The Study of Oxazolidone Formation
from 9,10-Epoxyoctadecane and Phenylisocyanate

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ABSTRACT: The formation of oxazolidone from 9,10-epoxy-octadecane and phenylisocyanate was studied. One branch of epoxidized vegetable oil with one epoxy group per chain corresponds to 9,10-epoxyoctadecane. This model could explain the probability of oxazolidone formation from natural oil-derived epoxides. Epoxidized natural oils are TG consisting of glycerin and three FA with or without one to three epoxy groups in the middle of the chain. To study oxazolidone formation from an internal epoxy group without possible interference from the side reactions on the ester group, 9,10-epoxyoctadecane was selected as the most appropriate model compound. Epoxy groups in the middle of a long aliphatic chain are of low reactivity toward isocyanates, and preparation of oxazolidones requires fairly harsh conditions such as high temperatures and catalysts, which also promote side reactions. The dominant side reaction is rearrangement of the epoxy groups. We found that the direction and magnitude of the rearrangement and the yield of any particular product depended on the catalyst used. Lithium chloride, aluminum trichloride, and zinc iodide catalyzed oxazolidone formation, along with the catalysis of side reactions such as ketone and carbonate formation. Aluminum trichloride showed the highest conversion of 9,10-epoxyoctadecane to oxazolidone. Aluminum triisopropoxide, triphenylantimony iodide, and imidazole did not catalyze the formation of oxazolidone. They were effective as catalysts of epoxy group rearrangement and promoted the formation of hydroxyl, ketone, and carbonate compounds. Hydroxyl groups reacted with isocyanate to produce urethane.

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KEY WORDS: Aliphatic epoxide, isocyanate, oxazolidone, rearrangement.

Oxazolidones are an important class of heterocyclic organic compounds containing a five-membered ring. They can be synthesized in many different ways, as reviewed by Dyen and Swern (1). Oxazolidone formation from diepoxides and diisocyanates has been studied extensively in the preparation of thermally stable polymers (2–7). Although reaction parameters such as reactant type, reaction temperature, and solvent play an important role, the catalysts have a decisive influence on the course of the reaction. Typical catalysts are Lewis acids, metal salts, alkoxides, and phosphorus-based compounds (8). Preparation of oxazolidones from epoxidized natural oils may be an important way of making new types of polymers. One of the primary uses for epoxidized natural oils is as additives for plastics. However, the epoxy group can be converted to hydroxyl (9,10), amine (11), or oxazolidone (12), resulting in the potential to synthesize olechemical products that can successfully replace petrochemically-based ones. Epoxidized oils are TG in which some FA have one or more epoxy groups in the middle of the chain. These internal epoxy groups are of lower reactivity toward isocyanates, and the preparation of oxazolidones from epoxidized natural oils requires fairly harsh conditions such as high temperatures and catalysts, which also promote side reactions. Possible side reactions include the rearrangement of epoxy groups; the degradation of ester groups; and the formation of isocyanurates, amides, and urethanes (12).

To study oxazolidone formation from an internal epoxy group on a long aliphatic chain, 9,10-epoxyoctadecane was selected as the most appropriate model compound. This compound avoids the possible interference of undesired reactions on ester groups or specific reactions of multiple epoxy groups on one FA chain.

Only a limited number of studies have been carried out on the reaction of isocyanates with the internal epoxy groups in an aliphatic chain (13–17). We found that epoxy group rearrangement is always present simultaneously with oxazolidone formation. The direction and magnitude of the rearrangement and the yield of any particular product depends on the catalyst used. The extent of the side reactions can be significant in the case of less reactive internal epoxides.

