chilled reaction mixture furnished colorless crystals (1.89 g) and two more crops (total 5.13 g) were subsequently obtained from the filtrate. These crystals were identified as the starting methiodide of IV (65% recovery) by melting point and infrared spectrum.

Other reactions for longer periods or in the absence of hydrated sodium acetate gave similar results.

An attempted reaction between the methiodide of IV and phenylhydrazine in refluxing absolute ethanol which contained glacial acetic acid, resulted in an 88% recovery of the methiodide.

Reaction of *o*-N,N-Trimethylbenzylamine (VIII) with *n*-Butyllithium and *n*-Butyl Nitrite.—A slight excess of a *ca.* 1.6 *M* solution of *n*-butyllithium in hexane (267 ml) was added to a stirred solution of VIII[9] (59.6 g, 0.4 mol) in dry ether (100 ml) under nitrogen; after 2–3 hr, a cream-colored precipitate separated. The mixture was stirred at room temperature for 18 hr, during which time more dry ether was added to make up for losses by evaporation. The suspension was then added during 40 min to freshly prepared *n*-butyl nitrite[10] (20.6 g, 0.2 mol) at 0° to give an orange suspension initially which, toward the end of the addition, changed to a deep red solution; stirring at 0° was continued for a further 1 hr. The reaction mixture was poured into stirred water (200 ml) and the brown aqueous layer separated from the brown organic layer, acidified (glacial acetic acid), and neutralized ($NaHCO_3$). Extraction with three 200-ml portions of ether and evaporation of the dried ($MgSO_4$) ether layer furnished a viscous brown oil (10.64 g, 28%) whose infrared spectrum (liquid film) was consistent with that expected for the required oxime (IX): ν_{max} 3220 (OH), 2940 and 2850 (aliphatic CH), 1455, 1175, 1098, 1020, 965, 841, 758 cm^{-1}. This oil could not be induced to crystallize and was thus allowed to react with methyl iodide directly.

Reaction of the Crude Oxime (IX) with Methyl Iodide.—Methyl iodide (2.85 g, 0.020 mol) was added during 1 min to a stirred solution of the crude oxime IX (3.25 g, 0.018 mol) in absolute ethanol (30 ml) and, after *ca.* 50 min, a solid precipitated. The reaction mixture was stirred for a further 70 min and then filtered to give the crude methiodide (3.29 g); a further crop (0.52 g) was obtained by dilution of the filtrate with ether (400 ml); thus the total yield was 3.81 g (65%). Crystallization, with chilling, afforded the pure quaternary methiodide X (2.88 g, 49%) as colorless acicular plates: mp 196° dec with gradual darkening above 160°; ν_{max} 3240 (OH), 1477, 1407, 1370, 1285, 977, 961, 896, 888, 780, 763, 720 cm^{-1}.

Anal. Calcd for $C_{11}H_{17}IN_2O$: C, 41.26; H, 5.35; I, 39.64; N, 8.75. Found: C, 41.12; H, 5.44; I, 39.81; N, 8.60.

Attempted Cyclization of X.—A slight excess of a *ca.* 1.6 *M* solution of *n*-butyllithium in hexane (6.7 ml) was added during 5 min to a white suspension of X (3.20 g, 0.01 mol) in dry THF (100 ml) at 0° under nitrogen; the suspension became reddish brown and finally brown. Trimethylamine was evolved, and the solution was stirred at 0° for 15 min and allowed to warm to room temperature. After 16 hr trimethylamine was still being evolved; after making up the loss of solvent by evaporation, the suspension was boiled under reflux for 24 hr with the addition of more dry THF (50 ml) during this time. Although trimethylamine was still being evolved, the chocolate-colored suspension was allowed to cool and then filtered to provide a sticky brown solid (2.66 g) whose infrared spectrum showed it to be crude recovered X. Evaporation of the filtrate gave a reddish brown oil (1.25 g) which was chromatographed on alumina (Fischer, 80–200 mesh). Six different fractions were eluted, but each one yielded only an intractable tar on evaporation (total amount of tar, 0.75 g).

A second reaction, using di-*n*-butyl ether as solvent, gave similar results (probably owing to decomposition of the lithio salt of X).

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[9] W. R. Brasen and C. R. Hauser, *Org. Syn.*, **34**, 61 (1954).

[10] W. A. Noyes, *ibid.*, **16**, 7 (1936).

