# 2-Oxazolidone Formation by Pyrolysis of β-Iodocarbamates. A Stereoselective Reaction[1]

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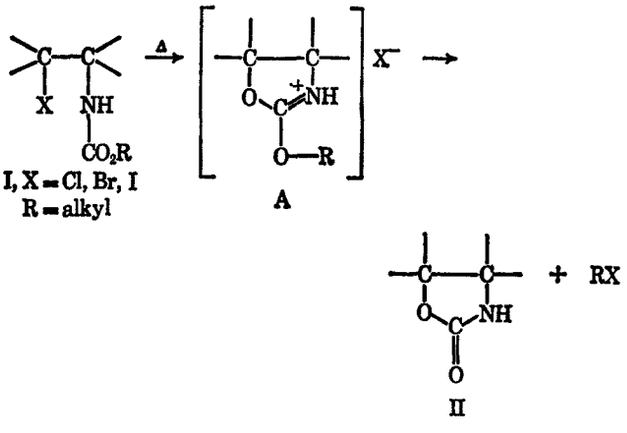
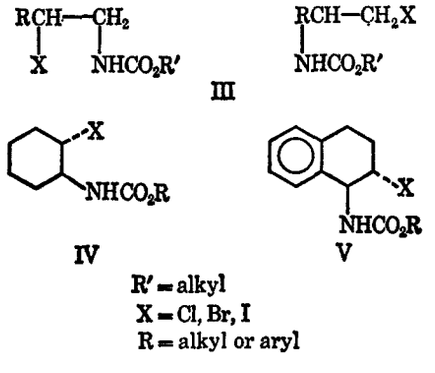
The pyrolytic cyclization of *threo*- and *erythro*-β-iodocarbamates from *cis*- and *trans*-2-butenes and -3-hexenes to 2-oxazolidones has been studied. The reaction is stereoselective, not stereospecific as with β-iodocarbamates from cyclic olefins. Selectivity of cyclization is greater with *erythro* than with *threo* isomers. The former yield 80–90% *trans*- and 10–20% *cis*-2-oxazolidones, the latter 70% *cis* and 30% *trans*. Ratios of isomers formed were determined by comparison of their nmr spectra with those of model 2-oxazolidones of known geometry.

The pyrolytic cyclization of β-halocarbamates (I) to 2-oxazolidones (II) has been the subject of a number of studies.[4-6] The mechanism of cyclization has been reported to involve intramolecular nucleophilic displacement of the halide ion by the carbonyl oxygen to yield an intermediate of type A.[5] Subsequent cleavage of the alkyl–oxygen bond by the departed halide ion yields II and alkyl halide. This process is similar to an




SN2 displacement and has been regarded as a stereospecific reaction.[5]

In all examples reported to date, however, the starting β-halocarbamates (I) have been terminally substituted (III),[6] where stereochemistry is not involved, or the carbamate and halogen functions are attached to a cyclic system (IV, V).[5,6] In the last two examples, stereospecific cyclization has indeed been observed (and confirmed by us) and is the basis for the above mechanism.[6]

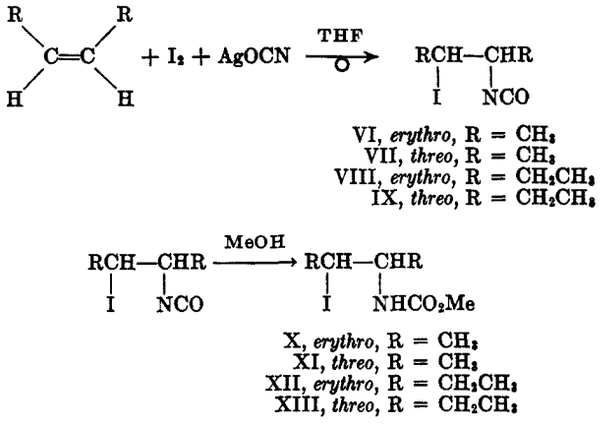



In this paper we are reporting (a) the pyrolytic cyclization of internal acyclic β-iodocarbamates of known stereochemistry and (b) the stereoselectivity of the cyclization.

## Results and Discussion

The model compounds selected for this study were the *erythro*- and *threo*-β-iodocarbamates (X–XIII). These were prepared by the addition of iodine isocyanate to *cis*- and *trans*-2-butene and *cis*- and *trans*-3-hexene followed by reaction with methanol as shown in Scheme I.

