Reversible Cycloelimination and Disproportionation Reactions in Aliphatic Amine Oxide–*N*,*N*-Dimethylhydroxylamine–Olefin Systems[1]

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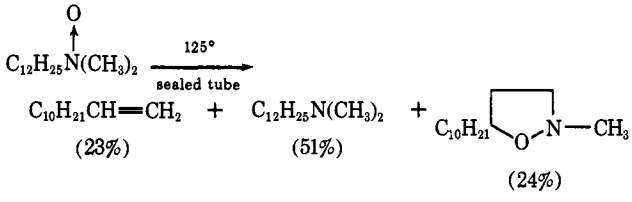
Abstract: The thermal decomposition of dimethyldodecylamine oxide at 125° in a sealed system produces 2-methyl-5-decylisoxazolidine (plus some olefin) and dimethyldodecylamine, rather than normal cycloelimination products. The anomalous products are suggested to result from a facile oxidation of *N*,*N*-dimethylhydroxylamine (DMHA) by tertiary amine oxide to *N*-methylnitrone, which is then trapped by olefin. The oxidation of DMHA by trimethylamine oxide in the presence of olefins at 100° constitutes a useful isoxazolidine synthesis. Heating DMHA with olefins at 125° (in the absence of tertiary amine oxides) *also* produces isoxazolidines, which suggests that DMHA can disproportionate to *N*-methylnitrone and dimethylamine. Unexpected coproducts of this reaction are isomeric dimethylalkylamines. Their formation constitutes the first substantial evidence that cycloaddition of DMHA to olefins, *i.e.*, *the reverse of the Cope cycloelimination reaction*, is an observable process.

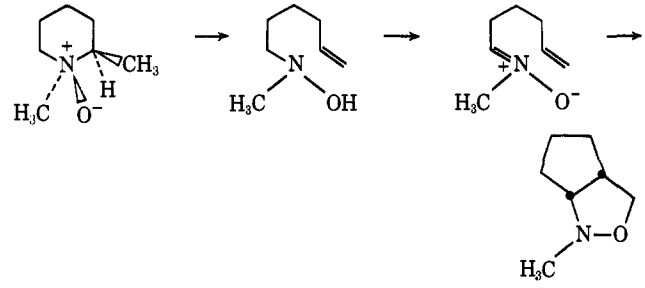
The pyrolysis of aliphatic amine oxides *in vacuo* to yield olefins and N,N-disubstituted hydroxylamines has been exploited synthetically by Cope and others.[2] Anticipated side reactions include the (Meisenheimer) rearrangement of a substituent from N to O, reduction of amine oxide to tertiary amine, and in some cases isomerization of the product olefin.

The present work includes a detailed study of the pyrolysis of a simple amine oxide, dimethyldodecylamine oxide (DDAO), under varied conditions. On slow pyrolysis *in vacuo* (<0.1 mm at 125°), DDAO produces only the expected 1-dodecene and *N*,*N*-dimethylhydroxylamine (DMHA). However, in a sealed tube at the same temperature no DMHA can be isolated, the yield of olefin is substantially reduced, and 2-methyl-5-decylisoxazolidine and dimethyldodecylamine are formed.



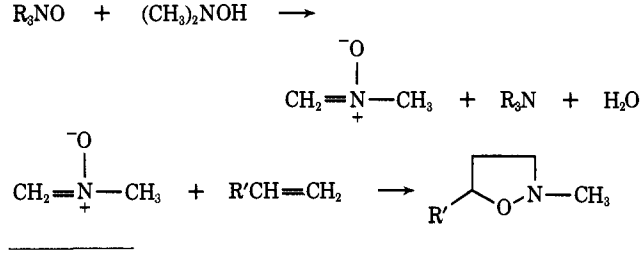
Pyrolysis in an open flask at atmospheric pressure leads to an intermediate product distribution. The structure of the isoxazolidine was firmly established on the basis of analytical, infrared, nmr, and mass spectral data, plus degradative reactions. No *N*,*N*-dimethyl-*O*-dodecylhydroxylamine, the most probable Meisenheimer rearrangement product,[3] was detected in the product, from investigations using a gc analytical technique which would have detected <0.2% yield.