Aminimides. VI.[1a,b] Synthesis of Aminimides from Carboxylic Acid Esters, Unsymmetrically Disubstituted Hydrazines, and Epoxides

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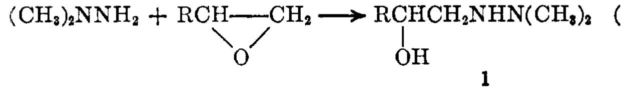
The reaction of unsymmetrically disubstituted hydrazines, epoxides, and carboxylic acid esters gives 1,1-disubstituted 1-(2-hydroxyalkyl- or aryl-)aminimides in excellent yields. Evidence is presented to support a primary reaction between the hydrazine and the epoxide to give an aminimine which subsequently reacts with the ester to give the aminimide. The aminimide may be pyrolyzed to give an isocyanate and a β-hydroxy tertiary amine which subsequently react to form a urethan.

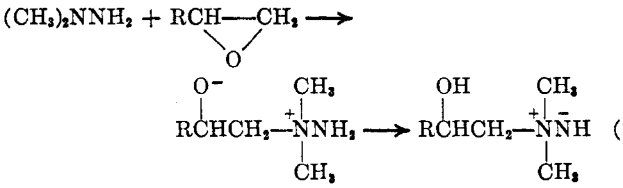
Very little mention is made in the literature concerning the reaction between unsymmetrically substituted hydrazines and epoxides. In fact, only two references[2,3] could be found, both of which support the attack of the unsubstituted nitrogen on the terminal epoxide carbon atom (eq 1).



$$(CH_3)_2NNH_2 + \underset{\diagdown\,O\,\diagup}{RCH\text{—}CH_2} \longrightarrow \underset{OH}{RCH}CH_2NHN(CH_3)_2 \quad (1)$$

1

It seemed more logical to us that the more nucleophilic substituted nitrogen would attack the epoxide to give the hydrazinium alkoxide 2 (eq 2). It is known



$$(CH_3)_2NNH_2 + \underset{\diagdown\,O\,\diagup}{RCH\text{—}CH_2} \longrightarrow \underset{}{\overset{O^-}{RCH}}CH_2\text{—}\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}NH_2 \longrightarrow \overset{OH}{RCH}CH_2\text{—}\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}\overset{-}{N}H \quad (2)$$

2 3

from prior work[4] that alkoxides react with 1,1,1-trisubstituted hydrazinium salts to give aminimines. If 2 is formed, then it is logical to assume an extraction of a nitrogen proton by the alkoxide to provide the aminimine 3.

Results and Discussion

Since it was known[5,6] that aminimines react with carboxylic acid esters to produce aminimides, we tested

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[1] (a) For paper V in this series, see B. M. Culbertson, E. A. Sedor, S. Dietz, and R. E. Fries, accepted for publication in *J. Polymer Sci., Part A-1.* (b) Presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., 1968. (c) Current address is Calgon Corp., Calgon Center, Box 1346, Pittsburgh, Pa. 15230.

[2] F. Ya. Perveev and V. Ershova, *Zh. Obshch. Khim.*, **30**, 3554 (1960).

[3] G. Benoit, *Bull. Soc. Chim. Fr.*, **6**, 708 (1939).

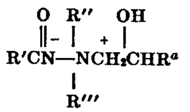
[4] R. Appel, H. Heinen, and R. Schollhorn, *Chem. Ber.*, **99**, 3118 (1966).

[5] H. W. Schiessl and R. Appel, *J. Org. Chem.*, **31**, 3851 (1966).

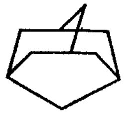
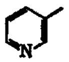
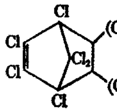
[6] W. J. McKillip and R. C. Slagel, *Can. J. Chem.*, **45**, 2619 (1967).

