Analytical photolyses were analyzed by GC on column A, temperature programmed from 150 to 250 °C, using naphthalene as an internal standard.

Direct Irradiation of (*Z*)-2-(2-Methylphenyl)-2-butene (10). Ten milliliters of 0.019 M **10** in benzene was irradiated through quartz for 5 h. GC analysis showed the presence of **9**, **11**, **12**, **13**, and **14**, which had the same retention times as authentic samples on three different columns (column A, column C, column D). Quantitation was done by GC, using naphthalene as an internal standard.

Direct Irradiation of (*E*)-2-(2-Methylphenyl)-2-butene (11). Ten milliliters of 0.021 M **11** in benzene was irradiated and analyzed as described for **10**.

Sensitized Irradiation of (*Z*)- and (*E*)-2-(2-Methylphenyl)-2-butene (10 and 11). Ten milliliters of a solution of a 0.04 M mixture of **10** and **11** (5:3, respectively) and 0.041 M xanthone in benzene was irradiated through Pyrex for 5.5 h. GC analysis (column C, temperature programmed from 85 to 180 °C) showed the presence of **9**. Quantitative GC employed naphthalene as an internal standard.

Irradiation of (*Z*)- and (*E*)-2-(2-Methylphenyl)-2-butene (10 and 11) in the Presence of Maleic Anhydride. A solution of 1.0 g (6.8 mmol) of a mixture of **10** and **11** (5:3, respectively) and 1.5 g (15.0 mmol) of maleic anhydride in 250 mL of acetonitrile was irradiated through quartz in the preparative photochemical apparatus for 5.5 h. The immersion well was cleaned several times during the irradiation to remove a polymer film that slowed the reaction. Distillation gave 0.4 g (24%) of **16**: bp 147–148 °C (0.35 mm); NMR ($CDCl_3$) δ 7.18 (m, 4 H, Ar), 3.85–2.81 (m, 4 H, H's on C-2, C-3, and C-4), 1.9–1.1 (m with s superimposed at 1.49, 5 H, CH_2 of ethyl and CH_3), 0.70 (t, J = 7 Hz, 3 H, CH_3 of ethyl); IR (neat) 1870, 1780, 735 cm^{-1}; MS, m/e 244 (molecular ion), 146 (base peak).

Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.70; H, 6.63.

Analytical photolyses were analyzed by GC (column C, temperature programmed from 85 to 200 °C), using naphthalene as an internal standard.

Irradiation of (*Z*)-2-(2-Methylphenyl)-2-butene (10) in the Presence of Maleic Anhydride. A solution of 0.50 g (3.4 mmol) of **10** and 0.75 g (7.5 mmol) of maleic anhydride in 275 mL of acetonitrile was irradiated through quartz in the preparative photochemical apparatus for 4.1 h. Workup as described for the photoproduct obtained by irradiation of the mixture of **10** and **11** and maleic anhydride gave 0.23 g (28%) of **16** with spectral properties identical with those of the sample of **16** obtained above.

Acknowledgment. We gratefully acknowledge support of this research by a grant from the National Science Foundation (CHE77-07881 A01). R.B. thanks the Marathon Oil Co. for summer support and the Boettcher Foundation for a fellowship.

Registry No. 1, 7399-49-7; 2, 1124-20-5; *cis*-3, 82902-68-9; 4, 42332-94-5; 5, 6962-60-3; *cis*-6, 82902-66-7; *cis*-7, 82902-67-8; 8, 1985-59-7; 9, 82902-62-3; 10, 82902-63-4; 11, 82902-64-5; 12, 82902-69-0; 13, 82902-70-3; 14, 34815-66-2; 15, 82902-65-6; 16, 82949-87-9; 17, 82902-76-9; (*Z*)-18, 82902-77-0; 19, 82902-73-6; 20, 82902-74-7; 27, 82917-41-7; 28, 82917-42-8; 29, 82902-71-4; 30, 82902-72-5; 32, 82902-75-8; maleic anhydride, 108-31-6; cyclohexene, 110-83-8; 2-benzyl-α,α-dimethylbenzenemethanol, 57732-89-5; 2-(3-methylphenyl)-2-propanol, 5208-37-7; methyl iodide, 74-88-4; methyl 3-methylbenzoate, 99-36-5; methyltriphenylphosphonium bromide, 1779-49-3; 1-(2-methylphenyl)-1-propanone, 2040-14-4; 1-(3-methylphenyl)-1-propanone, 51772-30-6; ethyltriphenylphosphonium bromide, 1530-32-1; 2-methylacetophenone, 577-16-2; 3-methylacetophenone, 585-74-0; xanthone, 90-47-1.

