Aminimides XIII Long Chain Aminimides and Isocyanates

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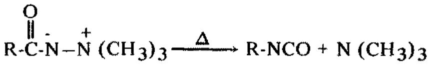
ABSTRACT

Aminimides were prepared from esters of stearic, oleic, linoleic, phenylstearic, 9,10-dihydroxystearic, ricinoleic and dimer acids. Thermolysis of the aminimides to isocyanates was carried out in a wiped film molecular still and by vacuum distillation of a bulk sample. The latter process is suitable only for small samples of the simple aminimides. Acyl N,N-dimethylhydrazides, which are aminimide precursors, can generally be prepared by dehydration of carboxylic acid-*unsym*-dimethylhydrazine mixtures. Details of the preparation of dimer acid diisocyanate by this route are presented. Some information on the use of long chain aminimides as emulsifiers for halocarbon mixtures, e.g., bromoform-water, is presented.

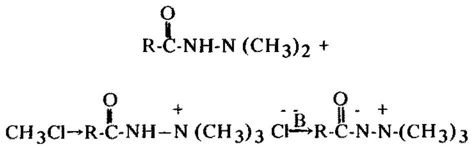
INTRODUCTION

Aminimides have been known for some time (1) but have received more attention recently because some of them undergo thermolysis to give an isocyanate and a tertiary amine (2,3).



$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}\overset{-}{N}{-}\overset{+}{N}(CH_3)_3 \xrightarrow{\Delta} R{-}NCO + N(CH_3)_3}$$

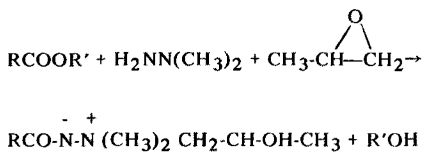
The aminimide moiety can be generated in several ways. For example, acyl N,N-dimethylhydrazides can be quaternized and the resulting salt treated with base to form the aminimide (4). A simpler route has been reported in which an ester, 1,1,1-trimethylhydrazinium chloride, and sodium alkoxide are mixed, and the aminimide forms directly (in situ route, 5). Since the hydrazinium salt is readily made and is stable, aminimide preparations by this route are quite convenient.



$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}NH{-}N(CH_3)_2 + CH_3Cl \rightarrow R{-}\overset{\overset{O}{\|}}{C}{-}NH{-}\overset{+}{N}(CH_3)_3\,\overset{-}{Cl} \xrightarrow{B} R{-}\overset{\overset{O}{\|}}{C}{-}\overset{-}{N}{-}\overset{+}{N}(CH_3)_3}$$

$$\mathrm{RCOOCH_3 + H_2N{-}\overset{+}{N}(CH_3)_3\,\overset{-}{Cl} + NaOCH_3 \rightarrow RCO{-}\overset{-}{N}{-}\overset{+}{N}(CH_3)_3 + 2MeOH + NaCl}$$

Recently a route was reported in which the sodium methoxide was unnecessary. In this route the reaction of an ester with 1,1-dimethylhydrazine and an epoxide gives the aminimide and an alcohol according to the following equation (6). Aminimides of this type can also be made by reaction of an epoxide such as propylene oxide with an acyl N,N-dimethylhydrazide (7). Thermolysis of these aminimides to isocyanates requires that the hydroxyl group be masked if R is normal.



$$\mathrm{RCOOR' + H_2NN(CH_3)_2 + CH_3{-}CH\overset{O}{\frown}CH_2 \rightarrow RCO{-}\overset{-}{N}{-}\overset{+}{N}(CH_3)_2\,CH_2{-}CH{-}OH{-}CH_3 + R'OH}$$

Isocyanate preparation via aminimide pyrolysis offers several advantages over the usual routes involving azide or phosgene. The isocyanate group can be generated at will in molecules that bear reactive groups such as amino or hydroxyl. Inexpensive substrates such as carboxylic acids or esters are used instead of amines or acid chlorides and the reactants are less corrosive and more easily handled.

Aminimides in the C_9-C_{15} range have been claimed (4) to be useful as cold water detergents and, more recently, a report on their surfactant properties was made (8). The purpose of this report is to describe the preparation of long chain aminimides by several routes, to describe a general and simple method for the preparation of acyl N,N-dimethylhydrazides, and to give some information on the use of aminimides as halocarbon emulsifiers.

