was isolated. Hence, nearly quantitative yields of piperazines became even more significant in view of this excess.

Experimental Section[13]

1,4-Di-*n*-butylpiperazine.—To a mixture of 64 g (1.0 mole) of piperazine in 500 ml of dry dimethylformamide was added dropwise with stirring 287.7 g (2.1 moles) of *n*-butyl bromide. The temperature was allowed to increase slowly to 100° during the addition and was held there with the aid of a water bath. After standing overnight at room temperature, the volatiles were removed on a rotary evaporator. The resulting gum was mixed with 500 ml of 20% aqueous sodium hydroxide and the water-insoluble oil was separated, dried over sodium sulfate, and distilled, bp 114° (10 mm), $n^{20}D$ 1.4539.

Anal. Calcd for $C_{12}H_{26}N_2$: N, 14.14. Found: N, 14.11.

1,4-Di-*n*-butyl-1-allylpiperazinium Bromide.—In 500 ml of dry acetone were mixed 19.8 g (0.1 mole) of 1,4-di-*n*-butylpiperazine and 14.5 g (0.12 mole) of allyl bromide. After standing for 72 hr at 25° a small quantity of a white precipitate was observed. The precipitate was removed by filtration and was found to be crude 1,4-di-*n*-butyl-1,4-diallylpiperazinium dibromide, mp 182–185°.

Anal. Calcd for N: 6.37. Found: 6.51.

The remaining liquid was evaporated leaving a gum which was converted into a white powder by washing with anhydrous ether. This product was shown into be 1,4-di-*n*-butyl-1-allylpiperazinium bromide, mp 134–136°.

Anal. Calcd for $C_{15}H_{31}BrN_2$: N, 8.73; mol wt, 319. Found: N, 8.55; mol wt, 319 (ebulliometrically in methyl ethyl ketone).

The infrared spectrum of this compound had the following characteristic piperazine bands[14] (KBr): 1348, 1145, 1108, 1030, and 935 cm^{-1}. A new band characteristic of the monoquaternized piperazines was found at 1212 cm^{-1}.

1,4-Diethyl-1-methylpiperazinium *p*-Toluenesulfonate.—In 50 ml of dry acetone were mixed 7.1 g (0.05 mole) of 1,4-diethylpiperazine and 1.9 g (0.01 mole) of methyl *p*-toluenesulfonate. After standing for 48 hr at 25°, the volatiles were removed at 70° and the resulting solid was recrystallized from acetone, mp 105–106°. The infrared spectrum was consistent with that of the expected product.

Anal. Calcd for $C_{16}H_{28}N_2O_3S$: N, 8.54. Found: N, 8.66.

Reaction of N-Substituted Aziridines with Alkylating Agents.—Into a small-mouth bottle was weighed 0.30 mole of the aziridine and the indicated volume of dry solvent was added. This mixture was placed in a thermostated 25° bath. Subsequently 0.03 mole of the alkylating agent was added with shaking. After 96 hr the bottles were removed from the bath, their contents were transferred to a rotary evaporator, and all volatiles were removed leaving either a powder or gummy residue. The residue was triturated with anhydrous diethyl ether resulting in the deposition of a white powder which was separated by filtration and dried. The piperazinium salts were subsequently recrystallized from acetone, vacuum dried, and analyzed.

In some cases the gummy residue did not solidify, but dissolved in the ether, thereby indicating polymer. Polymers which were not ether soluble were those containing functional groups such as those from 1-(2-hydroxyethyl)aziridine and 1-cyanoethylaziridine. It is also worth noting that those piperazines prepared from dihalides usually precipitated from the reaction mixture. This general procedure was used for all runs listed in Table III.

The poly(1-ethylaziridine) polymers prepared in reactions 10 and 12 were found to contain less than 3.0% piperazine rings ($C_4H_8N_2$) which was the analytical limit of the infrared method employed. This limit was established by preparing blends of 1,4-diethyl-1-methylpiperazinium *p*-toluenesulfonate and poly(1-ethylaziridine) and evaluating their infrared spectra.