Highly Stereo- and Regioselective Formation of 2-Oxazolone Telomers, Potential Synthetic Intermediates for Amino Sugars

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Free radical initiated reaction of 3-acyl-2-oxazolones proceeds smoothly in polyhalomethanes, which function as telogens, to give type **3** telomers of synthetic potential with high regio- and stereoselectivity, while the 3-alkyl derivatives failed to give such polyfunctional products. This particular telomerization can be controlled exclusively in the trans "head-to-tail" addition mode, as elucidated by ^1H and ^{13}C NMR and X-ray analysis of the products. Thus, the 3-benzoyl heterocycle **7** gave *trans*-4-chloro-5-(trichloromethyl)-2-oxazolidone (**8**) as a sole 1:1 adduct and two trans isomers of 4′-chloro-5-(trichloromethyl)[4,5′-bioxazolidinyl]-2,2′-dione (**9a,b**) as 2:1 telomers. Some characteristic reactions of the telomers are described.

Telomerization reactions capable of simultaneously attaining the stereoselective formation of carbon–carbon bonds and functionalization in a single step have great potential as a synthetic methodology for polyfunctional and complex molecules of biological interest.[1] Previously we explored a well-stereocontrolled telomerization reaction of vinylene carbonate with polyhalomethanes[2] and reported the synthetic utility of the polyfunctional products (viz., telomers) as versatile intermediates for stereoselective preparation of various monosaccharides including 2-deoxyaldoses.[1a,3] We next turned our attention to further application of such reactions to the 2-oxazolone heterocycle, which might serve as a building block for amino alcohols, including amino sugars.

Even though the 2-oxazolone skeleton was first reported in 1912,[4] 4,5-unsubstituted 2-oxazolones were not readily accessible until the practical synthesis reported by Scholz in 1976.[5] Such heterocycles were recently shown to be reactive enough to undergo smooth photocycloadditions and thermal cycloadditions to cyclobutane derivatives[6] and Diels–Alder products,[7] respectively, in contrast to the previous observation of extremely poor reactivities of the

(1) See, for example: (a) Kunieda, T.; Takizawa, T. *Heterocycles* **1977**, *8*, 661. (b) Tsuji, J. *Pure Appl. Chem.* **1979**, *51*, 1235.
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Scheme I

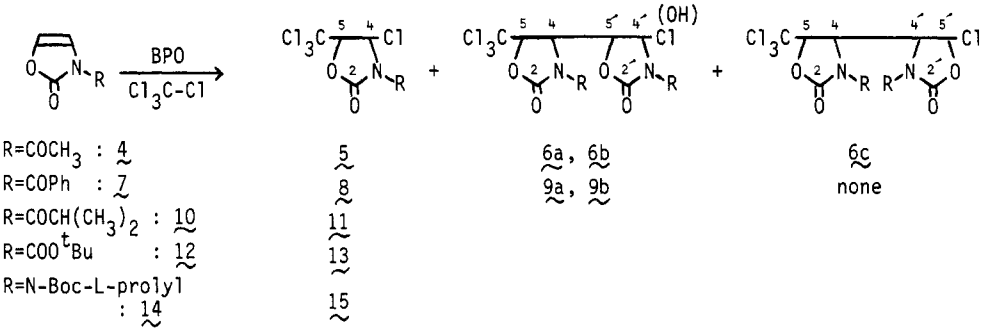


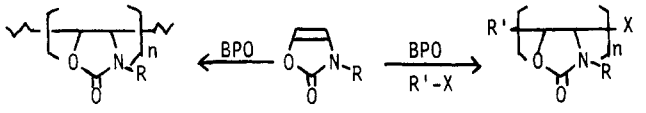
Table I. Telomerization of 3-Acyl-2-oxazolones with Carbon Tetrachloride[a]

oxazolone 1 (R)	molar ratio of 1/CCl_4	time, h	% yield (product)		
			$n = 1$	$n = 2$	higher telomers[b]
4 ($COCH_3$)	1:5	32	13.9 (5)	6.8 (6a-c)[c]	66.8 ($n = 5$)[d]
4 ($COCH_3$)	1:10	32	35.6 (5)	24.8 (6a-c)[e]	27.8 ($n = 4$)[f]
4 ($COCH_3$)	1:10	70	92.7 (5)[g]		
4 ($COCH_3$)	1:15	29	40.7 (5)	6.2 (6a,b)[h]	16.8
7 (COPh)	1:20	25	25.6 (8)	15.2 (9a,b)[i]	19.6 ($n = 3.5$)[j]
10 (CO-*i*-Pr)	1:12	31	36.4 (11)	9.0	15.0
14 (*N*-Boc-L-Pro)	1:30	60	68.0 (15)[g]		

[a] Benzoyl peroxide was used as a radical initiator. [b] Given in weight percent. [c] Isomer ratio of 5:5:1. [d] Anal. Calcd (Found): N, 8.87 (8.91). [e] Isomer ratio of 3.5:4:1. [f] Anal. Calcd (Found): N, 8.46 (8.35). [g] Catalyzed by $RuCl_2(PPh_3)_3$. [h] Isomer ratio of 1:1. No attempt was made to isolate 6c. [i] Isomer ratio of 1.3:1. [j] Anal. Calcd (Found): N, 6.00 (6.04).

derivatives.[8] They can be used for synthetic purposes by taking advantage of the excellent leaving ability of the 2-oxazolone moiety.[9]

It has been widely recognized that 1,2-disubstituted olefins are extremely difficult to homopolymerize under free-radical initiation, owing to the steric hindrance imposed by vicinal substitutes, with very few exceptions such as vinylene carbonate[10] and maleimide.[11] 3-Acyl-2-oxazolones, which can be regarded as internal olefins, were found to undergo smooth free-radical homopolymerization to give a type-2 polymer with a carbon–carbon backbone structure,[12] which is convertible to poly(1-amino-2-hydroxyethylene) with a $CH(OH)–CH(NH_2)$ repeating unit.



