Chemistry of Epoxy Compounds. XXII. Preparation of Some Long-Chain 2-Oxazolidones[1]

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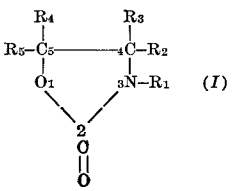
Abstract

Long-chain aliphatic compounds containing the 2-oxazolidone moiety have been prepared from *cis*- and *trans*-9-octadecene, methyl oleate, and elaidate, oleyl and elaidyl alcohols, and several long-chain terminal epoxides. The 2-oxazolidones prepared are substituted in the 4-, 4,5-, or 3,5-positions. The first two groups of oxazolidones are obtained by pyrolysis of β-iodocarbamates, prepared from terminal and internal monounsaturated compounds respectively by the addition of iodine isocyanate and by reaction with methanol. The last group is prepared by heating terminal epoxides with organic isocyanates in DMF containing a catalytic quantity of tetramethylammonium iodide or lithium chloride. Structures have been confirmed by elemental and spectral analysis.

Introduction

The 2-oxazolidones are an important class of heterocyclic compounds containing a five-membered ring. They have the general structure and numbering system shown (*I*):



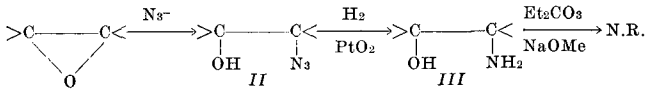
(*I*)

Although numerous 2-oxazolidones have been prepared with a wide variety of substituent groups (R=H or organic groups), a careful search of the literature (2) showed that the 2-oxazolidone moiety had not been introduced onto the alkyl chain of long-chain aliphatic compounds. This paper describes the preparation of some a) 4,5-disubstituted 2-oxazolidones from *cis*- and *trans*-9-octadecene, methyl oleate, and elaidate, also oleyl and elaidyl alcohols, and b) 4-substituted and 3,5-disubstituted 2-oxazolidones from long-chain terminal epoxides.

Results and Discussion

Initial studies were conducted on *cis*- and *trans*-9-octadecene as model compounds (3) with the object of obtaining the geometrical isomers of the 4,5-di-*n*-octyl-2-oxazolidones (*I*:R_1, R_3, $R_4 = H$ and R_2, $R_5 =$ *n*-octyl). Reaction of *cis*- and *trans*-9,10-epoxyoctadecane, obtained from the corresponding olefins by epoxidation (4), with potassium cyanate and a nucleophilic catalyst in aqueous dimethyl formamide at 120°, a reaction that furnishes 2-oxazolidones in fair-to-good yield from terminal long-chain epoxides (1), yielded unconverted starting-materials.

An alternative approach that had been successful with terminal olefins also was attempted. This consisted in conversion of the epoxides to the azidohydrins (*II*) by ring opening with azide ion, followed by catalytic hydrogenation over platinum oxide to the amino alcohols (*III*) and their attempted ring closure to the 2-oxazolidones by reaction in the conventional way with diethyl carbonate and sodium methoxide (Homeyer method) (2,5).



Although no difficulty was experienced in preparing the azidohydrins (*II*) or aminoalcohols (*III*) (6,7), the ring closure step was unsuccessful; starting materials (*III*) were recovered. No attempt was made to develop forcing conditions for ring closure.

The lack of success in preparing 2-oxazolidones from the epoxides by these two routes prompted an alternative procedure, which proved to be successful with the 9-octadecenes as well as with the four other long-chain compounds. This sequence is summarized in Fig. 1.

Iodine isocyanate adds stereospecifically to a *cis* (*trans*) double bond to yield the *threo* (*erythro*) adduct (8-10). Reaction with methanol converts the adduct to the corresponding carbamate without a change in stereochemistry. Pyrolysis at 150–180° is a smooth internal displacement, with inversion and elimination of methyl iodide (11,12), yielding the *cis* (*trans*) 2-oxazolidone. Two inversions are involved in proceeding from an internal unsaturated compound to the 2-oxazolidone; thus the 2-oxazolidone has the same geometrical configuration as the starting material.[3]

To assess the generality of the iodine isocyanate route, 2-oxazolidones were also prepared by pyrolysis of the iodocarbamates from 1-dodecene (12), 1-tetradecene, and 1-hexadecene. The products are 4-alkyl-2-oxazolidones (IV) (12), not the 5-isomers, because iodine isocyanate adds predominantly in Markownikow fashion (10). The structure of these products has been proven by chemical and physical means (12).