An earlier observation by Cope and LeBel[4] provides intramolecular precedent for formation of isoxazolidine and amine. They isolated a bicyclic isoxazolidine as a significant by-product of pyrolytic elimination, which also produced as the expected product an olefinic hydroxylamine.



The structure of the isoxazolidine was firmly established, and the mechanism of its formation was hypothesized to involve the intramolecular addition of an intermediate nitrone to the vinyl group. Although no mechanism for the oxidation of the hydroxylamine to the hypothetical nitrone was proposed by Cope and LeBel, it was observed that water and *N*-methyl-α-pipecoline, the reduction product of the amine oxide, were also formed.[4] Furthermore, independent syntheses which should have produced the unsaturated nitrone resulted in isoxazolidine formation.

Our work provides evidence that the tertiary amine oxide is directly responsible for oxidizing *N*,*N*-dialkylhydroxylamines to the hypothesized nitrones during pyrolysis and is reduced to tertiary amine in the process.[5]



(1) An abstract of this work was printed in the Book of Abstracts of the XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Mass., July 1971, Sect. O-C-4, p 47.

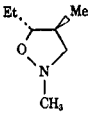
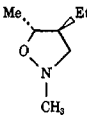
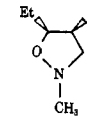
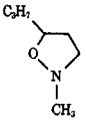
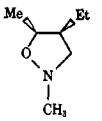
(2) A. C. Cope and E. R. Trumbull, *Org. React.*, **11**, 317 (1960).

(3) Aliphatic amine oxides *lacking* β hydrogens yield rearrangement products, among others, on pyrolysis [C. L. Bumgardner, *Tetrahedron Lett.*, 5499 (1966); J. I. Brauman and W. A. Sanderson, *Tetrahedron*, **23**, 37 (1967)]. Evidence has been obtained that rearrangement proceeds initially *via* homolytic cleavage of a C–N bond [U. Schoellkopf and H. Schaefer, *Justus Liebigs Ann. Chem.*, **683**, 42 (1965); J. P. Lorand, R. W. Grant, P. A. Samuel, E. O'Connel, and J. Zaro, *Tetrahedron Lett.*, 4087 (1969)]. If so, rearrangement of the dodecyl would be preferred to rearrangement of a methyl group.

(4) A. C. Cope and N. A. LeBel, *J. Amer. Chem. Soc.*, **82**, 4656 (1960).

(5) G. P. Schulman and W. E. Link [*J. Amer. Oil Chem. Soc.*, **41**, 329 (1964)] proposed that amine formation is accompanied by pro-

Table I. Product Yields from Reactions between DMHA and Isomeric Pentenes[a]

Olefin reacted	Recovered olefin	% yield, basic fraction[a]								
1-Pentene	1- and 2-Pentene (23%)	64	0	23[d]	23[d]	0	0	0	47	0
trans-2-Pentene	2-Pentene (43%)	42	3	10	0 (or small)	34	32	2–3	Small	1
cis-2-Pentene	2-Pentene (40%)	49	4	17	6	1	1	37	Small	31
Retention time[b] (min)			5.5	7.0	8.0	22.0	23.0	27.9	*c*	30.1

[a] Conditions: 2:1 DMHA–olefin, 125°, 18 hr. [b] Typical values utilizing gc conditions described in the Experimental Section. A minor quantity of an unidentified material with retention time of 15.1 min under the above conditions was observed. [c] This isomer emerged as a shoulder on the previous peak. [d] As noted by a referee, there is a discrepancy in the ratio of 1- to 2-alkyldimethylamines between these pentene results and those found in the case of dodecene. By nmr integrals and gc, the amine from 1-dodecene was largely 2-dodecyldimethylamine. However, the resolution of the two compounds by gc was insufficient to exclude the possibility that the 1-dodecyl isomer was not formed. [e] Approximate yields of the distilled basic fraction, calculated using an average molecular weight of 125.

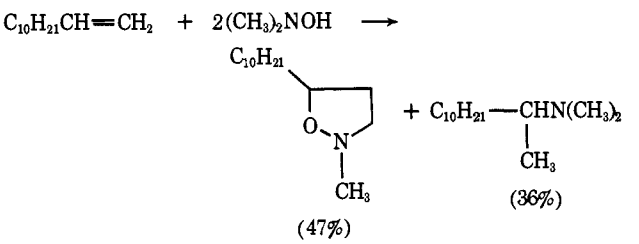
In amine oxide pyrolyses where the hydroxylamine cannot quickly escape from the vicinity of the amine oxide, the rate of this process is found to be comparable to that of the cycloelimination reaction.

