1,3-Oxazolidin-4-ones. Synthesis and Configuration of *cis* and *trans* Isomers.

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Mixtures of *cis* and *trans* 1,3-oxazolidin-4-ones were obtained by cyclodehydration, in the presence of *p*-toluenesulfonic acid or boron trifluoride etherate, of lactamide and *N*-methyllactamide with aromatic and aliphatic aldehydes. The products were separated by column (silica) chromatography and their configurations were determined.

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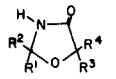
Staudinger and Ruzicka (1) condensed hydratropic amide with acetophenone by means of cold concentrated hydrochloric acid and obtained 2,5-diphenyl-2,5-dimethyl-4-oxazolidinone (**1a**) of unknown configuration. The same product (**1a**) was formed from acetophenone cyanohydrin and concentrated hydrochloric acid. A substance (**1b**) of similar nature, and also of unknown configuration, had previously been obtained from mandelonitrile with concentrated hydrochloric acid or by heating mandelamide with benzaldehyde (2). The same substance and other analogous to it have been noted as by-products of the Fischer oxazole synthesis (3).

Fischer, et al. (4) observed that amides of glycolic, lactic, mandelic, and 1-hydroxycyclohexanecarboxylic acid condense with acetone in the presence of hydrogen chloride to "amide-acetones" or 1,3-oxazolidin-4-ones (**1c-1f**). Cornforth and Cornforth (5) found that this method is not limited to acetone. Benzaldehyde and heptanal condensed with lactamide in the presence of *p*-toluenesulfonic or glacial acetic acid to give **1g** and **1h**, respectively; the presence of *cis* and *trans* forms was surmised, but not established. When Cornforth and Cornforth (5) prepared **1g**, Fischer's (6) so-called benzylidenelactamide ($C_{10}H_{11}NO_2$), m.p. 129-130°, they isolated a constitutional isomer that showed a rather unsharp melting point; the product softened at 60° and the melt was still turbid at 90°. To elucidate the structure and stereochemistry of these two products, we repeated their work and subjected the products to nmr analysis.



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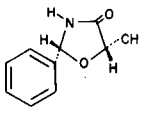
a, $R^1, R^3 = CH_3$; $R^2, R^4 = C_6H_5$
b, $R^1, R^3 = H$; $R^2, R^4 = C_6H_5$
c, $R^1, R^2 = H$; $R^3, R^4 = CH_3$
d, $R^1 = H$; $R^2, R^3, R^4 = CH_3$
e, $R^1 = H$; $R^2 = C_6H_5$; $R^3, R^4 = CH_3$
f, $R^1 = H$; R^2 = cyclohexyl; $R^3, R^4 = CH_3$
g, $R^1, R^3 = H$; $R^2 = CH_3$, $R^4 = C_6H_5$
h, $R^1, R^3 = H$; $R^2 = CH_3$; $R^4 = n\text{-}C_7H_{15}$

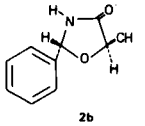
Results and Discussion.

When benzaldehyde was allowed to react with lactamide (molar ratio 1:1.1) in refluxing toluene (12 hours) in the presence of catalytic amounts of *p*-toluenesulfonic acid, with provision for continuous removal of water as it is formed, thin-layer chromatography (7) indicated the formation of two compounds in the approximate ratio of 1:3. Separation was achieved by silica chromatography. The compound with the higher R_F-value, isolated in 11-17% yield, had m.p. 89-92°, whereas the compound with the lower R_F-value (36-41% yield) had m.p. 131-134°. Both compounds have the general formula $C_{10}H_{11}NO_2$ (by CHN analysis and mass spectrum).

The compound with m.p. 131-134° has been assigned the *cis*-4-oxazolidinone structure **2a**, and the compound with m.p. 89-92° the *trans*-4-oxazolidinone structure **2b**. These assignments are based on their nmr spectra. For example, the deshielding effect of the phenyl group is expected to be greater for the proton at position-5 that is *cis* to it, and the effect of the methyl group, at C-5, is to deshield the proton remaining at C-5, so that its signal moves downfield. Thus, for the *trans* isomer **2b**, the combined deshielding effect of the two substituents, phenyl and methyl, will result in the signals from the ring protons each appearing at lower field than those from the corresponding protons in the *cis*-isomer **2a**. The chemical shifts observed (for DMSO-d6 solutions), δ 5.9 (2-H) and 4.2 ppm (5-H) for **2a** and 6.1 (2-H) and 4.4 ppm (5-H) for **2b**, indicate that these are the *cis* and *trans* isomers, respectively.



