Chemistry of Epoxy Compounds. XXI.[1] Reaction of Potassium Cyanate with Epoxides

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Reaction of potassium cyanate at 120–130° with terminal aliphatic epoxides in dimethylformamide containing controlled quantities of water and tetraethylammonium bromide catalyst yields 5-alkyl-2-oxazolidones in good yield (40–65%). Styrene oxide, 1,2-epoxy-2-methylpentane, and internal aliphatic epoxides do not yield 2-oxazolidones under these conditions. Under anhydrous conditions, terminal aliphatic epoxides yield "dimeric" 2-oxazolidones in low yield. The structures of the monomeric and "dimeric" 2-oxazolidones have been proved by independent, unequivocal synthesis.

Reaction of epoxides with numerous nucleophiles has been studied extensively from the synthetic and mechanistic viewpoints,[3] but no systematic study has been made of the scope and limitations of the reaction of epoxides with cyanate ion, a relatively weak nucleophile.[4] It was shown recently that cyanate ion has sufficient nucleophilicity to displace halide ion from certain organic halides.[5] We hoped, therefore, that nucleophilic ring opening of epoxides by cyanate ion would provide species with vicinal alkoxy and isocyanate functions that would immediately cyclize to 2-oxazolidones, thus providing a general synthesis of that heterocyclic system from readily available epoxides. This paper (a) describes the reaction of epoxides with potassium cyanate in the absence and presence of water to yield 2-oxazolidones, (b) defines the scope and limitations of the reaction, and (c) provides some information on the reaction mechanism. In selected cases to confirm structure, 2-oxazolidones were prepared from 1,2-amino alcohols by the well-known Homeyer method.[6]

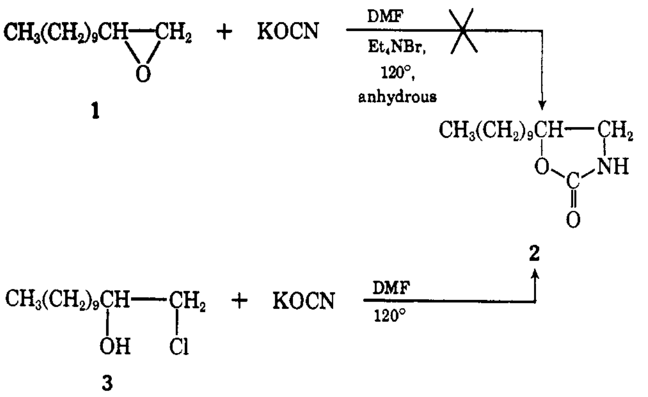
The only reaction of potassium cyanate with an epoxide is that reported by Thomsen in 1878 who allowed epichlorohydrin and potassium cyanate to react in an aqueous medium and obtained a chloromethyl-2-oxazolidone, mp 105°.[7] The position of the chloromethyl group on the oxazolidone ring (4 or 5) is still open to question.[8]

Reaction of organic isocyanates with epoxides, however, to produce N-substituted 2-oxazolidones has received extensive study.[9] Cyanate ion is reported to react with halohydrins to yield 2-oxazolidones.[10–12]

Results and Discussion

1,2-Epoxydodecane was used as the model epoxide in the initial studies. Since potassium cyanate decomposes in the presence of water, it was assumed that anhydrous systems would be required. When potassium cyanate and 1,2-epoxydodecane (**1**) were heated in dry dimethylformamide (DMF) to 120° in the presence of an initiating nucleophilic species, tetraethylammonium bromide, the epoxide slowly disappeared (no disappearance was observed in the absence of catalyst), and a white solid was obtained in small yield. This compound was assumed to be 5-decyl-2-oxazolidone (**2**) on the basis of its carbonyl absorption frequency in the infrared at 1760 cm^{-1}, the usual position of carbonyl in 2-oxazolidones. It was not identical with the authentic compound, prepared from 2-hydroxy-1-chlorododecane (**3**) and potassium cyanate,[10–12] based on mixture melting point, elemental analysis, and molecular weight. (See Scheme I.)

SCHEME I



Close examination of the infrared spectra of the two compounds in chloroform showed that the ratio of the C—H/C=O absorbance was about 2.5 times as high in the former (mp 101°) as in the latter (mp 88°). In all other respects the spectra were very similar but the band near 3500 cm^{-1} was unsplit in the former and was a doublet in the latter. Similar products were obtained from 1,2-epoxydecane, 1,2-epoxytetradecane, and 1,2-epoxyhexadecane under the same conditions.

