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Facile Conversion of 4-Halogeno-1,3-dioxolan-2-ones to 2-Oxazolidones[1]

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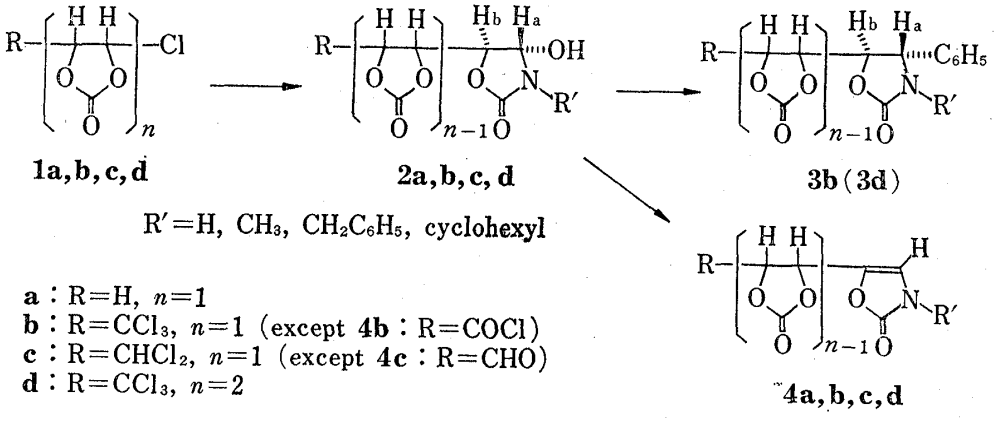
Telomers of vinylenecarbonate with tetrachloromethane, which possess the 4-chloro-1,3-dioxolan-2-one structure as a terminal ring, underwent smooth and selective conversion with primary aliphatic amines into 5-substituted 4-hydroxy-2-oxazolidones whose chemical reactions with the aid of acids, dehydration and phenylation, led to the corresponding 4-oxazolin-2-ones and 4-phenyl-2-oxazolidones, respectively. Treatment of 5-trichloromethyl-2-oxazolidinone with zinc-methanol resulted in the exclusive formation of 5-dichloromethyl-2-oxazolidone, in contrast to the corresponding 1,3-dioxolan-2-one system which suffered complete reductive ring-opening even under milder conditions.

Keywords——vinylenecarbonate telomer; 2-oxazolidone; 4-oxazolin-2-one; phenylation; dehydration

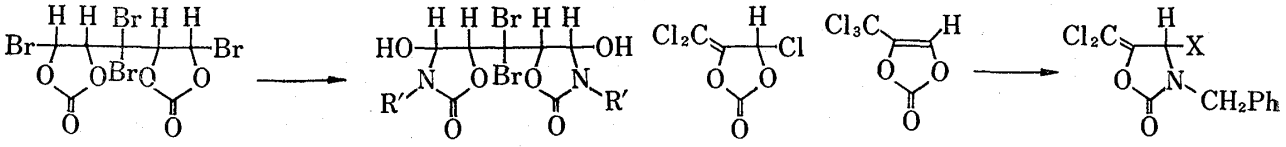
The 2-oxazolidones[3] are an important class of heterocyclic compounds because of a wide variety of potential uses in biological and industrial products. This paper describes the smooth conversion of 4-halogeno-1,3-dioxolan-2-ones into 4-hydroxy-2-oxazolidones and related heterocycles which may serve as versatile synthetic intermediates. The 4-halogeno-1,3-dioxolan-2-ones studied here include type (**1**) telomers[4] arising from free-radical telomerization of vinylene carbonate and the polyhalomethanes, broadening a useful route to such five-membered heterocycles.