TABLE I

PROPERTIES OF AMINIMIDES AND DATA ON THEIR FORMATION

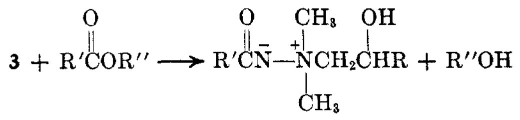


$$R'\overset{O}{\overset{\|}{C}}\overset{-}{N}-\underset{R'''}{\overset{R''}{\overset{+}{N}}}CH_2\overset{OH}{CH}R^a$$

Run no.	R′	R	Solvent, temp in °C	% yield	Mp, °C	TGA,[b] °C Onset	TGA,[b] °C Midpoint	Infrared absorption,[c] cm^{-1} $\overset{O}{\overset{\|}{C}}-N$	Infrared absorption,[c] cm^{-1} O—H	Anal., % Calcd C	Anal., % Calcd H	Anal., % Calcd N	Anal., % Found C	Anal., % Found H	Anal., % Found N
1	CH_3CH_2	CH_3	Isopropyl alcohol, 23	96	108.5–110	135	195	1600	3150	55.14	10.41	16.08	54.99	10.31	16.20
2	$CH_3(CH_2)_{10}$	CH_3	Isopropyl alcohol, 23	Quantitative	48–50	155	203	1570	3250	67.94	12.07	9.32	68.27	12.46	9.40
3	$CH_3(CH_2)_{10}$	$CH_3(CH_2)_5$	*t*-Butyl alcohol, 68	62	51.5–54.5	152	203	1570	3150	71.29	12.51	7.56	71.30	12.55	7.68
4	CF_3	CH_3	Isopropyl alcohol, 23	89	109–110	165	230	1650	3270	39.31	6.11	13.08	38.84	5.96	12.74
5	CF_3CF_2	CH_3	Isopropyl alcohol, 23	90.5	101–102	130	218	1660	3380	36.37	4.96	10.61	36.20	4.87	10.66
6	$CH_2{=}C(CH_3)$	CH_3	Isopropyl alcohol, 23	98	146.5–147.5	140	185	1580	3130	58.00	9.73	15.10	58.13	9.68	15.14
7	$CH_2{=}C(CH_3)$	H	*t*-Butyl alcohol, 23	88	78–80	139	188	1550	3120	55.78	9.36	16.26	56.05	9.18	16.25
8	$CH_2{=}C(CH_3)$	$CH_3(CH_2)_9$	Isopropyl alcohol, 23	Quantitative	64–66	155	187	1555	3225	69.17	11.61	8.96	69.30	11.51	9.07
9[a]	$CH_2{=}C(CH_3)$	CH_3	Isopropyl alcohol, 23	95	93–95	140	176	1555	3170	64.96	10.06	11.66	64.73	10.12	11.74
10	Ph	CH_3	*t*-Butyl alcohol, 23	94	122–125	168	211	1580	3125	64.84	8.16	12.61	65.20	8.11	12.71
11	Ph	Ph	*t*-Butyl alcohol, 23	90	146–147	162	195	1560	3090	71.80	7.09	9.85	71.89	7.12	9.81
12	Ph	*d*	*t*-Butyl alcohol, 55	55	182–183	175	208	1560	3180	68.66	8.45	10.74	68.42	8.22	10.81
13		CH_3	Isopropyl alcohol, 60	80	171 dec	...	...	1570	3150	68.53	10.06	9.99	68.38	10.05	9.83
14	$(EtO)_2P(O)(CH_2)_2$	CH_3	*t*-Butyl alcohol, 23	Quantitative	Oil	...	...	1600	3340	46.44	8.77	9.03	45.75	8.70	8.84
15		CH_3	Isopropyl alcohol, 23	Quantitative	116–118	175	225	1560	3325	59.17	7.68	18.82	59.38	7.62	18.85
16[e]	$-(CH_2)_4-$	CH_3	*t*-Butyl alcohol, 23	Quantitative	191–192	165	230	1570	3100	55.46	9.89	16.17	55.21	9.87	16.29
17[e]		CH_3	Isopropyl alcohol, 23	Quantitative	212 dec	205	277	1565	3100	42.80	5.62	8.68	42.50	5.64	8.65

[a] R′′ = R′′′ = CH_3 in all cases except run no. 9 where R′′ = R′′′ = $-(CH_2)_6-$. [b] Run on a Du Pont 950 thermogravimetric analyzer at 20°/min in nitrogen. [c] Run as mulls on a Perkin-Elmer 237B grating spectrophotometer. [d] Epoxide used was cyclohexene oxide. [e] The bisaminimides.

our hypothesis by allowing an unsymmetrically disubstituted hydrazine, an epoxide, and a carboxylic acid ester to react to see whether or not an aminimide (**4**) was produced (eq 3).