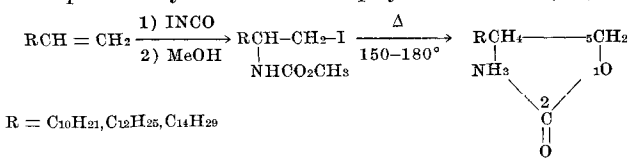


Table I lists the iodocarbamates formed by the addition of iodine isocyanate to unsaturated compounds, followed by reaction with methanol; Table II lists the 2-oxazolidones obtained by pyrolysis of the iodocarbamates.

Iodocarbamates are slightly unstable and develop color on exposure to light. On long storage they are slowly converted to 2-oxazolidones. Because of their lability there was no attempt to chromatograph them, but in several cases they were partially purified by recrystallization. Usually their iodine content was

[1] Presented at the AOCS Meeting, Washington, D.C., March 1968. Taken from the thesis of M. E. D. in partial fulfillment of the requirements for the Ph.D. degree, Temple University, June 1967.

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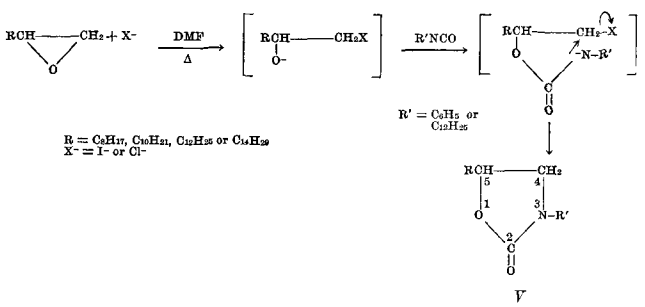
[3] Recent work has shown that the ring closure is stereoselective, not stereospecific.

low and their carbon content high, but since they yielded 2-oxazolidone of acceptable analytical purity, no special effort was made to obtain analytically pure iodocarbamates.

The pyrolytic conversion of β-iodocarbamates to 2-oxazolidones is readily monitored by infrared spectroscopy. The β-iodocarbamates have a carbonyl absorption band near 1730 cm^{-1} and an amide-II band near 1510 cm^{-1}. The 2-oxazolidones have a carbonyl band near 1760 cm^{-1} and the amide-II band is absent. The reaction can also be followed by observing the evolution of and collecting the methyl iodide produced, but such a procedure is not convenient on a small preparative scale.

The *cis*- and *trans*-4,5-di-*n*-octyl-2-oxazolidones, mp 15C and 23C respectively are crystalline solids that are readily purified by column chromatography. The 2-oxazolidones from unsymmetrical long-chain internally unsaturated compounds (methyl oleate and elaidate, oleyl and elaidyl alcohols) are mixtures of positional isomers. They could not be crystallized at low temperatures nor could they be distilled. Column chromatography was the only effective purification technique. The 4-alkyl-2-oxazolidones prepared from 1-olefins are crystalline solids, readily purified by solvent crystallization.

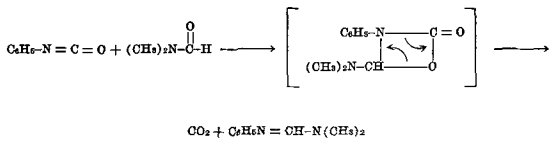
The six long-chain 2-oxazolidones are unsubstituted on nitrogen. Since there was available a series of pure long-chain terminal epoxides from an earlier study (1), it was decided to prepare a number of hitherto unreported 3,5-disubstituted 2-oxazolidones (*V*) by reaction of the epoxides with organic isocyanates in dimethyl formamide (DMF) by using tetramethylammonium iodide or lithium chloride as catalyst, as shown in the equations below:



V

Several 3,5-disubstituted 2-oxazolidones had been previously prepared by this procedure (1,13,14) from organic isocyanates and styrene oxide, glycidyl ethers, or terminal expoxides in which R, with one exception, contained fewer than four carbon atoms (13).

In the literature procedures, isocyanate, epoxide, and catalyst are heated in DMF, followed by removal of excess reactants and solvent by vacuum distillation. The residue is then recrystallized to analytical purity. To save time the reaction mixture was poured into water, and the product was extracted in some cases. Also, since phenyl isocyanate can react with DMF to yield a formamidine (*VI*) (15,16), as the following equation shows, in most cases it was preferred to add the isocyanate dropwise to the refluxing DMF solution of epoxide and catalyst (LiCl), thus guaranteeing an excess of epoxide relative to isocyanate at all times. (This procedure was suggested by John Herweh, Armstrong Cork Company.) Products are thereby easier to purify.



$$CO_2 + C_6H_5N{=}CH{-}N(CH_3)_2$$

VI

Table III lists the 3,5-disubstituted 2-oxazolidones which were prepared. All of the compounds were crystalline solids readily purified by recrystallization. The low yields in the table are more a reflection of the small scale of the preparation and recrystallization losses than of reaction inefficiency. Crude reaction products, obtained in almost quantitative yields, had infrared spectra that differed only slightly from those of the analytically pure products.