It has now become feasible to undertake telomerization of such heterocycles in the presence of chain-transfer agents. Radical telomerization of the 2-oxazolones proceeds smoothly in carbon tetrachloride to give novel polyfunctional telomers **3** which are not otherwise easily accessible with high stereo- and regioselectivity. Such products controlled in a low molecular weight range have great synthetic potential, particularly for amino sugars, since such a ring system is of broad utility as an α-amino-β-hydroxy synthon.[7,13]

Results and Discussion

Formation of Poly(3-acetyl-2-oxazolone). Treatment of deaerated 3-acetyl-2-oxazolone (**4**) with catalytic amounts of benzoyl peroxide (BPO) at 70 °C gave colorless homopolymer **2** (R = $COCH_3$; 72%; M_n = 30 by osmometry) whose ^1H NMR spectrum showed broad singlet peaks at δ 2.46 and 5.15 in an intensity ratio of 3:2, indicative of the absence of olefinic protons. In contrast, the 3-methyl derivative failed to give polymeric compounds under identical conditions. Recent work has revealed the synthetic utility of this type of polymer (**2**) as highly regio- and chemoselective protecting agents for amines and alcohols.[14]

Telomerization. Encouraged by the above findings of smooth carbon–carbon bond formation, 3-substituted 2-oxazolones were subjected to radical telomerization by gently refluxing their carbon tetrachloride solutions in the presence of initiator (BPO). The 4,5-unsubstituted oxazolones studied here include 3-acyl (acetyl, benzoyl and isobutyryl), 3-alkoxycarbonyl, and 3-alkyl derivatives. The 3-acetyl (**4**) and 3-benzoyl (**7**) compounds gave moderate yields of the $n = 2$ telomers which might serve as synthetic intermediates for aminopentoses and hexoses. Thus, chromatography of the telomerization products on silica gel gave, among several possible isomers, a single product (viz., **5** and **8**, respectively; see Scheme I) as a 1:1 adduct and two isomeric $n = 2$ telomers [**6a** (mp 153 °C) and **6b** (mp 169 °C), and **9a** (mp 148 °C) and **9b** (mp 182 °C), respectively] in nearly equal isomeric ratios in addition to higher telomers. Repeated careful attempts to isolate other isomers of the $n = 1$ and 2 telomers were unsuccessful, though small amounts of a third $n = 2$ isomer (**6c**, mp 160 °C) could be isolated by starting with **4** as the taxogen. It

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(10) Newman, M. S.; Addor, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 3789.
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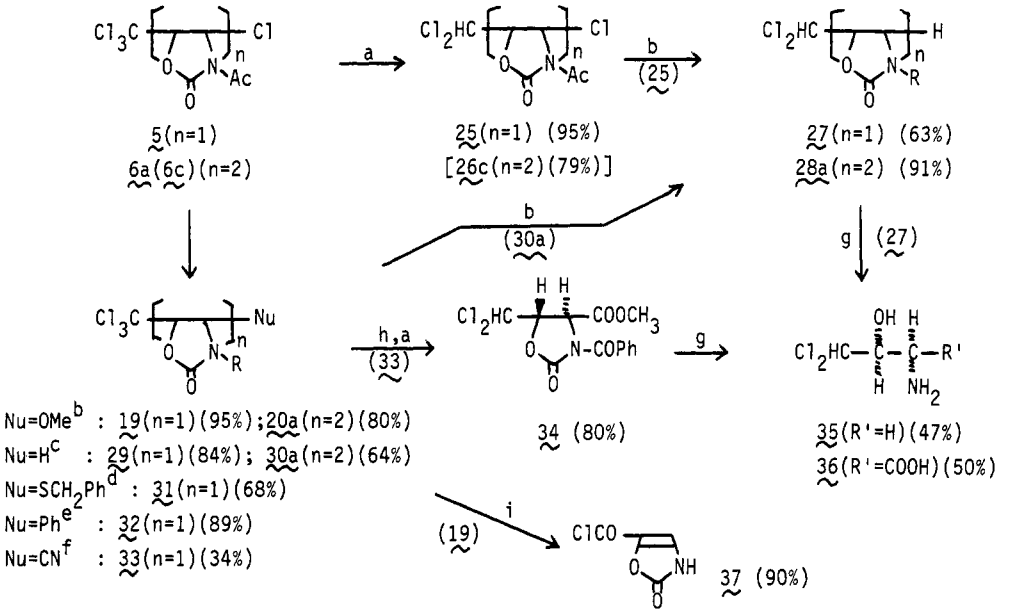
Scheme II[a]



[a] (a) $h\nu$/THF. (b) $NaBH_4$/THF. (c) MeOH. (d) $PhCH_2SH$. (e) $PhH/AlCl_3$. (f) $KCN/Bu_4N^+Br^-$. (g) 6N HCl. (h) MeOH/HCl. (i) CF_3COOH.