Since the reaction products from epoxides and potassium cyanate in anhydrous DMF have about twice the molecular weight and half the nitrogen content of the anticipated 2-oxazolidones, the reaction sequence in eq 1 is visualized in an anhydrous medium (where Nu: is the nucleophilic initiating species). Since no pro-

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Table I

"Dimeric" 2-Oxazolidones Prepared from Epoxides and Potassium Cyanate in Anhydrous DMF at 120°

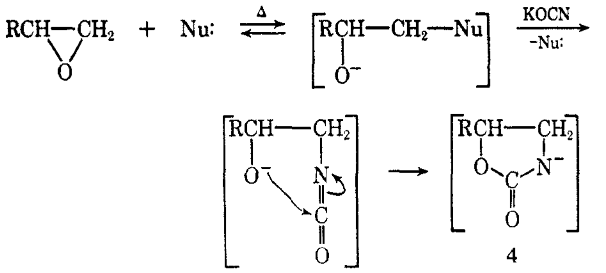
2-Oxazolidones	Registry no.	Mp, °C	C, %		H, %		N, %	
			Calcd	Found	Calcd	Found	Calcd	Found
3-(2-Hydroxydecyl)-5-*n*-octyl	14627-54-4	110–111	70.94	70.67	11.62	11.63	3.94	4.32
3-(2-Hydroxydodecyl)-5-*n*-decyl	14627-55-5	101–103	72.94	72.75	12.00	11.96	3.40	3.46
3-(2-Hydroxytetradecyl)-5-*n*-dodecyl	14627-56-6	105–107	74.46	74.66	12.28	11.90	2.99	3.20
3-(2-Hydroxyhexadecyl)-5-*n*-tetradecyl	14627-57-7	107–109	75.66	76.08	12.51	12.58	2.67	2.66

Table II

5-Alkyl-2-oxazolidones Prepared from Epoxides, Potassium Cyanate, and Water[a]

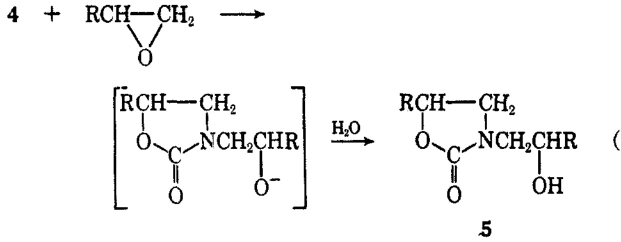
5-Alkyl-2-oxazolidones	Registry no.	Mp, °C	C, %		H, %		N, %	
			Calcd	Found	Calcd	Found	Calcd	Found
n-Octyl	7721-46-2	78–79	66.29	66.07	10.62	10.34	7.03	7.29
n-Decyl	7693-76-7	86.5–87.5	68.68	68.70	11.08	11.29	6.16	6.09
n-Dodecyl	14627-60-2	88–89	70.54	70.75	11.46	11.38	5.48	5.56
n-Tetradecyl	14627-61-3	94–95	72.04	71.99	11.73	11.78	4.94	4.87

[a] The molar ratio is 1:6:4.



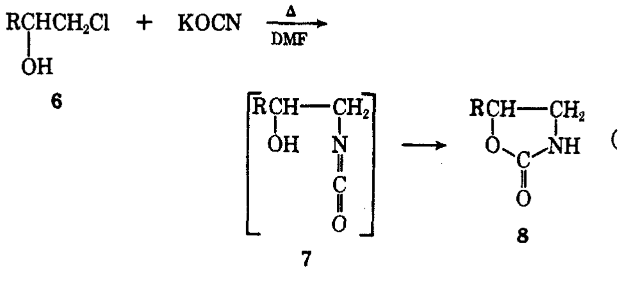
(1)

tonic species is present in anhydrous medium, **4** would be expected to react further with epoxide to form dimers, trimers, etc. (see eq 2). When the anhydrous reaction mixtures are quenched in water, the only crystalline product isolated is **5** (eq 2), the so-called "dimeric" 2-oxazolidone. This product would be expected to have an infrared spectrum analogous to that of a monomeric 5-substituted 2-oxazolidone but, since two alkyl groups are present for each carbonyl group, a high C—H/C=O absorbance ratio should be and is observed. The structure of these "dimeric" 2-oxazolidones was proven by independent synthesis to be described later. Table I lists the "dimeric" 2-oxazolidones prepared from epoxides and potassium cyanate in anhydrous DMF.



(2)

When chlorohydrins **6** react with potassium cyanate even in an anhydrous medium, monomeric 5-alkyl-2-oxazolidones **8** are obtained, although in poor yields, as a proton is available from the original hydroxyl group for reaction with the vicinal isocyanate function in the intermediate **7**.

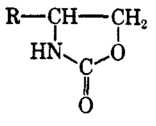


(3)

If the mechanism of formation of the "dimeric" products from epoxides and potassium cyanate in anhydrous DMF is indeed correct, a proton source in the reaction medium should neutralize the strongly basic alkoxyisocyanate precursors of **4** to yield **7** which should ring close to monomeric 5-alkyl-2-oxazolidones (**8**). Ethanol or *t*-butyl alcohol were used in stoichiometric quantities, based on epoxide, or in excess, but 2-oxazolidones were not obtained. However, when controlled quantities of water were used as the proton source, good yields (40–65%) of monomeric 5-substituted-2-oxazolidones were obtained from terminal aliphatic epoxides. Table II summarizes the results. All of the products had the expected spectral characteristics, in addition to correct elemental analyses.