The analytically pure disubstituted 2-oxazolidones, isolated from the reaction of organic isocyanates and long-chain terminal epoxides, are disubstituted in the 3,5-positions, not in the 3,4-, as shown by physical methods, mainly NMR. As described elsewhere in detail, the NMR spectra of 5-alkyl-2-oxazolidones are significantly different from those of the 4-isomers (3-substitution on nitrogen does not alter the argument).

In the case of known 5-alkyl derivatives, the signal of the methine proton, H_A (Table III), appears as a complex multiplet centered at about 4.6 ppm downfield from TMS. It is split by the two equivalent methlyene protons α to the oxazolidone ring and by the two nonequivalent protons H_B and H_C on the 4-position of the ring. Since the methine proton H_A in 5-alkyl derivatives is on a carbon atom attached to oxygen, a more electronegative atom than nitrogen, its signal should be (and is) farther downfield from TMS than the proton H_B and H_C (multiplet centered at about 3.5 ppm) on the 4-position of the ring (17).

In the case of 4-alkyl derivatives, the signal of the methine proton H_A moves slightly upfield to about 4.3-4.4 ppm, and the signal of H_B and H_C moves slightly downfield. Thus, in 5-alkyl-2-oxazolidones, the signals of the H_A proton and those of H_B and and H_C should be (and are) farther apart than in

TABLE I

β-Iodocarbamates by Addition of Iodine Isocyanate to Unsaturated Compounds, Followed by Reaction with Methanol

			Iodocarbamate							
			C%		H%		N%		I%	
Unsaturated compound	MP, °C	Yield, %	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
cis-9-Octadecene	25–6	38	53.0	53.9	8.89	9.14	3.09	3.02	28.0	25.5
trans-9-Octadecene	38.9	68	53.0	56.1	8.89	9.39	3.09	2.73	28.0	24.5
Methyl oleate	a	98[a]	50.7	53.5	8.12	8.35	2.82	3.02	25.5	21.2
Methyl elaidate	a	98[a]	50.7	54.5	8.12	8.80	2.82	2.18	25.5	20.5
Oleyl alcohol	a	98[a]	51.2	54.5	8.59	9.19	2.99	2.12	27.0	21.8
Elaidyl alcohol	a	98[a]	51.2	54.6	8.59	9.06	2.99	2.79	27.0	20.0
1-Dodecene	67.5–9	35	45.5	46.0	7.64	7.61	3.79	3.74	34.4	32.2
1-Tetradecene	74–5	17	48.4	49.1	8.11	7.89	3.53	3.56	31.9	30.0
1-Hexadecene	79–80	40	50.8	52.1	8.53	8.70	3.29	3.40	29.8	26.0

[a] Crude, isolated reaction products, obtained as oils.

the 4-isomers. This situation is always realized with known pairs of isomeric 5- and 4-alkyl-2-oxazolidones (12).

The 3,5-disubstituted compounds (Table III) described in this paper have NMR spectra analogous to those of known 5-alkyl-2-oxazolidones and are thus assigned the structure shown in Table III; the NMR spectra of the 4-alkyl 2-oxazolidones in Table II resemble those of known 4-substituted 2-oxazolidones.

Experimental Procedures

Equipment and Materials. Infrared spectra were obtained on a Perkin-Elmer Infracord, Model 137, by using either a thin liquid film or a 3–5% solution in chloroform or carbon tetrachloride in 0.096, 0.103, or 0.151-mm matched cells with sodium chloride windows.

When applicable, the extent of reaction was monitored by gas chromatography on a Wilkens Aerograph Autoprep Model A-700 by using the following columns (10 ft × 0.25 in.) as needed: 10% butanediol succinate, 10% SE-30, and 15% Apiezon-L, all on 60 mesh Anakrom ABS. NMR spectra were obtained with a Varian A60-A spectrometer.

Melting points were determined on a Thomas-Hoover Capillary Melting-Point Apparatus. Melting points and boiling points were uncorrected. Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, Del.

Column chromatography was performed with Florisil as the stationary phase. It was purchased from the Fisher Scientific Company and used directly.