Treatment of 4-chloro-substituted 1,3-dioxolan-2-ones with ammonia and primary aliphatic amines resulted in the smooth and preferential formation of crystalline isomers of 4-hydroxy-2-oxazolidones (**2**). The conversion would involve the primary formation of the acyclic urethanes (not isolated in pure forms) followed by smooth cyclization to lead to the isolation of hydroxy-oxazolidones. Thus, chloroethylenecarbonate derivatives (**1a—d**) were allowed to react with ammonia, methylamine, benzylamine and cyclohexylamine in methanol (or dimethylformamide) to give the corresponding hydroxyoxazolidones (**2a—d**) as colorless



1) This constitutes part VIII in "Studies on Telomers and Oligomers of Vinylene Carbonate." Part VII: T. Matsuura, T. Kunieda, and T. Takizawa, *Chem. Pharm. Bull.* (Tokyo), **25**, 239 (1977).
2) Location: *Hongo, Bunkyo-ku, Tokyo 113, Japan.*
3) M.E. Dyen and D. Swern, *Chem. Rev.*, **67**, 197 (1967).
4) T. Tamura, T. Kunieda, and T. Takizawa, *J. Org. Chem.*, **39**, 38 (1974).

crystals mostly in 70—85% yields.[5] These cyclic structures were established on the basis of the infrared (IR) and nuclear magnetic resonance (NMR) data which exhibited an intense band near 1760 cm^{-1} (characteristic of the oxazolidone carbonyl)[6,7] and a doublet signal at δ 5.1—5.4 (attributable to the Ha proton), respectively. And the configurational assignment is based on their small coupling constants[4,7a] (Table I) which are in agreement with *trans* value in compound (**2a**) (J_{cis}=6.0 Hz, J_{trans}=2.0 Hz). This reaction was applied to the compound (**5**) (*trans*-"*anti*"-*trans*)[8] derived from radical reaction of vinylene carbonate and bromoform (or carbon tetrabromide), to give bis-2-oxazolidone (**6**). Allylic chlorides (**7** and **8**), readily obtained from **1b** by dehydrochlorination with triethylamine,[9] gave dichloromethylene heterocycle (**9**) (X=OH) exclusively, which was also formed on the treatment of **2b** with phosphorus pentoxide in benzene.[10]



5 **6** : R′=CH_2Ph **7** **8** **9** : X=OH

Ph=phenyl

Arylation of 4-hydroxy-2-oxazolidones (**2b**) was performed in a 13% (v/v) concentrated sulfuric acid–benzene mixture[11] at room temperature to give *trans*-4-phenyl-5-trichloromethyl-2-oxazolidones (**3b**)[5] stereoselectively in over 80% yields without any detectable amounts of *cis*-isomers. The NMR spectral data of phenylation products (**3b**) showed the coupling constants of $J_{a,b}$ 3.0—4.5 Hz, strongly suggesting *trans*-stereochemistry[12] which would permit the hydrolytic conversion to *threo* amino-alcohols. On the other hand, under the similar conditions, compounds (**2d**) and (**9**) (X=OH) gave nearly quantitative yields of the dehydrated (**4d**) and the rearranged (**4b**), respectively, instead of arylation products (**3d**) and (**9**) (X=Ph) expected.

Treatment of **2b** and **2c** with trifluoroacetic acid at room temperature resulted in the smooth dehydration followed by almost simultaneous hydrolysis of tri- and di-chloromethyl groups to carboxylic acid chloride and aldehydes. This provides highly effective one-step route to 2-oxo-4-oxazolin-5-carboxylic acid chlorides (**4b**) (further characterized by esterification and the Friedel-Crafts reaction as methyl ester and phenyl ketone, respectively) and -5-carboxaldehyde (**4c**) which would be useful intermediates for the preparation of a wide variety of 5-substituted 4-oxazolin-2-ones. Similar dehydration of **2a** derived from vinylene carbonate, gave 4,5-unsubstituted 4-oxazolin-2-one (**4a**), though in low yield.