2a
(m.p. 131-134°)



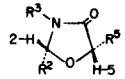
2b
(m.p. 89-92°)

N-Methyllactamide cyclocondensed with benzaldehyde in refluxing toluene (17 hours) in the presence fo TSA to give a 3:1 mixture of *cis*- and *trans*-3,5-dimethyl-2-phenyl-4-oxazolidinone (**3a,b**) (Table I), in 44% yield. Attempts to resolve this mixture by preparative thin-layer or silica chromatography using a variety of solvent systems were unsuccessful.

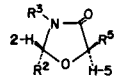
Lactamide reacted similarly in refluxing toluene (TSA) with trichloroacrolein, 3,5-dichlorobenzaldehyde, 2,6-dichlorobenzaldehyde, and 2,3,6-trichlorobenzaldehyde to give mixtures of the *cis*- and *trans*-4-oxazolidinones (**4a,b**,

Table I

1,3-Oxazolidin-4-ones



cis Isomer



trans Isomer

Compound	R^2	R^3	R^5	Isomer	Yield, %	M.p., °C	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found	Nmr Position in δ (ppm) 2-H	5-H	Solvent (a)
2a	C_6H_5	H	CH_3	*cis*	41	131-134	$C_{10}H_{11}NO_2$	67.8	67.8	6.2	6.2	7.9	7.9	5.9	4.2	D
2b	C_6H_5	H	CH_3	*trans*	17	89-92	$C_{10}H_{11}NO_2$	67.8	67.8	6.2	6.2	7.9	8.0	6.1	4.4	D
3a,b	C_6H_5	CH_3	CH_3	*cis-trans* (b)	44	oil	$C_{11}H_{13}NO_2$	69.1	69.2	6.8	6.9	7.3	7.1	5.9	4.4	D
4a	$Cl_2C=C(Cl)$-	H	CH_3	*cis*	25	111-114	$C_6H_6Cl_3NO_2$	31.2	31.2	2.6	2.5	6.1	6.1	6.47	4.3	D
4b	$Cl_2C=C(Cl)$-	H	CH_3	*trans*	6	99-101	$C_6H_6Cl_3NO_2$	31.2	31.3	2.6	2.5	6.1	6.0	6.48	4.4	D
5a	3,5-$Cl_2C_6H_3$	H	CH_3	*cis*	35	96-102	$C_{10}H_9Cl_2NO_2$	48.8	48.8	3.6	3.6	5.7	5.7	6.0	4.3	D
5b	3,5-$Cl_2C_6H_3$	H	CH_3	*trans*	14	124-127	$C_{10}H_9Cl_2NO_2$	48.8	48.8	3.6	3.6	5.7	5.7	6.1	4.4	D
6a	2,6-$Cl_2C_6H_3$	H	CH_3	*cis*	30	158-162	$C_{10}H_9Cl_2NO_2$	48.8	48.7	3.6	3.6	5.7	5.7	6.7	4.4	D
6b	2,6-$Cl_2C_6H_3$	H	CH_3	*trans*	20	135-136	$C_{10}H_9Cl_2NO_2$	48.8	48.9	3.6	3.6	5.7	5.8	6.8	4.4	D
7a (c)	2,3,6-$Cl_3C_6H_2$	H	CH_3	*cis*	14	131-133	$C_{10}H_8Cl_3NO_2$	42.8	42.6	2.8	2.8	4.9	4.9			
7b	2,3,6-$Cl_3C_6H_2$	H	CH_3	*trans*	38	117-121	$C_{10}H_8Cl_3NO_2$	42.8	42.7	2.8	2.8	4.9	4.9	6.7	4.4	D
8a	C_6H_5-CH=C(Cl)-(*trans*)	H	CH_3	*cis*	33	98-100	$C_{12}H_{12}ClNO_2$	60.6	60.3	5.0	5.0	5.9	5.9	6.75	4.5	D
8b	C_6H_5-CH=C(Cl)-(*trans*)	H	CH_3	*trans*	7	87-89	$C_{12}H_{12}ClNO_2$	60.6	60.5	5.0	5.0	5.9	6.2	6.75	4.5	D
9	C_6H_5	H	H	–	21	87-90	$C_9H_9NO_2$	66.3	65.9	5.5	5.5	8.6	8.5	6.05	4.2 (d)	C
10	C_6H_5	CH_3	H	–	13	oil	$C_{10}H_{11}NO_2$	67.8	67.8	6.2	6.3	7.9	7.7	5.8	4.2 (d)	C
11	2,6-$Cl_2C_6H_3$	H	H	–	10	167-170	$C_9H_7Cl_2NO_2$	46.5	46.6	3.0	2.9	6.0	5.9	6.9	4.3 (d)	C
12	2,6-$Cl_2C_6H_3$	CH_3	H	–	9	oil	$C_{10}H_9Cl_2NO_2$	48.8	48.7	3.7	3.6	5.7	5.4	6.8	4.4 (d)	C