EXPERIMENTAL PROCEDURE

Stearate, oleate and linoleate esters used in this work were all over 97% pure. Ethyl phenylstearate was prepared from phenylstearic acid in which the phenyl group was located mainly at positions C-8 through C-13 with lesser amounts of C-4 through C-17 isomers. Published procedures were used to prepare the dimethyl ester of dimer acid (97-99% dimer, Emery Empol 1010) (9), 1,1,1-trimethylhydrazinium chloride (10), and methyl *threo*-9,10-dihydroxystearate (11).

Isocyanate values were measured by the method described in Siggia (12). NMR spectra were run in deuterochloroform and are reported in terms of delta (δ, ppm).

1,1,1-Trimethylamine-2-Stearoylimide

Into a three-necked flask equipped with a stirrer and a reflux condenser was placed methyl stearate (10 g, 0.034 mole), *t*-butyl alcohol (100 ml) and 1,1,1-trimethylhydrazinium chloride (3.8 g, 0.034 mole). This mixture was stirred while sodium methoxide (1.8 g, 0.033 mole) was poured in. The resulting suspension was then heated to reflux and stirred 3 hr. After cooling, the *t*-butyl alcohol was stripped to give a white solid that was triturated twice with portions (75 ml each) of hot hexane. Concentration of the hexane gave 1,1,1-trimethylamine-2-stearoylimide (9.3 g, 82%) as a white powder. Recrystallization from hexane gave long, white needles mp 77-79 C. Calculated for $C_{23}H_{48}N_2O_2$: C, 71.82; H, 12.58; N, 7.28; Found: C, 71.78; H, 12.42; N, 7.39. The IR spectrum (Nujol) showed the 1580 cm^{-1} aminimide carbonyl absorption (3).

1,1,1-Trimethylamine-2-Oleoylimide and *cis*-8-Heptadecenyl Isocyanate

The aminimide was prepared as above and was purified by recrystallization from hexane at -80 C. The NMR spectrum showed absorptions at 0.72-2.3 (m, 31H, aliphatic chain), 3.50 (*s*, 9H, $\overset{-}{N}{-}\overset{+}{N}(CH_3)_3$) and 5.52 ppm (t, 2H, vinyl). The IR showed the 1580 cm^{-1} (liquid film) absorption.

On vacuum distillation, 1,1,1-trimethylamine-2-oleoylimide (3.7 g) was converted to *cis*-8-heptadecenyl isocyanate. At a pot temperature around 180 C trimethylamine was liberated and the isocyanate co-distilled at a head

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TABLE I

Emulsification of Halocarbon-Water Mixtures With Aminimides

Experiment	Organic phase	Aminimides	Wt %	Stability of emulsion
1	Trichloroethylene (1.45 g/cc)	TO[a]	1	About 24 hr, creaming
2	Trichloroethylene (1.45 g/cc)	TO	2	Over 48 hr
3	Trichloroethylene (1.45 g/cc)	DHPL[b]	1	About 24 hr, creaming
4	Trichloroethylene (1.45 g/cc)	DHPL	2	Over 48 hr
5	Trichloro trifluoroethane (1.69 g/cc)	TO	2	Over 48 hr, translucent
6	Trichloro trifluoroethane (1.69 g/cc)	DHPO[c]	2	Over 48 hr, translucent
7	Carbon tetrachloride (1.69 g/cc)	DHPR[d]	2	Over 30 hr
8	Bromoform (2.89 g/cc)	TO	2	Clear upper layer begins to appear at 15 hr
9	Bromoform (2.89 g/cc)	DHPL	2	Small droplet of liquid at 24 hr

[a] TO = Trimethylamine oleoylmide.

[b] DHPL = Dimethyl-(2-hydroxypropyl)amine linoleoylimide.

[c] DHPO = Dimethyl-(2-hydroxypropyl)amine oleoylimide.

[d] DHPR = Dimethyl-(2-hydroxypropyl)amine ricinoleoylimide.

temperature of 163 C at 0.4 mm pressure (75% yield). The resulting colorless oil showed NMR absorptions similar to those of the aminimide, except that the absorption at 3.50 ppm was gone and a new absorption at 3.28 ppm (*t*, 2H, -CH_2NCO) appeared. The IR spectrum (liquid film) had bands at 2270 (NCO) and 3310 cm^{-1} (CH = CH) and showed the double bond is still in the *cis* configuration. Calculated for $C_{18}H_{33}NO$: NCO, 15.05%; Found: 14;1%.