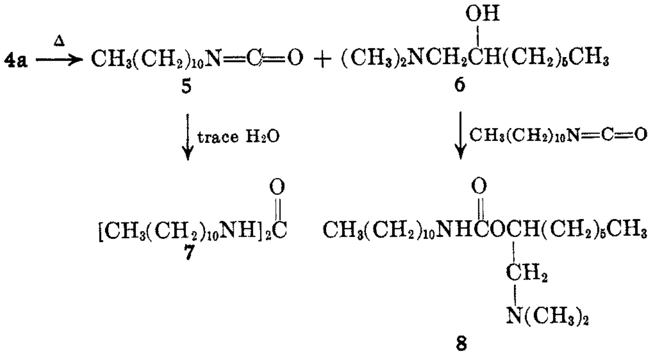


$$\mathbf{3} + \mathrm{R'\overset{O}{\overset{\|}{C}}OR''} \longrightarrow \mathrm{R'\overset{O}{\overset{\|}{C}}\bar{N}{-}\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{\overset{+}{N}}}}CH_2\overset{OH}{\overset{|}{C}}HR} + \mathrm{R''OH} \qquad (3)$$

4a, $R = CH_3(CH_2)_5$; $R' = CH_3(CH_2)_{10}$
b, $R = CH_3$; $R' = CH_2{=}CCH_3$
c, $R = H$; $R' = CH_2{=}CCH_3$
d, $R = CH_3$; $R' = CH_3CH_2$
e, $R = CH_3$; $R' = CF_3CF_2$
f, $R = CH_3$; $R' = C_6H_6$

The first reaction studied was with unsymmetrical dimethylhydrazine, 1-octene oxide, and ethyl laurate in *t*-butyl alcohol. Heating the reactants together at 68° for 8 hr resulted in a 62% yield of a waxy product identified as 1,1-dimethyl-1-(2-hydroxyoctyl)aminelaurimide (**4a**). The structure was determined by infrared (O–H absorption at 3150 and typical aminimide absorption at 1570 cm^{-1} in halocarbon mull) and nmr (CCl_4, τ; N-methyl peaks at 6.58 ppm gave the expected integration) spectroscopy, elemental analysis, and the products of pyrolysis. Pyrolysis of **4a** gave the expected results,[7] *i.e.*, the β-hydroxy tertiary amine **6**, the symmetrical urea **7**, and the urethan **8** (Scheme I). The isocyanate **5** may be isolated if the hydroxy group of **4a** is converted into the acetate ester prior to pyrolysis.

Scheme I



The Scope of the Reaction.—Further investigation showed that the scope of the reaction is very broad (Table I, p 1375). The ester may be aliphatic, fluorinated aliphatic, α,β-unsaturated, aromatic, or difunctional. The epoxide may be one of long- or short-chain α-olefins, of internal olefins, or of aromatically substituted olefins. The unsymmetrically disubstituted hydrazine may be an aliphatic substituted hydrazine such as 1,1-dimethylhydrazine or aminohexamethylenimine. It was found, however, that 1-methyl-1-phenylhydrazine did not react with propylene oxide, probably because of the reduced nucleophilicity of the nitrogen substituted by the phenyl group.

The effect of solvent on the reaction is shown in Table II. It is interesting to note that, with the exception of highly polar dimethyl sulfoxide, only the protonic solvents gave high yields of aminimide **4b**. Dimethyl sulfoxide, however, was shown to be an ineffective solvent in the *in situ* synthesis of aminimides from hydrazine halides, esters, and sodium methoxide.[6] The aminimide was formed in quantitative yield even if no solvent was used.

Table II

Effect of Solvent[a] on Yield of **4b**

Solvent	% yield
Benzene	9.6
t-Butyl alcohol	91.5
Dimethyl sulfoxide	88.0
Isopropyl alcohol	98.0
Methanol	97.0
Tetrahydrofuran	5.4
Water–ethyl alcohol	Quantitative
No solvent	Quantitative

[a] Reactions run at room temperature for 72 hr with 0.1 mol of each reactant in 50 ml of solvent.

Most of the reactions reported in Table I were run at room temperature for 16–48 hr with yields ranging from 88% to quantitative. In runs 3, 12, and 13, lower yields were obtained despite higher reaction temperatures. These lower yields are probably all attributable to a highly decreased rate of reaction due to steric hindrance at the reaction sites. Such is the case at least with the adamantane derivative (run 13) where the aminimide formed very slowly over a period of 22 hr even at 60°. Other less hindered aliphatic esters reacted much more readily.