(a) Solvent C: Deuteriochloroform; Solvent D: Hexadeuteriodimethyl sulfoxide. (b) Ratio 3:1. (c) Contains about 40% of **7b**. (d) These show vicinal coupling (CH_2 of ring) of 7H_z and *ca.* 2H_z coupling to 2-H.

Table II

2-Phenoxymethyl-1,3-oxa(and thia)zolidin-4-ones

Compound	R	R^3	R^5	X	Isomer	Yield, %	M.p., °C	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found	Nmr Positions in δ (ppm) 2-H	5-H	Solvent (a)
13a	H	H	CH_3	O	*cis*	13	84-86	$C_{11}H_{12}ClNO_3$	54.6	54.7	4.9	5.1	5.8	5.6	5.4	2.43	C
13b	H	H	CH_3	O	*trans*	9	134-137	$C_{11}H_{12}ClNO_3$	54.6	54.6	4.9	5.0	5.8	5.6	5.5	4.43	C
18a	CH_3	H	CH_3	O	*cis*	30	77-82	$C_{12}H_{14}ClNO_3$	56.3	56.5	5.5	5.4	5.5	5.2	5.5	4.40	C
18b	CH_3	H	CH_3	O	*trans*	18	136-140	$C_{12}H_{14}ClNO_3$	56.3	56.5	5.5	5.5	5.5	5.2	5.5	4.47	C
19a	CH_3	CH_3	CH_3	O	*cis*	25	oil	$C_{13}H_{16}ClNO_3$	57.9	58.2	5.9	6.2	5.2	4.8	5.3	4.37	C
19b	CH_3	CH_3	CH_3	O	*trans*	22	oil	$C_{13}H_{16}ClNO_3$	57.9	58.2	5.9	6.1	5.2	4.6	5.3	4.37	C
20	H	H	H	O	—	5	118-122	$C_{10}H_{10}ClNO_3$	52.7	52.5	4.4	4.4	6.2	6.1	5.4	4.2	C
21	CH_3	H	H	O	—	28	109-112	$C_{11}H_{12}ClNO_3$	54.6	54.7	4.9	5.0	5.8	5.7	5.6	4.3	C
22	CH_3	CH_3	H	O	—	11	oil	$C_{12}H_{14}ClNO_3$	56.4	56.3	5.6	6.0	5.5	5.6	5.4	4.3	C
23	Cl	H	H	S	—	20	134-136	$C_{10}H_9Cl_2NO_2S$	43.2	42.9	3.2	3.2	5.0	4.9	4.9	≈3.4	D

(a) Solvent C: Deuteriochloroform. Solvent D: Hexadeuteriodimethyl sulfoxide.

5a,b, **6a,b**, and **7a,b**), that were separated by silica chromatography (Table I). Again the *trans* isomers had higher Rf-values than the corresponding *cis* isomers.

α-Chlorocinnamaldehyde (m.p. 32-33°) and lactamide yielded two isomeric 4-oxazolidinones in the approximate ratio of 5:1. The major component **8a** was assigned the *cis* configuration and the minor component, the *trans* configuration, by comparison of their Rf values with those of other pairs of *cis-trans* isomers. The assignment of the configurations by the use of nmr data was inconclusive.