SCHEME I




Addition of iodine isocyanate to olefins proceeds in a clean *trans* manner,[7,8] yielding *threo* adducts from *cis*-olefins and *erythro* adducts from *trans*-olefins. Conversion of the isocyanate group to the methyl carbamoyl group by reaction with methanol does not affect the stereochemistry.

The diastereoisomeric pair, VI and VII, as well as VIII and IX, are distinguishable by their nmr spectra, summarized in Table I. The spectra of iodoisocyanates VI and VII are interpretable on the basis of the preferred conformations in Figure 1a and not with those previously suggested.[9] The signal of $H_a$ in conformer VIa, geminal to iodine,[10] appears at 4.24 ppm (TMS = 0), split into a quartet ($J$ = 7 Hz) by the adjacent

(1) Pseudohalogens. XIV. For XIII, see D. Saika and D. Swern, *J. Org. Chem.*, **33**, 4548 (1968).

(2) To whom inquiries should be addressed.

(3) The authors acknowledge with thanks support of this investigation by U. S. Public Health Service, Grants No. CA-07803, CA-07174, and CA-10439 of the National Cancer Institute.

(4) M. E. Dyen and D. Swern, *Chem. Rev.*, **67**, 197 (1967).

(5) C. Heathcock and A. Hassner, *Angew. Chem. Intern. Ed. Engl.*, **2**, 213 (1963).

(6) T. A. Foglia and D. Swern, *J. Org. Chem.*, **32**, 75 (1967).

(7) A. Hassner and C. Heathcock, *Tetrahedron*, **20**, 1037 (1964).

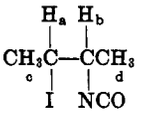
(8) A. Hassner, M. E. Lorber, and C. Heathcock, *J. Org. Chem.*, **32**, 540 (1967).

(9) A. Hassner and C. Heathcock, *Tetrahedron Lett.*, No. 19, 1125 (1964).

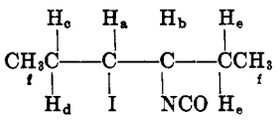
(10) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, p 84.

TABLE I

NMR SPECTRAL DATA FOR DIASTEREOMERIC IODOISOCYANATES



| | $H_a$[a] | $H_b$ | $H_c$ | $H_d$ |
|---|---|---|---|---|
| | δ | | | |
| *threo* VII | 4.22 (octet), $J_{ac}$ = 7.0, $J_{ab}$ = 3.0 (double quartet) | 3.15 (octet), $J_{bd}$ = 7.0, $J_{ba}$ = 3.0 (double quartet) | 1.95 (d), $J_{ac}$ = 7.0 | 1.40 (d), $J_{bd}$ = 7.0 |
| *erythro* VI | 4.24 (octet), $J_{ab}$ = 3.5, $J_{ac}$ = 7.0 (double quartet) | 3.45 (octet), $J_{ba}$ = 3.5, $J_{bd}$ = 7.0 (double quartet) | 1.93 (d), $J_{ac}$ = 7.0 | 1.42 (d), $J_{bd}$ = 7.0 |



| | $H_a$ | $H_b$ | $H_{cde}$ | $H_f$ |
|---|---|---|---|---|
| | δ | | | |
| *threo* IX | 4.12 (septet), $J_{ab}$ = 3.0, $J_{ac}$ = 4.5, $J_{ad}$ = 7.5 (double quartet) | 2.84 (sextet), $J_{ba}$ = 3.0, $J_{be}$ = 7.0 (double triplet) | 1.80 (m) | 1.02 (m) |
| *erythro* VIII | 4.14 (octet), $J_{ab}$ = 8.5, $J_{ac}$ = 5.5, $J_{ad}$ = 4.5 (double quartet) | 3.41 (sextet), $J_{ba}$ = 8.5, $J_{be}$ = 5.0, (double triplet) | 1.72 (m) | 1.06 (m), $J_{ef}$ = 7 |

[a] $J$ is given in cycles per second.

methyl group, each line of which is further split into a doublet ($J$ = 3.5 Hz) by a proton $H_b$ adjacent to the isocyanate group. $H_a$ in conformer VIIa also appears as a double quartet centered at 4.22 ppm; $J_{ab}$ is now 3 Hz while the coupling constant with the adjacent methyl group ($J_{ac}$) remains 7 Hz. This similarity in both chemical shift and coupling constant between $H_a$ and $H_b$ in both diastereomers indicates a similar magnetic environment and that the dihedral angle between $H_a$ and $H_b$ is very similar or the same. Accordingly, the nmr data are consistent with a *gauche* arrangement of $H_a$ and $H_b$ in both diastereomers, as in Figure 1a, and not the *gauche* and *anti* configurations previously assigned.[9] In both isomers, $H_b$ also appears as a double quartet centered at 3.45 (VIa) and 3.15 ppm (VIIa), respectively. Thus, as previously noted, the iodine atom by nature of its magnetic anisotropy exerts unequal shielding on the nucleus of $H_b$ in the two isomers.