An alternative explanation for the success in obtaining monomeric 2-oxazolidones by using controlled quantities of water is enhancement of the solubility of potassium cyanate which is known to be low in anhydrous DMF.[5] When substantially larger quantities of water were employed than those specified in the Experimental Section, 2-oxazolidones were not obtained, however. It is well known that reaction with water causes inorganic cyanates to decompose yielding ammonia among other products. It is probable that with the controlled quantity of water we have achieved a balance between solubility and rate of decomposition of potassium cyanate and proton availability. In all cases in which water was employed, ammonia was detected (odor).

Structures of the monomeric and "dimeric" 2-oxazolidones were proven by independent unequivocal synthesis. Reaction of potassium cyanate with terminal, aliphatic epoxides in the presence of water could yield the expected 5-alkyl-2-oxazolidones (**8**) by terminal attack or the isomeric 4-alkyl products of structure **9**. The fact that potassium cyanate reacts with terminal alkyl epoxides (water present) or the corresponding chlorohydrins (chlorine on the terminal



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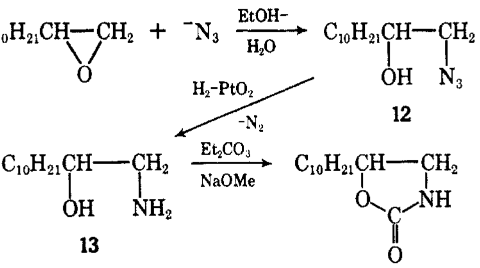
carbon atom) to yield identical 2-oxazolidones is not a proof of structure. Published cases are known in which nucleophilic displacement on vicinal halohydrins proceeds *via* the epoxide and the incoming nucleophile then does not attack the carbon atom to which the halogen had been originally attached.[13,14]

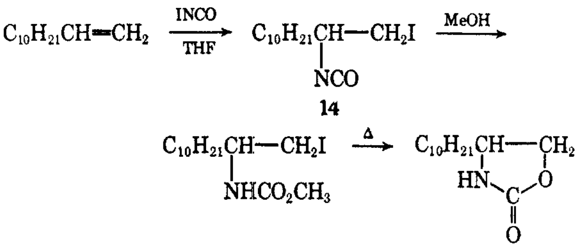
One pair of monomeric 2-oxazolidones was chosen for synthesis, namely, the 5- and 4-decyl-2-oxazolidones (**2** and **11**, respectively). The 5 isomer, mp 86.5–87.5°, was prepared by refluxing 1,2-epoxydodecane with aqueous–alcoholic sodium azide solution, a reaction known to proceed predominantly, if not exclusively, by terminal attack.[3] The product, 2-hydroxydodecyl azide (**12**), without purification, was reduced with hydrogen and platinum oxide to the corresponding amino alcohol **13** which was then cyclized with diethyl carbonate and sodium methoxide.[6] The sequence is summarized in eq 4.



(4)

2, mp 86.5–87.5°

4-Decyl-2-oxazolidone (**11**), mp 31.5–32.5°, was prepared from 1-dodecene by addition of preformed iodine isocyanate in tetrahydrofuran,[15] reaction of the resulting vicinal 1-iodo-2-dodecyl isocyanate (**14**) with methanol, and pyrolytic cyclization of the resulting iodocarbamate **15**[16] as illustrated in eq 5. Iodine isocyanate is known to add to terminal olefins almost exclusively in Markownikow fashion.[17]

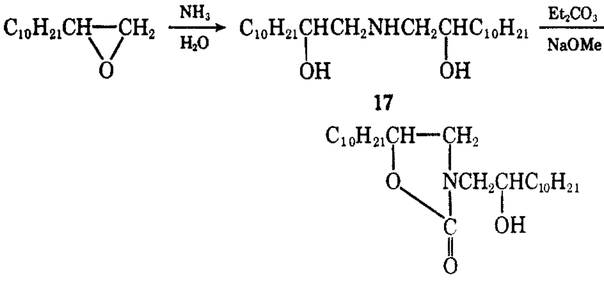


(5)

15 **11**, mp 31.5–32.5°

5-Decyl-2-oxazolidone, mp 86.5–87.5°, prepared from 1,2-epoxydodecane and potassium cyanate plus water was identical in every way (spectra, melting point, and mixture melting point) with the authentic compound. The other 5-alkyl-2-oxazolidones listed in Table II were also prepared unequivocally from the epoxides → hydroxy azides → hydroxy amines → 2-oxazolidones.

The "dimeric" product, 3-(2-hydroxydodecyl)-5-*n*-decyl-2-oxazolidone (**16**), mp 101–103°, was also synthesized by an independent route and was shown to be identical with the compound isolated from the reaction of 1,2-epoxydodecane with potassium cyanate in the absence of water. Reaction of 1,2-epoxydodecane with aqueous ammonia in a stirred autoclave yielded the secondary amine, bis(2-hydroxydodecyl)amine (**17**), which on reaction with diethyl carbonate and sodium methoxide yielded **16** (eq 6). It was identical in every respect (spectra, melting point and mixture melting point) with that obtained from 1,2-epoxydodecane and potassium cyanate in anhydrous DMF. The secondary amine, **17**, was the isolated reaction product rather than the primary amine, 1-amino-2-hydroxydodecane. We attribute this result to the higher solubility of the amino alcohol in unreacted epoxide than in aqueous ammonia. Subsequently, the other "dimeric" 2-oxazolidones listed in Table I were also synthesized unequivocally as just described.