Convincing experimental support for this proposal lies in the fact that trimethylamine oxide, a relatively thermally stable amine oxide lacking β-hydrogen atoms, is equivalent to DDAO as an oxidant for DMHA. In fact, heating equimolar quantities of an olefin with DMHA and trimethylamine oxide at 100°/20 hr constitutes a general and useful isoxazolidine synthesis. Yields of 97–98% pure isoxazolidines[6] range from 36 to 43%; unreacted olefin is recovered unchanged.

The results of a crossover experiment demonstrated that the olefin is an intermediate in the formation of the isoxazolidine. Heating equimolar quantities of DDAO and 1-decene at 125° produced a mixture of homologous (5-decyl and 5-octyl) isoxazolidines in 1:1.8 ratio.

To summarize, the differences in product distribution between vacuum and sealed tube pyrolyses of DDAO may be rationalized on the basis of secondary oxidation–reduction processes which follow cycloelimination. No primary thermal reaction other than cycloelimination is required to explain the present as well as earlier observations.

Reaction of Olefins and *N,N*-Dimethylhydroxylamine in the Abence of Amine Oxides. Tertiary amine oxides are not unique reagents for oxidizing DMHA. Stronger oxidants like hydrogen peroxide also react to produce methylnitrone which, as above, may be trapped as the isoxazolidine. More surprisingly, it was found that DMHA could function as its own oxidant, although it is noticeably less reactive than trialkylamine oxides in this respect. In reaction with dodecene, temperatures of 125° are required to achieve rates roughly comparable to those achieved by trimethylamine oxide at 100°. Along with the expected isoxazolidine, an unexpected product, 2-dodecyldimethylamine, is observed. Its structure was suggested by nmr spectral data, in which both the characteristic distorted C–CH_3 triplet displayed



by long *n*-alkyl chains and a second C–CH_3 signal split into a doublet, indicative of the CH_3–CH< grouping, were observed. The identity of this amine was confirmed by direct comparison of spectral data with that obtained from an authentic sample prepared from 2-dodecanone.

The isolation of 2-dodecyldimethylamine constitutes the first substantial evidence that the *reverse of the Cope cycloelimination reaction* of amine oxides is observable.[7] Though clearly possible in principle, there are no thermodynamic data to indicate whether the rate of the reverse of elimination would be fast enough to render the reaction observable. Central to the interpretation is the fact that the Cope elimination can only produce 1-dodecene from DDAO, while the reverse addition may produce either 1- or 2-dodecyldimethylamine oxide. It would be anticipated from the results described earlier that, should either of these amine oxides be formed, it would rapidly be reduced by DMHA to the corresponding tertiary amine. Also crucial to this interpretation is the fact that the oxidation of DMHA by amine oxides is irreversible and that one amine oxide does not oxidize another tertiary amine.[8] The tertiary amine thus represents a dead end in an otherwise mobile system that may be represented in part as shown in Scheme I. An important implication of these ideas is that olefin isomerization in amine oxide pyrolysis is more likely than was heretofore suspected. Whether it is observed will, like isoxazolidine formation, hinge on

duction of elemental oxygen. We could not substantiate this experimentally. As pointed out by a referee, J. E. Baldwin, A. K. Bhatnagar, S. C. Choi, and T. J. Shortridge, *J. Amer. Chem. Soc.*, 93, 4082 (1971), also looked for and failed to observe oxygen as a product of amine oxide pyrolysis.

(6) The 2–3% impurity is a tertiary amine, probably resulting from the direct reaction of DMHA with the olefin (see later).

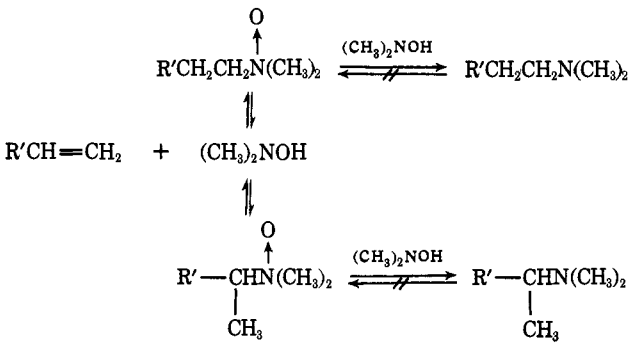
(7) This interpretation of the experimental data was first suggested by Professor W. von E. Doering.