Table II. Carbon-13 NMR Data for 2-Oxazolone Telomers and Assignments[a]

telomer	chemical shift							
	C_2 [b]	C_4	C_5	$C_{2'}$ [b]	$C_{4'}$	$C_{5'}$	CCl_3	$COCH_3$ or COC_6H_5
5	149.8	66.8	89.0				94.8	167.4, 23.4
6a	149.5	56.9	81.8	150.9	67.5	81.3	96.5	170.6, 167.6, 23.6, 23.5
6b	151.5	53.8	80.3	151.8	76.6	73.1	97.3	169.1, 169.0, 23.4, 23.1
6c	150.2	53.8	81.8	150.9	65.9	83.9	96.5	170.2, 24.5, 22.5
8	149.0	67.8	88.9				94.9	166.4, 133.5, 131.0, 129.3[c]
9a	150.1	57.3	81.7	153.2	68.4	81.7	96.7	169.2, 167.0, 133.9, 133.7[d]
9b	149.8	57.7	83.4	150.5	68.3	83.6	96.9	164.6, 169.5, 134.2, 133.4[e]

[a] In δ units (with Me_4Si as an internal standard). [b] The assignments may be reversed. [c] Additional peaks at δ 128.3 and 128.1. [d] Additional peaks at δ 131.0, 129.5, and 128.4. [e] Additional peaks at δ 131.0, 130.5, 130.1, 129.2, 128.5, and 128.1.

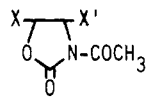
is noteworthy that only two $n = 2$ isomers are preferentially obtained among 32 possible head-to-tail and head-to-head isomers. Such selectivity is comparable to that in vinylene carbonate telomer formation.[2]

Telomer distribution depended heavily on the initial molar ratio of the reactants, as expected. Thus, ratios of 1:5 and 1:15 of **4** to carbon tetrachloride resulted in the 1:1 adduct (**5**) formation in 14% and 41% yields and in formation of higher telomers (average $n = 4$ products) in 70 and 20 wt % yields, respectively (Table I), and the ratio of 1:10 $4/CCl_4$ gave the best yields of the $n = 2$ telomers. The advantage of one-step formation of such polyfunctional compounds could outweigh the rather low yields obtained even under optimum conditions.

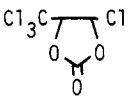
When the same telomerization conditions were applied to the oxazolones **10** and **12** with bulkier isobutyryl and *tert*-butoxycarbonyl groups, no products could be fully characterized except the 1:1 adducts **11** and **13**. The 3-alkyl 2-oxazolones (e.g., 3-benzyl and 3-propyl derivatives) gave none of the expected telomers under the same conditions.

Reaction of the oxazolone **4** with carbon tetrachloride catalyzed by dichlorotris(triphenylphosphine)ruthenium(II) $[RuCl_2(PPh_3)_3]$ resulted in the exclusive formation of the same 1:1 adduct **5** (93%) with negligible amounts of higher telomers even in the ratio of 1:10 $4/CCl_4$. Such a preferential formation is consistent with previous observations.[15] When this reaction was applied to 3-[*N*-(*tert*-butoxycarbonyl)-L-prolyl]-2-oxazolone (**14**), readily obtainable from diphenyl 2-oxo-3-oxazolinylphosphonate[9b] and N-protected L-proline, the 1:1 adduct **15** was formed in 30% diastereomeric excess, providing a route to asymmetric synthesis of the telomers.

Structures of Telomers. $n = 1$ Adduct. Structural assignments of **5** and **8** as 3-acyl-4-chloro-5-(trichloromethyl)-2-oxazolidinones were made on the bases of ^1H and ^{13}C NMR analysis and chemical conversion to the 4-phenyloxazolidinone **26** (Scheme II). The ^{13}C NMR data of the $n = 1$ telomers were assigned as shown in Table II by comparison with those of reference compounds such as 4- and 5-chloro-2-oxazolidinones (**16** and **17**) and vinylene carbonate derivative (**18**).[2] Selective decoupling of doublet



16 : X=H, X'=Cl
17 : X=Cl, X'=H



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peaks at δ 66.8 and 67.8 in the off-resonance spectra indicated that the chlorine atom is attached to the 4-position of **5** and **8**, indicative of an initial attack of the trichloromethyl radical at the 5-position.