(6)

16, mp 101–103°

After having developed a convenient set of conditions for obtaining monomeric 2-oxazolidones from terminal epoxides we explored the scope and limitations of the reaction of epoxides with potassium cyanate. Internal epoxides, such as *cis*-9,10-epoxyoctadecane, do not react with potassium cyanate at 120° in the presence or absence of water and with tetraethylammonium bromide, lithium chloride, or N,N-dimethylbenzylamine as catalyst. Reaction of the chlorohydrin, 9-hydroxy-10-chlorooctadecane, under the same conditions reconverted it cleanly into the epoxide, as shown by glpc.

Styrene oxide or 1,2-epoxy-2-methylpentane reacts rapidly with potassium cyanate in the presence or absence of water or nucleophilic initiating species. Infrared spectra, however, indicated that little or no 2-oxazolidone had formed. Chromatographic separation of crude reaction products on Florisil, a technique usually successful in isolating 2-oxazolidones from crude reaction mixtures,[18] did not yield any.

The reaction of potassium cyanate and water with epoxides in DMF to yield 2-oxazolidones is apparently limited to terminal alkyl epoxides. With these epoxides yields of 2-oxazolidones are satisfactory (40–65%) and are generally higher than are obtained in the two-step sequence, epoxide → amino alcohol → 2-oxazolidone.

In a search for a superior solvent for potassium cyanate a large number were screened, namely, ether, tetrahydrofuran, 1,2-dimethoxyethane, dioxane, chloroform, carbon tetrachloride, benzene, nitrobenzene, acetonitrile, dimethyl sulfoxide, pyridine, 1-methyl-2-pyrrolidone, ethanol, and *t*-butyl alcohol. At their

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boiling points, none was found to be substantially superior to DMF.

Sodium cyanate was used in several cases, but yields of 2-oxazolidones from terminal epoxides (in DMF) were lower than with the potassium salt. Dimethyl sulfoxide was used in several experiments but had no advantages over DMF.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Infracord, Model 137, using either thin films or 3–5% solutions (w/v) in chloroform in 0.096-mm, 0.103-mm, or 0.151-mm, matched sodium chloride cells.

Glpc was carried out with a Wilkens Aerograph Autoprep Model A-700, using the following columns (10 ft × 0.25 in.): 10% butanediol succinate on 60 mesh Anakrom ABS; 10% SE-30 on 60 mesh Anakrom ABS; or 15% Apiezon-L on 60 mesh Anakrom ABS.

Dimethylformamide was purified[19] by shaking it with potassium hydroxide, filtering, and shaking it with calcium oxide. It was then distilled at atmospheric pressure; only the center cut was used. All other solvents were of the highest quality and were used as received.

Potassium cyanate and tetraethylammonium bromide were purchased from J. T. Baker Chemical Co., Phillipsburg, N. J.; ammonium chloride from Allied Chemical, New York, N. Y.; sodium azide from Fisher Scientific Co., Fair Lawn, N. J. Potassium cyanate was dried at 60° under vacuum for several days before use. All other salts were used as received.

Column chromatography was performed using "Florisil," as the stationary phase. It was purchased from Fisher Scientific Co. and was used without prior conditioning.

Melting points were determined on a Thomas–Hoover capillary melting point apparatus. Melting points and boiling points are uncorrected. Molecular weights were determined on a Mechrolab osmometer, Model 301 A. Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, Del. and Micro-Tech Laboratories, Inc., Skokie, Ill.

Olefins and Epoxides Used.—1-Decene, 1-dodecene, 1-hexadecene, and 2-methyl-1-pentene were purchased from Humphrey Chemical Co., North Haven, Conn., and determined to be 95% pure by glpc. They were used without further purification.

Oleyl alcohol, "Adol-90," was purchased from Archer Daniels Midland Co., Minneapolis, Minn., and distilled through a 1-m adiabatic Vigreux Column, bp 173° (0.6 mm) and $n^{15}\mathrm{D}$ 1.4629. Its purity was 96.2% by glpc and 96.0% by iodine number. It was converted to *cis*-9-octadecene, bp 128–130° (0.5 mm), by a known procedure.[20]

1,2-Epoxydodecane was purchased from Chemical Intermediates and Research Laboratories, Cuyahoga Falls, Ohio, and redistilled, bp 89–90° (0.6 mm). 1,2-Epoxytetradecane was purchased from Archer Daniels Midland Co., Minneapolis, Minn., and was also redistilled, bp 103–104° (0.6 mm). Both were found to be at least 98% pure by glpc. Styrene oxide was purchased from Aldrich Chemical Co., Milwaukee, Wis., and was used without further purification.