Reaction of N-Alkylaziridines with Dimethylchloroethylamine and Diethylchloroethylamine.—The chloroethylamine was prepared by treating 0.031 mole of the corresponding hydrochloride with an excess of cold 20% aqueous sodium hydroxide and extracting with diethyl ether. The ether solution was dried over anhydrous sodium sulfate and this solution (20–30 wt % amine) was introduced into the bottle containing the aziridine–solvent mixture. The remainder of the procedure was the same as the preceding one.

The nmr spectrum of a D_2O solution of 1,1-dimethyl-4-phenethylpiperazinium chloride had signals (relative to sodium 1-trimethylsilylpropane-3-sulfonate) at δ 2.81 (4 H, singlet, NCH_2CH_2O methylenes), at 2.90 (4 H, multiplet, NCH_2 ring methylenes), at 3.18 (6 H, singlet, $^+NCH_3$), at 3.43 (4 H, multiplet, $^+NCH_2$ ring methylenes), and at 7.35 (5 H, singlet, phenyl ring).

Acknowledgment.—The author gratefully acknowledges the able assistance of C. L. Sechrest and R. M. Cook. Infrared spectra were obtained and interpreted by H. L. Spell and nmr data were furnished by R. P. Vander Wal.

(13) All melting points are uncorrected. Nmr spectra were obtained with a Varian Associates Model A-60 spectrophotometer equipped with a variable-temperature probe. The chemical shifts were measured using sodium 1-trimethylsilylpropane-3-sulfonate as an internal standard. Infrared spectra were obtained on a Beckman IR-9. Glpc data were taken on an F & M 810 chromatograph.

(14) P. J. Hendra and D. B. Powell, *Spectrochim. Acta*, **18**, 305 (1962).

Pseudo-Halogens. VIII.[1] New Synthesis of Aziridines and Oxazolidones

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Aziridines or 2-oxazolidones are readily prepared from unsaturated compounds by direct conversion into β-chlorocarbamates followed by reaction with base or by pyrolysis, respectively. Yields are good and are comparable with those from the corresponding iodocarbamates. β-Chlorocarbamates prepared from 1-olefins have chlorine on C-2 and nitrogen on C-1; the oxazolidones obtained, therefore, are the 5-alkyl isomers. Proof of structure of the 2-oxazolidones has been obtained by independent synthesis of one pair of 4- and 5-alkyl isomers.

Aziridines can be prepared by numerous synthetic pathways of which two of the most widely used are the Gabriel and Wenker methods, both of which require a suitably substituted β-amino alcohol.[3] Limitations of these two reactions have been adequately discussed and will not be repeated.

A voluminous literature also exists on the preparation of 2-oxazolidones.[4] The most important synthetic routes involve various ring-closing techniques on β-amino alcohols and β-halamines or their derivatives.

β-Amino alcohols and β-halamines are not always readily accessible in good yield and/or of known stereochemistry and often they are obtained by multistep sequences. Our interest in aziridines and 2-

(1) Pseudo-halogens. VII: T. A. Foglia and D. Swern, *J. Org. Chem.*, **31**, 3625 (1966).

(2) Work to be submitted in partial fulfillment of the requirements for the Ph.D. degree.

(3) P. E. Fanta in "Heterocyclic Compounds with Three and Four-Membered Rings," Part I, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 524–575, and references listed therein.

(4) M. E. Dyen and D. Swern, *Chem. Rev.*, in press. For a brief review of the literature to 1953, see J. W. Cornforth, "Heterocyclic Compounds," Vol. 5, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, pp 396–402.