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Table III. Proton NMR Data (δ) for 2-Oxazolone Telomers and Derivatives[a]

compd	chemical shift				
	H_4	H_5	$H_{4'}$	$H_{5'}$	$COCH_3$ [COC_6H_5]
5	6.33 (d, 1.7)	5.15 (d, 1.7)			2.53 (s)
6a	4.77 (dd, 1.5, 7.7)	4.89 (d, 1.5)	6.56 (d, 1.0)	4.88 (dd, 1.0, 7.7)	2.59 (s)
6b	4.81 (dd, 3.0, 7.0)	5.42 (d, 3.0)	5.84 (d, 5.0)	4.97 (dd, 5.0, 7.0)	2.39 (s), 2.32 (s)
6c	5.11 (dd, 2.4, 2.8)	4.67 (d, 2.4)	5.06 (dd, 0.7, 2.8)	6.27 (d, 0.7)	2.51 (s), 2.56 (s)
8	6.63 (d, 2.0)	5.23 (d, 2.0)			[7.8-7.3 (m)]
9a	5.25 (dd, 2.2, 6.3)	4.98 (d, 2.2)	6.72 (d, 2.7)	5.13 (dd, 2.7, 6.3)	[7.6-7.35 (m)]
9b	5.45 (dd, 2.0, 3.5)	5.01 (d, 3.5)	6.86 (d, 1.5)	5.11 (dd, 1.5, 2.0)	[7.7-7.2 (m)]
19	4.81 (d, 2.0)	5.12 (d, 2.0)			
20a	5.20 (dd, 2.5, 5.0)	4.90 (d, 2.5)	6.11 (d, 3.0)	4.78 (dd, 3.0, 5.0)	[7.85-7.3 (m)]
20b	5.38 (dd, 2.4, 3.6)	4.97 (d, 3.6)	6.08 (d, 2.0)	4.71 (dd, 2.0, 2.4)	[7.7-7.2 (m)]

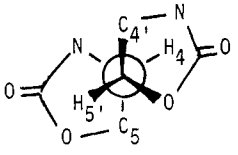
[a] Multiplicities and coupling constants (hertz) are given in parentheses.

The expected trans stereochemistry was substantiated by the small coupling constants, J = 1.7–2.0 Hz, between the ring protons, which were in good accord with trans values of the similar structures **16** and **17** (J_{trans} = 2.0–2.3 Hz, J_{cis} = 4.1–5.0 Hz;[16] Chart I).

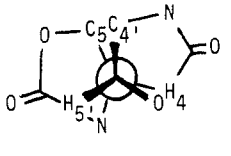
The structures of **11**, **13**, and **15** were established by methanolysis to yield **19**, identical with the product derived from **5** or **8**.

***n* = 2 Telomer.** On the basis of the above assignments, the ^{13}C NMR peaks of the n = 2 telomers were interpreted as shown in Table II. Spectral data (IR and ^1H NMR) showed the presence of a hydroxyl group in **6b** which presumably arose from hydrolysis of the highly unstable isomer (X = Cl) on silica gel during the course of isolation. Telomers **6a,b** and **9a,b** were proved to be the "head-to-tail" addition products with a trichloromethyl group at the 5-position of the heterocycle with the aid of the proton–carbon decoupling technique and were identified as 3,3′-diacyl-4′-chloro(or hydroxy)-5-(trichloromethyl)[4,5′-bioxazolidinyl]-2,2′-diones. Compounds **6a** and **9a** gave the same methoxy derivative **20a** on methanolysis followed by benzoylation, indicative of identical configurations. Similar chemical correlation of **6b** and **9b** was performed by their conversion to a common product, **20b**, which was distinctly different from **20a**.

Coupling constants between H_4 and $H_{5'}$ are 5.0–7.7 and 2.0–2.4 Hz for **a** and **b** isomers (except **6b**), respectively, which accord with the values of ~8 and ~3 Hz expected for the preferred conformations **21** (syn) and **22** (anti),



"syn" (21)



"anti" (22)

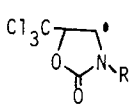
giving the least dipole–dipole interaction between the rings. Such data favor the trans-"syn"-trans structure for **20a** (hence **6a** and **9a**) and the trans-"anti"-trans configuration for **20b** (hence **6b**[17] and **9b**). These structures are analogous to those of vinylene carbonate telomers.[1a] X-ray analysis was performed to confirm the validity of the above assignments based solely on the spectral data.

The minor product 6c is anticipated to be the head-to-head addition product on the basis of the ^{13}C NMR data which showed trichloromethyl and chloro groups at the 5- and 4′-positions, respectively. Considerations similar to those given above led to the tentative assignment of trans-"anti"-trans stereochemistry as shown in Chart I.

