Aminimides. I. A general synthesis of aminimides from acyl hydrazides and their pyrolysis

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Acyclic, alicyclic, and aromatic bis-trimethylaminimides and a keto-substituted trimethylaminimide have been synthesized by a stepwise route of general applicability. Pyrolysis of the aliphatic aminimides resulted in a rearrangement to trimethylamine and isocyanate. The keto-isocyanate herein reported was synthesized in a convenient four-step sequence from dimethyl ketene dimer in a good yield, and provides an attractive new route to this type of difunctional compound. Pyrolysis of the bis-aminimides in the presence of polyhydroxylic materials gave polyurethanes.

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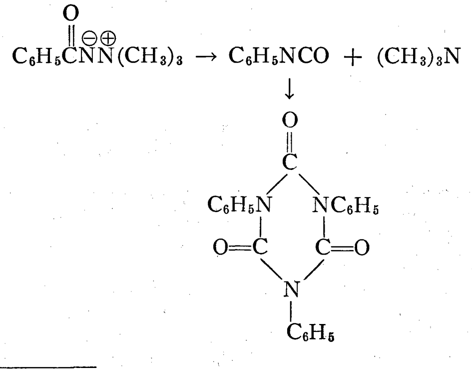
INTRODUCTION

The reported thermal rearrangement of trimethylamine benzimide to phenyl isocyanate (1)[1] prompted our investigation of the synthetic utility of this reaction. Subsequent to the initiation of this work, other workers (2) reported the thermolysis of trimethylamine benzimide.

The aminimide rearrangement, shown in eq. [1], is analogous to other carbon-to-nitrogen rearrangements, such as the Curtius, Schmidt, Hofmann, and Lossen rearrangements. Whether the rearrangement proceeds in a concerted fashion or by a nitrene intermediate has not been established firmly, although Wadsworth (3) has presented evidence for a concerted path in the pyrolysis of a cyclic aminimide. The mechanism is currently under study in our laboratories.

[1]


$$C_6H_5\overset{O}{\overset{\|}{C}}\overset{\ominus}{N}\overset{\oplus}{N}(CH_3)_3 \rightarrow C_6H_5NCO + (CH_3)_3N$$

In the previous reports on this reaction, phenyl isocyanate was isolated as the trimer, phenyl isocyanurate (1, 2). The tendency of aromatic isocyanates to trimerize when treated with heat and basic catalysts such as trimethylamine is well known (4). On the other hand, this tendency is much less pronounced for aliphatic isocyanates. Consequently, most of the present work was directed to the preparation and rearrangement of aliphatic aminimides.

RESULTS

Preparation

The route to the aminimides is outlined in eq. [2]. The acid hydrazides were usually prepared from the acid chlorides and unsymmetrical dimethylhydrazine. An alternate approach, the reaction of an ester and unsymmetrical dimethylhydrazine, has been reported to proceed poorly or not at all with aliphatic esters (5). 1,1-Dimethyl-2-(2,2,4-trimethyl-3-ketovaleryl)hydrazine (I) was prepared by opening the parent lactone with unsymmetrical dimethylhydrazine (eq. [3]).

For large-scale quaternizations of the acid hydrazide, methyl chloride was the reagent of choice since neutralization of the salt gives the aminimide and sodium chloride, which are easily separable. Neutralization of the methiodide salts leads to a mixture of the aminimide and sodium iodide, which are best separated by column chromatography. We have also observed

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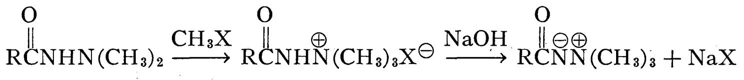
[1] We are indebted to Professor S. Wawzonek for the communication of these results before publication.

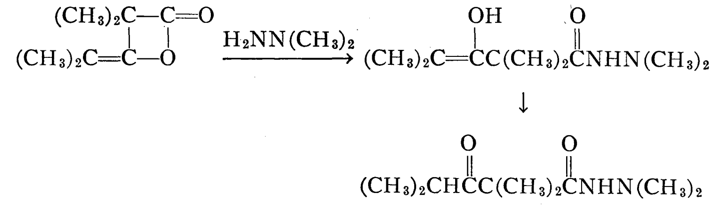
[2]



$$\mathrm{R\overset{O}{\overset{\|}{C}}NHN(CH_3)_2 \xrightarrow{CH_3X} R\overset{O}{\overset{\|}{C}}NH\overset{\oplus}{N}(CH_3)_3X^{\ominus} \xrightarrow{NaOH} R\overset{O}{\overset{\|}{C}}\overset{\ominus}{N}\overset{\oplus}{N}(CH_3)_3 + NaX}$$

X = I, Cl, or OTs

[3]



I

that column chromatography of the methyl chloride salts on neutral alumina leads directly to the aminimides.