TABLE I

AZIRIDINES FROM β-CHLOROCARBAMATES AND BASE

Aziridines	Bp (mm) or mp, °C	Yield,[a] %	C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found
2-Phenylaziridine	93–93.5[b]	60	75.6	75.7	5.92	5.90	11.8	12.1
7-Azabicyclo[4.1.0]heptane	156–157[b,c]	55	...	...	...	...	...	...
cis-2,3-Diphenylaziridine	82–84[d]	45	...	...	...	...	...	...
2-*n*-Octylaziridine	52–52.5 (0.05)	75	77.4	77.5	13.6	13.4	9.02	9.00
2-*n*-Decylaziridine	70–71 (0.1)	65	78.6	78.5	13.7	13.7	7.64	7.49
2-*n*-Hexadecylaziridine	51.5–52	70	80.8	80.4	13.9	13.6	5.27	5.04

[a] Pure products. [b] Phenyl urea derivative. [c] Lit.[5] mp 158–159°. [d] A. Weissberger and H. Bach, *Ber.*, **64**, 1095 (1931); **65**, 631 (1932).

TABLE II

5-ALKYL-2-OXAZOLIDONES BY PYROLYSIS OF β-CHLOROCARBAMATES

2-Oxazolidones	Mp, °C	Yield, %	C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found
n-Butyl-	88–9	80	58.7	58.2	9.15	9.06	9.78	9.88
n-Octyl-	78–9	65	66.3	66.4	10.6	10.3	7.03	7.06
n-Decyl-	86.5–7.5	60	68.7	68.8	11.1	10.9	6.16	6.32
Phenyl-	87–88	45[a]	...	...	...	...	...	...
cis-Cyclohexano [*b*]	54–55	65[b]	...	...	...	...	...	...
4,5-Diethyl- (*cis* + *trans*)	66–72	70	58.7	58.9	9.15	9.39	9.78	9.77

[a] G. Poos, J. Carson, J. Rosenau, N. Kelly, and J. McGowin, *J. Med. Chem.*, **6**, 266 (1963). [b] M. Mousseran, F. Winternitz, and M. Mousseran-Canet, *Bull. Soc. Chim. France*, 737 (1953).

oxazolidones has prompted us to seek alternate, direct procedures for obtaining them from unsaturated compounds, of which a wide variety of structural types of high purity are readily available.

In a recent paper,[1] we described the scope, mechanism, and limitations of the addition of N,N-dichlorourethan (DCU, **1**) to unsaturated compounds to obtain β-chlorocarbamates (**2**), often in high to almost quantitative yields. In this paper we are reporting the synthetic utility of β-chlorocarbamates in the preparation of aziridines and 2-oxazolidones.

$$>C{=}C< \xrightarrow[\text{2. aqueous } NaHSO_3]{\text{1. DCU (1)}} \underset{Cl\ \ NHCO_2C_2H_5}{>C{-}C<} \quad \textbf{2}$$

β-Iodocarbamates have been used for the synthesis of aziridines[5] and 2-oxazolidones[6] but less is known about the chemical reactivity of the corresponding β-chlorocarbamates. We have found that the chlorine atom in these compounds is extremely labile and is readily eliminated by base treatment to yield aziridines. In confirmation and extension of earlier literature reports,[7,8] 2-oxazolidones are readily obtained by pyrolysis of β-chlorocarbamates. In both reactions, yields are comparable with those from β-iodocarbamates.

Table I lists aziridines prepared from β-chlorocarbamate precursors by base treatment. A disadvantage of the chlorocarbamate route to aziridines is failure to obtain stereospecific addition of DCU (**1**) to disubstituted alkenes. The addition is a free-radical reaction and yields a mixture of stereoisomers.[1] With terminal olefins, where this problem does not exist, the chlorocarbamate route is rapid and efficient, and overall yields of aziridines are good. The terminal aliphatic aziridines listed in Table I are new compounds. The β-chlorocarbamate route to their preparation is preferred to the iodocarbamate route which we have also employed as a confirmatory preparative procedure. Styrene yields 2-phenylaziridine in about 60% yield by both methods.

