# The Synthesis and Spectral Properties of Stereoisomeric β-Bromo Carbamates and 2-Oxazolidinones

### RONALD A. WOHL

School of Chemistry, Rutgers University, The State University of New Jersey, New Brunswick, New Jersey 08903

Received June 6, 1973

cis- and trans-4,5-dimethyl-N-phenyl-2-oxazolidinone (5a and 6a), as well as cis- and trans-4,5-dimethyl-N- $(\alpha$ -naphthyl)-2-oxazolidinone (5b and 6b), have been prepared from the corresponding three and erythro  $\beta$ -bromo carbamates 3 and 4 by ring closure through elimination of hydrogen bromide by alcoholic potassium hydroxide. The ir and nmr spectra of the  $\beta$ -bromo carbamates and 2-oxazolidinones are discussed.

For a study about which we will report at a later date we needed stereoisomeric 2-oxazolidinones having substituents at carbon atoms 4 and 5 as well as at the nitrogen atom (see eq 1).

Possible synthetic precursors for such 2-oxazolidinones are  $\beta$ -amino alcohols,  $\beta$ -halo amines,  $\beta$ -halo alcohols, 1,2glycols,  $\beta$ -halo carbamates, and N-( $\beta$ -halo) carbamates of defined stereochemistry.<sup>1</sup> A number of stereoisomeric 2-oxazolidinones of established configuration around atoms 4 and 5 have been prepared; the early efforts were undertaken in connection with establishing the configurations of ephedrine and  $\psi$ -ephedrine.<sup>2</sup> Most of these synthetic pathways have used  $\beta$ -amino alcohols as precursors. Recently, the pyrolysis of N- $(\beta$ -iodo) carbamates has been used for the synthesis of 4,5-disubstituted 2-oxazolidinones.<sup>3,4</sup>

While this reaction is stereospecific in the case of cyclic carbamates, Foglia and Swern found this reaction to be stereoselective only in the case of acyclic carbamates derived from cis- and trans-2-butenes and -3hexenes.4b

A convenient route for the synthesis of stereoisomeric 4,5-disubstituted 2-oxazolidinones seemed to be the ring closure from the corresponding  $\beta$ -bromo carbamates by elimination of hydrogen bromide with base (see eq 1).



The  $\beta$ -bromo carbamates are readily available from the corresponding bromohydrins. This route does not

(1) For a recent review on 2-oxazolidinone chemistry see M. E. Dyen and D. Swern, Chem. Rev., 67, 197 (1967). (2) See references cited in ref 1.

(3) C. Heathcock and A. Hassner, Angew. Chem., Int. Ed. Engl., 2, 213 (1963);A. Hassner, M. E. Lorber, and C. Heathcock, J. Org. Chem., 32, 540 (1967)

(4) (a) T. A. Foglia and D. Swern, J. Org. Chem., 32, 75 (1967); (b) ibid., 34, 1680 (1969).

seem to have been used previously for the stereospecific synthesis of 2-oxazolidinones.<sup>1</sup>

#### **Results and Discussion**

three-3-Bromo-2-butanol (1) with phenyl or  $\alpha$ naphthyl isocyanate gave the three carbamates 3a and 3b, respectively. Ring closure by elimination of HBr with potassium hydroxide in ethanol then led in practically quantitative yield to the cis-4,5-dimethyl-Naryl-2-oxazolidinones 5a and 5b (eq 1).

erythro-3-Bromo-2-butanol (2) similarly led via the intermediate ervthro carbamates 4a and 4b to the trans-2-oxazolidinones 6a and 6b.

Ring closure steps such as the one used for the oxazolidinone ring formation are generally accepted to proceed with inversion at the carbon atom at which the bromine atom is displaced. The stereochemistry of the 2-oxazolidinones 5 and 6 is supported by their nmr spectra (see below).