(8) Numerous attempts were made to oxidize DDA with DMHA or Me_3NO in a sealed tube at 125°. Had oxidation occurred, some formation of olefin and/or isoxazolidine should have resulted. No evidence for these products, which are easily detected by gc, could be obtained. The remote possibility that some unusual direct addition of dimethylamine (an end product of the disproportionation of DMHA) or its salts to dodecene occurred under the reaction conditions was also excluded by control experiments.

Table II. Mass Spectral Element Map Data on Isomeric Dimethylethylisoxazolidines

Nominal *m/e*	Formula	Relative intensity data: *trans*-2,4-Dimethyl-5-ethyl	*trans*-2,5-Dimethyl-4-ethyl	*cis*-2,4-Dimethyl-5-ethyl	*cis*-2,5-Dimethyl-4-ethyl
39	C_3H_3	39	82	43	48
40	C_3H_4	13	14	16	2.7
41	C_3H_5	63	87	80	76
42	C_3H_6	65	92	83	46
	C_2H_4N	73	(100)	(100)	(100)
43	C_3H_7	22	33	19	28
	C_2H_5N	74	40	82	44
→	C_2H_3O	10	69	8.0	45
44	C_2H_6N	41	45	41	34
45	C_2H_5O	7.6	28	1.5	2.9
	CH_3NO	13	2.2	7.2	1.9
50	C_4H_2	1.7	22	5.3	1.6
51	C_4H_3	1.7	44	1.1	1.4
52	C_4H_4	1.0	30	0.8	1.2
53	C_4H_5	5.2	8.5	3.4	3.3
54	C_4H_6	1.7	2.2	1.1	2.3
55	C_4H_7	36	1.4	36	35
→	C_3H_3O	6.8	1.8	9.5	1.4
56	C_4H_8		15	45	
→	C_3H_6N	29	2.7	15	2.5
57	C_3H_7N	12	8.1	5.1	6.6
→	C_3H_5O	9.6	4.9	18	3.1
58	C_3H_6O	13	21	7.4	2.7
60	C_2H_6NO	(100)	92	61	50
69	C_4H_5O	32.3	4.9	9.1	1.4
78	C_4H_6N	3.3	1.3	2.3	2.1
80	C_4H_8N	14	13	13	11
→ 81	C_4H_9N	12	0.4	7.8	0.8
82	$C_4H_{10}N$	5.2	0.4	1.3	
129	$C_7H_{15}NO$	18	19	17	11

Scheme I



details of experimental conditions as well as on the molecular structures involved.[9]

Reaction of DMHA with Pentenes. Investigation of the olefin–DMHA reaction was extended to the three isomeric *n*-pentenes. The results of these investigations are tabulated in Table I. 1-Pentene yielded a single isoxazolidine product presumed to be structurally analogous to the dodecene derived homolog. Essentially complete resolution of the complex mixtures formed from each of the 2-pentenes was achieved by gc. The isomeric amines were identified by direct comparison with authentic samples. The structures of the isoxazolidines from *cis*- and *trans*-2-pentene were assigned on the following bases.

(1) Four isomeric isoxazolidines were observed, two each from *cis*- and *trans*-2-pentene. This observation strongly suggests stereospecific addition of methylnitrone to form structurally isomeric but stereochemically similar adducts. Huisgen[10] has noted that numerous 1,3-dipolarophiles, including nitrones, add to olefins initially in a cis manner, without exception. The stereochemical relationship of the 4,5 substituents was assigned on this basis.