Table II summarizes the results on preparation of 2-oxazolidones from β-chlorocarbamates. Pyrolysis of β-chlorocarbamates was conducted on the neat liquids in a nitrogen atmosphere at 150–190° (preferred procedure) or in refluxing acetic acid. In the absence of solvent, pyrolyses were monitored by running the reactions about 10° above the temperature at which bubbling of ethyl chloride was first observed and then continuing the reaction until gas evolution ceased (usually less than 1 hr). Ethyl chloride could be isolated in a cold trap in almost quantitative yield; yields of pure 2-oxazolidones were usually 60–80%. Since 2-oxazolidones have a carbonyl stretching frequency at 1760 and the amide II band at about 1510 cm^{-1}, present in β-chlorocarbamates, is absent, the conversion of β-chlorocarbamates into oxazolidones can also be readily monitored by infrared spectroscopy.

The structure of the 2-oxazolidones, and consequently that of the β-chlorocarbamates, was proven by chemical and physical methods. The products are 5-alkyl-2-oxazolidones (**3**) and not the 4-substituted isomers (**4**). For structure determination one pair of isomeric 2-oxazolidones was selected for synthesis by unequivocal methods from 1-dodecene as shown in Scheme I.

Authentic 4-decyl-2-oxazolidone (**4**), mp 31.5–32.5°, was prepared by pyrolysis of the β-iodocarbamate obtained by adding preformed iodine isocyanate to 1-dodecene followed by reaction with methanol.[9] Iodine isocyanate is an electrophilic reagent that adds in Markovnikov fashion,[5] placing the iodine on the terminal carbon atom of 1-dodecene, with nitrogen becoming attached to C-2. Pyrolysis yields the 4-alkyl-2-oxazolidone (**4**) in good yield.

(5) A. Hassner and C. Heathcock, *Tetrahedron*, **20**, 1037 (1964); *J. Org. Chem.*, **29**, 3640 (1964); *Tetrahedron Letters*, **No. 6**, 393 (1963); **No. 19**, 1125 (1964).

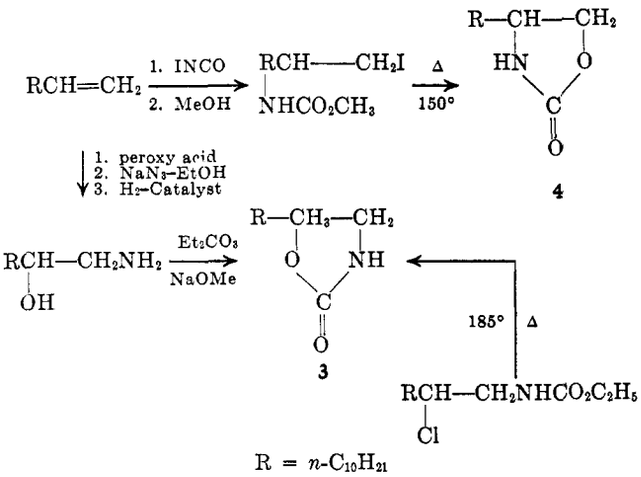
(6) C. Heathcock and A. Hassner, *Angew. Chem. Intern. Ed. Engl.*, **2**, 213 (1963); Dow Chemical Co. French Patent 1,331,404 (1963).

(7) E. Katchalski and D. Ben-Ishai, *J. Org. Chem.*, **15**, 1067 (1950).

(8) H. Najer, P. Chabrier, and R. Giudicelli, *Compt. Rend.*, **238**, 690 (1954).

(9) S. Rosen and Daniel Swern, *Anal. Chem.*, **38**, 1392 (1966).

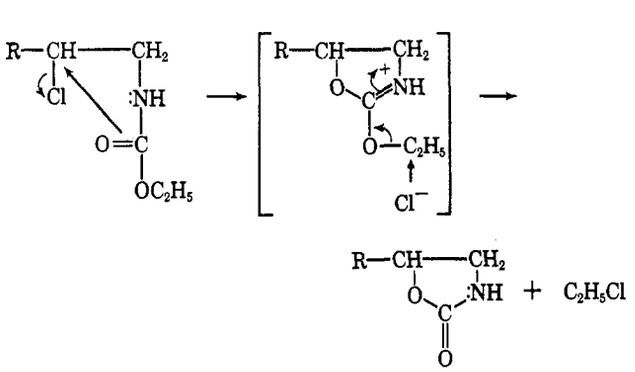
SCHEME I



Authentic 5-decyl-2-oxazolidone (**3**), mp 86.5–87.5°, was prepared from 1-dodecene by epoxidation followed by ring opening with azide ion and then catalytic hydrogenation. The intermediate, 2-hydroxy-*n*-dodecylamine, was ring closed by the Homeyer method.[10,11]