Pyrolysis of a larger sample of 1,1,1-trimethylamine-2-oleoylimide (139 g) in a wiped film molecular still gave a 71% yield of *cis*-8-heptadecenyl isocyanate. Operating parameters for the still were: jacket temperature, 230-250 C; pressure, 3-5 mm; condenser temperature, 45 C. The pale yellow product was decolorized with charcoal to give a colorless oil (82 g) with an isocyanate value of 14.1%.

1,1,1-Trimethylamine-1-Linoleoylimide and *cis,cis*-8,11-Heptadecadienyl Isocyanate

A sample of 1,1,1-trimethylamine-2-linoleoylimide was purified by preparative thin layer chromatography. The resulting oil showed NMR absorptions at 5.54 (*m*, 4H, vinyl hydrogen), 3.50 (*s*, 9H, $\bar{N}$-$\overset{+}{N}(CH_3)_3$), 2.86 (*t*, 2H, C=C-CH_2-C=C) and 2.4-0.7 ppm (*m*, balance of aliphatic hydrogen).

Vacuum distillation of the crude aminimide (11.7 g) gave the isocyanate (5.0 g, 50% yield) as a colorless oil, bp 163 C at 0.4 mm pressure. The IR spectrum (liquid film) showed absorptions at 3010 and 1650 (CH=CH), 2270 (NCO) and 1745 cm^{-1} (weak, COOR). The NMR spectrum showed the 3.50 ppm band was gone and a new absorption at 3.23 ppm (*t*, 2H, -CH_2NCO) appeared.

1,1,1-Trimethylamine-2-Phenylstearoylimide and Phenylheptadecyl Isocyanate

The aminimide was an oil with IR absorptions (liquid film) at 1580 (carbonyl), 1500, 765 and 710 cm^{-1} (aromatic) and NMR absorptions at 7.42 (*s*, 5H, phenyl), 3.42 (*s*, 9H, $\bar{N}$ $\overset{+}{N}(CH_3)_3$) and 2.2-0.7 ppm (*m*, 34H, balance of aliphatic hydrogen). Vacuum distillation of this material (5 g) resulted in the liberation of trimethylamine but no isocyanate was recovered. Instead a greenish glass with a strong IR band at 1680 cm^{-1} remained as a pot residue. The isocyanate was prepared by heating the aminimide in xylene at reflux for 3 days. The xylene was then stripped and the residue distilled in a molecular still to give a 20-30% yield of isocyanate.

1,1,1-Trimethylamine-2-(*threo*-9,10-Dihydroxystearoyl) Imide

The product was recrystallized from hexane-benzene as a white powder mp 73-74 C. Calculated for $C_{21}H_{44}N_2O_3$: Hydroxyl Value, 302; C, 67.68; H, 11.91; N, 7.51. Found: Hydroxyl Value, 334; C, 68.06; H, 11.85; N, 7.47. On heating, trimethylamine was liberated and a translucent resin formed.

1,1,1-Trimethylamine-2-Ricinoleoylimide

The aminimide is a clear, very viscous oil that is water soluble. The NMR spectrum shows absorptions at 5.60-5.32 (*m*, 2H, vinyl), 3.62 (*m*, 2H, CHOH, OH buried) 3.38 (*s*, 9H $\bar{N}$ $\overset{+}{N}(CH_3)_3$) and 2.40-0.68 ppm (*m*, 29H, balance of aliphatic hydrogen). Calculated for $C_{21}H_{42}N_2O_2$: C, 71.14; H, 11.93; N, 7.90. Found: C, 71.20; H, 12.02; N, 7.74.

General Procedure-Preparation of N,N-Dimethylhydrazides

To a glass-lined autoclave containing benzene solvent was charged a carboxylic acid (1 mole-eq) and *unsym*-dimethylhydrazine (4 mole-eq). The autoclave was sealed and heated to 150 C for 24 hr. On cooling the autoclave to room temperature the contents, which formed two layers (aqueous and organic), were decanted. The organic layer was stripped on a rotary evaporator. The residue was dissolved in methanol and passed through an alkaline ion exchange column to remove unreacted or, in the case of diacids, partially reacted materials. The methanol was then stripped and the product purified by recrystallization or distillation.