(2) The distinction between positional isomers rests on high-resolution mass spectroscopy. Element map data on each of the pure isomers (isolated by gc) are given in Table II. Each isomer displayed a parent peak having the expected formula and a characteristic C_2H_6NO fragment. Furthermore, several fragments could reasonably be assumed to result from rupture of the C_4–C_5 bond, permitting distinction between positional isomers to be made. For example, the peak intensities of the C_3H_3O, C_3H_5O, and C_4H_9N fragments, which would be expected to originate predominately from the 2,4-dimethyl-5-ethyl stereoisomers, were comparatively intense in two isoxazolidines, one each from *cis*- and *trans*-2-pentene. In the other two the C_2H_3O fragment was comparatively intense, a result compatible with the 2,5-dimethyl-4-ethyl structures. The corresponding $C_5H_{11}N$ fragment was not evident in any of the four isomers.

(3) The facile reductive opening of the ring in the dodecene derived product to form 3-hydroxydodecylmethylamine, whose structure was established by diacetylation, pyrolytic elimination of acetic acid, and oxidative cleavage to the two expected fatty acids, provides chemical support for the isoxazolidine ring suggested by the mass spectral data.

A notable feature of the cycloadditions of the two reagents, nitrone and DMHA, is the different pattern of substituent effects. While nitrone addition yields pri-

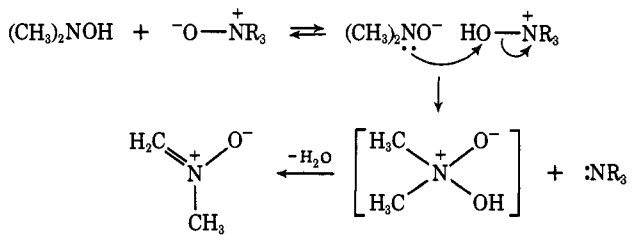
(9) While not usually observed, instances of olefin isomerization have been noted by Cope and Trumbull.[2]

(10) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, 2, 565, 633 (1963).

marily a single isomer from 1-olefin and significant amounts of both isomers from 2-, the reverse is true of the addition of DMHA. It was also established that 1-olefins are more reactive in this system than 2-olefins. The recovered olefin from a reaction of 1-hexene, 2-pentene, and DMHA (1:1:4 mole ratio) was 83% 2-pentene and 17% 1-hexene. This observation rationalizes the fact that 1-pentene was observed to isomerize while 2-pentene was not. This fact also helps explain the appearance of larger quantities of 1-pentyldimethylamine from *cis*-2-pentene than of 3-pentyldimethylamine from 1-pentene. The phase heterogeneity of the neat olefin–DMHA reaction systems precludes detailed kinetic interpretation of these data.

Possible Path of DMHA Oxidation. The oxidation of DMHA by amine oxide occurs with surprising facility. Oxidizing reagents are typically electrophilic in nature, yet the proposition that the electron-rich oxygen of an amine oxide constitutes an electrophilic site is not attractive. In addition, there are the experimental facts that the amine and the isoxazolidine are inert to amine oxides. The amine is $\sim 10^5$ *more* basic than DMHA, and for it to be grossly less nucleophilic is unlikely. The possibility that DMHA is unusually nucleophilic due to the α oxygen is diminished by the observed inertness of the isoxazolidines.

The singular structural feature of DMHA which does offer a plausible explanation for its reactivity is the acidic OH group.[11] One may think of this reaction as proceeding *via* an essential preliminary proton transfer, followed by nucleophilic displacement of the nitrogen of the DMHA anion on the peroxide-like oxygen of the cationic species.



$R_3N^+–O^-$ in the equation might be either a trialkylamine oxide or the amine oxide tautomer of DMHA. The presumed low proportion of the latter species in DMHA offers a plausible qualitative explanation for its comparatively low reactivity.

The species in brackets is the unknown dimethylnitronic acid. This nitrogen analog of dimethylphosphinic acid should dehydrate readily to the nitrone, much as "orthonitric acid," were it to be formed, would tend to yield nitric acid.[12] In addition, nitronic acids (particularly those lacking α hydrogens) easily decompose to nitroxide and (presumably) hydroxy radicals. This alternative reaction course, as well as side reactions of the nitrone, offer a reasonable explanation for the *ca.* 60% loss of DMHA in the isoxazolidine synthesis.[15,16]

(11) Salts of DMHA may be formed easily with sodium hydride in monoglyme; these are readily alkylated by dodecyl bromide on nitrogen to yield DDAO.