Infrared Spectra of  $\beta$ -Bromo Carbamates.<sup>5</sup>—The infrared spectra of the carbamates 3 and 4 generally agree well with literature data.<sup>6-9</sup> They show  $\nu(NH)_{free}$ at ca. 3500 cm<sup>-1</sup>, the amide I and II bands at ca. 1742 and  $1532 \text{ cm}^{-1}$ , symmetric and asymmetric methyl bending frequencies at ca. 1447 and 1384 cm<sup>-1</sup>, skeletal frequencies corresponding to the -CNHC==0 group at ca. 1335 and 1318 cm<sup>-1</sup>, and skeletal frequencies corresponding probably to the -COO group at ca. 1210, 1105, and 1075  $\rm cm^{-1.5}$ 

Nmr Data and Conformational Analysis of  $\beta$ -Bromo **Carbamates**—The nmr data of the  $\beta$ -bromo carbamates 3 and 4 are summarized in Table I. It can be seen from this table that the two three carbamates on one side and the two erythro carbamates on the other side behave very similarly.

The three compounds 3 may assume a priori the three conformations 3-I (gauche), 3-II (gauche), and 3-III (anti) (and their mirror images). For the erythro compounds 4 the three corresponding conformations are 4-I (gauche), 4-II (gauche), and 4-III (anti) (and their mirror images).

Turning our attention first to the vicinal coupling constant  $J_{ab}$ , it is seen that the values for the erythro compounds are slightly larger (4.2 Hz) than those for the corresponding three compounds (3.8 and 4.0 Hz). It has been found in many stereoisomeric series of the

(8) S. Pinchas and D. Ben-Ishai, J. Amer. Chem. Soc., 79, 4099 (1957).

(9) A. R. Katritzky and R. A. Jones, J. Chem. Soc., 676 (1960).

<sup>(5)</sup> See paragraph at end of paper regarding supplementary material.(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1966.

<sup>(7)</sup> L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen and Co., London, 1968.

|  |                    | TABLE I  |                    |                    |              |
|--|--------------------|--|--------------------|--------------------|--------------|
|  | NMR DATA OF        | 8-Bromo Carbam   | IATES <sup>a</sup> |                    |              |
|  | 。C<br>ArNC:<br>。H  | $ \begin{array}{cccc} H_{a} & H_{b} \\  & &   \\ H_{3}C & CCH_{3} & d \\  & &   \\ O & Br \\ \end{array} $ |                    |                    |              |
|  |                    |  |                    |                    |              |
| Carbamate  | Ha                 | Hp   | Hc                 | H <sub>d</sub>     | He           |
| 2-(threo-3-Bromobutyl)                             | 4.95 (oct)         | 4.12 (oct)   | 1.66 (d)           | 1.33 (d)           | 6.87-7.5 (m) |
| carbanilate ( <b>3a</b> )                          | $J_{\rm ab} = 3.8$ | $J_{\rm ba} = 3.8$   | $J_{\rm ea} = 6.8$ | $J_{\rm db} = 6.4$ |              |
| 2-(threo-3-Bromobutyl)-                            | 5.02 (oct)         | 4.15 (oct)   | 1.67 (d)           | 1.38 (d)           | 7.07-8.0 (m) |
| $N$ -( $\alpha$ -naphthyl) carbamate ( <b>3b</b> ) | $J_{\rm ab} = 4.0$ | $J_{\rm ba} = 4.0$   | $J_{\rm ca} = 6.8$ | $J_{\rm db} = 6.5$ |              |
| 2-(erythro-3-Bromobutyl)                           | 4.85 (oct)         | 4.23 (oct)   | 1.65 (d)           | 1.34 (d)           | 6.85-7.5 (m) |
| carbanilate (4a)                                   | $J_{\rm ab} = 4.2$ | $J_{\rm ba} = 4.2$   | $J_{ca} = 6.8$     | $J_{\rm db} = 6.4$ |              |
| 2-(eruthro-3-Bromobutyl)-                          | 4.89 (oct)         | 4.28 (oct)   | 1.69 (d)           | 1.40 (d)           | 6.90-8.0 (m) |
| $N$ -( $\alpha$ -naphthyl) carbamate (4b)          | $J_{\rm ab} = 4.2$ | $J_{\text{ba}} = 4.2$  | $J_{\rm ca} = 6.8$ | $J_{\rm db} = 6.3$ |              |
|  |                    | $\Delta H(\text{erythr})$  | o-threo)           |                    |              |
| Ar = phenyl  | -0.10              | +0.11  | -0.01              | +0.01              |              |
| $Ar = \alpha - naphthyl$                           | -0.13              | +0.13  | +0.02              | +0.02              |              |
|  |                    |  |                    |                    |              |