1,2-Epoxydecane, bp 95–96° (11.3–11.7 mm), 1,2-epoxyhexadecane, bp 144–145° (0.75 mm), 1,2-epoxy-2-methylpentane, bp 104–105°, and *cis*-9,10-epoxyoctadecane were prepared from the corresponding olefins by a modification of a known procedure.[21] In general, the olefin (0.5 mole) was added dropwise during the course of 1 hr at 20–30° to a stirred mixture of peroxyacetic acid (114 g, 0.6 mole) (Becco 40% peracetic acid in glacial acetic acid containing 1% by weight of sulfuric acid) and sodium acetate (2.5 g, 0.03 mole). When the exothermic reaction had ceased, the reaction mixture was allowed to stir at room temperature overnight, with the exception noted below. The mixture was poured into water (200 ml) and extracted several times with ether. The combined extracts were washed first with aqueous sodium carbonate until neutral and then with water. After drying, the solvent was evaporated. *cis*-9,10-Epoxyoctadecane was used as obtained; 1,2-epoxydecane and 1,2-epoxyhexadecane were distilled.

Because the derived epoxide is very sensitive to acetic acid, 2-methyl-1-pentene was added to the peroxy acid–sodium acetate mixture dropwise over a period of 2.5 hr while the temperature was maintained at 10–15°. Stirring was continued for another 0.5 hr and the reaction mixture was poured into water (500 ml) containing excess sodium carbonate. The product was extracted several times with ether, the ether solution was washed with water and dried, and the solvent was removed. Purification was by distillation.

Reaction of Epoxides with Potassium Cyanate in the Absence of Water. "Dimeric" 2-Oxazolidones.—In a 50-ml, three-necked, round-bottom flask fitted with a mechanical stirrer, rubber septum, and reflux condenser topped by a calcium chloride drying tube were placed dimethylformamide (25 ml), tetraethylammonium bromide (0.2 g), potassium cyanate (4.1 g, 0.05 mole), and the epoxide (0.025 mole). The reactants were stirred and heated to 120–130° in an oil bath for 10 hr. Samples were withdrawn through the rubber septum so that the disappearance of epoxide could be followed by glpc. At the end of the reaction, stirring was continued as the flask and its contents together with the oil bath cooled to room temperature. The reaction mixture was then poured into 200–300 ml of water and extracted several times with ether or chloroform. The combined extracts were washed with water and dried; the solvent was then evaporated under vacuum. The resulting solids were then recrystallized (Table I).

1. **3-(2-Hydroxydecyl)-5-*n*-octyl-2-oxazolidone.**—The product was prepared from 1,2-epoxydecane (3.9 g) in 4% yield based on epoxide. It was extracted with ether and recrystallized from carbon tetrachloride, mp 110–111°. The infrared spectrum ($CHCl_3$) showed bands at 3550 (OH), 1760 (carbonyl), 1460, and 1270 cm^{-1}.

2. **3-(2-Hydroxydodecyl)-5-*n*-decyl-2-oxazolidone.**—The product was prepared from 1,2-epoxydodecane (4.6 g) in 1% yield based on epoxide. It was extracted with ether and recrystallized from carbon tetrachloride, mp 101–103°. The infrared spectrum ($CHCl_3$) showed bands at 3550 (OH), 1755 (carbonyl), 1455, and 1265 cm^{-1}. The calculated molecular weight was 411; that found was 448.

3. **3-(2-Hydroxytetradecyl)-5-*n*-dodecyl-2-oxazolidone.**—The product was prepared from 1,2-epoxytetradecane (5.3 g) in 1.5% yield based on epoxide. It was extracted with ether and recrystallized from carbon tetrachloride, mp 105–107°. The infrared spectrum ($CHCl_3$) showed bands at 3500 (OH), 1755 (carbonyl), 1460, and 1205 cm^{-1}.

4. **3-(2-Hydroxyhexadecyl)-5-*n*-tetradecyl-2-oxazolidone.**—The product was prepared from 1,2-epoxyhexadecane (6.0 g) in 6% yield based on epoxide. It was extracted with chloroform and recrystallized from carbon tetrachloride, mp 107–109°. The infrared spectrum ($CHCl_3$) showed bands at 3495 (OH), 1750 (carbonyl), 1460, and 1260 cm^{-1}.

Preparation of 5-Alkyl-2-Oxazolidones from 1,2-Epoxyalkanes, Potassium Cyanate, and Water.—As just described, dimethylformamide (25 ml), tetraethylammonium bromide (0.2 g), potassium cyanate (12.2 g, 0.150 mole), water (1.8 ml, 0.10 mole), and epoxide (0.025 mole) were stirred and heated to 120–130° for 5 hr. Work-up was the same as in the previous description. Results are in Table II.

1. **5-*n*-Octyl-2-oxazolidone** was prepared from 1,2-epoxydecane (3.9 g) in 63% yield. It was extracted with ether and recrystallized from ethanol, mp 78–79°.[18] The infrared spectrum ($CHCl_3$) showed bands at 3500 and 3300 (NH, doublet), 1750 (carbonyl), 1220, and 1070 cm^{-1}.