Tetrahydrofuran was purified by treating it with potassium hydroxide overnight, filtering, and shaking it over sodium. It was then distilled at atmospheric pressure, retaining only the center cut; it was stored over calcium hydride in the dark and used as needed. Dimethylformamide (DMF) was purified by a literature procedure (18). All other solvents were of the highest quality and were used as received.

Silver cyanate was prepared from pure potassium cyanate and silver nitrate (19). Iodine was the triply sublimed grade. Phenyl isocyanate was purchased from the Eastman Organic Chemicals and dodecyl isocyanate from the City Chemical Corporation. Both isocyanates were used as received.

Oleyl alcohol, "Adol-90," purchased from the Archer Daniels Midland Company, was distilled through a one-meter adiabatic Vigreux column. The main fraction, bp 173 C/0.6 mm and $n_D^{15} = 1.4629$, was shown to be 96% pure by GLC and iodine number. Elaidyl alcohol, mp 34.5–35.5C, was prepared by selenium isomerization of the purified oleyl alcohol (20,21).

The *cis*- and *trans*-9-octadecene were prepared from oleyl and elaidyl alcohol respectively (3). The olefins were distilled before use.

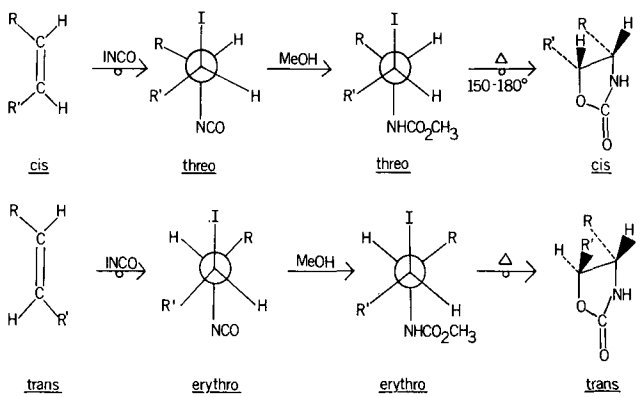
Oleic acid, "Emery 3528R," purchased from Emery Industries, was esterified by refluxing it for 3 hr with excess methanol (2 ml/g of acid), containing 1% concentrated sulfuric acid based on oleic acid. The reaction mixture was poured into excess water, and the upper layer was washed until the washings were neutral. After drying overnight under vacuum in a stream of inert gas, the ester was distilled as described above. The main fraction, bp 165C/0.7 mm and $n_D^{25} = 1.4506$, was shown to be 96–97% pure by GLC and iodine number.

Elaidic acid, mp 44.5C, was prepared from the oleic acid by isomerization with nitrous acid (22). Methyl elaidate was obtained from elaidic acid as described under the preparation of methyl oleate.

The 1-decene and 1-hexadecene were purchased from the Humphrey Chemical Company. They were greater than 95% pure (GLC) and were used for subsequent epoxidation without further purification. The 1,2-epoxydecane, bp 95–6C/11.3–11.7 mm, and 1,2-epoxyhexadecane, bp 144–5C/0.75 mm, were prepared from the corresponding olefins by epoxidation with peroxyacetic acid (4). The *cis*- and *trans* 9,10-epoxyoctadecane were prepared from *cis*- and *trans*-9-octadecene respectively in the same manner (4) and were used without distillation.

The 1,2-epoxydodecane, bp 89–90C/0.6 mm and 1,2-epoxytetradecane, bp 103–4C/0.6 mm, were purchased from Chemical Intermediates and Research Laboratories and Archer Daniels Midland Company respectively. The epoxides were fractionally distilled before use; both were found to be at least 98% pure (GLC) after distillation.

2-Oxazolidones from Unsaturated Compounds and Iodine Isocyanate. General Procedure (Fig. 1). Io-



(R = *n*-octyl and R′ = *n*-octyl, $-(CH_2)_7CO_2CH_3$ or $-(CH_2)_7CH_2OH$)

FIG. 1. The 2-oxazolidones from unsaturated compounds and iodine isocyanate.

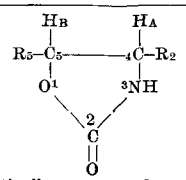
dine (25.4 g; 0.10 mole) was dissolved in tetrahydrofuran (150 ml) in a three-neck, round-bottom flask, fitted with a mechanical stirrer and a low temperature thermometer and wrapped in aluminum foil to keep out light. The stirred solution was cooled to −50C, silver cyanate (20 g, 0.12 mole) was added in one portion, and stirring was continued at −50C for 1.5 hr (23). The unsaturated compound (0.10 mole) in tetrahydrofuran (50 ml) was added in one portion, and stirring was continued for an additional 2 hr at −50C. The cooling bath was then removed, and the flask and contents were allowed to come to room temperature with stirring. The reaction mixture was filtered, and the insoluble solids were thoroughly washed with tetrahydrofuran. The combined filtrate and washings were evaporated to about one-third of the original volume in a rotating vacuum evaporator, without heating.