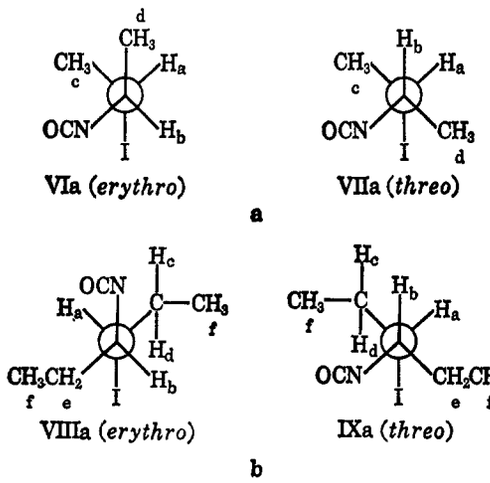


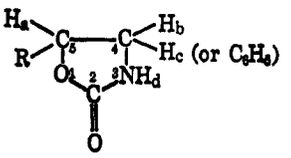

Figure 1

Interpretation of the nmr spectra of iodoisocyanates VIII and IX is based on conformations VIIIa and IXa in Figure 1b. In the *erythro* isomer (VIIIa) the *anti* conformation is assigned to $H_a$ and $H_b$ because of their large coupling constant ($J_{ab}$ = 8.5 Hz) and the deshielding effect on $H_b$ of the iodine atom as in VIa. $H_a$ is seen at 4.14 ppm, split into an octet (two overlapping quartets) by $H_b$ ($J_{ba}$ = 8.5 Hz) and the two nonequivalent methylene protons[11] $H_c$ and $H_d$ ($J_{ac}$ = 5.5; $J_{ad}$ = 4.5 Hz). The signal of $H_b$ appears at 3.41 ppm split into a triplet by the adjacent methylene group ($J_{be}$ = 5 Hz) each line of which is further split by $H_a$ ($J_{ba}$ = 8.5 Hz). In the *threo isomer* (IXa) $H_a$ and $H_b$ are assigned the *gauche* conformation by the identity of their coupling constant with $J_{ab}$ in *threo* isomer VIIa. $H_a$ appears at 4.12 ppm as a septet (overlapping double quartet), split by the two nonequivalent methylene protons $H_c$ ($J_{ac}$ = 4.5 Hz) and $H_d$ ($J_{ad}$ = 7.5 Hz),[11] each line further split by $H_b$ ($J_{ab}$ = 3 Hz). $H_b$ is seen at 2.84 ppm, split into a triplet by the adjacent methylene group ($J_{be}$ = 7 Hz) each line of which is further split into a doublet by $H_a$ ($J_{ba}$ = 3 Hz). The alternate *gauche* conformation of IXa in which $H_b$ is deshielded by the iodine atom (as in VIIIa) is eliminated in view of its chemical shift.

Conversion of iodoisocyanates VI–IX into the corresponding methyl iodocarbamates (X–XIII) does not alter the original stereochemistry. This was corroborated by their nmr spectra, which are very similar to those of the parent iodoisocyanates. The major differences in the spectra, aside from the expected methoxy signal at 3.70 ppm, is a general down-

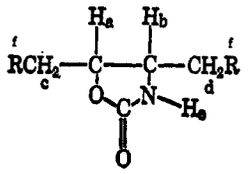
(11) L. M. Jackman, "Applications of NMR Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, pp 99–103.

TABLE II
NMR SPECTRA
2-Oxazolidones



| | δ | | | |
|---|---|---|---|---|
| | $H_a$ | $H_b$[b] | $H_c$ | $H_d$ |
| 4,5-Diphenyl | | | | |
| *cis* XV | 6.02 (d), $J_{ab}$ = 8.5 | 5.28 (d), $J_{ba}$ = 8.5 | | 6.88 (s) |
| *trans* XVI | 5.24 (d), $J_{ab}$ = 7.5 | 4.76 (d), $J_{ba}$ = 7.5 | | 6.70 (s) |
| 5-Phenyl[a] | | | | |
| XVII | 5.52 (dd), $J_{ab}$ = 8.5, $J_{ac}$ = 7.5 | 3.90 (t), $J_{ba}$ = $J_{bc}$ = 8.5 | 3.42 (dd), $J_{cb}$ = 8.5, $J_{ca}$ = 7.5 | 6.82 (s) |