 $^{a}$  With respect to tetramethylsilane as internal standard. J values are observed splitting values in hertz.



type  $CH_3CHXCHYCH_3$  that the vicinal coupling constant is larger in the erythro series than in the three series. The general interpretation is that the anti conformation is more stable in the erythro series, where it is frequently the dominant conformer, than the anti conformation in the three series.<sup>10a</sup>

In our case the relatively small value of the vicinal coupling constant precludes this. The percentage of the anti conformation 4-III for the erythro compounds may be estimated at about 33%, assuming a value of 9.6 Hz for  $J_{anti}$  and 1.5 Hz for  $J_{gauche}$ :<sup>11</sup>  $J_{ab} = (0.67 \cdot 1.5 + 0.33 \cdot 9.6) = 4.2$  Hz.

For the three compounds the estimated percentages of the anti conformation 3-III are only approximately 2-5% lower, corresponding to a decrease in the coupling constant of 0.2-0.4 Hz.

Addressing ourselves now to the chemical shifts of the

(10) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969: (a) p 291 ff; (b) p 163 ff; (c) p 286 ff; (d) p 234 ff; and references cited therein.

(11) Compare the value of  $J_{\rm ois} = 8.5$  Hz in the *cis*-2-oxazolidinones **5** discussed in this paper as well as the value of  $J_{\rm anti}$  in compounds of similar structure known to exist preferentially in the anti conformation. The estimated value of 33% is presumably close to the upper limit considering the perhaps somewhat low estimates for both  $J_{\rm gauche}$  and  $J_{\rm anti}$ .

methine protons, it can be seen from Table I that the proton  $H_a$  appears at lower field in the three series whereas the proton  $H_b$  appears at higher field.

The protons  $H_a$  are vicinal to the bromine atom and the observed behavior corresponds to that of the 2,3dibromobutanes 7a, where the signal of the DL (corresponding to threo) isomer appears at lower field than that of the meso (corresponding to erythro) compound.<sup>10b,12</sup>

 $H_b$ , on the other hand, is vicinal to the carbamate group and the behavior is analogous to that of the 2,3diacetoxybutanes 7b, where the signal of the DL isomer also appears at higher field than that of the meso compound.<sup>10b,12a</sup>



The chemical shift differences in  $H_a$  and  $H_b$  between the two stereoisomeric series of  $\beta$ -bromo carbamates show that the corresponding protons are in *different* magnetic environments. The difference in the population of the anti conformers 3-I and 4-I is too small in the present case to account solely for the magnitude of the chemical shift differences, and we will concentrate therefore on the ratio of the two gauche conformations I:II.

The treatment has to take into account the orientation of all vicinal groups with respect to each other. These orientations are listed in Table II. Not included are the orientations of the two vicinal protons  $H_a$  and  $H_b$ , which have been taken *a priori* to be gauche in the conformations I and II and anti in the conformation III.

It can be seen from Table II that with respect to the three conformations I, II, and III the environment around  $H_a$  is different for both the three and the erythro

 <sup>(12) (</sup>a) A. A. Bothner-By and C. Naar-Colin, J. Amer. Chem. Soc., 84, 743 (1962);
 (b) F. A. L. Anet, ibid., 84, 747 (1962).