(12) Salts of nitronic acids ought to be the primary intermediates in the addition of organometallic compounds to nitroalkanes. Evidence that aliphatic nitronic acids undergo elimination reactions to produce a nitrone intermediate may be seen in the unusual reaction (in some cases) of excess organometallic compounds with nitroalkanes

$$C_2H_5ZnI + C_2H_5NO_2 \longrightarrow CH_3CH(C_2H_5)N(OH)C_2H_5$$[13]

and

$$PhCH_2NO_2 + PhMgBr \longrightarrow Ph_2CHN(OH)Ph$$[14]

(13) J. Bewad, *Ber.*, 40, 3065 (1907).

(14) A. Dornow, H. Gehrt, and F. Ische, *Justus Liebigs Ann. Chem.*, **585**, 220 (1954).

Experimental Section

Nmr spectra were determined on a Varian HA-100 spectrometer. Infrared data were determined on a Perkin-Elmer Model 621 grating spectrophotometer. Mass spectral element map data on the pentene–DMHA reaction products were determined on fractions collected from the gc using a Varian MAT SM-1 mass spectrometer operating at a resolution of 10,000. The mass of each ion was determined relative to the fragment peaks of perfluorokerosene. All the reported ions were within 3 mmu of the calculated mass for that formula.

Thermal Decomposition of DDAO. DDAO (4.23 g, 18.4 mmol) was heated in a sealed tube for 0.5 hr at 125°. The crude reaction mixture was mixed with dilute hydrochloric acid and extracted with pentane, using ethanol to break emulsions. The pentane extracts were evaporated at room temperature or below to yield 1-dodecene (0.71 g, 4.2 mmol, 23%). The acidic layer was basified with potassium hydroxide and extracted three times with hexane. Gc analysis at 179° on a silicone column, using peak area corrections from a known mixture, indicated that a 1:2.1 mole ratio of isoxazolidine–DDA was formed, in 75% total yield.

The amine and isoxazolidine could be separated by column chromatography on silica gel, provided the latter was deactivated by slurrying in 2-propanol. Otherwise, carbonyl-containing artifacts resulted. After the deactivated column was washed with hexane, a sample of up to 5 g of mixture could be chromatographed on a column 25 × 250 mm. The sample was added to the column in 2-propanol; elution with hexane yielded any remaining olefin. Elution with a 25:75 2-propanol–acetone mixture yielded the isoxazolidine, and elution with methanol yielded the tertiary amine. Comparison of yields from the column chromatography with gc data suggested that the amine was never quantitatively eluted.

Pyrolysis of small samples of crystalline DDAO at 125° bath temperatures and 0.05 mm yielded virtually no residue (0.75%) and only trace amounts (≪1%) of long chain basic products.

5-Decyl-2-methylisoxazolidine. 1-Dodecene (168 g, 1.0 mol), DMHA[17] (61 g, 1.0 mol), and trimethylamine oxide dihydrate (111 g, 1.0 mol) were stirred in a condenser-equipped flask heated in a 100° bath for 20 hr. After cooling, the upper phase was separated. Distillation yielded 62% unreacted olefin and 36% isoxazolidine, bp 91° (0.5 mm). Yields ranged between 36 and 43% typically. The isoxazolidine was about 98% pure, the impurity being most likely dimethyl-2-dodecylamine. Tetradecene reacted similarly. The lower phase from these reactions was water soluble and darkly colored.

Nmr data on the isoxazolidine (in $CDCl_3$ with external tetramethylsilane reference): τ 9.12 (t, ω-CH_3), 8.72 (s, $-CH_2-$), 9.16–8.24 (broad, weak), 7.66 (weak), 7.33 (s, NCH_3), 6.82 (broad), 5.95 (broad). Infrared bands (neat, CsBr windows): 2961, 2933, 2859, 1087 cm^{-1} (S); 1466, 1379, 1013, 927, 801, 721, 496, 460 cm^{-1} (M); 1433, 1342, 1285, 1214, 1181, 585 cm^{-1} (W). Conventional mass spectral data supporting the structure included a strong (base) peak at *m/e* 70 ($C_3H_4NO^+$) and a strong $C_2H_6NO^+$ (mass60) (methylnitrone) peak.