5) On the preliminary pharmacological evaluation, compounds (**2b**) (R′=H) and (**3b**) (R′=H) showed significant anticholinergic and analgesic activities, respectively, in oral administration to mice at the level of 100 mg/kg. For these tests, we are indebted to Dr, T. Kobayashi, The Mitsubishi-Yukayakuhin Research Laboratories.

6) R. Gompper and H. Herlinger, *Chem. Ber.*, **89**, 2825 (1956).

7) J.C. Sheehan and F. Guziec, Jr., *J. Org. Chem.*, **38**, 3034 (1973); *a*) *cf.*) F.A.L. Anet, *J. Am. Chem. Soc.*, **84**, 747 (1962). see also ref. 12.

8) K. Hosoda, T. Kunieda, and T. Takizawa, *Chem. Pharm. Bull.* (Tokyo), **24**, 2427 (1976).

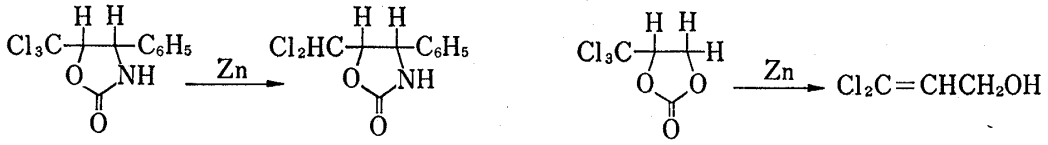
9) Experimental details will be reported elsewhere together with the findings on synthetic utility of these reactive compounds.

10) This process probably involves hydrolysis of 4-chloro-5-dichloromethylene-2-oxazolidone (at the stage of work-up) which would arise from the allylic rearrangement of 5-trichloromethyl-4-oxazolin-2-one initially formed.

11) *cf.*) D. Ben-Ishai, I. Satati, and Z. Berler, *J. Chem. Soc. Chem. Commun.*, 349 (1975); D. Ben-Ishai, Z. Berler, and J. Altman, *ibid.*, 905 (1975).

12) J.E. Herweh, T.A. Foglia, and D. Swern, *J. Org. Chem.*, **33**, 4029 (1968); J.E. Herweh and W.J. Kauffman, *Tetrahedron Letters*, **1971**, 809; S. Futagawa. T. Inui, and T. Shiba, *Bull. Chem. Soc. Japan*, **46**, 3308 (1973); H. Suda, T. Takita, T. Aoyagi, and H. Umezawa, *J. Antibiotics*, **29**, 100 (1976).

Contrary to the quite facile and complete ring-opening (at 0°) of 4-trichloromethyl-1,3-dioxolan-2-one[4] (**11**) to allyl alcohol (**12**) by the familiar reductive cleavage of β-trichloro ether,[13] the 2-oxazolidone ring was stable when **3b** (R′=H) was treated with zinc in boiling methanol, resulting in the exclusive formation of the dichloromethyl compound (**10**).



3b **10** **11** **12**

The method described herein would provide a route from $n=3$ telomers to 5-polyhydroxypentyl-2-oxazolidones and -4-oxazolin-2-ones, a potential source of C-nucleoside analogs.[14]

Experimental

Melting points were obtained on a Yanaco melting point apparatus and are uncorrected. Infrared spectra were recorded in nujol mull, unless otherwise stated, with a JASCO-Model-IR-S or a JASCO-IRA-1 Grating spectrophotometer. NMR spectra were determined on a Hitachi R-24 spectrometer (60 MHz) using tetramethylsilane (TMS) as an internal standard. 4-Chloro-1,3-dioxolan-2-one and the 5-substituted derivatives were prepared by chlorination of ethylenecarbonate and by the free radical telomerization of vinylene carbonate in the medium of carbon tetrachloride, respectively, according to the procedures previously reported.[4]

General Procedure for 4-Hydroxy-2-oxazolidones——The methanolic solutions (0.5—2.0M) of 4-chloro-1,3-dioxalan-2-ones (**1a—d**, **5**, **7** and **8**) and amines in molar ratios of about 1 to 2 (1 : 4 for compound **5**) were stirred at room temperature for 0.5—3 hr. Then, the low-boiling materials were removed *in vacuo* and the residue was taken up in methylene chloride, and washed with 2N hydrochloric acid and successively with water.