Several mono and dicarboxylic acids were treated in this manner and the pure N,N-dimethylhydrazides were obtained in 60-80% yields. Application of this method to dimer acid is reported in detail.

Dimer Acid Diaminimide and Diisocyanate

Di-N,N-dimethylhydrazide: Into a glass-lined, two liter autoclave containing benzene (700 ml) was placed dimer acid (283 g, 0.5 moles) and unsymmetrical dimethylhydrazine (120 g, 2.0 moles). The autoclave was sealed and heated to 110 C for 24 hr. The resulting solution was cooled, stripped and the residue dissolved in 80% methanol. The methanol solution was then passed through a strongly basic ion exchange column (Rexyn 201 converted to OH form with NaOH) to remove unreacted or partially reacted dimer acid. After another stripping, the product was a pale yellow glass (Gardner 1-2) with IR absorption (liquid film) at 3210 (N-H), 1670 (amide I) and 1545 cm^{-1} (amide II).

Quaternization: The di-N,N-dimethylhydrazide (216 g, 0.331 moles) was added to a glass-lined, two liter autoclave containing benzene (300 ml) and acetonitrile (450 ml). Methyl chloride gas was then added to the autoclave until a constant pressure of 45 psig was attained. The autoclave was sealed and heated at 75 C under autogenous pressure for 12 hr.

After it had been cooled and vented, the autoclave was opened and the solid white mass it contained was broken up and filtered. On drying under vacuum the product turned light brown and became gummy. The yield in this step was quantitative.

Dimer diaminimide: The quaternary chloride (200 g, 0.266 moles) was dissolved in dilute methanol and passed through a strongly basic (Rexyn 201) ion exchange column in order to convert the salt to the aminimide. After stripping, a very viscous liquid resulted (155 g, 86% of theory). The aminimide carbonyl absorption at 1575 cm^{-1} (liquid film) was the only carbonyl absorption observed in the IR spectrum.

Dimer diaminimide (in situ route): In a two liter three-necked flask fitted with a stirrer, thermometer and reflux condenser were placed methanol (150 ml) and sodium (4.6 g, 0.2 moles). After the sodium had reacted, the methanol was stripped. Anhydrous isopropyl alcohol (300 ml), dimer acid dimethyl ester (60 g, 0.10 moles) and 1,1,1-trimethylhydrazinium chloride (22 g, 0.20 moles) were then added to the flask and the mixture heated at 50 C and stirred for 4 days.

The mixture was then cooled, filtered through filter aid and reduced to nonvolatiles. These were dissolved in chloroform and again passed through filter aid. The chloroform was removed and the residue dissolved in 80% methanol and passed through a strongly basic ion exchange column. Solvents were finally removed to give dimer diaminimide (57.5 g, 85% of theory) as a very viscous liquid.

Dimer diisocyanate: A thin film molecular still with carbon blades, externally heated to 270-285 C and with an internal pressure of 0.5 mm Hg was used to decompose the aminimide. The dimer diisocyanate was recovered in a 75% conversion (average of several runs) with NCO values 12-13% (theory 15.02%). The mobile liquid was nearly colorless and has exhibited a shelf stability in excess of 1 year.

1,1-Dimethyl-1-(2-Hydroxypropyl)-2-Stearoylimide

Methyl stearate (20 g, 0.067 moles), *unsym*-dimethylhydrazine (5 g, 0.083 moles), propylene oxide (5 g, 0.083 moles) and isopropyl alcohol (100 ml) were added to a Wheaton bottle. The bottle was sealed and heated on a steam bath overnight. The contents were cooled, stripped under vacuum and recrystallized from hexane to give the pure product in essentially qualitative yield, mp 72-73 C. Calculated for $C_{23}H_{48}N_2O_2$: C, 71.82; H, 12.58; N, 7.28. Found: C, 71.78; H, 12.42; N, 7.39.

The related oleate, linoleate and ricinoleate derivatives used as emulsifiers were prepared similarly. Commercially available esters were used for these preparations and the products were not purified.

Emulsification Studies

Some of the long chain aminimides were checked as emulsifiers for halocarbon-water mixtures. In a typical example, water (20 ml) and 1,1-dimethyl-1-(2-hydroxypropyl)-2-oleoylimide (1 g) were shaken together to form a thick, foamy mixture. Trichlorotrifluoroethane (20 ml) was then added and the mixture shaken by hand for ca. 1 min. The resulting emulsion was translucent and free flowing (example 6). Additional examples are listed in Table I.