Pyrolysis of the β-chlorocarbamate prepared from 1-dodecene and DCU gave an oxazolidone, mp 86.5–87.5°, in 60% yield. The compound was identical in every respect with **3** (infrared and nmr spectra, melting point; mixture melting point determination showed no depression). Thus, DCU adds to 1-olefins to place the nitrogen on the terminal carbon atom. Previously we had shown that addition of DCU to styrene also yields the anti-Markovnikov product.[1]

The iodine isocyanate and DCU routes to 2-oxazolidones complement each other, the former yielding 4-alkyl- and the latter 5-alkyl-2-oxazolidones in good yields from 1-olefins. A suggested mechanism of formation of 5-alkyl-2-oxazolidones from β-chlorocarbamates is shown. Although the chlorine is secondary, it is readily displaced on pyrolysis as well as by base. β-Chlorocarbamates are stable for long periods and they are insensitive to laboratory illumination. Iodocarbamates darken on storage in the laboratory and should be used promptly.



Experimental Section[12]

β-Chlorocarbamates.—Their preparation has been described.[1]

Aziridines from β-Chlorocarbamates (Table I). 2-*n*-Octylaziridine.—A typical procedure is given in detail. Ethyl N-(2-chloro-*n*-decyl)carbamate (4.0 g, 0.015 mole) in 95% ethanol (15 ml) was added in one portion to a solution of potassium hydroxide (4.5 g, 0.08 mole) in 95% ethanol (35 ml). The solution was heated at 50° for 4 hr, poured into water (100 ml), and extracted with ether (three 30-ml portions). The combined extracts were dried over anhydrous sodium sulfate and the ether was removed in a rotary evaporator. The residual oil was distilled under vacuum to yield 2-*n*-octylaziridine, bp 52–52.5° (0.05 mm) and $n^{25}D$ 1.4525, a colorless liquid (1.8 g, 70% yield). Infrared (neat) showed 3350 (NH), 3000, 2950, 1470, 1100, 860, 830, 725 cm^{-1}.

2-*n*-Decylaziridine.—Prepared in 60% yield, as described above, from ethyl N-(2-chloro-*n*-dodecyl)carbamate (10 g, 0.034 mole), it had bp 70–71° (0.1 mm) and $n^{25}D$ 1.4534. Infrared (neat) showed 3350 (NH), 3000, 2950, 1470, 1095, 1055, 885, 860, 725 cm^{-1}.

2-*n*-Hexadecylaziridine.—Prepared in 70% yield from ethyl N-(2-chloro-*n*-octadecyl)carbamate (2.8 g, 0.007 mole), the product, mp 51.5–52.5°, was purified by recrystallization from hexane at −20°. Infrared (CCl_4) showed 3400 (NH), 2950, 2900, 1470, 1100, 1050, 890, 860 cm^{-1}.

2-Phenylaziridine.—Prepared from ethyl N-(2-chloro-2-phenylethyl)carbamate (4.6 g, 0.02 mole), it was isolated as the phenylurea derivative as follows. The crude aziridine (*ca.* 2 g) after evaporation of the ether was dissolved in hexane (50 ml) and phenyl isocyanate (3 ml) was added in one portion. After 1 hr, the solid was filtered and recrystallized from 95% ethanol, mp 93–93.5° (3 g, 65% yield). Infrared (Nujol) showed 3350 (NH), 1670 (carbonyl), 1600 (C=C), 1550 (amide II), 750, 690 cm^{-1}.

7-Azabicyclo[4.1.0]heptane.—Prepared from *trans*-ethyl N-(2-chlorocyclohexyl)carbamate (4.1 g, 0.02 mole). The phenylurea derivative was isolated (2.4 g, 55% yield); the crude product had mp 156–157° (lit.[5] mp 158°). Infrared (Nujol) showed 3350 (NH), 1650 (carbonyl), 1600 (C=C), 1540 (amide II), 1370, 1320, 1210, 755, 700 cm^{-1}.