2. **5-*n*-Decyl-2-oxazolidone** was prepared from 1,2-epoxydodecane (4.6 g) in 65% yield. It was extracted with ether and recrystallized from ethanol, mp 86.5–87.5.[18] The infrared spectrum ($CHCl_3$) showed bands at 3550 and 3350 (NH, doublet), 1760 (carbonyl), 1240, 1080, and 980 cm^{-1}.

3. **5-*n*-Dodecyl-2-oxazolidone** was prepared from 1,2-epoxytetradecane (5.3 g) in 41% yield. It was extracted with ether and recrystallized from ethanol, mp 88–89°. The infrared spectrum ($CHCl_3$) showed bands at 3550 and 3350 (NH, doublet), 1760 (carbonyl), 1240, and 1080 cm^{-1}.

4. **5-*n*-Tetradecyl-2-oxazolidone** was prepared from 1,2-epoxyhexadecane (6.0 g) in 58% yield. It was extracted with chloroform and recrystallized from ethanol, mp 94–95°. The infrared

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TABLE III

AMINO ALCOHOLS

Amino alcohol	Registry no.	Method	Mp, °C	C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found
2-Hydroxydodecylamine	4054-54-0	A	51.52	71.63	71.49	13.52	13.22	6.96	6.70
2-Hydroxytetradecylamine	14627-63-5	A	64–65	73.30	73.26	13.62	13.56	6.11	5.91
2-Hydroxyhexadecylamine	14627-64-6	A	94–95.5	74.64	74.35	13.70	13.01	5.44	4.95
Bis(2-hydroxydodecyl)amine	4153-94-0	B	103–104	74.74	74.24	13.33	13.14	3.63	3.73
Bis(2-hydroxytetradecyl)amine[a]	14627-66-8	B	98–100	76.13	75.37	13.46	13.44	3.17	3.65

[a] *Anal.* Calcd for O: 7.24. Found: 7.51.

spectrum ($CHCl_3$) showed bands at 3525 and 3325 (NH, doublet), 1760 (carbonyl), 1485, 1220, and 1080 cm^{-1}.

5. **5-Phenyl-2-oxazolidone, Attempted Unsuccessfully.**—Styrene epoxide disappeared with or without a catalyst under the conditions of the reaction, but the product gave no spectral evidence of the formation of a 2-oxazolidone.

6. **4,5-Di-*n*-octyl-2-oxazolidone, Attempted Unsuccessfully.**—*cis*-9,10-Epoxyoctadecane did not disappear under the conditions of the reaction.

7. **5-Methyl-5-*n*-propyl-2-oxazolidone, Attempted Unsuccessfully.**—1,2-Epoxy-2-methylpentane disappeared with or without a catalyst under the conditions of the reaction, but the product gave no spectral indication of the formation of a 2-oxazolidone.

Preparation of 5-Alkyl-2-oxazolidones from Chlorohydrins and Potassium Cyanate.—The 1,2-chlorohydrins of dodecane and tetradecane were prepared by reaction of the corresponding epoxide with an excess of an ethereal solution of approximately 0.3 *N* in HCl. Excess acid was neutralized with aqueous sodium acetate and the ether solution was washed with water and dried. The solvent was removed, giving quantitative yields of the chlorohydrins. No attempt was made to separate the isomers formed.

In a 50-ml, three-necked, round-bottom flask fitted with a mechanical stirrer, reflux condenser, and rubber septum were placed dimethylformamide (25 ml), potassium cyanate (4.1 g, 0.05 mole), and the chlorohydrin (0.025 mole).[10,11] The reactants were stirred and heated to 120–130° for approximately 5 hr. Samples were withdrawn through the rubber septum to follow disappearance of chlorohydrin by glpc. At the end of the reaction the hot solution was filtered to remove the inorganic salts. The dimethylformamide was then distilled off using a water aspirator and the crude residual product was recrystallized. The products obtained were identical with those obtained from the epoxides, potassium cyanate, and water, as just described, and from the corresponding amino alcohols by reaction with diethyl carbonate.

1. **5-*n*-Decyl-2-oxazolidone.**—The product was recrystallized from ethanol to give a 1% yield of a white solid, mp 87–87.5°. It showed no melting point depression upon admixture with the authentic 2-oxazolidone synthesized from either the epoxide or the amino alcohol and the infrared spectra were superimposable.

2. **5-*n*-Dodecyl-2-oxazolidone.**—The product was recrystallized from ethanol to give a 1.5% yield of white solid, mp 85–85.5°. It showed no melting point depression upon admixture with the authentic 2-oxazolidone synthesized from either the epoxide or the amino alcohol and the infrared spectra were superimposable.

Preparation of 2-Oxazolidones from Amino Alcohols (Homeyer Method).[6] Method A.—In a 1-l. flask fitted with a heating mantle and reflux condenser were placed sodium azide (7.8 g, 0.12 mole), ammonium chloride (6.5 g, 0.12 mole), and the epoxide (0.10 mole). Enough ethanol and water were added to give a homogeneous solution. The reaction mixture was then refluxed for 48 hr, poured over a large amount of ice and allowed to cool. The product was extracted with several portions of ether. The ether extracts were washed with water, dried, and filtered; the solvent was then evaporated under vacuum to afford the 1-azido-2-hydroxyalkane. The infrared spectrum (neat) showed characteristic bands at 3400 (OH), 2110, and 1270 (N_3) cm^{-1}.