<sup>*a*</sup> a = anti; g = gauche.

series, but that the environment of  $H_b$  is identical for the two series.

The observed chemical shift difference of  $H_b$  then leads us to the conclusion that the ratio I:II must be quite *different* in the three and the erythre series. While it is not possible, unfortunately, to evaluate any of the ratios I:II in the two stereoisomeric series, the implication follows that *at least* three of the four gauche conformations or at least five out of the total of six conformations are present in significant proportions in the conformational equilibria discussed.

Foglia and Swern have investigated  $\beta$ -iodo isocvanates 7c and N-( $\beta$ -iodo) carbamates 7d.<sup>4b</sup> The general behavior found is similar to that of our compounds, with slightly smaller vicinal coupling constants of 3.0 and 3.5 Hz for the three and erythre series, except that the chemical shifts  $H_b$  (in formulas 7c and 7d) are practically identical in both the three and erythro compounds. Foglia and Swern concluded that their compounds existed only in the two gauche conformations 3-I and 4-I, respectively (iodo in place of bromo, NCO or NHCOOMe in place of OCONHAr). As can be seen from Table II, another interpretation is compatible with their data. Namely, the compounds can exist in all four gauche conformations, provided that the ratios I: II are accidentally very similar but not close to 1 in both stereoisomeric series.<sup>13</sup>

No explanation is readily apparent why in all the carbamates discussed as well as in the 2,3-diacetoxybutanes  $7b^{12a}$  the anti conformation 4-III is not the dominant conformer in the erythro series, as in so many other erythro or meso compounds studied.<sup>10a,12</sup>

Infrared Spectra of 2-Oxazolidinones.<sup>5</sup>—The value of the C=O stretching frequency (amide I band) lies at ca. 1750 cm<sup>-1</sup> in the typical region of other 2oxazolidinones, specifically N-aryl-2-oxazolidinones and similar five-membered lactams.<sup>7,8,14,15</sup> Mecke, Mecke, and Lüttringhaus have, in a detailed examination of the parent compound, 2-oxazolidinone, listed five skeletal frequencies.<sup>16</sup> All 2-oxazolidinones examined show corresponding bands at ca. 1215, 1078, 1060, 915,

(15) J. E. Herweh, T. A. Foglia, and D. Swern, J. Org. Chem.,  ${\bf 33},\,4029$  (1968).

and 765 cm<sup>-1</sup>. It appears that these five skeletal bands, perhaps besides the band around  $915 \text{ cm}^{-1}$  which, being less intense, seems only marginally useful, are suitable as a diagnostic tool for recognizing the 2-oxazolidinone structure.

The band around  $1050 \text{ cm}^{-1}$  has also been pointed out by Pinchas and Ben-Ishai.<sup>7</sup>

Nmr Spectra of 2-Oxazolidinones.<sup>17</sup>—The nmr data of the 2-oxazolidinones examined agree well with those of similar oxazolidinones reported by other authors.<sup>46,15</sup> The two cis oxazolidinones 5a and 5b thus have a 4-H-5-H coupling constant of ca. 8 Hz, whereas the corresponding trans compounds 6a and 6b have a coupling constant of ca. 6.0 Hz.<sup>4b</sup> Generally, cis proton coupling is larger than trans proton coupling in five-membered rings, which cannot deviate appreciably from planarity as expected from the Karplus rule.<sup>10c,18,19</sup> The 4 and 5 methyl groups absorb at higher field in the cis oxazolidinones ( $\delta$  ca. 1.12 and 1.45 ppm, respectively) than in the corresponding trans isomers ( $\delta$  *ca*. 1.24 and 1.52 ppm, respectively). The 4 and 5 methine protons, on the other hand, appear at lower field in the cis compounds ( $\delta$  ca. 4.43 and 4.93 ppm, respectively) than in the trans isomers ( $\delta$  3.98 and 4.24 ppm, respectively). This effect can be attributed mainly to the diamagnetic anisotropy of the C-methyl bond and is found in many cis-trans isomer pairs of planar three- to five-membered ring compounds.<sup>10d</sup> A more detailed discussion has been given elsewhere.<sup>19</sup>