DISCUSSION

The preparation of aminimides from fatty esters proceeds as it does with other esters, however, some materials do present problems in purification. When the in situ route to trimethylaminimides is used, pure dry alkoxide must be used; otherwise the reaction will not go to completion. If this happens, for example, with oleate or linoleate esters, the aminimide product cannot be easily freed of residual ester and it will co-distill on thermolysis. Of interest, particularly in the preparation of fatty aminimides, is the route involving dehydration of fatty acid-*unsym* dimethylhydrazine mixtures to give the corresponding acyl N,N-dimethylhydrazides. The formation of hydrazides by this route is general, and any unreacted acid can be removed from the N,N-dimethylhydrazide because of solubility or acidity differences. The subsequent reactions, alkylation and neutralization, go in practically quantitative yields. Triglycerides react readily via the in situ route to give the aminimide; however in a sample tried (hydrogenated tallow), the glycerine could not be removed from the product and it prevented the formation of isocyanate on thermolysis.

Thermolysis of fatty aminimides gives isocyanates, but several methods of decomposition can be used depending on the amount and structure of aminimide to be decomposed. For preparation of small amounts (<10 g) of isocyanates from aminimides of stearate, oleate and linoleate, a simple, inefficient vacuum distillation works reasonably well. Around 150-180 C the sample begins to liberate trimethylamine and the isocyanate distills as a colorless liquid. When this method is applied to larger batches of aminimide, the yields of isocyanate decrease and the amounts of pot residue increase. Apparently the trimethylamine that is generated cannot be removed as fast as it is formed and it catalyzes the formation of isocyanate telomers. Attempted vacuum distillation of phenylstearate or dimer acid aminimides gave trimethylamine but no isocyanate was isolated, even in small batches.

Of greater utility are decompositions in a wiped film molecular still, or in an inert high-boiling solvent such as xylene or mesitylene. Dimer acid diisocyanate, for example, was formed in good yield on molecular distillation of the related diaminimide. Solvent decompositions are also quite effective, though no attempt was made to optimize the process in this case.

Long chain aminimides show a wide range of solubilities. Trimethylaminimides from oleate, linoleate and phenylstearate, for example, are miscible with hexane and ethanol and, when shaken with water at low levels (<10% w/w), form a clear to translucent gel. Those from more hydroxylated acids such as 9,10-dihydroxystearic or ricinoleic are water soluble. As a class of compounds, long chain aminimides are good emulsifiers especially for halocarbons and other systems requiring high HLB (13) values. Table I summarizes results on some emulsions prepared from halocarbons. Even mixtures with large density differences such as bromoform (2.80 g/cc) water were easily emulsified. Admixture of the aminimide and water resulted in a gelatinous mixture, as indicated above, but the emulsions had usually about the same viscosity as water.

REFERENCES

1. Sisler, H.H., G.M. Omietanski and B. Rudner, Chem. Revs. 57:1021 (1957).
2. Wawzonek, S., and R.C. Gueldner, J. Org. Chem. 30:3031 (1965).
3. McKillip, W.J., L.M. Clemens and R. Haugland, Can. J. Chem. 45:2613 (1967).
4. Brocklehurst, P., Brit. Pat. 1,003,926 (1963).
5. McKillip, W.J., L.M. Clemens and R. Haugland, Can. J. Chem. 45:2619 (1967).
6. Slagel, R.C., J. Org. Chem. 33:1374 (1968).
7. Sedor, E.A., R.E. Freis and R.A. Grimm, presented in part at the ACS Second Central Meeting, Columbus, Ohio, June 1970.
8. Kameyama, E., Y. Minegishi and T. Kuwamura, Kogyo Kagaku Zasshi 73:1018 (1970).
9. Clinton, R.O., and S.C. Laskowski, J. Am. Chem. Soc. 70:3135 (1948).

10. Appel, R., H. Heinen and R. Schollhorn, Chem. Ber. 99:3118 (1966).
11. Hilditch, T.P., J. Chem. Soc. 1926:1834.
12. Siggia, S., "Quant. Org. Anal. via Functional Groups," Third Edition, John Wiley and Sons, New York, 1967, p. 559, 561.
13. Becher, P., "Emulsions, Theory and Practice," Second Edition, American Chemical Society Monograph No. 162, Reinhold Publishing Corp., New York, 1965, p. 233.

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