The bis-aminimides and their precursors are reported in Table I. The quaternary salts lacking analytical data are those which were not purified but were converted directly into the aminimides. The aminimides were hygroscopic, crystalline compounds which began to decompose at temperatures slightly above the melting point. These compounds all exhibited the aminimide band (1) in the infrared in the range 1 550 to 1 580 cm^{-1}.

Rearrangement

Both trimethylamine 2,2,4-trimethyl-3-ketovalerimide and bis-trimethylamine sebacimide gave the corresponding isocyanates in a good yield when pyrolyzed. No dimer or trimer products were observed.

The reaction also appears to be a good method for the *in situ* preparation of isocyanates. Thus, both bis-trimethylamine azelaimide and isophthalimide gave polyurethane elastomers when heated in the presence of a hydroxyl-terminated polyester having a molecular weight of about 1 000.

The decomposition temperatures of the aminimides are considerably higher than those of the corresponding azides, indicating that trimethylamine is a poorer leaving group than nitrogen. Nevertheless, the decomposition of the aminimides from the solid state appears to be hazard free, with little heat evolution; thus the rearrangement offers a convenient and safe synthesis of isocyanates.

EXPERIMENTAL

All melting points and boiling points are corrected. The infrared spectra were obtained on a Perkin–Elmer 237B grating spectrophotometer. The elemental analyses were performed by Huffman Laboratories, Inc., Wheatridge, Colorado.

1,1-Dimethyl-2-(2,2,4-trimethyl-3-ketovaleryl)hydrazine (I)

Sixty grams (1.0 mole) of 1,1-dimethylhydrazine was added to 140 g (1.0 mole) of 2,2,4-trimethyl-3-hydroxy-3-pentenoic acid lactone (Eastman). The temperature of the mixture rapidly increased to 110°. An additional 20 g of 1,1-dimethylhydrazine was added and the mixture was refluxed for 6 h. When the reaction was cooled to room temperature, a quantitative deposit of white crystals (200 g) was obtained. A single recrystallization from Skellysolve B – benzene gave 160 g (80%) of the hydrazine, m.p. 76–78°.

Anal. Calcd. for $C_{10}H_{20}N_2O_2$: C, 59.97; H, 10.07; N, 13.99. Found: C, 60.39; H, 10.04; N, 13.89.

1,1,1-Trimethyl-2-(2,2,4-trimethyl-3-ketovaleryl) hydrazinium Iodide

A solution of 34.2 g (0.1 mole) of 1,1-dimethyl-2-(2,2,4-trimethylpentan-3-one) acid hydrazide and 14.2 g (0.1 mole) of methyl iodide in 150 ml of acetonitrile was refluxed for 24 h. Removal of the solvent gave 47 g (97%) of a pale-yellow crystalline solid, m.p. 173–176°. Recrystallization from methanol–ether gave 40 g, m.p. 176–177.5° (decomp.)

Anal. Calcd. for $C_{11}H_{23}N_2O_2I$: C, 38.60; H, 6.77; N, 8.19. Found: C, 38.80; H, 6.72; N, 7.56.

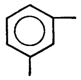
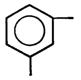
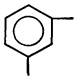
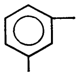
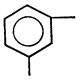
Trimethylamine 2,4,4-Trimethyl-3-ketovalerimide

A solution of 17.1 g (0.05 mole) of the hydrazinium iodide in 30 ml of water was titrated to the phenolphthalein end point with 47.3 ml of 1.06 *N* alcoholic potassium hydroxide. The solution was evaporated to dryness and extracted three times with 50 ml portions of chloroform. Evaporation of the chloroform yielded 10.0 g of the crude aminimide, m.p. 117–120°. Recrystallization from methanol–ether yielded 8.9 g, m.p. 121–121.5°.

Anal. Calcd. for $C_{11}H_{22}N_2O_2$: C, 61.65; H, 10.35; N, 13.07. Found: C, 61.85; H, 10.26; N, 12.88.