The Boiling Points of the Oxazolidinones.-The stereoisomeric 2-oxazolidinones were analyzed by glc on a QF-1 column. For both the N-phenyl compounds 5a and 6a (column temperature 220°) and the N-( $\alpha$ -naphthyl) compounds **5b** and **6b** (column temperature 250°) the trans-2-oxazolidinones 6a and 6b had a lower retention time, indicating a lower boiling point than the cis isomers. We have observed the same relationship with numerous other heterocyclic three- to five-membered rings possessing two vicinal alkyl substituents.<sup>196,20</sup> This behavior is reminiscent of the von Auwers' rule, or rather of the "extended von Auwers' rule",<sup>21</sup> originally applied (occasionally with erroneous conclusions) to cis-trans isomeric cyclohexane derivatives, according to which the cis compound has the higher boiling point, refractive index, and density, but the lower molar refraction. Recent modifications of the von Auwers' rules have been called the "Allinger rule" and the "conformational rule."22-24 According

(16) (a) R. Mecke, R. Mecke, and A. Lüttringhaus, Chem. Ber., 90, 975
(1957); (b) R. Mecke, Jr., and R. Mecke, Sr., *ibid.*, 89, 343 (1956); (c) see also A. R. Katritzky and A. P. Ambler in "Physical Methods in Heterocyclic Chemistry," Vol. 2, Academic Press, New York, N. Y., 1963, pp 161, 219 ff.
(17) See paragraph at end of paper regarding supplementary material.

(17) See paragraph at end of paper regarding supplementary intervents.
 (18) S. Sternhell, Quart. Rev., Chem. Soc., 23, 236 (1969).

(19) S. Stermen, guarantee, one boost, 27, 200 (1972);
 (19) (a) R. A. Wohl and D. F. Headley, J. Org. Chem., 37, 4401 (1972);
 (b) R. A. Wohl and J. Cannie, *ibid.*, 38, 1787 (1973).

(20) R. A. Wohl, unpublished data.

(21) The boiling point, although frequently quoted, is not included in the original von Auwers' rule. See the comments in ref 23. The rule, including the reference to the boiling point, has therefore been called the "extended Auwers' rule".<sup>23</sup>

(22) (a) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, p 172 ff;
(b) M. Hanack, "Conformation Theory," Academic Press, New York, N. Y., 1965, pp 86, 142.

(23) H. van Bekhum, A. van Veen, P. E. Berkaade, and B. M. Wepster, Recl. Trav. Chim. Pays-Bas, **80**, 1310 (1961).

(24) N. L. Allinger, Experientia, 10, 328 (1954); J. Org. Chem., 21, 915 (1956); J. Amer. Chem. Soc., 79, 3443 (1957); 80, 1953 (1958); 81, 232 (1959). N. L. Allinger and R. J. Cirby, Jr., J. Org. Chem., 26, 933 (1961).

<sup>(13)</sup> A ratio I:II of 1 would make the magnetic environment around  $H_{\rm a}$  equal for both the three and erythre series and should therefore result in practically equal values of  $H_{\rm a}$ .

<sup>(14)</sup> H. K. Hall, Jr., and R. Zbinden, J. Amer. Chem. Soc., 80, 6428 (1958).

## $\beta$ -Bromo Carbamates and 2-Oxazolidinones

to the latter, "the isomer with the smaller molar volume has the greater heat content." The higher boiling point can then be related to the smaller molecular volume, although the origin of the relationship is not very clear. Van Bekhum and coworkers have suggested that the boiling point should be excluded from any statement of the von Auwers' rule since it frequently fails for the boiling point.23

The examples where the extended von Auwers' rule fails consist of cyclohexane rings with very bulky or very polar substituents. We have, on the other hand, not been able to find an example where the rule fails in three- to five-membered rings with two vicinal alkyl substituents, such as occur very frequently in heterocyclic compounds. The extended von Auwers' rule in this restricted context has occasionally been of use to us for the tentative assignment of configuration until a more rigorous proof of stereochemistry could be obtained.