Single-Crystal X-ray Analysis of *n* = 2 Telomer (6a). A colorless rhombic crystal recrystallized from methylene chloride–*n*-hexane was used for the X-ray diffraction work. The final difference electron-density map showed positive and negative residual peaks around the chlorine atoms of the trichloromethyl group, suggesting a rotational movement. Incomplete approximation of the movement with the temperature factors may have resulted in the rather high value of R (0.107). The bond lengths and angles are normal. The averages of the differences in the corresponding bond lengths and angles between the two crystallographically independent molecules are 0.011 Å and 0.91°, respectively, while the averages of their standard deviations are 0.008 Å and 0.5°. Most of the large differences involve terminal atoms. The internal rotation about the C_4–C_5 bond is such that C_5 and $C_{4'}$ (as well as N_3 and $O_{1'}$) are situated in a trans position to each other. One of the chlorine atoms of the trichloromethyl group is in a gauche–gauche position with respect to O_1 and C_4.

Thus, the structures of the **a** series isomers have been conclusively established as "syn" forms, and therefore "anti" forms are assignable to the **b** series. It has also been proved that only the trans-addition mechanism is operative in this type of telomerization.

Reaction Pathways. From the structures thus determined, the present telomerization is a typical chain-transfer reaction involving radical intermediates such as **23** and **24** followed by chlorine abstraction in a trans



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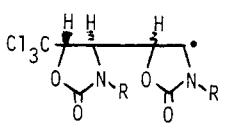

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fashion. Regio- and stereoselectivity may be explained in terms of relative radical stabilities as well as steric effects imposed by N substituents.

Chemical Reactivities. The synthetic versatility of the telomers is demonstrated by some representative reactions performed starting with **5** and **6a** (Scheme II).

Trichloromethyl groups were smoothly converted to dichloromethyls (convertible to aldehyde functions[18]) by UV irradiation in THF[19] without any other functional groups being affected, as shown in the conversion to **25** and **26c**. Treatment with borohydride resulted in a simulta-

(16) The relative magnitudes of the J values in five-membered rings may prove of use for empirical assignment of configuration in some instances. Cf.: Herweh, J. E.; Foglie, T. A.; Swern, D. *J. Org. Chem.* **1968**, *33*, 4029. Kaufman, W. J.; Herweh, J. E. *Ibid.* **1972**, *37*, 1842. Futagawa, S.; Inui, T.; Shiba, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3308.

(17) The configuration of the hydroxyl group at $C_{4'}$ is uncertain.

(18) Takahata, H.; Kunieda, T.; Takizawa, T. *Chem. Pharm. Bull.* **1975**, *23*, 3017.

(19) Mitsuo, N.; Kunieda, T.; Takizawa, T. *J. Org. Chem.* **1973**, *38*, 2255.

neous reductive removal of the secondary 4-chloro and 3-acyl groups to give **29** and **30a** as well as **27**. Compound **27** was further converted to the amino alcohol **35**. The highly reactive 4-chloro group could be easily displaced by nucleophiles such as alcohols and thiols to give the corresponding trans products **19**, **20a**, and **31**, whose stereochemistry was based on ^{1}H NMR data. The alkoxy derivative **19** thus formed gave excellent yields of the acid chloride **38** on treatment with trifluoroacetic acid. This reaction has a precedent of one-step conversion to the acid chloride and aldehyde from 5-trichloromethyl and 5-dichloromethyl derivatives, respectively.[20] Under Friedel–Crafts conditions, an aryl group was readily introduced at the C_4 position to give **32** in addition to acetophenone. Such a reaction was not observed in the vinylene carbonate telomers such as **18**. These reactivities permit the stereoselective conversion of **5** through the cyanation product **33** (trans) to the dichloro α-amino acid **36** (armentomycine analogue),[21] which possesses significant growth inhibitory activity against some microorganisms.

Facile and high-yield conversions such as those illustrated here open up a convenient route to diaminopentoses and hexoses[22] from the telomers **6a** (**9a**) and **6b** (**9b**) as well as **6c**.

Experimental Section

Melting points were determined in a Yanaco micro melting point apparatus and are uncorrected. IR spectra were taken on a JASCO DS-701G spectrometer. ^{1}H NMR spectra were recorded on a 100-MHz JEOL FX-100(FT) or a 60-MHz Hitachi R-24 NMR spectrometer in $CDCl_3$ solvent with Me_4Si as an internal standard, unless otherwise specified. The former instrument was also used for ^{13}C work.

3-Acetyl-2-oxazolone[5] (4). This compound was prepared by a slight modification of the reported procedure.[5] A large-scale chlorination of the oxazolidinone was smoothly performed with radical initiator (BPO) instead of the photochlorination procedure employed originally. Thus, Cl_2 gas was vigorously bubbled through a suspension of 3-acetyl-2-oxazolidinone (150 g) in CCl_4 (2 L) at 80 °C in the presence of BPO (0.4 g). Once the reaction started, the mixture was kept under gentle reflux by controlling the introduction of Cl_2 gas. After most of the starting material had been consumed as monitored by ^{1}H NMR spectroscopy, the solvent was removed in vacuo to leave an oil, which ^{1}H NMR data showed to contain 60% of isomeric monochlorides [^{13}C NMR for **16** δ 66.8 (C_4), 71.4 (C_5); for **17** δ 52.7 (C_4), 83.7 (C_5)]. Both chlorides, whose separation could be effected by careful chromatography on silica gel, were used for the following dehydrochlorination. Heating at 120–140 °C gave 3-acetyl-2-oxazolone (**4**) in 40% overall yield: mp 35 °C (from ether); bp 100–104 °C (16 mmHg) [lit.[5] bp 110 °C (24 mmHg)].