TABLE I

Bis-aminimides and precursors

R	X	Melting point (°C)	Yield (%)	Calculated (%) C	Calculated (%) H	Calculated (%) N	Found (%) C	Found (%) H	Found (%) N
$R(CONHN(CH_3)_2)_2$									
—(CH$_2$)$_7$—		117.5–118.5	44	—	—	—	—	—	—
—(CH$_2$)$_8$—		136.5–137.5	77	58.71	10.56	19.56	57.86	10.27	19.13
CH$_2$CH— | | CH$_2$CH— (*trans*)*		207	60	52.61	8.83	24.54	52.27	8.58	23.68
		255–256	75	57.58	7.52	22.39	57.80	7.09	22.39
$R(CONH\overset{\oplus}{N}(CH_3)_3X^{\ominus})_2$									
—(CH$_2$)$_7$—	I	172–174.5 (decomp.)	87	32.39	6.16	10.07	32.66	6.00	9.65
—(CH$_2$)$_7$—	OTs	170–172 (decomp.)	81	54.01	7.50	8.69	53.79	7.28	8.02
—(CH$_2$)$_8$—	Cl	240 (decomp.)	72	—	—	—	—	—	—
CH$_2$CH— | | CH$_2$CH— (*trans*)*	I	207–216 (decomp.)	99	—	—	—	—	—	—
	I	203–206 (decomp.)	96	—	—	—	—	—	—
	Cl	193 (decomp.)	75	—	—	—	—	—	—
$R(CO\overset{\ominus}{N}\overset{\oplus}{N}(CH_3)_3)_2$									
—(CH$_2$)$_7$—	OTs†	146–147.5	50	59.96	10.74	18.65	60.18	10.36	18.43
—(CH$_2$)$_8$—	Cl†	142–144	78	61.11	10.90	17.82	60.68	10.70	17.18
CH$_2$CH— | | CH$_2$CH— (*trans*)*	I†	177–179	60	56.22	9.44	21.86	55.81	9.42	21.29
	I†	251	96	60.41	7.97	20.13	59.91	7.94	19.64
	Cl†	251	70	—	—	—	—	—	—

*From the *trans*-diacid chloride (Sohio).
†Of the starting salt.

Bis-1,1-dimethyl-2-sebacylhydrazine

The preparation of bis-1,1-dimethyl-2-sebacylhydrazine is typical of the general procedure for preparing the acid hydrazides from the parent acid chloride.

A solution of 99.2 g (0.830 equivalent) of sebacyl chloride in 150 ml of hexane was added slowly (1.5 h) to a stirred solution of 117 g (1.95 equivalents) of 1,1-dimethylhydrazine in 200 ml of hexane, the reaction temperature being kept at 5–10°. After the addition, the mixture was stirred at room temperature for another 12 h and then filtered; the solids thus obtained were dissolved in 800 ml of water and treated with 33.2 g (0.830 mole) of sodium hydroxide dissolved in 300 ml of water. The resultant solution was then stripped of volatiles on the flash evaporator and the solid residue was extracted with 3 × 400 ml of hot acetone. Evaporation of a portion of the combined acetone extracts and cooling gave a first crop of crystals (79 g, 67%), m.p. 134–137°. Further concentration of the filtrate gave an additional 9.9 g (7%) with the same melting point. A small portion of the combined crops, when twice recrystallized from ethanol–acetone, gave the analytical sample, m.p. 136.5–137.5°.

Bis-1,1,1-trimethyl-2-azelaylhydrazinium Iodide

This preparation is typical of the hydrazinium salts prepared with either methyl iodide or methyl tosylate.

A solution of 13.6 g (0.10 equivalent) of bis-1,1-dimethyl-2-azelaylhydrazine and 28 g (0.20 equivalent) of methyl iodide in 40 ml of methanol was refluxed for 24 h. Removal of the solvent gave 27.6 g of a yellow solid, m.p. 168–173°. Recrystallization from methanol–ether gave 24.2 g (87%), m.p. 170–173°. Two further recrystallizations gave the analytical sample, m.p. 172–174.5°.

Bis-1,1,1-trimethyl-2-sebacylhydrazinium Chloride

This preparation is an example of larger scale quaternizations with methyl chloride.

In a 2 l Parr bomb equipped with a stirrer, 111 g (0.388 mole) of bis-1,1-dimethyl-2-sebacylhydrazine was partly dissolved in a solution consisting of 275 ml of isopropanol, 100 ml of water, and 2 g of sodium bicarbonate. The bomb was heated to 100° and the total pressure was adjusted to 70 p.s.i. by the addition of methyl chloride gas. The pressure was maintained until the uptake of methyl chloride was no longer evident (about 5 h). The bomb was cooled and the product recrystallized as flat plates (93 g), m.p. 237–240° (decomp.). Evaporation of the mother liquor and crystallization of the residue gave an additional 15 g (total yield 72%).