The hydroxy azide, without further purification, was dissolved in absolute ethanol (200 ml); a small amount of Adams catalyst (PtO_2) was added; and the mixture was stirred for 48 hr under approximately 800 psi of hydrogen pressure at room temperature. No pressure change was observed as the hydrogen absorbed exactly balanced the nitrogen evolved. After filtration of the solution with the aid of Filter-cel, the ethanol was evaporated and the resulting solid was recrystallized from hexane (Table III). Infrared spectra ($CHCl_3$) of the amino alcohols showed bands at 3500 (broad, OH, NH), 2990, and 1475 cm^{-1}.

The amino alcohol (0.02 mole) was placed in a 50-ml, round-bottom flask with diethyl carbonate (12 g, 0.1 mole); a small amount of the latter (2 ml) was distilled off in order to purge the system of water. The mixture was allowed to cool and a small amount of freshly prepared sodium methoxide (approximately 0.3 g) was then added. The reaction mixture was refluxed for 1.5–2 hr and then ethanol (2–3 ml) was distilled off. The residual material was allowed to cool, poured into water, and extracted with ether. The ether was evaporated and the residual product was recrystallized from ethanol. In each case the 2-oxazolidone formed was identical with the corresponding substance synthesized by the other methods described.

Method B.—The epoxide (0.5 mole) and aqueous ammonium hydroxide (500 ml, approximately 7.5 moles) were placed in a stirred autoclave and heated to 160° overnight under endogeneous pressure (about 400 psi). The reaction mixture was allowed to cool and was extracted several times with chloroform. After drying the extract and evaporating the solvent, a white soapy solid was obtained which was then recrystallized. The infrared spectra ($CHCl_3$) showed bands at 3500 (broad, OH, NH), 2990 (C–H), and 1460 cm^{-1} (Table III).

The secondary amine was then converted to the 2-oxazolidone as described under method A.

1. **5-*n*-Decyl-2-oxazolidone.**—2-Hydroxydodecylamine was prepared by method A from 1,2-epoxydodecane (18.4 g), ammonium chloride, and sodium azide dissolved in ethanol (500 ml) and water (200 ml), followed by reduction over Adams catalyst. The amino alcohol was prepared in 60% yield based on epoxide, and the oxazolidone in 63% yield based on amino alcohol; the over-all yield was 38%.

2. **5-*n*-Dodecyl-2-oxazolidone.**—2-Hydroxytetradecylamine was prepared by method A from 1,2-epoxytetradecane (21.2 g), ammonium chloride and sodium azide dissolved in ethanol (500 ml) and water (350 ml), followed by reduction over Adams catalyst. The amino alcohol was prepared in 58% yield based on epoxide, and the oxazolidone in 67% yield based on amino alcohol; the over-all yield was 39%.

3. **5-*n*-Tetradecyl-2-oxazolidone.**—2-Hydroxyhexadecylamine was prepared by method A from 1,2-epoxyhexadecane (24.0 g), ammonium chloride, and sodium azide dissolved in ethanol (500 ml) and water (400 ml), followed by reduction over Adams catalyst. The amino alcohol was prepared in 86% yield based on epoxide, and the oxazolidone in 70% yield based on amino alcohol; the over-all yield was 60%.

4. **3-(2-Hydroxydodecyl)-5-*n*-decyl-2-oxazolidone.**—The amino alcohol, bis(2-hydroxydodecyl)amine, was prepared from 1,2-epoxydodecane (93 g) in 21% yield using method B. It was recrystallized from ethanol and converted to the oxazolidone in 18% yield based on amino alcohol; the over-all yield was 4%. The oxazolidone was recrystallized from carbon tetrachloride. This product was identical with the corresponding product obtained from the reaction between potassium cyanate and the epoxide in the absence of water.

5. **3-(2-Hydroxytetradecyl)-5-*n*-dodecyl-2-oxazolidone.**—The amino alcohol, bis(2-hydroxytetradecyl)amine, was prepared from 1,2-epoxytetradecane (106 g) in 25% yield using method B. It was recrystallized from heptane and converted

to the oxazolidone in 8.5% yield based on amino alcohol; the over-all yield was 2%. The oxazolidone was recrystallized from carbon tetrachloride. This product was identical with the corresponding product obtained from the reaction between potassium cyanate and the epoxide in the absence of water.

Registry No.—Potassium cyanate, 590-28-3.

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Structural Isomer Distribution in Ring Polymers of Propylene Oxide

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The structural isomer distributions in the cyclic dimer and tetramer of propylene oxide formed by the homogeneous catalyst BF_3 have been determined and found to be random. By a combination of gas chromatography, nuclear magnetic resonance, and mass spectroscopy, four out of four of the geometrical isomers of the dimer and 22 out of 23 of the geometrical isomers of the tetramer have been observed, the majority isolated, characterized, and assigned to a structural configuration.