Anhydrous methanol (200 ml) was added to the concentrated solution, and it was stirred overnight at room temperature in the dark. (Refluxing should be avoided to minimize iodine loss by displacement and/or elimination.) The reaction mixture was poured into water (300–400 ml) containing sufficient sodium bisulfite to destroy any remaining iodine, and it was extracted several times with ether. The ether extracts were combined, washed several times with water, and dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated under vacuum

TABLE II

2-Oxazolidones[a] by Pyrolysis of β-Iodocarbamates

2-Oxazolidone	MP, °C	Yield, %[b]	C%		H%		N%	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
cis-4,5-di-*n*-Octyl	15–6	65	73.3	73.2	12.0	12.0	4.50	4.67
trans-4,5-di-*n*-Octyl	22.5–3.5	78	73.3	73.2	12.0	12.1	4.50	4.54
cis-4(5)-*n*-Octyl-5(4)-(7-carbomethoxyheptyl)	oil	50	67.6	67.6	10.5	10.5	3.94	3.87
trans-4(5)-*n*-Octyl-5(4)-(7-carbomethoxyheptyl)	oil	70	67.6	68.1	10.5	10.5	3.94	3.82
cis-4(5)-*n*-Octyl-5(4)-(8-hydroxyoctyl)	oil	52	69.7	69.4	11.4	11.4	4.28	4.01
trans-4(5)-*n*-Octyl-5(4)-(8-hydroxyoctyl)	oil	45	69.7	69.6	11.4	11.4	4.28	4.08
4-*n*-Decyl	31.5–2.5	55	68.7	68.6	11.1	11.0	6.16	6.08
4-*n*-Dodecyl	46–7	88	70.5	70.7	11.5	11.6	5.48	5.42
4-*n*-Tetradecyl	54–5	34	72.0	72.2	11.7	11.5	4.94	4.75

[a] 

$R_5 = H_C$ in the last three cases listed in the table.

[b] Analytically pure products, based on iodocarbamates.

at room temperature, and the residue, if solid, was purified by recrystallization. Infrared spectra (neat or in chloroform solution) revealed that the isocyanate absorption band near 2280 cm^{-1} had completely disappeared and new bands near 3500 (N-H), 1730 (C=O), and 1510 (amide-II) cm^{-1} had appeared. These last three absorptions are characteristic of β-iodocarbamates. Table I lists the β-iodocarbamates prepared.

A portion of the β-iodocarbamate (approximately 5 g) was pyrolyzed neat (11) at 150–80C under a blanket of nitrogen, and the resulting residue was purified either by recrystallization or chromatography on Florisil (specific cases follow). Table II lists 2-oxazolidones obtained by the procedures just described.

cis-4,5-Di-n-Octyl-2-Oxazolidone. Methyl N-(*threo*-9-iodo-10-octadecyl)carbamate, mp 25–6C (recrystallized from acetone), was obtained in 38% yield from *cis*-9-octadecene (25.2 g, 0.10 mole). Pyrolysis, followed by chromatography, gave the 2-oxazolidone in 65% yield, based on iodocarbamate; over-all yield from olefin was 25%.

Purification was by column chromatography of the crude pyrolyzate (2.4 g dissolved in a minimum of pentane) on Florisil (200 g). Successive elution with pentane (1200 ml) and 50% ether-pentane (2800 ml) gave the analytically pure 2-oxazolidone, mp 15–6C, in the last eluates. Its infrared spectrum in $CHCl_3$ showed bands at 3500 and 3300 (N-H doublet), 1760 (C=O), 1470, 1400, and 1105 cm^{-1}.

trans-4,5-Di-n-Octyl-2-Oxazolidone. Methyl N-(*erythro*-9-iodo-10-octadecyl)carbamate, mp 38–9C (recrystallized from acetone), was obtained in 68% yield from *trans*-9-octadecene (25.2 g, 0.10 mole). Pyrolysis, followed by chromatography, gave the 2-oxazolidone in 78% yield, based on iodocarbamate; over-all yield from olefiin was 53%.