The rearrangement of the epoxy group is initiated by a strain in the epoxy ring. The normal angles of 109°29′ between atoms of saturated hydrocarbons are decreased to about 60° for the epoxy ring. At a higher temperature or by the effect of some catalysts, the ring isomerizes to more stable functional groups, such as a carbonyl or hydroxyl group (18). A high temperature, usually about 400°C, causes epoxy group rearrangement without any catalyst, producing primarily carbonyl groups. The mechanism and type of product from the catalyzed rearrangements depend on the acidity of the catalyst. Protic and Lewis acids give mostly carbonyl compounds, ketones, and aldehydes (19), whereas basic catalysts produce predominantly allylic alcohols. The bases used most frequently for rearrangement studies are potassium *t*-butoxide, *t*-butyllithium, and lithium dialkylamides (18).

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Trimerization is a reaction of the isocyanate groups. The product of this reaction is a thermally stable six-member iso-cyanurate ring. Its formation is promoted by higher reaction temperatures and by specific catalysts (5). We studied the effect of six catalysts on oxazolidone formation using 9,10-epoxyoctadecane and phenylisocyanate.

EXPERIMENTAL PROCEDURES

Materials. Samples were prepared using phenylisocyanate (99% purity) from Fisher Scientific (Fairlawn, NJ) and 9,10-epoxyoctadecane prepared in our laboratory. The phenyliso-cyanate was distilled under vacuum before use. 9,10-Epoxy-octadecane was prepared from 9-octadecene by epoxidation with perchlorobenzoic acid. Dimethyl formamide (DMF; Fisher) was dried over 4-Å molecular sieves and distilled before use. Catalysts (lithium chloride, aluminum trichloride, aluminum triisopropoxide, triphenylantimony iodide, zinc io-dide, and imidazole; Fisher) were used as supplied.

Methods. The IR spectra were recorded on a Perkin-Elmer Spectrum 1000 FTIR spectrometer. Samples were prepared as thin films on a KBr or NaCl salt plate. The IR absorption band of the carbonyl group in the oxazolidone ring was in the region of 1750–1760 cm^{-1}. NMR experiments were performed on a Bruker Avance DPX-300 (Karlsruhe, Germany), 300 MHz with a 5-mm broadband probe. Field desorption (FD) MS, CI-MS, and EI-MS were carried out on a Finnigan MAT 95Q mass spectrometer (San Jose, CA) using direct run in the FD and CI mode. The gas used for CI-MS was isobutene. TLC was performed on Florisil 6-nm plates (Fisher). The eluent was a mixture of hexane and diethyl ether in a volume ratio of 85:15.

Synthesis. Catalyst (0.35 g), DMF (20 g), and 9,10-epoxy-octadecane (6.7 g; 0.025 mol) were added to a three-necked round-bottomed flask equipped with a reflux condenser and mixed with a magnetic stirrer. The catalyst content was 1% of the total weight of the reaction mixture. Phenylisocyanate (3.7 g; 0.03 mol) dissolved in 5 g of DMF was then added dropwise over 2 h. The mixture was stirred and heated in the oil bath at 156°C (b.p. of DMF). The reaction continued for an additional 2 h after the total quantity of phenylisocyanate was added. The solvent was removed by distillation at high vacuum after the reaction was completed. The residue consisted of unreacted isocyanate, epoxide, and reaction prod-ucts. A series of subsequent purification techniques was car-ried out to separate the unreacted starting materials from the reaction products described herein. In the first step, the residue was dissolved in acetone, and water was added to neu-tralize the remaining isocyanate. The reaction of water and isocyanate produced urea, which was removed by precipita-tion by cooling at −16°C overnight followed by filtration. When triisocyanurate was formed, it precipitated along with urea, but it was not detected by the FTIR analysis. Acetone and excess water were evaporated from the filtrate, and the residue was dissolved in hexane and cooled at −16°C overnight. The unreacted epoxide and residual urea precipi-

tated and were separated from the solution by filtration. Hexane was removed from the filtrate by distillation, and the residue was dissolved in methanol and cooled at −16°C overnight. The solid precipitate was separated from the solute by filtration. Methanol was evaporated from the filtrate by distillation, yielding a yellow liquid. The solid precipitate and the yellow liquid residue were the resulting reaction products, and both were analyzed by FTIR and TLC. The precipitate was a pure compound with an R_f value of 0.97 in the TLC analysis. The yellow liquid residue was a mixture of several compounds, free of the starting materials, with R_f values of 0.65, 0.82, 0.91, and 0.97. The significant differences in R_f enabled the components to be separated and subsequently the structure to be determined. The chemical structure of the solid precipitate and composition of the yellow liquid residue are explained below.