An example of how the rate of reaction increases with temperature is shown in Table III. Aminimide **4b** forms readily at 80° in 2 hr or less, whereas at room temperature only a 50% yield is obtained after 2 hr.

Table III

Effect of Temperature[a] on Yield of **4b**

Temp, °C	% yield
Room temperature	50
40	76
60	91
80	95

[a] Two-hour reaction with 0.1 mol of reactants in 50 ml of isopropyl alcohol.

One would expect the reaction rates to increase with increasing electron-withdrawing ability of the group on the ester if the aminimine is the attacking species on the ester carbonyl.[5,6] This was found to be the case as shown from the rate data in Figure 1. At the initial stages of the reaction, it is apparent that the relative order of rates is $CF_3CF_2{-} > CH_2{=}CCH_3 \geqslant C_6H_5{-} > CH_3CH_2{-}$.

Mechanism.—The work just described suggests that the reaction probably proceeds through the intermediate aminimine (eq 2). To establish this, we tried the reaction in isopropyl alcohol with no ester present. After 4 days at room temperature, the solvent was evaporated *in vacuo* at room temperature to give a very hygroscopic, heat-sensitive, viscous oil whose analysis agreed with **3** ($R = CH_3$). Reaction of the oil with methyl methacrylate in isopropyl alcohol gave **4b** in near quantitative yield.

These results lead us to seriously question the earlier work by Perveev[2] and Benoit[3] which supports eq 1.

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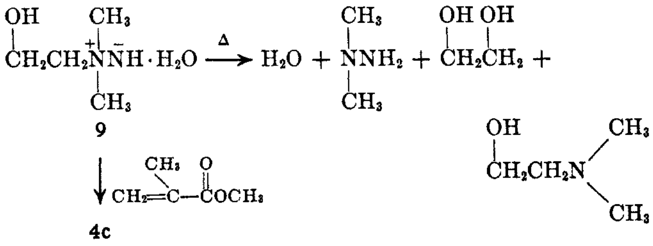
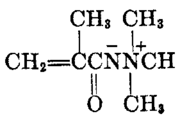
[7] W. J. McKillip, L. M. Clemens, and R. Haugland, *Can. J. Chem.*, **45**, 2613 (1967).

Benoit[3] carried out the reaction of 1,1-dimethylhydrazine and ethylene oxide in water. Conceding that the solvent might make some difference, we repeated Benoit's work. Evaporation of the water *in vacuo* at 40° or lower gave a very hygroscopic, white crystalline solid in quantitative yield. This material was identified as the monohydrate of **3** (R = H) or **9**, by infrared and nmr spectroscopy, elemental analysis, and, finally by its reaction with methyl methacrylate to give a quantitative yield of **4c**. Similar results were obtained using propylene oxide. Benoit[3] distilled his reaction product to obtain what he identified as **1** (R = H). Distillation of our product (**9**) (decomposition starts at 86°) proceeded to give the products shown in Scheme II with no trace of **1** (R = H) as a product. The products that we observed were not surprising since pyrolysis of hydrazinium hydroxides, which are probably the same as aminimine hydrates, have been shown to give similar products.[8] For example, 1,1,1-trimethylhydrazinium hydroxide was pyrolyzed to give water, 1,1-dimethylhydrazine, methyl alcohol, and trimethylamine all analogous to the products of Scheme II as well as nitrogen, ammonia, dimethylamine, and N,N,N',N'-tetramethyldiaminomethane.[9] Our decomposition was carried out at reduced pressure, and we did not attempt to isolate any gaseous products.

SCHEME II



To provide further evidence that hydrazinium hydroxides are actually aminimine hydrates, we prepared 1,1,1-trimethylhydrazinium hydroxide in isopropyl[10] alcohol and added methyl methacrylate. Trimethylamine methacrylimide (**10**)[11] was obtained in high yield.



$CH_2{=}\overset{CH_3}{C}\underset{O}{\overset{\|}{C}}\overset{-}{N}\underset{CH_3}{\overset{CH_3}{\overset{+}{N}}}CH_3$

10

Consequently, our work has shown that the synthesis of aminimide from *unsym*-disubstituted hydrazines, epoxides, and esters follows the general pathway outlines in eq 1 and 2.