Only one condensation product would be expected from the reaction of glycolamide and *N*-methylglycolamide with aldehydes. Indeed, the 4-oxazolidinones **9**, **10**, **11**, and **12** were the only products that were isolated (10-20% yield) from the cyclodehydration of benzaldehyde and 2,6-dichlorobenzaldehyde with both glycolamide and *N*-methylglycolamide. Compounds **9**, **10**, and **12** show vicinal coupling to 2-H. This can be explained by admitting a coupling effect that extends through five bonds and across the carbonyl group. A similar long range coupling across the lactone group of the 1,3-dioxolan-4-one ring between protons that are *trans* has been observed by Baron and Hollis (8) and Cort and Stewart (9).

4-Chlorophenoxyacetaldehyde reacted with lactamide (molar ratio 1:1) in refluxing toluene (5 hours) in the presence of TSA to give a dark reaction mixture from which the desired 2-(4-chlorophenoxymethyl)-5-methyl-1,3-oxazolidin-4-one (**13a**) was isolated in low (4%) yield. The formation of the *trans* isomer **13b** was indicated (by tlc), but a pure sample of **13b** was not isolated.

The major product of the above reaction was the acyclic compound (**14**), isolated in 22.5% yield, for which combustion analysis indicated it to have the empirical formula $C_{14}H_{19}ClN_2O_5$. Clearly, its formation is the result of the elimination of one molar equivalent of water from the reaction between 4-chlorophenoxyacetaldehyde

Scheme 1

and lactamide in the molar ratio of 1:2 (Scheme 1). Based on the proton and ^{13}C spectra, it is concluded that the most likely structure for the 1:2 condensation product is that represented by **14**. Structures such as **15**,**16**, and **17** in which one carbon atom is bonded to two oxygen atoms are unlikely because there is no C resonance with the expected shift of 90-100 ppm. For this reason alone, there is doubt that any of **15**, **16**, or **17** is correct. Furthermore, structure **17** is incorrect because there is no quaternary C resonance in the observed spectrum; **16** is incorrect because it has either four or zero exchangeable H's, whereas there are two H's that exchange upon addition of deuterio-trifluoroacetic acid, and **15** would be expected to show two methyl, two carbonyl, and three methine resonances. The ^{13}C spectrum does indeed contain two methyl and three methine C resonances, but only one carbonyl resonance. The proton spectrum contains two methyl doublets, but only two kinds of methine H resonances. These observations suggest the presence of more symmetry than that contained in **15**. However, the presence of only one carbonyl resonance is surprising. Also, the shift of 53.5 ppm for the methine C attached to both O and N atoms is not as large as might have been anticipated. Hence, there is still a possibility that structure **14** is not correct either, although it fits the nmr data better than **15**, **16** or **17**.

The low yield of **13a** (4%) and the failure to isolate **13b** from the above reaction prompted the search for a more suitable dehydrating reagent for reactions involving phenoxyacetaldehydes and α-hydroxycarboxamides. Farines and Soulier (10) have recently shown that 4-dioxolanones may be prepared under mild conditions from α-hydroxycarboxylic acids and carbonyl compounds in the presence of equimolar amounts of boron trifluoride etherate. When this technique was applied to the reaction of 4-chlorophenoxyacetaldehyde with lactamide, both **13a** (13%) and **13b** (9%) were isolated after two hours of reaction time at ambient temperature.

Both lactamide and *N*-methyllactamide reacted with 4-chloro-2-methyl phenoxyacetaldehyde in ether-tetrahydrofuran (29 hours, 20-25°), containing 1.1 equivalents of boron trifluoride etherate, to give the respective pairs of isomeric 4-oxazolidinones (**18a**,**b** and **19a**,**b**) in 20-30% yield (Table II). Whereas the conformational assignment of **18a** and **18b** could still be based on differences in chemical shift values (δ 5-H 4.40 vs. 4.47 ppm), such a distinction was no longer apparent in the case of the *N*-methyl analogs (**19a** and **19b**). Their conformational assigment is based on the fact that, as a rule, all *cis* isomers have lower Rf values than the corresponding *trans* isomers.

Glycolamide, *N*-methylglycolamide and mercaptoacetamide on treatment with one equivalent of 2-chloro-, 2,4-dichloro-, and 2-chloro-4-methylphenoxyacetaldehyde in the presence of 1.1 equivalent of boron trifluoride etherate gave the 4-oxazolidinones (**20**, **21**, **22** and **23**) in low (5-28% yields (Table II). In the nmr spectra of these compounds, there is too much interference and noise for determination of vicinal coupling, which is probably near 7 Hertz and about 1 Hertz coupling to 2-H as above for **9**, **10**, and **12**.