RESULTS AND DISCUSSION

FTIR spectra of the liquid residue, before separation by TLC, showed that different catalysts affected the reaction between epoxy and isocyanate groups in different ways. Lithium chlo-ride, aluminum trichloride, and zinc iodide gave products with the typical absorption bands for ketone (1715 cm^{-1}), ox-azolidone (1756 cm^{-1}), and carbonate (1812 cm^{-1}) (Fig. 1). The other three catalysts (aluminum triisopropoxide, tri-phenylantimony iodide, and imidazole) gave urethane (1730 cm^{-1}) instead of oxazolidone and ketone (Fig. 2). Carbonate was produced by triphenylantimony iodide and in traces by aluminum triisopropoxide but not by imidazole.

The product with a FTIR absorption band at 1756 cm^{-1} (Fig. 3D) was oxazolidone, as shown by Dyen and Swern (13) and others (15–17). Its R_f value, obtained by TLC analysis, was 0.82. The shifts in the ^{1}H NMR spectrum for a pure com-pound were at ε 4.0 and 4.3 ppm (Fig. 4), typical for the pro-tons on the oxazolidone ring. Additionally, the ^{13}C NMR shift at 54 and 85 ppm for the oxazolidone ring C-atoms in the proximity of oxygen and nitrogen, respectively, proved that
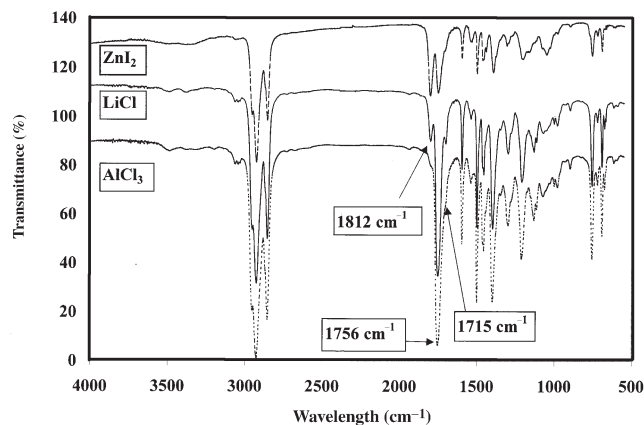

FIG. 1. FTIR spectra of the liquid product synthesized with zinc iodide, lithium chloride, and aluminum trichloride as catalysts.
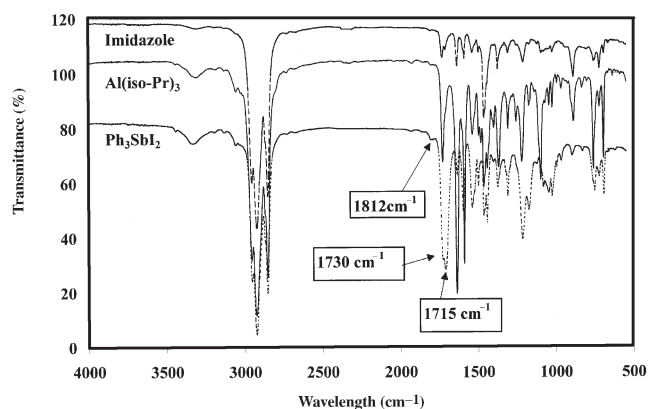
FIG. 2. FTIR spectra of the liquid product synthesized with imidazole, triphenylantimony iodide, and aluminum triisopropoxide as catalysts.
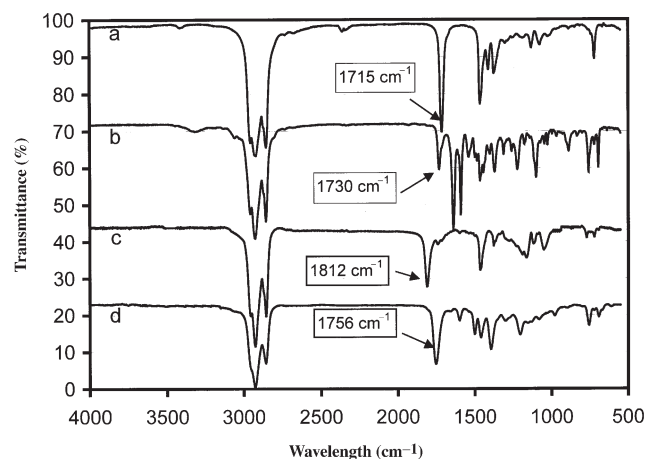