Table I. 4-Hydroxy-2-oxazolidones

Compound (R′)	Isolated yield, %	mp, (°C)	Recrystn. solvent	Formula	Analysis % Calcd. (Found) C	H	N	NMR $J_{a,b}$, Hz
2a ($CH_2C_6H_5$)	85	134—135	CH_2Cl_2–acetone	$C_{10}H_{11}O_3N$	62.16 (61.95)	5.73 (5.76)	7.24 (7.24)	2.0
2b (H)	74	133—135	CH_2Cl_2–acetone	$C_4H_4O_3NCl_3$	21.77 (21.87)	1.81 (1.81)	6.34 (6.23)	2.2
2b (CH_3)	76	137—140	CH_3OH	$C_5H_6O_3NCl_3$	25.59 (25.74)	2.56 (2.48)	5.97 (5.75)	2.0
2b ($CH_2C_6H_5$)	33	150—151	CH_2Cl_2–benzene	$C_{11}H_{10}O_3NCl_3$	42.51 (42.23)	3.22 (3.18)	4.51 (4.45)	2.0
2b (cycl-C_6H_{11})	72	115—116	$(C_2H_5)_2O$	$C_{10}H_{14}O_3NCl_3$	39.70 (39.80)	4.66 (4.64)	4.63 (4.87)	2.0
2c ($CH_2C_6H_5$)	20	116—117	benzene	$C_{11}H_{11}O_3NCl_2$	47.83 (47.60)	3.99 (3.95)	4.80 (4.80)	2.0
2d (cycl-C_6H_{11})	70	167—168	CH_2Cl_2–acetone	$C_{13}H_{16}O_6NCl_3$	40.15 (39.62)	4.12 (4.08)	3.60 (3.39)	—a)
6	10	183—185	CH_2Cl_2–acetone	$C_{21}H_{20}O_6N_2Br_2$	45.32 (45.55)	3.60 (3.63)	5.04 (4.78)	—a)
9 (X=OH)	44b) 40c)	149—150	benzene	$C_{11}H_9O_3NCl_2$	48.18 (48.12)	3.28 (3.54)	5.11 (4.73)	—

a) not determined, *b*) from **7**, *c*) from **8**

13) T.B. Windholz and D.B.R. Johnston, *Tetrahedron Letters*, **1967**, 2555.
14) W. Asbun and S.B. Binkley, *J. Org. Chem.*, **31**, 2215 (1966); J.M.J. Tronchet and M.F. Perret, *Helv. Chim. Acta*, **53**, 648 (1970); *ibid.*, **54**, 683 (1971); H. Ogura and H. Takahashi, *J. Org. Chem.*, **39**, 1374 (1974) *etc.*

The organic layer was dried (Na_2SO_4) and evaporated *in vacuo* to give the products which were purified by recrystallization or chromatography on silica gel (methylene chloride as an eluting solvent) (Table I).

Products thus obtained had the following spectral properties.

3-Benzyl-4-hydroxy-2-oxazolidone (**2a**: R′=CH_2Ph): IR 1755 and 3270 cm^{-1}, NMR (CH_3CN) δ 3.96 (1H, d.d, J=10 Hz and 2 Hz), 4.18 (1H, d, J=15 Hz), 4.31 (1H, d.d, J=6 Hz and 10 Hz), 4.48 (1H, d, J=8 Hz, OH), 4.54 (1H, d, J=15 Hz), 5.08 (1H, d,d,d, J=2 Hz, 6 Hz and 8 Hz), 7.25 (5H, s).

4-Hydroxy-5-(trichloromethyl)-2-oxazolidone (**2b**: R′=H): IR 1740 and 3300 cm^{-1}, NMR (CH_3CN) δ 4.84 (1H, d, J=2.2 Hz), 5.40 (1H, d, J=2.2 Hz).