EXPERIMENTAL

Representative synthesis procedures are described.

Starting Materials.

Intermediate aldehydes and α-hydroxycarboxamides prepared by reported procedures had analytical and physical constants in agreement with reported values.

N-Methylglycolamide.

This compound was prepared in 98% yield from ethyl glycolate and methylamine in ethanol (24 hours, ambient temperature), m.p. 40-42°; ir: 3350 (NH) and 1650 cm^{-1} (C=O); nmr (DMSO-d6): 2.6 (3, NCH_3), 2.6 (1.NH), 3.8 (2, CH_2) and 5.2 ppm (1, OH).

N-Methyllactamide.

This compound was prepared analogously in 94% yield; ir: *ca.* 3400 (OH, NH), 1670 (C=O) and 1550 cm^{-1} (amide II); nmr (DMSO-d6): 1.2 (3, CH_3), 2.5 (3, NCH_3), 3.9 (1, CH), 5.4 (1, OH) and 7.6 ppm (1, NH).

4-Chloro-2-methylphenoxyacetaldehyde Diethyl Acetal.

A solution containing 142.5 g. (1.0 mole) of 4-chloro-*o*-cresol, 60 g. (1.1 mole) of sodium methoxide and 197 g. (1.0 mole) of bromocaetaldehyde diethyl acetal in 450 ml. of dimethylformamide was heated at 130-135° with stirring for 6 hours. The cooled reaction mixture was poured into water and extracted with ether. The combined ether extracts were washed with 5% sodium hydroxide and water and dried (magnesuim sulfate). Removal of the solvent gave 141.5 g. (55%) of acetal with an estimated purity of greater than 95% (by tlc.).

4-Chloro-2-methylphenoxyacetaldehyde.

A solution containing 141.5 g. (0.55 mole) of the above acetal, 100 ml. of glacial acetic acid and 60 ml. of concentrated sulfuric acid in 950 ml. of water was refluxed (5 hours), cooled and extracted with ether. The ethereal layer was washed with 5% sodium bicarbonate, dried (magnesium sulfate), and evaporated to give 97.2 g. (96%) of aldehyde having a purity of greater than 95% (by glc and tlc).

4-Chloro- and 2,4-dichlorophenoxyacetaldehyde were prepared analogously.

cis-5-Methyl-2-phenyl-1,3-oxazolidin-4-one (**2a**) and *trans*-5-Methyl-2-phenyl-1,3-oxazodidin-4-one (**2b**).

(a). Condensation in the Presence of *p*-Toluenesulfonic Acid.

A mixture containing 10.6 g. (0.1 mole) of benzaldehyde, 9.8 g. (0.11 mole) of lactamide and 0.2 g. of *p*-toluenesulfonic acid in 600 ml. of toluene was refluxed for 12 hours, while water was removed aceotropically. The reaction mixture was concentrated to dryness and the product was puridied by silica chromatography (silica gel: Grace, grade 62; eluent (by volume): hexane, ethyl acetate, THF = 80:16:4) to give 2.2 g. (11%) of **2b** (faster moving), a colorless crystalline solid; m.p.: 89-92° (from ether); ir (potassium bromide): 3210 (NH), 1720 and 1685 cm^{-1} (C=O): nmr (DMSO-d6): 7.4 (5, CH=), 9.10 (1, NH), 1.3 (3, CH_3), 6.1 (1, 2-H), and 4.4 ppm (1, 5-H).

The second fraction consisted of **2a** (slower moving), 7.0 g. (41%) and melted at 131-134° (from ether); ir (potassium bromide): 3180 (NH) 1715 and 1680 cm^{-1} (C=O); nmr (DMSO-d6): 7.3 (5, CH=), 9.05 (1, NH), 1.3 (3, CH_3), 5.9 (1, 2-H), and 4.2 ppm (1, 5-H). The mass spectra of both **2a** and **2b** are identical: m/e 176, 177 (M^+); 132; 131; 106, 105, 104; 92, 91, 90; 79, 78, 77; 68; 56, 55; 52, 51; 45, 44; 39; 29, 28.

(b). Condensation in the Presence of Boron Trifluoride Etherate.