*cis*- and *trans*-Alkyl-2-oxazolidones



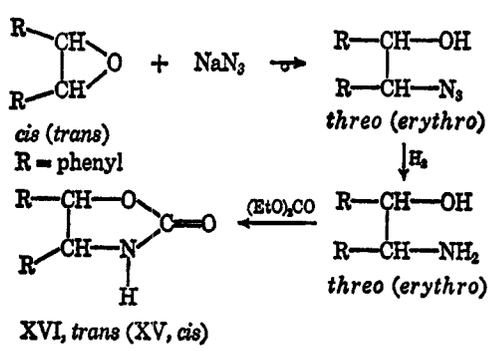
| | δ | | | |
|---|---|---|---|---|
| | $H_a$ | $H_b$[b] | $H_{c,d}$ | $H_e$ |
| 4,5-Dimethyl, R = H | | | | |
| *cis* XIX | 4.80, $J_{ab}$ = 8.5, $J_{ac}$ = 7.0 (double quartet) | 3.98, $J_{ba}$ = 8.5, $J_{bd}$ = 7.0 (double quartet) | 1.34 (d), 1.20 (d), $J$ = 7.0 | 6.82 (s) |
| *trans* XVIII | 4.22 (quintet), $J_{ab}$ = $J_{ac}$ = 7.0 | 3.56 (quintet), $J_{ba}$ = $J_{bd}$ = 7.0 | 1.26 (d), 1.10 (d), $J$ = 7.0 | 6.74 (s) |
| 4,5-Diethyl, R = $CH_3$ | | | | |
| *cis* XXI | 4.52, $J_{ab}$ = 5.5, $J_{ac}$ = 7.5, 1,1,2,2,1,1 sextet (double triplet) | 3.70, $J_{ba}$ = 5.5, $J_{bd}$ = 7.5 (double triplet) | 1.54 (m), 7.26 (s) | 1.02 (m) |
| *trans* XX | 4.12 (q), $J_{ab}$ = $J_{ac}$ = 5.5 | 3.40 (q), $J_{ba}$ = $J_{bd}$ = 5.5 | 1.58 (m), 6.98 (a) | 0.98 (m) |

[a] Coupling constants (cycles per second) obtained by treating with trifluoracetic acid and deuterium oxide to remove proton on nitrogen. [b] $H_b$ always shows small splitting of <0.5 cps due to coupling with proton $H_d$.

field shift of $H_b$ to approximately 3.2 ppm and the further splitting of $H_b$ by the proton attached to nitrogen.

Before continuing with the investigation of the stereochemistry of pyrolysis of methyl β-iodocarbamates, it was necessary to be able to distinguish between *cis*- and *trans*-2-oxazolidones by nmr. Model 2-oxazolidones of known structure and stereochemistry were required for determination of coupling constants and chemical shifts. The compounds selected were the isomeric *cis*- and *trans*-4,5-diphenyl-2-oxazolidones (XV and XVI), prepared by the reaction sequences shown in Scheme II.

SCHEME II




The starting materials, *cis*- and *trans*-stilbene epoxides, were prepared in the conventional manner by epoxidation of *cis*- and *trans*-stilbene, respectively.[12] Nucleophilic attack on the epoxides by azide ion converted them into the *threo*- and *erythro*-azidohydrins, respectively. The stereochemistry of this reaction is known to proceed with inversion.[13] Hydrogenation of the azidohydrins gave the known *threo*- and *erythro*-amino alcohols which were then cyclized to the *cis*- and *trans*-2-oxazolidones by a modification of the Homeyer method.[14,15]

To obtain the geminal coupling constant of methylene protons on a 2-oxazolidone ring, 5-phenyl-2-oxazolidone (XVII) was prepared; its structure is well established.[6]

The nmr spectra of the model 2-oxazolidones are summarized in Table II. In the *cis* isomer (XV), $H_a$ appears at 6.02 ppm (TMS = 0), split into a doublet ($J_{ab}$ = 8.5 Hz) by $H_b$, also seen as a doublet upfield at 5.28 ppm.