***cis*-2,3-Diphenylaziridine.**—Prepared from an approximately equimolar mixture of *threo*- and *erythro*-ethyl N-(2-chloro-1,2-diphenylethyl)carbamate (6.1 g, 0.02 mole), the crude aziridine was crystallized from hexane to yield the *cis* isomer (1.8 g, 45% yield, mp 82–84° (lit.[3] mp 83–84°). Infrared (CCl_4) showed 3330 (NH), 1595 (C=C), 1490, 1440, 1180, 1070, 1050, 930, 865, 725, 695 cm^{-1}.

2-Oxazolidones from β-Chlorocarbamates (Table II). 5-*n*-Butyl-2-oxazolidone. A. Neat Pyrolysis.—Ethyl N-(2-chloro-*n*-hexyl)carbamate (2.12 g, 0.01 mole) was placed in a flask equipped with a thermometer, nitrogen inlet tube, and an exit tube leading to a Dry Ice–acetone cold trap. The carbamate was heated at 180° under nitrogen until evolution of ethyl chloride ceased. Ethyl chloride was collected in the cold trap, weight 0.53 g (calcd 0.65 g). The residue was cooled and recrystallized from 75% ether–hexane to yield 5-*n*-butyl-2-oxazolidone (1.1 g, 80% yield), mp 88–89°. Infrared (CCl_4) showed 3250 (NH), 1760 (carbonyl), 1240, 1095, 960 cm^{-1}.

B. Solvent Method.—The carbamate (4.24 g, 0.02 mole) was refluxed in glacial acetic acid (50 ml) for 18 hr. The reaction mixture was poured into water (100 ml) and the aqueous layer was neutralized with 3 *M* sodium hydroxide solution. The mixture was extracted with ether (three 50-ml portions) and the combined ether extracts were dried and evaporated to dryness. The residue (1.42 g, 50% yield), mp 88–89°, was recrystallized from 75% ether–hexane. It was identical with the product obtained in A.

5-*n*-Octyl-2-oxazolidone.—Prepared by pyrolysis of neat ethyl N-(2-chloro-*n*-decyl)carbamate (2.64 g, 0.01 mole) at 160–170°, the product was recrystallized from hexane (1.3 g, 65% yield), mp 83–84°. Infrared (CCl_4) showed 3300 (NH), 1760 (carbonyl), 1235, 1100, 955 cm^{-1}.

5-*n*-Decyl-2-oxazolidone (3).—Prepared by pyrolysis of neat ethyl N-(2-chloro-*n*-dodecyl)carbamate (2.9 g, 0.01 mole) at 185–190°, the product was recrystallized from hexane (1.4 g, 60% yield), mp 86.5–87.5°. Infrared (CCl_4) showed 3350 (NH), 1760 (carbonyl), 1230, 1080, 950 cm^{-1}.

5-Phenyl-2-oxazolidone.—Prepared by pyrolysis of neat ethyl N-(2-chloro-2-phenylethyl)carbamate (2.28 g, 0.01 mole) at 170–175°, the crude product in a minimum of chloroform was placed on a Florisil column (1.5 g of crude oxazolidone–30 g

(10) A. H. Homeyer, U. S. Patent 2,399,118 (1946).

(11) B. J. Ludwig, W. A. West, and D. N. Farnsworth, *J. Am. Chem. Soc.*, **76**, 2891 (1954).