#### **Experimental Section**

General Procedures .--- Melting points were taken on a Fisher-Johns melting point apparatus and are corrected. Infrared spectra were taken on a Perkin-Elmer 137 sodium chloride spectrophotometer. Methylene chloride was used as a solvent. Gas chromatography was done on a Varian Model 90P gas chromatograph. Most of the work was done with an 8-ft column of 10% QF-1 on Gas-Chrom Q. Nmr spectra were taken on a Varian T-60 nmr spectrometer. Tetramethylsilane was used as internal standard. The elemental analyses were performed by Hoffmann-La Roche, Inc., Nutley, N. J., to whom we would like to extend our thanks.

threo- and erythro-3-Bromo-2-butanol.-1 and 2, respectively, were prepared essentially according to the method of Winstein and Lucas,<sup>25</sup> by addition of HOBr to cis- and trans-2-butene, respectively, using, however, N-bromosuccinimide in place of N-bromosuccinimide. The bromohydrins were found to be >99%pure as judged by ir and nmr data and gc analysis as originally assumed by Winstein and Lucas. 1 and 2 each gave only one peak on gas chromatography on a 6-ft 15% Carbowax 20M on Gas-Chrom R column. A mixture of the two compounds was easily separated at  $115^{\circ}$ , the compounds having retention times of 8.6 and 10.4 min, respectively, at a flow rate of 100 ml/min.

Preparation of Carbamates.<sup>26</sup>—A mixture of bromohydrin (10.0 g, 65 mmol) and phenyl or  $\alpha$ -naphthyl isocyanate (64-65 mmol) was kept for 1 hr at 95-100°. After cooling, the mostly solid residue was triturated twice with cold pentane and then extracted with three to five portions of hot petroleum ether (bp  $30-60^{\circ}$ ) or ligroin. The combined petroleum ether or ligroin fractions were evaporated to about 150 ml and then allowed to cool for crystallization. The obtained product was recrystallized from petroleum ether or ligroin.

**2**-(*threo*-**3**-Bromobutyl) carbanilate (**3**a) was obtained as white crystals (56%), mp 64.5-65° (from petroleum ether).

Anal. Calcd for C<sub>11</sub>H<sub>14</sub>BrNO<sub>2</sub>: C, 48.55; H, 5.19; N, 5.15; Br, 29.36. Found: C, 48.37; H, 5.15; N, 5.15; Br, 29.64.

 $2-(threo-3-Bromobutyl)-N-(\alpha-naphthyl)$  carbamate (3b) was obtained as slightly yellowish crystals (71%), mp 99.5–100° (from ligroin, bp 90–120°).

Calcd for C<sub>15</sub>H<sub>16</sub>BrNO<sub>2</sub>: C, 55.92; H, 5.01; N, 4.35. Anal. Found: C, 56.32; H, 5.03; N, 4.30.

2-(erythro-3-Bromobutyl) carbanilate (4a) was obtained as white crystals (62%), mp 56-56.5° (from petroleum ether).

(25) S. Winstein and H. J. Lucas, J. Amer. Chem. Soc., 61, 1576 (1939). (26) See paragraph at end of paper regarding supplementary material.

Anal. Calcd for C<sub>11</sub>H<sub>14</sub>BrNO<sub>2</sub>: C, 48.55; H, 5.19; N, 5.15; Br, 29.36. Found: C, 48.53; H, 5.11; N, 5.15; Br, 29.59.

2-(erythro-3-Bromobutyl)-N-( $\alpha$ -naphthyl) carbamate (4b) was obtained as white, fluffy crystals (41%), mp 128-129° (from ligroin, bp 90–120°).