3-Methyl-4-hydroxy-5-trichloromethyl-2-oxazolidone (**2b**: R′=CH_3): IR 1740 and 3280 cm^{-1}, NMR CH_3CN) δ 3.90 (3H, s), 4.67 (1H, d, J=2 Hz), 5.15 (1H, d, J=2 Hz).

3-Benzyl-4-hydroxy-5-(trichloromethyl)-2-oxazolidone (**2b**: R′=CH_2Ph): IR 1740 and 3360 cm^{-1}, NMR (CH_3CN) δ 4.23 (1H, d, J=15 Hz), 4.65 (1H, d, J=15 Hz), 4.78 (1H, d, J=2 Hz), 5.06 (1H, d, J=2 Hz), 7.28 (5H, s).

3-Cyclohexyl-4-hydroxy-5-(trichloromethyl)-2-oxazolidone (**2b**: R′=C_6H_{11}): IR 1782 and 3300 cm^{-1}, NMR ($CDCl_3$) δ 1.35—1.90 (11H, m), 4.75 (1H, d, J=2 Hz), 5.36 (1H, d, J=2 Hz), 7.85 (1H, broad, OH).

3-Benzyl-4-hydroxy-5-(dichloromethyl)-2-oxazolidone (**2c**: R′=CH_2Ph): IR 1735 and 3210 cm^{-1}, NMR (CH_3CN) δ 4.28 (1H, d, J=15 Hz), 4.63 (1H, d, J=15 Hz), 4.73 (1H, d.d, J=2 and 3.7 Hz), 5.07 (1H, d, J=2 Hz), 6.08 (1H, d, J=3.7 Hz), 7.31 (5H, s).

3-Cyclohexyl-4-hydroxy-5-(2-oxo-5-trichloromethyl-1,3-dioxolan-4-yl)-2-oxazolidone (**2d**: R′=C_6H_{11}): IR 1755, 1810 and 3380 cm^{-1}.

Dibromethylene-5,5′-bis([3-benzyl-4-hydroxy-2-oxazolidone] (**6**): IR 1758 and 3220 cm^{-1}.

3-Benzyl-4-hydroxy-5-(dichloromethylene)-2-oxazolidone (**9**: X=OH): IR 1680, 1765 and 3310 cm^{-1}, NMR (CH_3CN) δ 4.22 (1H, d, J=15 Hz), 4.60 (1H, d, J=15 Hz), 5.50 (1H, s), 7.25 (5H, s). This was also prepared from **2b**. To a solution of **2b** (R′=benzyl) (60 mg, 0.19 mmole) in benzene (15 ml) was added phosphorus pentoxide (10 mg) and the mixture was stirred at room temperature for 45 min. The solvent was removed *in vacuo* and purification of the product by chromatography on silica gel (CH_2Cl_2) gave **9** (20 mg, 37%) (as colorless crystals, mp 149—150°) which was identical with the above authentic compound.

Phenylation Procedure——To a solution of **2b** (*ca.* 2 mmole) in benzene (40 ml) was added concentrated sulfuric acid (6 ml) under ice-cooling and the mixture was stirred at room temperature for 3 hr. Then, the solution was poured onto ice-cold water (50 ml) and the benzene layer separated and dried (magnesium sulfate). Removal of the solvent *in vacuo* followed by recrystallization gave the phenylation products (**3b**), which showed the following properties.

4-Phenyl-5-trichloromethyl-2-oxazolidone (**3b**: R′=H) (86% yield): mp 166—167° (from CH_2Cl_2–ether as colorless prisms), IR 1775 and 3270 cm^{-1}, NMR ($CDCl_3$) δ 4.83 (1H, d, J=4 Hz), 5.05 (1H, d, J=4 Hz), 6.69 (1H, broad s, NH), 7.46 (5H, s). *Anal.* Calcd. for $C_{10}H_8O_2NCl_3$: C, 42.81; H, 2.87; N, 4.99. Found: C, 42.82; H, 2.84; N, 4.93.