Boron trifluoride etherate, 22.5 g. (0.158 mole) was added to a solution of 8.9 g. (0.1 mole) of lactamide and 10.6 g. (0.1 mole) of benzaldehyde in 100 ml. of tetrahydrofuran and 150 ml. of ether. After 24 hours, the reaction mixture was washed with 100 ml. of 10% sodium acetate, 100 ml. of water, dried (magnesium sulfate), and concentrated. The residual colorless solid was purified by silica chromatography to give 3.1 g. (17%) of **2b**, m.p. 89-92° (from ether-hexane), and 6.4 g. (36% of **2a**, m.p. 131-134° (from ether-hexane).

cis-2-(4-Chlorophenoxymethyl)-5-methyl-1,3-oxazolidin-4-one (**13a**), *trans*-2-4-chlorophenoxymethyl-5-methyl-1,3-oxazolidin-4-one (**13b**) and 2-(2-Amino-1-methyl-2-oxoethoxy)-*N*-(2-(4-chlorophenoxy-1-hydroxyethyl) propanamide (**14**).

(a). Condensation in the Presence of *p*-Toluenesulfonic Acid.

A mixture of lactamide, 16.9 g. (0.19 mole), 32.3 g. (0.19 mole) of 4-chlorophenoxyacetaldehyde and 0.2 g. of *p*-toluenesulfonic acid in 500 ml. of toluene was refluxed with stirring for 5 hours, while water was removed azeotropically. Toluene was removed under reduced pressure, and the residue, which contained at least three major components (by tlc); one near the base line, was purified by silica chromatography (eluent (by volume)): THF, ethyl acetate, hexane = 4:30:66). The first fraction contained **13b**, but could not be obtained in pure form (see under (b) below. The second fraction, 1.1 g. (4%), was identified as **13a**, m.p. 84-86°; ir (potassium bromide): 3420, 3200 (NH) and 1725 cm^{-1} (C=O); nmr (deuteriochloroform): 7.0 (4, CH=), 4.0 (2, OCH_2), 8.5 (1, NH), 1.35 (3, CH_3), 5.4 (1, 2-H), and 4.43 ppm (1, 5-H); mass spectrum (70 eV): m/e 241, 243* (M^+, 1 Cl-isotope abundance); 142, 144*; 128; 111; 113; 100*; 75, 77; 63, 64; 55; 45*; 43, 42; 15.

The third fraction, **14**, was a white crystalline solid, 7.1 g. (22.5%), m.p. 169-170° (from ethyl acetate); ir (potassium bromide): 3400 (NH) and 1670 cm^{-1} (C=O); mass spectrum (70 eV): m/e 241, 243 (1 Cl-isotope abundance), 203 (no Cl), 189, 170, 172, 153, 141, 128, 117, 114, 100, 95, 90, 75, 72, 45, 44, 43, 28, 18, 15; nmr (deuteriochloroform): (DMSO-d6): 1.2 (6, $(CH_3)2$), 4.0 (4, OCH_2 and $(OCH)_2$), 5.7 (2, NH and OH), 5.9 (1, O-CH-N), 7.1 (4, CH=), and 8.05 and 8.2 ppm (2, NH_2).

Anal. Calcd. for $C_{14}H_{19}ClN_2O_5$: C, 50.7; H, 5.8; N, 8.4. Found: C, 50.8; H, 5.7; N, 8.3.

(b). Condensation in the Presence of Boron Trifluoride Etherate.

A solution containing 8.5 g. (0.05 mole) of 4-chlorophenoxyacetaldehyde, 5.0 g. (0.055 mole) of lactamide and 14.2 g. (0.1 mole) of boron trifluoride etherate in 250 ml. of anhydrous ether was stirred at ambient temperature for 2 hours, washed with 5% sodium carbonate and water, dried (magnesium sulfate), and evaporated. Separation by silica chromatography of the residual solid gave 0.6 g. (9%) of **13b**, a white crystalline solid, m.p. 134-137°; ir (potassium bromide): 3210 (NH) and 1730 cm^{-1} (C=O); nmr (deuteriochloroform): 7.0 (4, CH=), 4.0 (2, OCH_2), 8.5 (1, NH), 1.40 (3, CH_3), 5.5 (1, 2-H), and 4.43 ppm (1, 5-H).

The slower moving, *cis* isomer (**13a**) was obtained in 1.2 g. (13%) yield, m.p. 82-86°; ir (potassium bromide): 3210 (NH) and 1730 cm^{-1} (C=O).

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