Degradation of 2-Methyl-5-decylisoxazolidine.[4] The isoxazolidine (532.6 mg) in 15 ml of acetic anhydride was hydrogenated over a mixture of prereduced Adams catalyst and W-2 Raney nickel at 50 psi for 65 hr. The catalysts were filtered and the acetic anhydride was evaporated. The residue was distilled through a Hickman still at a bath temperature of 140–165° (0.038 mm). The distillate, which still showed hydroxyl absorption in the ir, was reacetylated twice by heating on a steam bath for 1 hr with 2 ml of acetic anhydride and 2 drops of dry pyridine. The solvents were removed *in*

(15) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. II, W. A. Benjamin, New York, N. Y., 1966, p 394.

(16) A. K. Hoffmann, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *J. Amer. Chem. Soc.*, **86**, 639 (1964).

(17) The DMHA utilized in this work was prepared by pyrolysis of commercial aqueous dimethyl-*n*-alkylamine oxides *in vacuo* in a wiped film continuous laboratory reactor developed for this purpose.

vacuo and the residue was distilled again, yielding 570 mg of an ester–amide. *Anal.* Calcd for $C_{18}H_{35}NO_3$: C, 69.0; H, 11.3; N, 4.5. Found: C, 70.2; H, 11.5; N, 4.6. Nmr and infrared data were consistent with the expected structure.

This ester–amide (307.4 mg) was pyrolyzed, under nitrogen, until infrared spectra showed that the ester carbonyl had disappeared. A temperature of 300° for 45 min was necessary. The residue was distilled at a bath temperature of 130° (0.04 mm); yield, 106.6 mg. *Anal.* Calcd for $C_{16}H_{31}NO$: C, 75.8; H, 12.3; N, 5.5. Found: C, 75.5; H, 11.6; N, 5.6. Nmr and infrared spectra were consistent with the alkenylmethylacetamide structures expected.

The mixture of olefinic amides was cleaved by the periodate–permanganate method, and the fatty acid methyl esters produced were analyzed by gas chromatography.[18] These analyses showed 58.8% of the double bonds to be at the $\Delta^{2,3}$ position and 40.1% at the $\Delta^{3,4}$ position.

Reaction of 1-Dodecene with Dimethylhydroxylamine. 1-Dodecene (4.0 g, 23.8 mmol) and DMHA (2.9 g, 47.6 mmol) were heated in a heavy-wall sealed tube at 125° for 15 hr. Pentane and water were added, the mixture was acidified, and the pentane phase was extracted with water. The combined aqueous phases were basified and hexane was extracted. The solvent was evaporated and the product analyzed by gc. The products were *N,N*-dimethyl-2-dodecylamine (36%) and 5-decyl-2-methylisoxazolidine (47%).

The amine was isolated by column chromatography as described in the DDAO decomposition section (above). It possessed two C–CH_3 groups according to the nmr spectrum ($CDCl_3$), one the usual distorted triplet characteristic of long chain compounds, and superimposed on this a doublet at τ 9.08 (J = 3.5 Hz). In addition, a methylene peak at τ 8.74 and a $N(CH_3)_2$ peak at τ 7.82 were observed. A strong mass 72 peak ($C_4H_{10}N^+$) in the conventional mass spectrum was observed, in agreement with the assigned structure.

The compound isolated was identical with an authentic sample prepared as follows

$$C_{10}H_{21}C(=O)CH_3 + NH_2OH \longrightarrow C_{10}H_{21}C(=NOH)CH_3$$

The reaction took place in refluxing ethanol for 90 min, and the product was recrystallized from ethanol–water, mp 42.0–42.2°. *Anal.* Calcd for $C_{12}H_{25}NO$: C, 72.4; H, 12.6; N, 7.0. Found: C, 73.0; H, 12.6; N, 7.0. Infrared and nmr spectra were consistent with the structure

$$C_{10}H_{21}C(=NOH)CH_3 + H_2 \longrightarrow C_{10}H_{21}CH(NH_2)CH_3$$

The oxime was hydrogenated in ethanol over Raney nickel (5.5 hr at 50 psi), bp 45–46° (0.07 mm). Gc analysis revealed only a single peak and nmr and elemental analyses were consistent with the expected structure

$$C_{10}H_{21}CH(NH_2)CH_3 + CH_2O/HCO_2H \longrightarrow C_{10}H_{21}CH[N(CH_3)_2]CH_3$$

The amine (1.85 g, 10 mmol) was refluxed with 3.4 g of 36% formalin and 3.4 g of 90% formic acid for 24 hr. Isolation of the basic products yielded somewhat impure (gc) dimethylalkylamine. Collection of the major peak from the gc and redistillation from a Hickman still (pot 80° (0.1 mm)) yielded a pure sample identical with the major amine product of the 1-dodecene–DMHA reaction (infrared, nmr, and mass spectral comparisons).