Purification by column chromatography (5 g of crude product on 200 g of Florisil), essentially as described above, gave the analytically pure 2-oxazolidone, mp 22.5–23C, in the last eluates (100% ether). Its infrared spectrum in $CHCl_3$ was essentially identical with that of the *cis*-isomer.

cis - 4(5)-n-Octyl - 5(4)-7-Carbomethoxyheptyl)-2-Oxazolidone. Methyl N- [*threo*-8(9)-iodo-9(8)-(1-carbomethoxyheptadecyl)] carbamate, yellow oil, was obtained in 98% yield from methyl oleate (29.6 g, 0.10 mole). Pyrolysis, followed by chromatography, gave the 2-oxazolidone in 50% yield, based on iodocarbamate; over-all yield from methyl oleate was 49%.

Purification was by column chromatography of the crude pyrolyzate (3 g of crude product on 200 g of Florisil). Successive elution with ether (1700 ml), 10% acetone-ether (1400 ml), and 20% acetone-ether (1200 ml) gave the analytically pure 2-oxazolidone in the last eluates. Its infrared spectrum (neat) showed bands at 3300 (N-H), 1750 (C=O), 1460, 1430, 1235, 1190, and 1160 cm^{-1}.

trans-4(5)-n-Octyl-5(4)-(7-Carbomethoxyheptyl)-2-Oxazolidone. Methyl N-[*erythro*-8(9)-iodo-9(8)-(1-carbomethoxyheptadecyl)] carbamate, yellow oil, was obtained in 90% yield from methyl elaidate (29.6 g, 0.10 mole). Pyrolysis, followed by chromatography, gave the 2-oxazolidone in 70% yield, based on iodocarbamate; over-all yield from methyl elaidate was 63%.

Purification by column chromatography (4 g of crude product on 200 g of Florisil), essentially as described above, gave the analytically pure 2-oxazolidone in the last eluates (25% acetone-ether). Its infrared spectrum in $CHCl_3$ showed bands at 3350 and 3350 (N-H doublet), 1760 (C=O), 1470, 1440, 1400, 1230, 1185, and 1110 cm^{-1}.

cis-4(5)-n-Octyl-5(4)-(8-hydroxyoctyl)-2-Oxazolidone. Methyl N-[*threo*-9(10)-iodo-10(9)-(1-hydroxyoctadecyl)] carbamate, yellow oil, was obtained in 98% yield from oleyl alcohol (26.8 g, 0.10 mole). Pyrolysis, followed by chromatography, gave the 2-oxazolidones in 52% yield, based on iodocarbamate; over-all yield from oleyl alcohol was 51%.

Purification by column chromatography (3 g of crude product on 200 g of Florisil), essentially as described above, gave 1.8 g of almost pure 2-oxazolidone in the last eluates. A portion of this material (0.9 g on 75 g of Florisil) was rechromatographed to obtain the analytically pure compound (0.83 g) in the last fractions (50% acetone-ether). Its infrared spectrum (neat) showed bands at 3300 (N-H, O-H, broad), 1760 (C=O), 1460, 1390, 1240, and 1055 cm^{-1}.

trans-4(5)-n-Octyl-5(4)-(8-hydroxyoctyl)-2-Oxazolidone. Methyl N- [*erythro* - 9(10 - iodo - 10(9) - (1-hydroxyoctadecyl)] carbamate, yellow oil, was obtained in 98% yield from elaidyl alcohol (26.8 g, 0.10 mole). Pyrolysis, followed by chromatography, gave the 2-oxazolidone in 45% yield, based on iodocarbamate; over-all yield from elaidyl alcohol was 43%.

Purification by column chromatography (3 g of

crude product on 200 g of Florisil), essentially as described above, gave the analytically pure 2-oxazolidone in the last eluates (10% acetone-ether). Only one chromatographic separation was required to obtain the compound. Its infrared spectrum in $CHCl_3$ showed bands at 3500 and 3300 (N-H, O-H, doublet), 1760 (C=O), 1460, 1395, 1235, and 1105 cm^{-1}.

4-n-Decyl-2-Oxazolidone. Methyl N-(1-iodo-2-dodecyl)carbamate, mp 67.5-9C (recrystallized from hexane), was obtained in 35% yield from 1-dodecene (16.8 g, 0.10 mole). Pyrolysis, followed by recrystallization from hexane, gave the analytically pure 2-oxazolidone, mp 31.5–2.5C (12), in 55% yield based on iodocarbamate; over-all yield from olefin was 19%. Its infrared spectrum in $CHCl_3$ showed bands at 3500 and 3300 (N-H doublet), 1760 (C=O), 1400, and 1240 cm^{-1}.