Anal. Calcd for  $C_{13}H_{16}$  BrNO<sub>2</sub>: C, 55.92; H, 5.01; N, 4.35; Br, 24.80. Found: C, 55.99; H, 4.99; N, 4.20; Br, 25.00.

Preparation of 2-Oxazolidinones from  $\beta$ -Bromo Carbamates.-A solution of 840 mg (15 mmol) of potassium hydroxide in 6 ml of absolute ethanol was added to a hot solution of carbamate (15 mmol) in 12 ml of absolute ethanol and the mixture was heated in a 95° water bath for 10 min with occasional shaking. The precipitated potassium bromide was filtered off and the filtrate was evaporated at the rotary evaporator to dryness. The residue was taken up in ether and filtrated again to remove any small additional amount of potassium bromide. The solution was then evaporated again and the residue was distilled and/or recrystallized.

cis-4,5-Dimethyl-N-phenyl-2-oxazolidinone (5a) was obtained as an oil (2.84 g, 99%). Distillation at 141-143° (0.2 mm), low-temperature recrystallization from isopropyl alcohol, and washing with petroleum ether yielded colorless crystals, mp 42- $42.5^{\circ}$ .

Anal. Caled for C<sub>11</sub>H<sub>13</sub>NO<sub>2</sub>: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.04; H, 6.92; N, 7.23.

Ring closure with aqueous sodium hydroxide gave only about 50% yield beside about 50% of basic compounds.<sup>27</sup>

is-4,5-Dimethyl-N-( $\alpha$ -naphthyl)-2-oxazolidinone (5b) was obtained as colorless crystals (3.57 g, 99%), mp after repeated re-crystallization from isopropyl alcohol 138–140°. Anal. Caled for  $C_{15}H_{15}NO_2$ : C, 74.67; H, 6.27; N, 5.81. Found: C, 74.89; H, 6.43; N, 5.71.

trans-4,5-Dimethyl-N-phenyl-2-oxazolidinone (6a).—Distillation of the crude product (3.67 g, 99%) at  $120-122^{\circ} (0.05 \text{ mm})$ gave a colorless liquid which solidified. After two recrystallizations from isopropyl alcohol, colorless crystals, mp 63-63.5°, were obtained.

Anal. Caled for C<sub>11</sub>H<sub>13</sub>NO<sub>2</sub>: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.00; H, 6.99; N, 7.23. trans-4,5-Dimethyl-N-( $\alpha$ -naphthyl)-2-oxazolidinone (6b).—De-

colorization of the crude material (3.61 g, 100%) with activated charcoal and recrystallization from isopropyl alcohol gave almost colorless crystals, mp 112.5-113°. Anal. Calcd for C<sub>15</sub>H<sub>18</sub>NO<sub>2</sub>: C, 74.67; H, 6.27; N, 5.81.

Found: C, 74.59; H, 6.44; N, 5.70.

Acknowledgment.-We wish to thank the Rutgers Research Council for financial support.

Registry No.-1, 19773-41-2; 2, 19773-40-1; 3a, 41594-13-2; 3b, 41594-14-3; 4a, 41594-15-4; 4b, 41594-16-5; 5a, 41594-17-6; 5b, 41594-18-7; 6a, 41594-19-8; 6b, 41594-20-1; phenyl isocyanate, 103-71-9;  $\alpha$ -naphthyl isocyanate, 86-84-0; di- $\alpha$ naphthylurea, 607-56-7.

Supplementary Material Available .-- Detailed tables showing the ir frequencies of all compounds examined, a table containing detailed nmr data of all 2-oxazolidinones examined, and full details for the preparation of all carbamates described in this paper will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105  $\times$  148 mm, 20  $\times$ reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-73-3858.

(27) Cf. R. Adams and J. B. Segur, J. Amer. Chem. Soc., 45, 785 (1923).