(12) Melting and boiling points are uncorrected. An infrared 137-B and a Varian A-60 nmr spectrometer were used. Analyses were by Micro-Analysis, Inc., Wilmington, Del.

of Florisil) and eluted successively with hexane (75 ml), 50% ether–hexane (50 ml), ether (150 ml), and then chloroform (50 ml). The pure oxazolidone was obtained from the ether eluate; it had mp 87–88° (lit.[13] mp 87–87.5°) (0.76 g, 45% yield). Infrared ($CHCl_3$) showed 3520, 3350 (NH), 1760 (carbonyl), 1220, 1070, 970, 695 cm^{-1}.

cis-**Cyclohexano**[*b*]-**2-oxazolidone.**—Prepared by pyrolysis of neat ethyl N-(2-chlorocyclohexyl)carbamate (2.06 g, 0.01 mole) at 180–185°, the crude product in a minimum of chloroform was placed on a Florisil column (1.5 g of crude oxazolidone–30 g of Florisil). Elution successively with hexane (50 ml) and 25% ether–hexane (50 ml) afforded 0.32 g of unconverted starting material. Further elution with 50% ether–hexane (50 ml) and 75% ether–hexane (100 ml) gave a colorless oil. Low-temperature recrystallization from ether–hexane yielded the pure oxazolidone, mp 54–55° (lit.[14] mp 55–56°) (0.76 g, 65% yield). Infrared (CCl_4) showed 3300 (NH), 1760 (carbonyl), 1220, 995, 955 cm^{-1}.

cis- **and** *trans*-**4,5-Diethyl-2-oxazolidone.**—Prepared by neat pyrolysis of an approximately equimolar mixture of *erythro*- and *threo*-ethyl N-(2-chloro-1,2-diethyl ethyl)carbamate (2.08 g, 0.01 mole) at 180–185°, the crude product in a minimum of chloroform was placed on a Florisil column (1.4 g of crude oxazolidone–25 g of Florisil) and eluted successively with hexane (50 ml), 50% ether–hexane (100 ml), and ether (150 ml). The ether eluates on evaporation yielded a colorless oil which was recrystallized from ether–hexane. Crystals were obtained that analyzed perfectly for the expected oxazolidone but the melting range (66–72°) indicated that the product (1.04 g, 70%) was a mixture of *cis* and *trans* isomers. Infrared ($CHCl_3$) showed 3540, 3350 (NH), 1760 (carbonyl), 1230, 985 cm^{-1}.

1-Iodo-2-(N-Carbomethoxy)amino-*n***-dodecane.**—Prepared from 1-dodecene (8.4 g, 0.05 mole) by reaction with preformed iodine isocyanate in tetrahydrofuran at −50° followed by reaction with methanol,[9] the iodocarbamate was recrystallized from 25% ether–hexane (6.5 g, 35% yield), mp 67.5–69°. Infrared (CCl_4) showed 3400 (NH), 1710 (carbonyl), 1510 (amide II), 1250, 1100, 900 cm^{-1}.

4-*n***-Decyl-2-oxazolidone** (**4**).—The iodocarbamate described above (2.5 g, 0.007 mole) was heated at 150° in a nitrogen atmosphere until methyl iodide evolution ceased. The crude reaction product was recrystallized from hexane at −20° (0.8 g, 55% yield), mp 31.5–32.5°. Infrared (CCl_4) showed 3300 (NH), 1760 (carbonyl), 1240, 1050, 940 cm^{-1}.

Anal. Calcd for $C_{13}H_{25}NO_2$: C, 68.7; H, 11.1; N, 6.16. Found: C, 68.6; H, 11.0; N, 6.08.

2-Hydroxy-*n***-dodecylamine.**—1,2-Dodecane epoxide[15,16] (18.4 g, 0.10 mole) in ethanol (500 ml) was added in one portion to a solution of sodium azide (7.8 g, 0.12 mole) and ammonium chloride (6.5 g, 0.12 mole) in water (200 ml), and the solution was refluxed for 48 hr. The reaction mixture was poured into water (800 ml) and extracted with ether (four 100-ml portions). The ether solution was dried over anhydrous sodium sulfate and the ether was removed in a rotary evaporator. The crude residual azidohydrin (21.3 g, 94% yield) was dissolved in ethanol (300 ml) and hydrogenated at room temperature in a stirring autoclave for 48 hr at 780 psi with platinum oxide catalyst (0.50 g). The solution was filtered and evaporated to dryness. The crude amino alcohol was recrystallized from hexane (12.5 g, 62% yield), mp 51–52°. Infrared (CCl_4) showed 3500 (OH), 3400 (NH), 1480, 1070 cm^{-1}.