SCHEME 1

FIG. 3. FTIR spectra of the reaction products of phenylisocyanate and 9,10-epoxyoctadecane: (a) 9-octadecanone; (b) N-phenyl-8-octadecenyl-10-urethane; (c) 9,10-octadecylene carbonate; (d) 3-phenyl-4,5-dioctyl-2-oxazolidone.
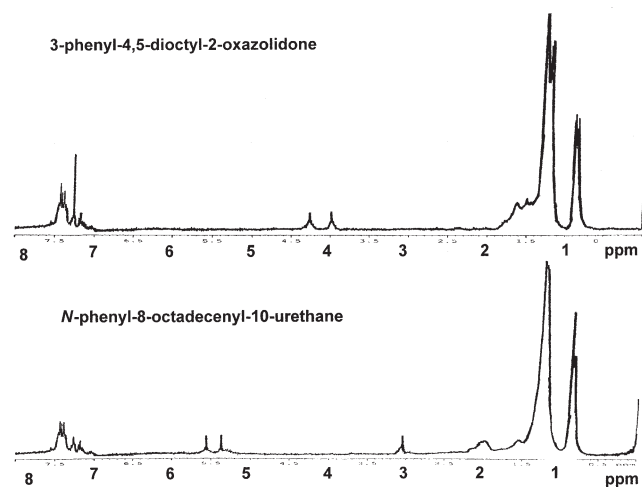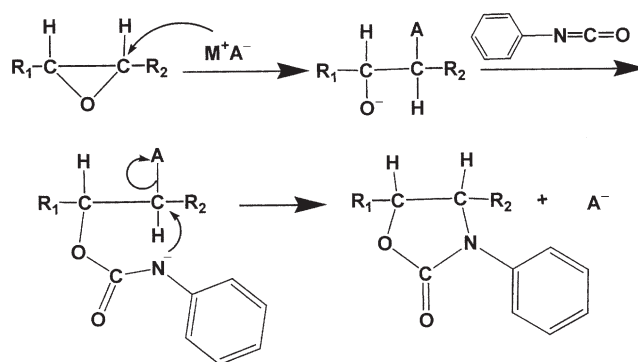

FIG. 4. ^{1}H NMR spectra of 3-phenyl-4,5-dioctyl-2-oxazolidone and N-phenyl-8-octadecenyl-10-urethane.

the product was 3-phenyl-4,5-dioctyl-2-oxazolidone. Oxazolidone formation from epoxides and isocyanates in the presence of LiCl or ZnI_2 or other Lewis acid catalysts proceeded according to Scheme 1 (13).

The chemical structure of both isocyanates and epoxides affects the oxazolidone formation process. The order of activity of epoxide and isocyanate in oxazolidone formation is the same: aliphatic > alicyclic > aromatic (17). The aromatic ring increases steric hindrances to the formation of the oxazolidone ring. We found that the structure of isocyanate had a considerably lower effect on this reaction than the structure of epoxides.