3-Substituted 2-Oxazolones. 3-Benzoyl[5] (**7**), 3-isobutyryl (**10**), and 3-[*N*-(*tert*-butoxycarbonyl)-L-prolyl) (**14**) derivatives were prepared from equimolecular amounts of diphenyl 2-oxo-3-oxazolinylphosphonate[9b] and the corresponding acids in the presence of triethylamine.[9b] Compound **10**: bp 117 °C (17 mmHg); IR (film) 3180, 1785, 1735 cm^{-1}; ^{1}H NMR δ 7.28 (d, J = 2.0 Hz, 1 H), 6.85 (d, J = 2.0 Hz, 1 H), 3.73 (septet, J = 7.0 Hz, 1 H), 1.23 (d, J = 7.0 Hz, 6 H). Compound **14**: $[\alpha]_D$ −54.0° (*c* 2, acetone); IR (film) 3160, 1790, 1735, 1695 cm^{-1}; ^{1}H NMR (run at 68 °C) δ 7.17 (d, J = 2.0 Hz, 1 H), 6.80 (d, J = 2.0 Hz, 1 H), 5.35 (dd, J = 4.0 Hz, J' = 8.0 Hz, 1 H), 4.5 (m, 2 H), 2.40 (m, 1 H), 1.94 (m, 3 H), 1.37 (s, 9 H). 3-(Butoxycarbonyl)-[9a] (**12**), 3-methyl-,[5] and 3-benzyl-2-oxazolones[20] were obtained by essentially same procedures as reported previously. In the same way as for the 3-benzyl compound, the 3-propyl derivative was prepared: bp 80–85 °C (3 mmHg); IR (film) 3150, 1740 cm^{-1}; ^{1}H NMR δ 6.78 (d, J = 2.0 Hz, 1 H), 6.60 (d, J = 2.0 Hz, 1 H), 3.49 (t, J = 7.0 Hz, 2 H), 1.70 (sextet, J = 7.0 Hz, 2 H), 0.90 (t, J = 7.0 Hz, 3 H).

Poly(3-acetyl-2-oxazolone) (2, R = $COCH_3$). A mixture of 3-acetyl-2-oxazolone (4 2.5 g, purified by recrystallization from ether) and BPO (15 mg) was deaerated and heated at 75 °C for 6 h. The resulting polymer was dissolved in acetone (8 mL) and added to methylene chloride (100 mL) dropwise. The deposited precipitates were washed with CH_2Cl_2 and dried in vacuo: yield 1.8 g (72%); M_n 30 by the osmometric method; [η] 0.24 (DMF at 30 °C); mp 300 °C dec; IR (KBr) 1800, 1710 cm^{-1}; NMR (acetone-d_6) δ 5.15 (br s, 2 H), 2.46 (br s, 3 H).

Telomerization of 3-Acyl-2-oxazolones. General Procedure. A solution of the oxazolones and polyhalomethanes (telogen) in a definite ratio was refluxed (at 80 °C) under an N_2 atmosphere while catalytic amounts of BPO were added at 2-h intervals. The starting oxazolones were almost completely consumed within 30 h as monitored by TLC. The excess telogen was removed in vacuo, and the resulting low telomers were separated by chromatography on silica gel. The n = 1 and n = 2 telomers were eluted from the column with benzene and CH_2Cl_2, respectively. Higher telomers ($n \geq 3$) were obtained as an isomeric mixture by elution with acetone.

3-Acetyl-2-oxazolone Telomers. A solution of 3-acetyl-2-oxazolone (**4**) (5.08 g) in CCl_4 (61.6 g, 10 equiv) gave the following telomers on treatment as described above.

3-Acetyl-4-chloro-5-(trichloromethyl)-2-oxazolidinone (5). Recrystallization from *n*-hexane gave colorless prisms: mp 56 °C; 4.0 g (35.6%); IR (KBr) 1810, 1728 cm^{-1}. Anal. Calcd for $C_6H_5NO_3Cl_4$: C, 25.62; H, 1.78; N, 4.98. Found: C, 25.79; H, 1.75; N, 4.90.

3,3′-Diacetyl-4′-chloro-5-(trichloromethyl)[4,5′-bioxazolidinyl]-2,2′-dione (Trans-"Syn"-Trans) (6a). Recrystallization from CCl_4 gave colorless prisms: mp 153 °C, 0.80 g (9.8%); IR (KBr) 1795, 1739 cm^{-1}. Anal. Calcd for $C_{11}H_{10}N_2O_6Cl_4$: C, 32.35; H, 2.45; N, 6.86. Found: C, 32.03; H, 2.40; N, 6.43.