In the *trans* isomer (XVI), $H_a$ is seen at 5.24 ppm as a

(12) T. W. Findley, D. Swern, and J. T. Scanlan, *J. Amer. Chem. Soc.*, **67**, 412 (1945).
(13) R. D. Guthrie and D. Murphy, *J. Chem. Soc.*, 5288 (1963).
(14) A. H. Homeyer, U. S. Patent 2,399,118 (1946); R. J. Ludwig, W. A. West, and D. N. Farnsworth, *J. Amer. Chem. Soc.*, **76**, 2891 (1954).
(15) M. S. Newman and A. Kutner, *ibid.*, **73**, 4199 (1951).

doublet ($J_{ab}$ = 7.5 Hz), while $H_b$ is a doublet at 4.76 ppm. The difference in the chemical shift of $H_a$ and $H_b$ in the two isomers is ascribed to the shielding effect of the benzene rings attached to the adjacent carbon atoms in the *trans* isomer. In 5-phenyl-2-oxazolidone (XVII), $H_a$ is a double doublet at 5.52 ppm, coupled to the *cis* proton $H_b$ ($J_{ab}$ = 8.5 Hz) and the *trans* proton $H_c$ ($J_{ac}$ = 7.5 Hz). $H_b$ appears at 3.90 ppm split into a triplet ($J_{ba,bc}$ = 8.5 Hz) by the *cis* proton $H_a$ and the geminal proton $H_c$. $H_c$, shielded by the benzene ring, is seen at 3.42 ppm as a double doublet coupled to protons $H_a$ and $H_b$.

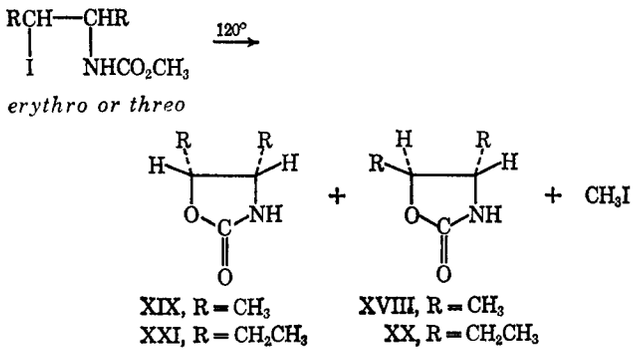
β-Iodocarbamates X–XIII were then pyrolyzed as neat liquids in a nitrogen atmosphere at 120°. The pyrolyses were monitored by disappearance of the methoxy signal in the nmr of the carbamates and by ir. The liberated methyl iodide was isolated in a cold trap usually in nearly quantitative yield; yields of 2-oxazolidones were essentially quantitative and the products were shown to be >97% pure by nmr.

Pyrolysis of methyl *erythro*-N-(3-iodo-2-butyl) carbamate (X) was complete after 1 hr. Examination of the reaction mixture by nmr and glpc showed it to be an 80:20 mixture of two compounds. After a cleanup distillation (no change in composition in the distillate), the two components were separated by preparative glpc and identified as the geometric isomers of 4,5-dimethyl-2-oxazolidone by elemental analysis, ir and nmr. The assignment of stereochemistry was made by analysis of their nmr spectra, listed in Table II. The major component, *trans*-4,5-dimethyl-2-oxazolidone (XVIII) showed $H_a$ and $H_b$ as quintets ($J$ = 7.0 Hz) centered at 4.22 and 3.56 ppm, respectively. The methyl protons appeared as doublets ($J$ = 7.0 Hz) at 1.26 and 1.10 ppm. The *trans* configuration is assigned since the coupling constant of $H_a$ and $H_b$ is of the same magnitude as that in the model *trans* compound XVI. Since all hydrogen–hydrogen coupling constants in the *trans* isomer are of the same magnitude the hydrogens appear as equivalent hydrogens. Accordingly, $H_a$ and $H_b$ are seen as quintets.

The minor component from the *erythro* isomer was identified as *cis*-4,5-dimethyl-2-oxazolidone (XIX) from its nmr spectrum (Table II). Assignment of the *cis* configuration is based on the magnitude of the coupling constant of $H_a$ with $H_b$.

Pyrolysis of methyl *threo*-N-(3-iodo-2-butyl) carbamate (XI) also gave a mixture of isomeric 2-oxazolidones, the composition of which was 70% *cis* and 30% *trans*.