4-n-Dodecyl-2-Oxazolidone. Methyl N-(1-iodo-2-tetradecyl)carbamate, mp 74–5C (recrystallized from hexane), was obtained in 17% yield from 1-tetradecene (19.6 g, 0.10 mole). Pyrolysis, followed by crystallization from hexane, gave the analytically pure 2-oxazolidone, mp, 46–7C, in 88% yield, based on iodocarbamate; over-all yield from olefin was 15%. Its infrared spectrum in $CHCl_3$ was essentially the same as that of 4-*n*-decyl-2-oxazolidone.

4-n-Tetradecyl-2-Oxazolidone. Methyl N-(1-iodo-2-hexadecyl)carbamate, mp 79–80C (recrystallized from acetone), was obtained in 40% yield from 1-hexadecene (22.4 g, 0.10 mole). Pyrolysis, followed by chromatography, gave the 2-oxazolidone in 34% yield, based on iodocarbamate; over-all yield from olefin was 14%.

Purification by column chromatography (1.1 g, of crude product on 75 g of Florisil), essentially as described earlier, gave an almost analytically pure 2-oxazolidone in the last eluates (20% acetone-ether). The product was recrystallized from hexane; mp 54–5C.

3,5-Disubstituted 2-Oxazolidones from Epoxides and Organic Isocyanates (Table III). Method A. DMF (25 ml), organic isocyanate (0.03 mole), epoxide (0.025 mole), and tetramethylammonium iodide (0.2 g), were placed in a 50-ml, three-neck, round-bottom flask, fitted with a mechanical stirrer and a reflux condenser topped by a calcium chloride drying tube. The third neck was sealed with a rubber septum. The reactants were stirred and heated to 150–60C for 4–5 hr with periodic withdrawal of samples through the rubber septum by means of a hypodermic syringe to follow the disappearance of isocyanate and epoxide by GLC. The reaction mixture was then allowed to cool to room temperature, poured into water (200–300 ml), and extracted several times with a suitable solvent (see below). The water-washed extracts were dried and filtered; the solvent was evaporated under vacuum. The residual solids were purified by recrystallization. *Method B.* DMF (25 ml), lithium chloride (0.2 g), and epoxide (0.025 mole) were heated to reflux, and isocyanate (0.03 mole) was added dropwise over a 2–2.5-hour period. After an additional two hours, the reaction mixture was worked up as in Method A. *Method C.* This was the same as Method A except that at the end of the reaction period the DMF was removed by vacuum distillation and the residual solid was recrystallized. *Method D.* This was the same as Method B with the removal of DMF by vacuum distillation.

3-Phenyl-5-Octyl-2-Oxazolidone. This was prepared in 41% yield by Method D from 1,2-epoxyhexadecane (3.9 g) and phenyl isocyanate (3.6 g). Recrystallization from hexane yielded the pure compound, mp 69.5–70C. Its infrared spectrum in $CHCl_3$ showed bands at 1770 (C=O), 1610, 1510, 1500, 1420, 1320, 1220, 1140, and 685 cm^{-1}.

3-Phenyl-5-n-Decyl-2-Oxazolidone (13). This was prepared in 25% yield by Method C from 1,2-epoxydodecane (4.6 g) and phenyl isocyanate (3.6 g). Recrystallization from petroleum ether (bp 30–60C) yielded the pure compound, mp 68.5–9C.

Its infrared spectrum in CCl_4 was essentially identical with that of the previous compound.

3-Phenyl-5-n-Dodecyl-2-Oxazolidone. This was prepared in 10% yield by Method C from 1,2-epoxytetradecane (5.3 g) and phenyl isocyanate (3.6 g). Recrystallization from heptane yielded the pure compound, mp 74–5C. Its infrared spectrum in CCl_4 was essentially the same as those of the previous compounds.

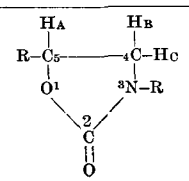
3-Phenyl-5-n-Tetradecyl-2-Oxazolidone. This was prepared in 16% yield by Method A from 1,2-epoxyhexadecane (6.0 g) and phenyl isocyanate (3.6 g). After extraction with ether, the crude product was recrystallized from hexane to yield the pure compound, 79–9.5C. Its infrared spectrum in $CHCl_3$ was essentially the same as those of the previous compounds.