The reactivity of the epoxy ring in the oxazolidone formation reaction depends on its position in the compound and the type of neighboring substituents. Kadurina and coworkers (17) found the steric hindrances around the epoxy group to be determining factors in the formation of cyclic oxazolidone structures. The terminal aliphatic epoxides are much more active than the groups in the middle of the aliphatic chain. We found as well that steric effects played a decisive role in the syntheses of oxazolidones from long-chain aliphatic epoxides. The group in the middle of the long aliphatic chain is less reactive, so higher temperatures must be applied. However, this results in isomerization of the epoxy group along with oxazolidone formation.

The ketone FTIR spectrum (Fig. 3A) showed a typical absorption band at 1715 cm^{-1}. Its R_f value, obtained by TLC analysis, was 0.97. The proton NMR spectrum (Fig. 5) showed the characteristic shift at δ 2.4 ppm for the protons closest to the carbonyl group, and ^{13}C NMR, with the shift at δ 212 ppm for the carbonyl carbon, confirmed that the product was an aliphatic ketone. EI-MS readings showed the fragmentation pattern typical of an aliphatic ketone. The highest m/z was 268, and the major scission of the C–C bonds occurred at the carbonyl group, giving two strong peaks of m/z 141 (41%) and m/z 155 (55%). This was the characteristic decomposition pattern of 9-octadecanone. The elemental analysis proved the same. The calculated ratios of C, H, and O for 9-octadecanone were 80.59, 13.43, and 5.97%, respectively. The experimentally determined ratios of C, H, and O were 80.82, 12.80, and 6.38%, respectively. Formation of 9-octadecanone was the result of the rearrangement of an epoxy group
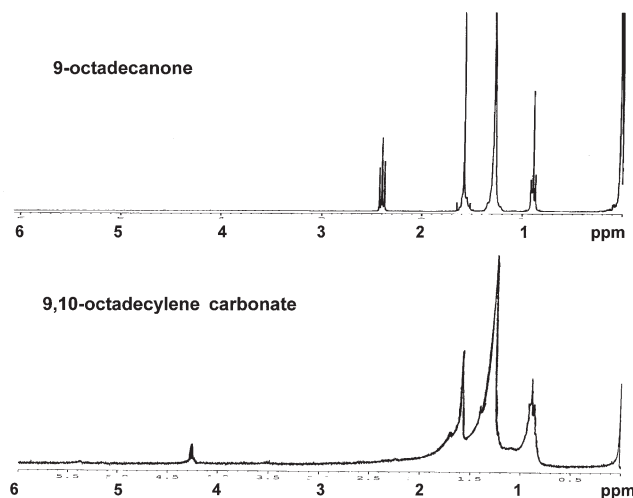
FIG. 5. ^{1}H NMR spectra of 9-octadecanone and 9,10-octadecylene carbonate.

typical for the acid-catalyzed rearrangement. Canonica *et al.* (20) and Walens *et al.* (21) also found that the rearrangement of the epoxy group in the middle of the chain of FA esters catalyzed by BF_3 produced ketones. The catalysts produced a ketone according to the reaction in Scheme 2 (18).

The FTIR spectra of the compound with a strong carbonyl absorption band at 1812 cm^{-1} (Fig. 3C) indicated the presence of a carbonate group. When separated by TLC, the compound showed an R_f value of 0.91. Analysis of the pure compound by high-resolution FD/CI-MS separated the molecular ion (MH)$^+$ of *m/z* 313, corresponding to the formula $C_{19}H_{37}O_3$, and two diagnostic ions, (MH − H_2CO_3)$^+$ of *m/z* 251 (5%) and (MH − CO_2)$^+$ of *m/z* 269 (6.2%). The diagnostic ions corresponded to the formulas $C_{18}H_{35}$ and $C_{18}H_{37}O$, respectively. The ^{1}H NMR spectrum chemical shift of δ 4.2 ppm (Fig. 5), typical of a carbonate ring, confirmed that the product was 9,10-octadecylene carbonate. The structure of the compound was as shown in Scheme 3.