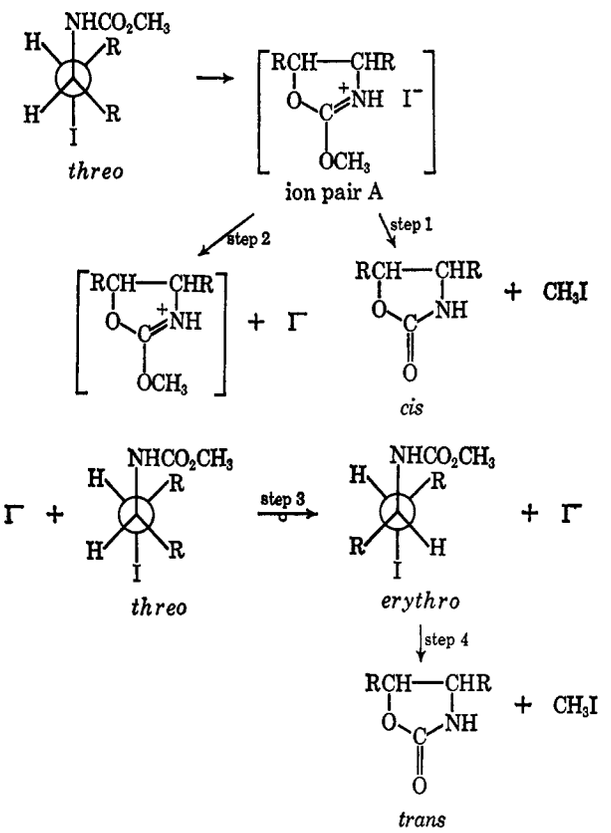
Pyrolysis of diastereomeric *erythro*- and *threo*-methyl N-(4-iodo-3-hexyl) carbamates XII and XIII also gave




a mixture of *cis*- and *trans*-2-oxazolidones as shown by nmr. The isomer distribution from the *erythro* isomer was 90% of the expected *trans* (XX, Table II) and only 10% *cis* (XXI); from the *threo* isomer, the ratio was 70:30 with the expected *cis* isomer predominating. The assignment of stereochemistry was based on their nmr spectra, as in the dimethyl cases.

The pyrolytic cyclization of *erythro*- and *threo*-β-iodocarbamates, therefore, is a nonstereospecific cyclization although it is stereoselective. However, cyclization of *erythro* isomers, to yield predominantly *trans*-2-oxazolidones, is more stereoselective than pyrolysis of *threo* isomers that yield mainly *cis*-2-oxazolidones.

SCHEME III




A suggested mechanism to account for the lack of stereospecificity is shown in Scheme III using a *threo*-iodocarbamate as a prototype. The initial step involves formation of the previously proposed intermediate ion pair A from the β-iodocarbamate. This intimate ion pair can now proceed to the *cis*-2-oxazolidone (step 1) or dissociate to the free ions (step 2). The liberated iodide ion can undergo an identity reaction (SN2) with another molecule of *threo*-iodocarbamate to give the diastereomeric *erythro* isomer (step 3). The *erythro* isomer can then cyclize to *trans*-2-oxazolidone (step 4). Isomerization of *erythro* and *threo* isomers has been previously observed in the iodide ion-catalyzed conversion of acyl aziridines into oxazolines.[16]

The lower stereoselectivity observed in the pyrolytic cyclization of *threo*-iodocarbamates can be attributed to a higher degree of crowding of alkyl groups in approach-

(16) H. W. Heine, D. C. King, and L. A. Portland, *J. Org. Chem.*, **31**, 2662 (1966).

ing the transition state for 2-oxazolidone formation (*trans*, antiparallel arrangement of the iodine and carbamoyl groups). Thus in *threo*-iodocarbamates the identity reaction suggested may become more competitive than in *erythro* isomers.

## Experimental Section

**Materials and Equipment.**—The olefins used were the purest commercial reagents; glpc indicated >98%. Iodine isocyanate was prepared by the method of Rosen and Swern.[17] Infrared spectra were obtained on a Perkin-Elmer Infracord, Model 137. Nmr were obtained on a Varian A-60A spectrometer using TMS as internal standard. The samples were run as 10% solutions in chloroform. Glpc was carried out on a Wilkens Aerograph Autoprep, Model A-700. Refractive indices were taken on a Bausch and Lomb refractometer. Microanalyses were performed by Microanalysis Inc., Wilmington, Del.

