmol) in dry mesitylene (10 ml) in a 50-ml separable reaction flask was heated at 160 °C for 3 h with stirring under a nitrogen atmosphere. The work-up of the reaction product was performed in the same way as the case of the thermolysis of **4e** under dilute conditions. Cyclic urethane (**7a**, 0.22 g, 37% yield based on **4a**) as a distillate, a 0.31 g of residue, and a 0.02 g of chloroform-insoluble solid were afforded. A thermolysis of aminimides (**4b—f**) under concentrated conditions was carried out using a similar procedure.

The results of thermolytic reactions, including α-hydroxyl type aminimides (**4g,h**), are presented in Table 2.

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