All the catalysts produced 9,10-octadecylene carbonate except imidazole, which did not give any, and aluminum triisopropoxide, which gave traces. The highest yield was obtained in the reaction with zinc iodide (Table 1). It can be assumed that this product was a result of the chemical reaction between the epoxy groups and carbon dioxide. Since the first copolymerization of epoxides and carbon dioxide by Inoe *et al.* (22), this reaction has been studied extensively. Zinc salts are known to be the most efficient catalysts for this copolymerization (23). The reaction is shown in Scheme 4.
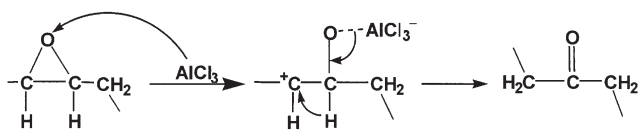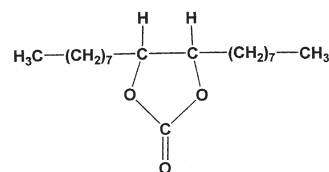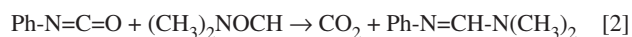

SCHEME 3

The CO_2 in our experiments could have originated from traces of humidity that reacted with isocyanate to produce carbon dioxide according to the following reaction:

$$Ph\text{-}N{=}C{=}O + H_2O \rightarrow Ph\text{-}NH_2 + CO_2 \qquad [1]$$

or from the reaction of isocyanate and DMF:

$$Ph\text{-}N{=}C{=}O + (CH_3)_2NOCH \rightarrow CO_2 + Ph\text{-}N{=}CH\text{-}N(CH_3)_2 \quad [2]$$

The FTIR spectra of the compound with a strong carbonyl absorption band at 1730 cm^{-1} (Figs. 2 and 3B) indicated the presence of a urethane group that was produced with triphenylantimony iodide, aluminum triisopropoxide, and imidazole. The R_f value for the urethane product was 0.65, which was very distinctive from oxazolidone and other products. The ^{1}H NMR urethane chemical shift at δ 3.1 ppm (Fig. 4) was for the proton on the octadecene carbon chain that was bonded to the urethane group. The chemical shifts of δ 5.4 and 5.6 ppm were assigned to protons bonded to the C-9 and C-10 atoms in the double bond of the octadecene chain. The chemical shifts from δ 7.0 to 7.6 ppm were characteristic of the protons on the *para* and *ortho* carbons of the phenylene ring. The ^{13}C NMR shifts at δ 73 ppm, for the C-atom in the octadecylene chain bonded to the urethane group, and at 155 ppm, for the C-atom in the urethane group, were typical of a urethane group bonded to an aliphatic chain.

The origin of the urethane compound in this reaction can be explained by the rearrangement of the epoxy group to an allylic alcohol. This rearrangement takes place in the presence of basic catalysts, as shown in Scheme 5 (18).

We also found that using aluminum triisopropoxide as the catalyst specifically produced a high yield of allylic alcohol in the rearrangement of epoxy groups (18). This alcohol reacted immediately with isocyanate to produce *N*-phenyl-8-octadecenyl-10-urethane. The overall reaction with aluminum triisopropoxide as the catalyst is described in Scheme 6.
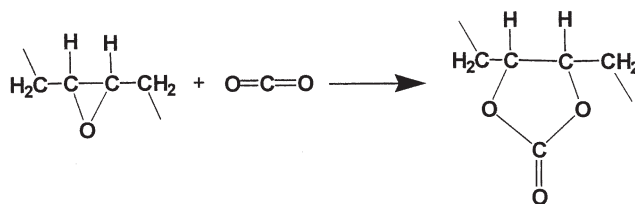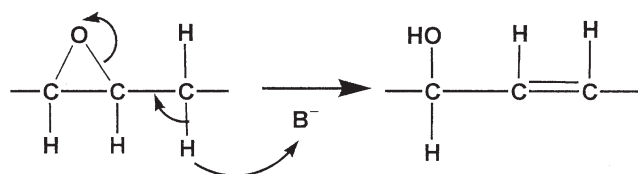