**Additions of INCO to Olefins. General Procedure.** ***erythro*-4-Iodo-3-hexyl Isocyanate (VIII).**—Into a 500 ml three-necked flask equipped with a mechanical stirrer and condenser 25.0 g (0.15 mol) of freshly prepared silver cyanate and 200 ml of tetrahydrofuran (distilled from LAH) were placed. The stirred mixture was cooled to −35° and *trans*-3-hexene (10.0 g, 0.12 mol) was added followed by iodine (25.4 g, 0.10 mol) in one portion. The reaction temperature rose to −20° where it was held for 2 hr at which time the solution became colorless. The reaction mixture was allowed to come to room temperature, solids were filtered from the solution, washed with THF and the solvent was then removed from the filtrate at room temperature in a rotary vacuum evaporator. The residue was distilled to give VIII (20 g, 80% yield): bp 62–64° (0.30 mm); $n^{25}$D 1.5122; ir (neat) 3000, 2280 (-NCO), 1460, 1330, 1180, 950, 890, 820, and 800 cm$^{-1}$.

*Anal.* Calcd for $C_7H_{12}INO$: C, 33.1; H, 5.08; N, 5.52; I, 50.0. Found: C, 33.0; H, 5.01; N, 5.72; I, 49.8.

**Methyl N-*erythro*-4-iodo-3-hexylcarbamate (XII)** was prepared by adding VIII to 50 ml of anhydrous methanol and allowing the solution to stand for 18 hr in the dark. Vacuum evaporation of excess methanol gave a quantitative yield of XII as a viscous oil which solidified on cooling to −30°: mp 45–46°; ir ($CHCl_3$) 3500 (N–H), 3000, 1720 (C=O), 1520 (amide II), 1240, 1110, 990 and 870 cm$^{-1}$.

*Anal.* Calcd for $C_8H_{16}INO_2$: C, 33.7; H, 5.66; N, 4.91; I, 44.5. Found: C, 33.4; H, 5.91; N, 4.87; I, 44.0.

***threo*-4-Iodo-3-hexyl Isocyanate (IX)** was prepared from *cis*-3-hexene (10.0 g, 0.12 mol) in 75% yield by the described procedure: bp 66° (0.25 mm); $n^{23}$D 1.5125; ir (neat) 3000, 2260 (NCO), 1460, 1330, 1300, 1180, 1140, 1120, 920, 900, 840 and 790 cm$^{-1}$.

**Methyl N-*threo*-4-iodo-3-hexylcarbamate (XIII)** was prepared from IX as described for the *erythro* isomer. The crude residue was a viscous oil which could not be induced to crystallize. Its ir spectrum was similar to that of the *erythro*-iodocarbamate. Its nmr indicated it to be >98% pure.

***erythro*-3-Iodo-2-butyl isocyanate (VI)** was prepared from *trans*-2-butene in 70% yield: bp 49–50° (1.0 mm) [lit.[9] bp 57–59° (1.5 mm)]. The iodocarbamate, methyl *erythro*-N-(4-iodo-3-butyl)carbamate (X), was prepared as already described. The pure carbamate was a viscous oil obtained in quantitative yield: ir (neat) 3350 (NH), 2990, 1725 (C=O), 1510 (amide II), 1220, 1100 and 860 cm$^{-1}$.

*Anal.* Calcd for $C_6H_{12}INO_2$: C, 28.0; H, 4.71; N, 5.45; I, 49.4. Found: C, 28.7; H, 4.83; N, 5.50; I, 48.6.

***threo*-3-Iodo-2-butyl isocyanate (VII)** was prepared in 75% yield from *cis*-2-butene by the described procedure: bp 50–51° (1.0 mm) [lit.[9] bp 57–59° (1.5 mm)]. The iodocarbamate, methyl *threo*-N-(4-iodo-3-butyl)carbamate (XI), was prepared in 90% yield, mp 28–29°. Its ir spectrum was similar to that of the *erythro* isomer.

*Anal.* Calcd for $C_6H_{12}INO_2$: C, 28.0; H, 4.71; N, 5.45; I, 49.4. Found: C, 28.4; H, 4.77; N, 5.70; I, 48.5.

***cis*- (XIX) and *trans*-4,5-Dimethyl-2-oxazolidone (XVIII).**—*erythro*- or *threo*-methyl-N-(3-iodo-2-butyl)carbamate (X or XI) (12.65 g, 0.05 mol) was pyrolyzed at 120° until the evolution of methyl iodide ceased. The crude residue was cooled and examined by nmr and glpc. Both *cis* and *trans* isomers were present in the ratio of 20:80 from the *erythro*-iodocarbamate and 70:30 from the *threo*-iodocarbamate. Yields in both cases were quantitative and the residues were free of starting carbamate (nmr). The residues from the pyrolyses had identical boiling points [101–103° (0.15 mm)]. They were separated by preparative glpc employing a 5 ft × ⅜ in. column packed with 10% butanediol succinate on Anakrom 60 mesh at 185° with a helium flow of 200 ml/min.