3-Benzyl-4-phenyl-5-(trichloromethyl)-2-oxazolidone (**3b**: R′=CH_2Ph) (81% yield): mp 84—85° (from *n*-hexane–ether), IR 1782 cm^{-1}, NMR ($CDCl_3$) δ 3.62 (1H, d, J=15 Hz), 4.47 (1H, d, J=4.5 Hz), 4.71 (1H, d, J=4.5 Hz), 4.86 (1H, d, J=15 Hz), 7.20 (5H, s), 7.31 (5H, m). *Anal.* Calcd. for $C_{17}H_{14}O_2NCl_3$: C, 55.09; H, 3.78; N, 3.80. Found: C, 55.23; H, 3.88; N, 3.72.

TABLE II. 4-Oxazolin-2-ones

Compound (R′)	Isolated yield, %	mp (°C)	Recrystn. solvent	Formula	Analysis % Calcd. (Found) C	H	N
4a ($CH_2C_6H_5$)	20[a,b]	(125—8/0.2 mm)		$C_{10}H_9O_2N$	68.57 (67.91)	5.14 (5.14)	8.00 (7.82)
4b (H)	96[a] 87[c]	>300	CH_2Cl_2	$C_4H_2O_3NCl$	32.57 (33.01)	1.37 (1.54)	9.50 (9.66)
4b ($CH_2C_6H_5$)	95[a]	116—117	CH_2Cl_2	$C_{11}H_8O_3NCl$	55.40 (55.11)	3.38 (3.70)	6.00 (6.00)
4b (cyclo-C_6H_{11})	96[a]	96— 97	CH_2Cl_2	$C_{10}H_{12}O_3NCl$	52.29 (52.57)	5.27 (5.30)	6.10 (5.83)
4b (CH_3)	98[a] 70[c]	162—164	CH_2Cl_2	$C_5H_4O_3NCl$	37.15 (36.97)	2.48 (2.46)	8.67 (8.43)
4c ($CH_2C_6H_5$)	96[a]	110—111	CCl_4–benzene	$C_{11}H_9O_3N$	65.02 (64.62)	4.43 (4.38)	6.89 (6.71)
4d (cyclo-C_6H_{11})	97[c]	150—151	CH_2Cl_2–$(C_2H_5)_2O$	$C_{13}H_{14}O_5NCl_3$	42.13 (41.96)	3.81 (3.85)	3.78 (3.56)

a) with trifluoroacetic acid, *b*) based on vinylene carbonate, *c*) with concentrated sulfuric acid

3-Cyclohexyl-4-phenyl-5-(trichloromethyl)-2-oxazolidone (**3b**: R′=C_6H_{11}) (74% yield): mp 126—127° (from *n*-hexane–ether), IR 1760 cm^{-1}, NMR ($CDCl_3$) δ 1.0—1.7 (11H, m), 4.70 (1H, d, J=3 Hz), 4.88 (1H, d, J=3 Hz), 7.46 (5H, s). *Anal.* Calcd. for $C_{16}H_{18}O_2NCl_3$: C, 52.98; H, 5.00; N, 3.86. Found: C, 52.97; H, 5.02; N, 4.13.

Dehydration Procedure with Trifluoroacetic Acid——The solutions of 4-hydroxy-2-oxazolidones (*ca.* 1 mmole) (**2b, c**) in trifluoroacetic acid (2 ml) were refluxed for 2 hr and the solvent was removed *in vacuo* to give the crystalline acid chlorides (**4b**) and the aldehyde (**4c**) nearly quantitatively. The products were further purified by recrystallization from CH_2Cl_2 or CCl_4–benzene (Table II). Spectral data of the products are as follows.