Structure of the Hydroxyaminimides.—Table I shows the infrared absorption of the carbonyl function in the aminimides to be at 1550–1660 cm^{-1}, depending on R'. As has been described previously,[12,13] the absorption is at too low a frequency for a typical acylhydrazinium-type carbonyl group and thus resonance form **11** must contribute to the over-all structure of

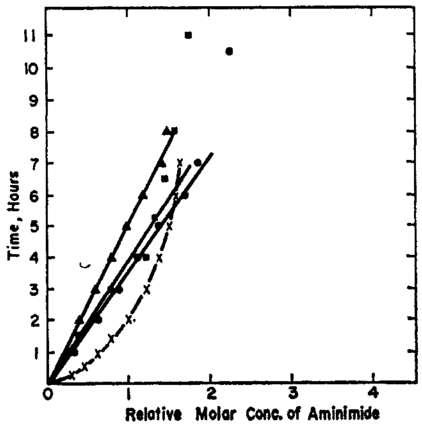
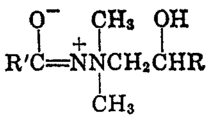


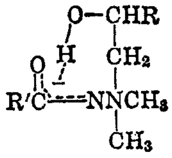
Figure 1.—The relative rates of formation of ●, **4b**, ▲, **4d**, × **4e**, and ■, **4f**.

the compound. The actual structure probably involves a distribution of the negative charge over the nitrogen, carbon, and oxygen atoms,[12] the degree depending mainly on R'.



$R'\overset{O^-}{C}{=}\underset{CH_3}{\overset{CH_3}{\overset{+}{N}}}CH_2\overset{OH}{C}HR$

11



12

It is interesting to note the exceptionally low frequency of the O–H stretch (Table I) indicating a strong hydrogen bond between the hydroxyl proton and the negative charge center, either inter- or intramolecular or both. The molecule is properly situated to form a *quasi* six- or eight-membered ring depending on whether the negative charge is closer to the nitrogen or oxygen atom. The infrared spectrum of **4b** in chloroform at three dilutions (1, 4.5, and 19%) showed a strong bonded O–H stretching at 3230 cm^{-1} with only a very weak free O–H stretch at 3655 cm^{-1}. This result indicates that the hydrogen bonding is mainly, if not entirely, intramolecular as in **12**.

Experimental Section[14]

General Synthesis of Aminimides in Table I.—A mixture of 0.1 equiv of each reactant (*i.e.*, ester, *unsym*-disubstituted hydrazine and epoxide) in 50–100 mol of the solvent indicated was allowed to stir at the temperature indicated for 16–48 hr, as was convenient. Exceptions include run 3 which was carried out at room temperature for 72 hr and then at 68° for 8 hr, run 12 at 55° for 48 hr, and run 13 at 60° for 22 hr. The preferred reaction vessel was a pressure bottle stirred magnetically, although a simple flask with an efficient condenser was also suitable. At the end of the reaction period, the solvent was removed *in vacuo* to give the crude yield. Most compounds were recrystallized two or three times from benzene or ethyl acetate to provide the analytical samples. The long-chain alkyl derivatives were recrystallized from hexane.

Pyrolysis of 1,1-Dimethyl-1-(2-hydroxyoctyl)aminelaurimide (4a).—Pyrolysis of 2.0 g of the aminimide was carried out in a Carius tube at 160° for 2 hr. Cooling provided a partially solid

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[8] H. H. Sisler and G. M. Omietanski, *Chem. Rev.*, **57**, 1031, 1033 (1957).

[9] F. Klages, G. Nober, F. Kircher, and M. Bock, *Ann.*, **547**, 1 (1941).

[10] G. L. Braude and J. H. Cogliano, U. S. Patent 3,225,101 (1965).

[11] R. C. Slagel and A. E. Bloomquist, *Can. J. Chem.*, **45**, 2625 (1967).

[12] S. Wawzonek and E. Yeakey, *J. Amer. Chem. Soc.*, **82**, 5718 (1960).

[13] T. A. Sokolova, L. A. Ovsyannikova, and N. P. Zapevalova, *Zh. Org. Khim.*, **2**, 818 (1966).