Reaction of Pentenes with Dimethylhydroxylamine. A pentene (14.0 g, 0.2 mol, purchased from Chemical Samples Co., Columbus, Ohio) and DMHA (24.4 g, 0.4 mol) were sealed in a tube and heated at 125° for 18 hr (autoclave). After cooling in ice, the tube was opened and aqueous 5% hydrochloric acid (0.45 mol) added. The olefin phase was separated, and the aqueous phase was saturated with potassium carbonate, with agitation and cooling. The organic phase was separated, dried over molecular sieves, and distilled at 25° into a Dry Ice cooled receiver. The basic products were analyzed by gc on a 10 ft × 0.25 in. 15% Carbowax 20M on Chromosorb column (isothermally at 45° till the amines came off (8 min), then programmed manually to 140° over 15 min). Isomeric pentyldimethylamines were identified by direct gc comparison with authentic samples. Yields were calculated from peak areas after applying an appropriate correction factor (0.94) to the amine peaks. Products are listed in Table I in order of emergence. Pertinent mass spectral element map data are listed in Table II.

Synthesis of *N,N*-Dimethyl-*O*-dodecylhydroxylamine. *N*-Hydroxyurethane and *N*-dodecoxyurethane were prepared by the procedure of Fuller and King.[19]

Dodecoxyamine. Potassium hydroxide (22.4 g, 0.4 mol) in 400 ml of water was added to dodecoxyurethane (27.3 g, 0.1 mol) at room temperature with stirring. The mixture was refluxed 8 hr. The cooled reaction was then extracted two times with hexane and once with ether; the organic phase was dried over potassium hydroxide and then over potassium carbonate (21.6 g). The sample was dissolved in a 1:3 mixture of alcohol–water, acidified with 2 *N* hydrochloric acid, and extracted with hexane. The alcohol–water layer was then basified with potassium hydroxide; the product was extracted with ether, dried over potassium hydroxide, and distilled to yield 7.7 g of dodecoxyamine (45%), bp 69–75° (0.006 mm). *Anal.* Calcd for $C_{12}H_{27}NO$: C, 71.6; H, 13.5; N, 6.7. Found: C, 71.9; H, 13.5; N, 6.8. The nmr showed a triplet at τ 6.35 ($-CH_2CH_2O-$) and the infrared spectrum a band at 1580 cm^{-1} (NH_2 bending mode), both consistent with the *O*-alkyl structure.

***N,N*-Dimethyl-*O*-dodecylhydroxylamine.** Dodecoxyamine (5.0 g, 24.9 mmol), formalin (10 ml, 100 mmol), and 90% formic acid (20.4 ml, 400 mmol) were combined, stirred, and refluxed for 58 hr. Volatile materials were evaporated under vacuum, the residue was dissolved in water, and the solution was made basic with potassium carbonate. Extraction with ether and hexane and drying over potassium carbonate, followed by distillation, yielded 4.4 g of product. Infrared spectra at this point showed carbonyl impurities to be present, so the product was refluxed in 50 ml of alcohol containing 2.5 g of potassium hydroxide. Redistillation yielded 4.1 g (72%), bp 97–98° (0.8 mm). *Anal.* Calcd for $C_{14}H_{31}NO$: C, 73.3; H, 13.6; N, 6.1. Found: C, 71.7; H, 13.2; N, 5.9. Nmr, infrared, and mass spectral data were consistent with the expected structure. For example, an intense peak in the mass spectrum was observed at *m/e* 61, corresponding to $(CH_3)_2N^+OH$. This was not observed in the isoxazolidine spectra. The structure was firmly established by reductive cleavage over W-2 Raney nickel in ethanol to dodecanol and dimethylamine. Gc analyses of the basic fraction from the DDAO decomposition (above) failed to reveal any evidence for formation of this material in the decomposition. Gc of known mixtures suggested that 0.2% of the *O*-dodecyl compound would have easily been detected.

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