*Anal.* Calcd for $C_5H_9NO_2$: C, 52.2; H, 7.88; N, 12.2. Found: C, 51.9; H, 8.19; N, 12.1.

***cis*- (XXI) and *trans*-4,5-Diethyl-2-oxazolidone (XX).** Pyrolysis of methyl *erythro*-N-(4-iodo-3-hexyl)carbamate (XII, 5.70 g, 0.02 mol) at 120° for 1 hr produced the theoretical amount of methyl iodide (2.8 g). The crude residue was cooled and examined by nmr, which indicated a 10:90 mixture of *cis*- and *trans*-2-oxazolidones of >98% purity. It was chromatographed on Florisil to give a colorless liquid of the same isomeric composition: ir (neat) 3320 (NH), 2980, 1750 (C=O), 1510 (amide II), 1220, 1150 and 970 cm$^{-1}$.

*Anal.* Calcd for $C_7H_{13}NO_2$: C, 58.7; H, 9.15; N, 9.78. Found: C, 58.5; H, 9.26; N, 9.54.

Pyrolysis of methyl *threo*-N-(4-iodo-3-hexyl)carbamate (XIII, 5.70 g, 0.02 mol) at 120° for 1.5 hr gave the theoretical quantity of methyl iodide. The crude product partially crystallized on cooling. Examination by nmr indicated a 70:30 mixture of *cis*- and *trans*-isomeric 2-oxazolidones. The crude residue was dissolved in a minimum of ether and cooled to −30° to deposit white crystals, mp 79–80°, whose nmr spectrum indicated it to be pure *cis* isomer (XXI): ir ($CHCl_3$) 3540, 3350 (NH), 3000, 1760 (C=O), 1230 and 985 cm$^{-1}$.

*Anal.* Calcd for $C_7H_{13}NO_2$: C, 58.7; H, 9.15; N, 9.78. Found: C, 58.8; H, 8.91; N, 9.76.

**5-Phenyl-2-oxazolidone (XVII)** was prepared in 55% yield by pyrolysis of neat ethyl N-(2-chloro-2-phenylethyl)carbamate, mp 87–88° (lit.[6] mp 87–87.5°).

***erthro*-1,2-Diphenylaminoethanol.**—*trans*-Stilbene oxide[18] (9.80 g, 0.05 mol) in ethanol (250 ml) was added in one portion to a solution of sodium azide (3.9 g, 0.06 mol) and ammonium chloride (3.3 g, 0.06 mol) in water (100 ml), and the solution was refluxed for 18 hr. The reaction mixture was poured into water (400 ml) and extracted with four 50-ml portions of ether. The ether solution was dried over anhydrous sodium sulfate and the solvent removed on a rotary evaporator. The crude residual azidohydrin was dissolved in ethanol (150 ml) and hydrogenated at room temperature in a stirring autoclave for 24 hr at 700 psi with platinum oxide catalyst (0.50 g). The solution was filtered and evaporated to dryness. The crude amino alcohol was recrystallized from aqueous alcohol, mp 163–165° (75% yield) (lit.[19] mp 165–166°).

***threo*-1,2-Diphenylaminoethanol** was prepared in 80% yield from *cis*-stilbene oxide[20] by the above procedure, mp 127–28° (lit.[19] mp 127–28°).

***cis*-4,5-Diphenyl-2-oxazolidone (XV)** was prepared from *erythro*-1,2-diphenylaminoethanol (4.25 g, 0.02 mol) and diethyl carbonate (40 g, 0.32 mol) by the method of Newman and Kutner.[15] The crude product was recrystallized from 80% aqueous methanol, mp 195–196° (55% yield) (lit.[15] mp 193.5–195.5°).

***trans*-4,5-Diphenyl-2-oxazolidone (XVI)** was prepared in 45% yield from *threo*-1,2-diphenylaminoethanol as described for the *cis* isomer, mp 161–163° (lit.[21] mp 161–162°).

**Registry No.**—VI, 19190-92-2; VII, 19190-93-3; VIII, 19202-65-4; IX, 19190-94-4; X, 19190-74-0; XI, 19190-75-1; XII, 19190-76-2; XV, 19202-66-5; XVI, 19190-95-5; XVII, 7693-77-8; XVIII, 19190-96-6; XIX, 19190-97-7; XX, 19190-98-8; XXI, 19190-99-9.

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