[14] Melting points and boiling points are uncorrected. The infrared spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer. The nmr spectra were obtained on a Varian A-60A spectrometer in the solvent indicated using tetramethylsilane as an internal standard except with deuterium oxide where 3-trimethylsilyl-1-propanesulfonic acid was used as the standard. Elemental analyses were performed by Huffman Laboratories, Inc., Wheatridge, Colo.

mass. The solid was filtered and washed with hexane to give 0.2 g of a white crystalline material, mp 103–105°. The infrared (3340, 1625, 1590 cm^{-1}) spectrum, elemental analysis, and melting point (lit.[15] mp 103°) show the structure to be symmetrical diundecylurea.

Anal. Calcd for $C_{23}H_{48}N_2O$: C, 74.93; H, 13.12; N, 7.60. Found: C, 74.43; H, 12.96; N, 7.46.

The filtrate was evaporated to give 1.8 g of a colorless liquid. Distillation gave 0.4 g of a colorless oil, bp 45° (0.35 mm), n^{22}_{D} 1.4367. This oil was identified as N,N-dimethyl-1-amino-2-octanol by comparing the boiling point, refractive index, and infrared spectrum with those of the known material made from 1-octene oxide and dimethylamine in isopropyl alcohol at room temperature.

The pot residue from the above distillation was filtered to give another 0.2 g of the urea. The remaining viscous oil showed infrared absorption bands at 3340 and 1725 cm^{-1}, among others, indicating the presence of urethane. We were unable to purify this material sufficiently to obtain a satisfactory elemental analysis. However, reaction of the known isocyanate with the known amino alcohol gave a product showing the same infrared spectrum.

Aminimide **4a** was treated with an equimolar amount of acetic anhydride in benzene[16] to provide 1,1-dimethyl-1-(2-acetoxyoctyl)aminelaurimide, identified by the disappearance of the 3150-cm^{-1} absorption bands in the infrared spectrum and the appearance of a band at 1745 cm^{-1}. The acetate was pyrolyzed at 150° (0.05 mm) to give an oil which was immediately fractionally distilled to give a 39% yield of pure undecyl isocyanate, bp 77–84° (0.05 mm), identified by the boiling point [lit.[17] bp 103° (3 mm)], infrared spectrum (sharp band at 2270 cm^{-1} for a thin film), and conversion into symmetrical diundecylurea.

Reaction of 1-Methyl-1-phenylhydrazine, Propylene Oxide, and Methyl Methacrylate.—Equimolar (0.05 mol) amounts of the reactants were placed in 50 ml of isopropyl alcohol and sealed in a pressure bottle. The reaction was allowed to stir at room temperature for 16 hr. A sample was removed and evaporated to give only the starting hydrazine. The reaction was continued for 4 hr at 80° and for 1.5 hr on the steam bath with the same result.

Rate Study of Aminimide Formation.—Solutions were made up with 0.01 mol of distilled unsymmetrical dimethylhydrazine, propylene oxide, and the ester (methyl methacrylate, ethyl propionate, ethyl perfluoropropionate, and methyl benzoate) in 20 ml of isopropyl alcohol. The solutions were immediately transferred to a 0.1-mm liquid infrared cell. The reactions were run at 23 ± 1°. Formation of the corresponding aminimide was followed by the increasing intensity of the band at 1550–1675 cm^{-1}. Each reaction was allowed to continue for at least 7 hr with spectra recorded periodically.

Several concentrations were made of each authentic aminimide in isopropyl alcohol and plotted *vs.* the absorbance of the 1550–1675-cm^{-1} infrared band. The absorbance of the experimental runs described above was then related to the known concentration plot to give the results shown in Figure 1.

Synthesis of 3 (R = CH_3).—Freshly distilled unsymmetrical dimethylhydrazine (0.1 mol) and propylene oxide (0.1 mol) were dissolved in 60 ml of Spectral Grade isopropyl alcohol. A portion was sealed in a vial which remained at room temperature for 4 days. The solvent was evaporated *in vacuo* at room temperature over phosphorus pentoxide to give a very viscous hygroscopic oil. The analytical sample was transferred under dry nitrogen.

Anal.[18] Calcd for $C_5H_{14}N_2O$: C, 50.81; H, 11.94. Found: C, 51.32; H, 11.95.