SCHEME 2

SCHEME 4

TABLE 1
Products of the Reaction of 9,10-Epoxyoctadecane and Phenylisocyanate

| Catalyst	Reaction product, wt%			
	3-Phenyl-4,5-dioctyl-2-oxazolidone	9-Octadecanone	N-Phenyl-8 octadecenyl-10-urethane	9,10-Octadecylene carbonate
Lithium chloride	40	50	0	10
Aluminum trichloride	65	30	0	5
Aluminum triisopropoxide	0	30	70	Traces
Triphenylantimony iodide	0	60	30	10
Zinc iodide	30	30	0	40
Imidazole	0	10	90	0

Results showed that the rearrangement of the epoxy group plays a dominant role in the reaction between an aromatic isocyanate and a fatty epoxide when the epoxy group is in the middle of the chain. The direction and magnitude of side reactions and the yield of any reaction product depend on the catalyst used (Table 1).

Lithium chloride, aluminum trichloride, and zinc iodide produced 3-phenyl-4,5-dioctyl-2-oxazolidone with 9-octadecanone and 9,10-octadecylene carbonate as the side products. The other three catalysts produced no oxazolidone, and the rearrangement of the epoxy group toward a hydroxyl and ketone was the main reaction. The products of catalysis with aluminum triisopropoxide were N-phenyl-8-octadecenyl-10-urethane and 9-octadecanone, with 9,10-octadecylene carbonate produced in traces. Triphenylantimony iodide gave N-phenyl-8-octadecenyl-10-urethane, 9-octadecanone, and 9,10-octadecylene carbonate. Imidazole produced N-phenyl-8-octadecenyl-10-urethane and 9-octadecanone. The conversion of epoxide to the reaction products was over 90% for all catalysts except imidazole. This catalyst gave a conversion of about 20%. Obviously, the epoxy group in the middle of the long hydrocarbon chain cannot easily be converted to oxazolidone with a good yield. The highest conversion to oxazolidone (65%) can be reached with aluminum trichloride as catalyst, although side reactions still occur.

The acidity or basicity of the catalyst clearly plays a dominant role in the reaction of an internal epoxy group and isocyanate. Lewis acid catalysts aluminum trichloride, lithium chloride, and zinc iodide produced oxazolidone in the reaction between epoxide and phenylisocyanate, along with some side products. Catalysts with a more basic character, such as imidazole and aluminumtriisopropoxide, promoted the epoxy group rearrangement toward allylic alcohol formation. Surprisingly, triphenylantimony iodide, known as a very good oxazolidone formation catalyst (24), produced no oxazolidone in this case but rather produced 9-octadecanone, allylic
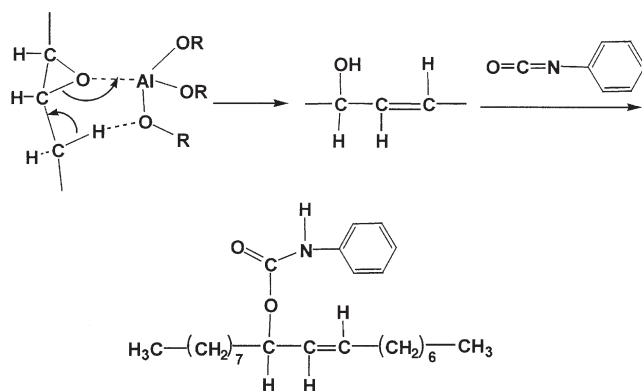
SCHEME 6

alcohol, and 9,10-octadecylene carbonate, all epoxy group rearrangement products.

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SCHEME 5

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