2-Oxo-4-oxazolin-5-carboxylic Acid Chloride (**4b**: R′=H): IR 1625, 1715, 1760 and 3140 cm^{-1}. Methyl Ester: mp 210—211° (from MeOH–CH_2Cl_2 as colorless needles), IR 1635, 1710, 1740, 3160 and 3200 cm^{-1}, NMR (CH_3CN) δ 4.07 (3H, s), 7.74 (1H, s), 7.93 (1H, s, NH). *Anal.* Calcd. for $C_5H_5O_4N$: C, 41.95; H, 3.52; N, 9.79. Found: C, 41.92; H, 3.45; N, 9.81.

2-Oxo-3-benzyl-4-oxazolin-5-carboxylic Acid Chloride (**4b**: R′=CH_2Ph): IR 1608, 1735 and 1770 cm^{-1}, NMR (CH_3CN) δ 4.85 (2H, s), 7.40 (5H, s), 8.00 (1H, s). Methyl Ester: mp 104—105° (from MeOH–CH_2Cl_2 as colorless needles), IR 1632, 1755 and 3115 cm^{-1}, NMR (CH_3CN) δ 3.80 (3H, s), 4.76 (2H, s), 7.33 (5H, s). *Anal.* Calcd. for $C_{12}H_{11}O_4N$: C, 61.28; H, 4.68; N, 5.06. Found: C, 61.04; H, 4.62; N, 6.21. 3-Benzyl-5-benzoyl-4-oxazolin-2-one: This was prepared in 99% yield under the Friedel-Craft conditions ($AlCl_3$ as a catalyst) and recrystallized from ether–CH_2Cl_2 to give colorless prisms, mp 94—95°, IR 1623 and 1777 cm^{-1}, NMR ($CDCl_3$) δ 4.87 (2H, s), 7.31 (1H, s), 7.40 (5H, s), 7.57—7.95 (5H, m). *Anal.* Calcd. for $C_{18}H_{12}O_3N$: C, 73.10; H, 4.69; N, 5.02. Found: C, 73.07; H, 4.66; N, 5.22.

2-Oxo-3-cyclohexyl-4-oxazolin-5-carboxylic Acid Chloride (**4b**: R′=C_6H_{11}): IR 1603, 1750 and 3100 cm^{-1}, NMR ($CDCl_3$) δ 1.3—2.1 (11H, m), 7.75 (1H, s). Methyl Ester: mp 136—137° (from *n*-hexane–CH_2Cl_2 as colorless needles), IR 1620, 1750 and 3110 cm^{-1}, NMR ($CDCl_3$) δ 1.3—2.1 (11H, m), 3.84 (3H, s), 7.38 (1H, s). *Anal.* Calcd. for $C_{11}H_{15}O_4N$: C, 58.67; H, 6.67; N, 6.22. Found: C, 58.61; H, 6.63; N, 6.12.

2-Oxo-3-methyl-4-oxazolin-5-carboxylic Acid Chloride (**4b**: R′=CH_3): IR 1610, 1735 and 1785 cm^{-1}, NMR ($CDCl_3$) δ 3.53 (3H, s), 7.75 (1H, s).

3-Methyl-5-benzoyl-4-oxazolin-2-one: mp 160—165° (from CH_2Cl_2), IR 1603, 1635, 1775 and 3130 cm^{-1}, NMR ($CDCl_3$) δ 3.34 (3H, s), 7.33 (1H, s), 7.38—7.93 (5H, m). *Anal.* Calcd. for $C_{11}H_9O_3N$: C, 65.02; H, 4.43; N, 6.90. Found: C, 64.90; H, 4.46; N, 6.89.

2-Oxo-3-benzyl-4-oxazoline-5-carboxyaldehyde (**4c**: R′=CH_2Ph): IR 1610, 1673 and 1770 cm^{-1}, NMR ($CDCl_3$) δ 4.80 (2H, s), 7.30 (1H, s), 7.32 (5H, s), 9.20 (1H, s).