The aminimine (0.05 mol) was again placed in 50 ml of isopropyl alcohol and 0.05 mol of methyl methacrylate was added. The resulting solution stirred at room temperature for 24 hr. A quantitative yield of the aminimide **4b** resulted in evaporation of the solvent (by melting point, mixture melting point, and infrared spectrum).

Synthesis of 9.—Freshly distilled unsymmetrical dimethylhydrazine (12.0 g, 0.2 mol) was dissolved in 100 ml of water and placed in a pressure bottle which was cooled with an ice bath. Ethylene oxide (4.4 g, 0.1 mol) was added and the bottle was then sealed. The reaction proceeded at ice bath temperature for 1 hr after which the bath warmed to room temperature and remained there for a total reaction time of 16 hr. The solvent was evaporated *in vacuo* at 40° to provide 13 g of a white crystalline solid. A sample of the solid was dried *in vacuo* at 23° over phosphorus pentoxide for 48 hr. The dried sample had mp 83° with decomposition at 86°. The infrared spectrum (halocarbon mull) showed absorption at 3400, 3240, 3120, 3030, 2820, 2700, 1650, and 1475 cm^{-1}, etc. The nmr spectrum (τ, D_2O) showed six protons at 6.63 (N-methyl protons) and four protons in a multiplet centered at 6.18 ppm.

Anal. Calcd for $C_4H_{14}N_2O_2$: C, 39.32; H, 11.55; N, 22.94. Found: C, 39.54; H, 11.27; N, 23.02.

The hydrate 9 (0.01 mol) was dissolved in 10 ml of isopropyl alcohol along with 0.01 mol of methyl methacrylate. The solution was stirred for 16 hr at room temperature. Evaporation of the solvent and drying the product *in vacuo* over phosphorus pentoxide gave a near-quantitative yield of **4b** as determined by melting point, mixture melting point, and the infrared spectrum.

Reaction of Unsymmetrical Dimethyl Hydrazine and Propylene Oxide in Water.—The above procedure was repeated except that equimolar amounts of the reactants were used. A quantitative yield of product was obtained. The dried sample had mp 83° with decomposition at 90°. The infrared spectrum (nujol mull) showed absorption at 3420, 3250, 3160, 3030, and 1660 cm^{-1}, etc. The nmr spectrum (τ, D_2O) showed a doublet at 8.83, two peaks at 6.52 and 6.58 (N-methyl protons), and a multiplet at 5.58 ppm in an expected area ratio of 3:6:1, respectively.

Anal. Calcd for $C_5H_{16}N_2O_2$: C, 44.09; H, 11.84; N, 20.57. Found: C, 44.53; H, 11.62; N, 20.11.

Reaction with methyl methacrylate, as above, gave a near-quantitative yield of **4b**.

Pyrolysis of 9.—The aminimine hydrate 9 (28 g) was pyrolyzed at 115° (30 mm). A colorless liquid distilled at 39–47° totalling 17.4 g. Redistillation of the liquid gave a first fraction containing water and unsymmetrical dimethylhydrazine, both identified by glpc (6-ft dimethylpolysiloxane on Chromosorb W column). Unsymmetrical dimethylhydrazine was also identified by comparing its methyl iodide salt with known 1,1,1-trimethylhydrazinium iodide (melting point, mixture melting point, and infrared spectrum). The second, and last, fraction had bp 125–128°, n^{25}_{D} 1.4274, and was shown to be N,N-dimethyl-1-amino-2-hydroxyethane by comparison of the infrared spectrum and the methyl iodide salt (mp 263°, mixture melting point not depressed) with those of the known material.

The pot residue from the pyrolysis contained starting material and ethylene glycol. The latter was identified by its infrared spectrum and glpc retention time.

Reaction of Trimethylhydrazinium Hydroxide with Methyl Methacrylate.—1,1,1-Trimethylhydrazinium chloride (5.5 g, 0.05 mol) was dissolved in 200 ml of isopropyl alcohol and then passed over a Dowex 1-X4 ion-exchange column (200 g of resin) in the hydroxyl form.[10] Excess methyl methacrylate was added to the effluent and the mixture was allowed to stir at room temperature overnight. Evaporation of the solvent gave a quantitative yield of **4b** identified by comparing the melting point, mixture melting point, and infrared spectrum with those of authentic **4b**.

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(18) The Dumas nitrogen determination was not satisfactory. This is not surprising since the determination uses a carbon dioxide purge and it is known that aminimines react with carbon dioxide; see ref 4.