Bis-trimethylamine Isophthalimide

A solution of 4.80 g of bis-1,1,1-trimethyl-2-isophthalylhydrazinium iodide in 10 ml of water was treated with 11.1 ml of 1.60 *N* aqueous sodium hydroxide and evaporated to dryness. A 1.00 g portion of the dry solid residue was chromatographed on neutral alumina, with 10% methanol – 90% benzene as eluent. Evaporation of the eluate gave 2.6 g (96%, dried *in vacuo*) of the aminimide, m.p. 248°, which gave a negative test for I^- ion.

Pyrolysis of Bis-trimethylamine Sebacimide

A well-dried 5.0 g sample of the aminimide was placed in a small, pear-shaped flask set up for a short-path distillation at a water pump. The flask was immersed in an oil bath. As the bath temperature approached 200°, trimethylamine was evolved rapidly from the melt and the product began to distill. A total of 2.5 g (80%) of octamethylene diisocyanate, b.p. 165–168° at 14 mm, n_D^{25} 1.4542, was collected. A slightly brown residue was left in the pot. Redistillation gave 1.9 g, b.p. 153–155° at 12 mm, n_D^{25} 1.4533 (reported (6) b.p. 146–148° at 11 mm). The dimethylurethane had m.p. 113–114° (reported (6) m.p. 111–112°).

Pyrolysis of Trimethylamine 2,4,4-Trimethyl-3-ketovalerimide

The aminimide (6.28 g) was placed in the short-path distillation apparatus at an aspirator pressure of 13 mm. The surrounding heating bath was heated rapidly to 190–200°, whereupon trimethylamine was evolved vigorously from the melt and the product began to distill with a head temperature of 65°. The head temperature began to rise slowly to 160° as some of the undecomposed starting material began to distill (sublime) over. The contents of the receiver weighed 5.2 g; there was no pot residue. When left, the starting material almost completely crystallized from the liquid product. The liquid portion was redistilled to give 3.4 g (75%) of 2-isocyanato-2,4-dimethylpentan-3-one, b.p. 69° at 12 mm, n_D^{25} 1.4304. On redistillation, the material boiled between 173–174° at 731 mm, n_D^{25} 1.4304. The infrared spectrum showed the isocyanate group as a doublet at 2 250 (vs) and 2 200 cm^{-1} (s) and the keto group at 1 725 cm^{-1}.

Anal. Calcd. for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.04. Found: C, 62.10; H, 8.51; N, 9.14.

The isocyanate could also be obtained from the methiodide salt without isolation of the aminimide. In this procedure, 10.3 g (0.0300 mole) of the keto-methiodide salt was titrated to the phenolphthalein end point with 28.2 ml of 1.06 *N* alcoholic KOH. The mixture was evaporated to dryness. A 10.0 g portion of the residue was then placed in a flask set up for a short-path distillation at atmospheric pressure. With the bath temperature in the range of 200–240°, the isocyanate distilled over at a head temperature range of 60–170° (the early vapors were entrained in trimethylamine). The cloudy liquid distillate was redistilled to give 2.92 g (72%) of a clear liquid, b.p. 71–74° at 14 mm, n_D^{25} 1.4307.

The isocyanate readily reacted with water to yield the urea as long needles. After three recrystallizations from methanol, the analytical sample melted at 166–168° and remelted at 170–172°.

Anal. Calcd. for $C_{15}H_{28}N_2O_3$: C, 63.35; H, 9.92; N, 9.85. Found: C, 63.50; H, 9.68; N, 10.01.

In Situ Pyrolysis

In a small aluminium dish on an asbestos pad on a hot plate, 0.766 g (0.055 equivalent) of bis-trimethylamine isophthalimide, 5.010 g (0.051 equivalent) of a hydroxyl-terminated polyester (prepared from adipic acid, diethylene glycol, and trimethylol propane, hydroxyl value 57), and a drop of stannous octoate were mixed at 140° with the bulb end of a thermometer. When the maximum amount of aminimide dissolved, the cup was transferred to the bare metal surface of the hot plate (about 250°). Profuse evolution of trimethylamine and foaming took place as the temperature of the thermometer rapidly rose to about 240°. The sample quickly changed to a tacky yellow elastomer and the cup was removed from the hot plate.

An infrared spectrum of the elastomeric film showed the characteristic urethane NH absorption at 3 320 cm^{-1} (s), the ester and urethane carbonyl band at 1 760 – 1 680 cm^{-1} (vs), phenyl absorption at 1 600 cm^{-1}, and the urethane "amide II" band at 1 530 cm^{-1}.

Similar results were obtained in the pyrolysis of bis-trimethylamine azalaimide with the polyester.

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