3-Benzyl-4-oxazolin-2-one (**4a**): This was prepared by direct dehydration with trifluoroacetic acid of the carbamates derived from vinylene carbonate and benzylamine without isolation of **2a**. IR (neat) 1750 and 3150 cm^{-1}, NMR ($CDCl_3$) δ 4.70 (2H, s), 6.48 (1H, d, J=2.0 Hz), 6.75 (1H, d, J=2.0 Hz), 7.28 (5H, s).

3-Cyclohexyl-4-oxazolin-5-(2-oxo-5-trichloromethyl-1,3-dioxolan-4-yl)-2-one (**4d**: R′=C_6H_{11})——This provides a typical procedure for dehydration with conc. sulfuric acid. To a solution of **2d** (R′=cyclohexyl) (0.85 g, 2.18 mmole) in benzene (30 ml) was added concentrated sulfuric acid (4 ml), and it was stirred at room temperature for 5 hr. Then the solution was poured into ice–water (50 ml) and the benzene layer separated and dried (magnesium sulfate). After removal of the solvent, recrystallization of the resulting product from ether–CH_2Cl_2 afforded **4d** (0.8 g, 97%) as colorless needles, mp 150—151° (decomp.), IR 1658, 1746 and 1820 cm^{-1}, NMR ($CDCl_3$) δ 1.3—2.1 (11H, m), 5.31 (1H, d, J=5 Hz), 6.98 (1H, s).

4-Phenyl-5-(dichloromethyl)-2-oxazolidone (**10**)——The mixture of **3b** (R′=H, 0.2 g, 0.71 mmole) and zinc powder (0.2 g) in methanol (10 ml) was refluxed for 3 hr. The insoluble materials were filtered off and the filtrate was evaporated *in vacuo*. Chromatography of the residue on silica gel (CH_2Cl_2) gave **10** (0.12 g, 68%) as colorless prisms, mp 129—130° (from *n*-hexane–ether), IR 1775 cm^{-1}, NMR ($CDCl_3$) δ 4.62 (1H, t, J=4 Hz), 5.00 (1H, d, J=4 Hz), 5.92 (1H, d, J=4 Hz), 6.36 (1H, s, NH), 7.39 (5H, s). *Anal.* Calcd. for $C_{10}H_9O_2NCl_2$: C, 48.80; H, 3.69; N, 5.69. Found: C, 48.56; H, 3.79; N, 5.99.

3,3-Dichloro-2-propen-1-ol (**12**)——A solution of 4-(trichloromethyl)-1,3-dioxolan-2-one(**11**)[4] (2.5 g) 12 mmole) in methanol (10 ml) was cooled to 0° and zinc powder (5 g) was added under vigorous stirring. After being kept at this temperature for 30 min, no starting material was detected on the thin-layer chromatography plate. After removal of the insoluble materials and the solvent, the residue was distilled under reduced pressure to give **12** (0.75 g, 50%) as a colorless liquid, bp 68—70°/15 mm. (lit.[15] bp 75—77°/20 mm), IR (neat) 1625 and 3350 cm^{-1}, NMR ($CDCl_3$) δ 4.20 (2H, d, J=6 Hz), 4.28 (1H, s), 6.05 (1H, t, J=6 Hz). *p*-Nitrobenzoate: mp 68—69° (from *n*-hexane), IR 1610 and 1730 cm^{-1}, NMR ($CDCl_3$) δ 4.95 (1H, d, J=7 Hz), 6.17 (1H, t, J=7 Hz), 8.17 (2H, d, J=9.5 Hz), 8.25 (2H, d, J=9.5 Hz). *Anal.* Calcd. for $C_{10}H_7O_4Cl_2N$: C, 43.48; H, 2.54; N 5.07. Found: C, 43.43; H, 2.64; N, 5.26.

15) L.F. Hatch and S.D. Zimmerman, *J. Am. Chem. Soc.*, 79, 3091 (1957).