3-n-Dodecyl-5-n-Octyl-2-Oxazolidone. This was prepared in 40% yield by Method B from 1,2-epoxydecane (3.9 g) and dodecyl isocyanate (6.3 g). After extraction with ether, the crude product was recrystallized from hexane to yielded the pure compound,

TABLE III

3,5-Disubstituted 2-Oxazolidones[a] Prepared from Epoxides and Organic Isocyanates

2-Oxazolidones	MP, °C	Yield, %[b]	C%		H%		N%	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
Phenyl-5-octyl	69.5–70	41	74.1	74.2	9.15	9.04	5.09	5.31
Phenyl-5-decyl(13)	68.5–69	25	.....	.....	....	.....	4.62	4.79
Phenyl-5-dodecyl	74–5	10	76.1	76.1	10.0	9.85	4.23	4.44
Phenyl-5-tetradecyl	79–9.5	16	76.9	76.6	10.4	10.1	3.90	4.09
Dodecyl-5-octyl	50.5–51.5	40	75.2	75.2	12.3	12.3	3.81	4.00
Dodecyl-5-decyl	61–2	50	75.9	76.0	12.5	12.6	3.54	3.71
5-Didodecyl	69.5–70.5	74	76.5	76.4	12.6	12.5	3.31	3.30
Dodecyl-5-tetradecyl	63.5–64.5	48	77.1	77.4	12.7	12.8	3.10	3.30

[a] 

[b] Analytically pure products.

mp 50.5–1.5C. Its infrared spectrum in $CHCl_3$ showed bands at 1760 (C=0), 1500, 1460, 1375, and 1265 cm^{-1}.

3-n-Dodecyl-5-n-Decyl-2-Oxazolidone. This was prepared in 50% yield by Method D from 1,2-epoxydodecane (4.6 g) and dodecyl isocyanate (6.3 g), Recrystallization from hexane yielded the pure compound, mp 61–2C. Its infrared spectrum in $CHCl_3$ was essentially the same as that of the previous compound.

3,5-di-n-Dodecyl-2-Oxazolidone. This was prepared in 74% yield by Method B from 1,2-epoxytetradecane (5.3 g) and dodecyl isocyanate (6.3 g). After extraction with $CHCl_3$, the crude product was recrystallized from heptane to yield the pure compound, 69.5–70.5C. Its infrared spectrum in $CHCl_3$ was essentially the same as that of the previous compound.

3-n-Dodecyl-5-n-Tetradecyl-2-Oxazolidone. This was prepared in 48% yield by Method B from 1,2-epoxyhexadecane (6.0 g) and dodecyl isocyanate (6.3 g). After extraction with ether, the crude product was recrystallized from hexane to yield the pure compound, mp 63.5–4.5C. Its infrared spectrum in $CHCl_3$ was essentially the same as that of the previous compound.

threo-9-Amino-10-Hydroxyoctadecane. A solution of sodium azide (7.8 g, 0.12 mole), ammonium chloride (6.5 g, 0.12 mole), and *cis*-9,10-epoxyoctadecane (26.8 g, 0.10 mole) in ethanol (500 ml) and water (400 ml) was refluxed for 48 hr and then poured into a large quantity of water. The insoluble material was extracted with ether, and the ether solution was washed with water, dried, and filtered. Evaporation of the ether yielded the azidohydrin (infrared spectrum in $CHCl_3$ showed bands at 3400 (OH), 2110, and 1270 (azide) cm^{-1} (6,7).

Without purification the azidohydrin was dissolved in absolute ethanol (200 ml), a small quantity of PtO_2 was added, and the mixture was stirred for 48 hr at room temperature under a hydrogen pressure of approximately 800 psi. The solution was filtered with the aid of Filter-cel, the filtrate was evaporated to dryness, and the residue was recrystallized from heptane. The product, *threo*-9-amino-10-hydroxyoctadecane, mp 56.5–8C, was obtained in 36% over-all yield from the epoxide. Anal. calcd. for $C_{18}H_{39}NO$: C, 75.5; H, 13.8; N, 4,91. Found: C, 75.8; H, 13.6; N, 4.69. Its infrared spectrum (and that of the *erythro* isomer below) in $CHCl_3$ showed the expected bands at 3500 (N-H, O-H, broad), 2990, and 1475^{-1}.

erythro-9-Amino-10-Hydroxyoctadecane. This was prepared in 21% yield from *trans*-9,10-epoxyoctadecane (26.8 g, 0.10 mole) by the procedure just described with the *cis*-epoxide. Its melting point was 84.5–5.5°. Anal. found: C, 75.6; H, 13.5; N, 4.71.

Reaction of the amino alcohols with diethyl carbonate and sodium methoxide (Homeyer reaction) (5) yielded only unchanged starting-materials.

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