In addition to a high molecular weight residue, a distillable liquid (in yields up to 60%) is obtained from the reaction of propylene oxide with triethyloxonium tetrafluoroborate or boron trifluoride. Analysis by gas chromatography, nuclear magnetic resonance, and mass spectroscopy has shown this liquid to be ring polymers of propylene oxide (designated as $(PO)_n$ where n, the number of PO units in the ring, is 2, 4, 5, and higher). This paper establishes the ring nature and structural isomer distributions (head to tail, head to head, and tail to tail) of $(PO)_2$ and $(PO)_4$.

Experimental Section

The details of the synthesis of the ring polymers of propylene oxide are given elsewhere.[1]

Separation of isomers of $(PO)_n$ by gas chromatography was possible by the use of glpc columns containing Carbowax 20M plus various metal salts, prepared in the following way. Anhydrous $AgNO_3$, $CuCl_2$, $CdCl_2$, or $NiCl_2$ was dissolved in methanol followed by addition of Carbowax 20M in dichloromethane. The mixture was stirred until homogeneous. Chromosorb CL (60–80 mesh) was added and the solvent removed by evaporation. The resulting columns had a composition of 1.0% (w/w) metal salt, 20% (w/w) Carbowax 20M. The packing was poured into copper tubing having dimensions of 0.25 in. × 10 ft. The $AgNO_3$ packing was used for preparative purposes and a $^3/_8$ in. × 10 ft. column was made to accommodate a larger sample size. All columns were conditioned overnight at 200° prior to use.

$(PO)_n$ fractions were collected at the exit of an F & M Model No. 720 gas chromatograph in 2, mm (o.d.) glass capillary tubing, coiled to increase trapping efficiency. A separation of the $(PO)_4$ mixture into four preliminary fractions was made on the $AgNO_3$–Carbowax 20M preparative column. Each fraction was then further separated by use of one or more of the other metal salt columns. The separated materials were examined by nmr and mass spectroscopy.

The majority of the proton nmr spectra of the isomers of $(PO)_n$ were obtained at 100 MHz using a Varian HA-100 spectrometer in conjunction with a time averaging computer. Spectra of the separated isomers (in $CDCl_3$) were obtained at room temperature. For purposes of interpretation, the spectra of a few isomers were obtained at 60 MHz using a Varian A-60 spectrometer. Mass spectra of glpc fractions were obtained using a Consolidated Electrodynamics Corporation mass spectrometer (Model no. 21-103C) using a source temperature of 300°, an ionizing potential of 70 ev, and an ionizing current of 20 μa.

Results

1. $(PO)_2$, 2,5- and 2,6-Dimethyldioxanes.—The lowest boiling fraction of the BF_3-catalyzed reaction of propylene oxide was determined by vapor phase osmometry to have a molecular weight in the range of 112 to 118. Infrared spectra showed the presence of C–O stretching vibrations and the absence of a characteristic hydroxyl frequency. Using the glpc column $NiCl_2$–Carbowax, this distillate separated into six peaks. Nmr analysis showed the first two of these peaks (in order of elution and constituting about 5% of the fraction) to be the *cis* and *trans* isomers of 2-ethyl-4-methyl-1,3-dioxolane easily identifiable by the characteristic resonance patterns of the $O_2\mathit{CH}CH_2CH_3$ and $O_2CHCH_2\mathit{CH}_3$ protons. The last four glpc peaks all had nmr spectra consisting of a single methyl region doublet (due to spin–spin coupling) and similar methine and methylene regions and so correspond to the *cis* and *trans* isomers of 2,5- and 2,6-dimethyldioxane.

TABLE I

SOME MAJOR MASS PEAKS OF ISOMERS OF 2,5- AND 2,6-DIMETHYLDIOXANE[a,b]

Glpc fraction[c]	m/e							Mole % of total
	44	57	58	59	72	101	116	
A	0.988	2.04	0.200	0.440	2.67	1.88	5.19	33
B	0.575	1.36	0.682	1.74	2.77	2.85	5.57	18
C	0.932	1.98	0.197	0.450	2.76	2.15	4.82	22
D	0.625	1.32	0.676	1.78	3.17	3.27	5.25	27

[a] Expressed as % Σ 28. [b] BF_3 was the catalyst. [c] In order of elution from a $NiCl_2$–Carbowax 20M column.

These assignments are confirmed by the mass spectra presented in Table I. The spectra of all four isomers displayed identical cracking patterns differing only in relative intensities. A high-intensity parent ion peak was observed at m/e 116 (2 × 58) and a low-intensity, pressure-dependent, parent ion plus one peak at m/e 117. Nothing was observed at higher values of m/e and a significant M − 15 peak was observed. The relative intensities of some other mass peaks are given in Table I. For the 2,5- and 2,6-dimethyldioxanes, structural configuration is expected to be more important than geometrical configuration

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[1] J. L. Down, J. Lewis, B. Moore, and G. Wilkinson, *J. Chem. Soc.*, 3767 (1959); R. J. Kern, *J. Org. Chem.*, **33**, 388 (1968).