Anal. Calcd for $C_{12}H_{26}NO$: C, 71.63; H, 13.52; N, 6.96. Found: C, 71.49; H, 13.22; N, 6.70.

5-*n***-Decyl-2-oxazolidone** (**3**).—Prepared from the amino alcohol (5.0 g, 0.025 mole) and diethyl carbonate (10 g, 0.08 mole) by Homeyer's method,[10] the crude product was recrystallized from ethanol (3.6 g, 63% yield), mp 86–87.5°. The product was identical with that from the pyrolysis of N-(2-chloro-*n*-dodecyl)-carbamate already described. Infrared (CCl_4) showed 3300 (NH), 1760 (carbonyl), 1240, 1095, 955 cm^{-1}.

Anal. Calcd for $C_{13}H_{25}NO_2$: C, 68.68; H, 11.08; N, 6.16. Found: C, 68.85; H, 11.05; N, 6.09.

Acknowledgment.—The authors acknowledge with thanks support of this investigation by Public Health Service Research Grants No. CA-07803 and CA-07174 from the National Cancer Institute.

(13) See Table II, footnote *a*.

(14) See Table II, footnote *b*.

(15) D. Swern, G. N. Billen, and J. T. Scanlan, *J. Am. Chem. Soc.*, **68**, 1504 (1946).

(16) Commercial peroxyacetic acid (40%), with sodium acetate added to neutralize sulfuric acid, was employed. The distilled reaction product was >97% 1,2-epoxydodecane (glpc).

Azetidinyl Ketones. II.[1] Synthesis, Epimerization, and Nuclear Magnetic Resonance Spectra of 1-*t*-Butyl-2-phenyl-3-benzoylazetidines

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trans-α-(Bromomethyl)chalcone (**1**) reacts with *t*-butylamine in solvent pentane to give 2-[α-(N-*t*-butylamino)-benzyl]acrylophenone (**2**) as the kinetically favored product which readily rearranges in more polar solvent media to the thermodynamically more stable α-[(N-*t*-butylamino)methyl]chalcone (**3**) and no evidence for an azetidinyl ketone is observed. When **2** or **3** was treated with hydrogen bromide followed by reaction with base, **2** produced the *cis*-1-*t*-butyl-2-phenyl-3-benzoylazetidine (**4**) while **3** gave *trans* isomer **5**; *cis* isomer **4** is readily converted into *trans* isomer **5** by sodium methoxide in methanol. Spectral studies, especially nmr and deuteration of the azetidines, were employed to assign the configurations. The mechanism and stereochemistry of the reactions leading to these stereospecific cyclizations to produce the arylaroylazetidines in good yield are discussed.

In a preliminary communication[3] concerning the study of mobile ketoallyl systems, it was reported that *trans*-α-(bromomethyl)chalcone (**1**) in solvent pentane reacts with 2 molar equiv of *t*-butylamine to give exclusively, in high yield, the rearranged substitution product, 2-[α-(N-*t*-butylamino)benzyl]acrylophenone (**2**). This compound under the proper conditions may be induced to rearrange quantitatively to the thermodynamically more stable isomeric form, α-[(N-*t*-butylamino)methyl]chalcone (**3**).

Although **2** is reasonably stable with respect to isomerization either in the crystalline state or in solvent pentane, in solvent chloroform (and other slightly polar solvents) it readily rearranges to **3**. Even in solvent pentane, however, **2** reacts readily with added *t*-butylamine to give **3**. The rearrangement **2** → **3** was then suggested to involve a four-membered-ring dipolar intermediate (X).

(1) See N. H. Cromwell and Earl Doomes, *Tetrahedron Letters*, **No. 34**, 4037 (1966), for the first announcement of the synthesis of 2-aryl-3-aroylazetidines.

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(3) R. P. Rebman and N. H. Cromwell, *Tetrahedron Letters*, **No. 52**, 4833 (1965).