3,3′-Diacetyl-4′-hydroxy-5-(trichloromethyl)[4,5′-bioxazolidinyl]-2,2′-dione (Trans-"Anti"-Trans) (6b). This telomer was recrystallized from CH_2Cl_2 as colorless prisms: mp 169 °C; 0.98 g (12.0%); IR (KBr) 3400, 1815, 1728 cm^{-1}. Anal. Calcd for $C_{11}H_{11}N_2O_7Cl_3$: C, 33.91; H, 2.85; N, 7.19. Found: C, 33.61; H, 2.88; N, 7.14.

3,3′-Diacetyl-5-(trichloromethyl)-5′chloro[4,4′-bioxazolidinyl]-2,2′-dione (Trans-"Anti"-Trans) (6c). This was recrystallized from *n*-hexane–CCl_4 as colorless prisms: mp 160 °C; 0.24 g (3.0%); IR (KBr) 1815, 1728 cm^{-1}. Anal. Calcd for $C_{11}H_{10}N_2O_6Cl_4$: C, 32.38; H, 2.45; N, 6.86. Found: C, 32.63; H, 2.56; N, 6.98.

3-Benzoyl-2-oxazolone Telomers. As described for the 3-acetyl derivative, telomerization of 3-benzoyl-2-oxazolone (**7**,[5] 2.8 g) with CCl_4 (27.4 g, 12 equiv) in the presence of BPO gave the following telomers in addition to the unchanged material (0.19 g) and 4-chloro-5-benzoxy-2-oxazolidinone: mp 142–143 °C; 0.08 g (1.5%); IR (KBr) 1801, 1742, 1701 cm^{-1}; ^{1}H NMR δ 7.96 (dd, 2 H), 7.8–7.25 (m, 8 H), 6.80 (s, 1 H), 6.40 (s, 1 H). Anal. Calcd for $C_{17}H_{12}NO_5Cl$: C, 59.06; H, 3.50; N, 4.05. Found: C, 58.78; H, 3.46; N, 3.95.

3-Benzoyl-4-chloro-5-(trichloromethyl)-2-oxazolidinone (8). This compound was recrystallized from *n*-hexane as colorless prisms: mp 58–59 °C; yield 1.3 g (25.6%); IR (KBr) 1814, 1710 cm^{-1}. Anal. Calcd for $C_{11}H_7NO_3Cl_4$: C, 38.52; H, 2.06; N, 4.08. Found: C, 38.72; H, 2.03; N, 4.11.

3,3′-Dibenzoyl-4′-chloro-5-(trichloromethyl)[4,5′-bioxazolidinyl]-2,2′-dione (Trans-"Syn"-Trans) (9a). This was obtained as colorless prisms from *n*-hexane–CH_2Cl_2: mp 146–148 °C; 0.34 g (8.6%); IR (KBr) 1808, 1685 cm^{-1}. Anal. Calcd for $C_{21}H_{14}N_2O_6Cl_4$: C, 47.40; H, 2.65; N, 5.26. Found: C, 47.34; H, 2.65; N, 5.18.

3,3′-Dibenzoyl-4′-chloro-5-(trichloromethyl)[4,5′-bioxazolidinyl]-2,2′-dione (Trans-"Anti"-Trans) (9b). This was obtained as colorless prisms from *n*-hexane–CH_2Cl_2: mp 181–182 °C; 0.22 g (5.6%); IR (KBr) 1800, 1705 cm^{-1}. Anal. Calcd for $C_{21}H_{14}N_2O_6Cl_4$: C, 47.40; H, 2.65; N, 5.26. Found: C, 47.47; H, 2.68; N, 5.35.

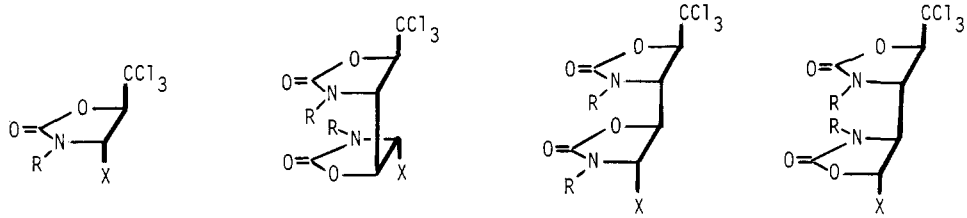
Further elution with acetone gave higher telomers as a mixture; yield 0.55 g (19.6 wt %).

(20) Matsuura, T.; Kunieda, T.; Takizawa, T. *Chem. Pharm. Bull.* **1977**, *25*, 1225.

(21) (a) Argoudelis, A. D.; Herr, R. R.; Mason, D. J.; Pyke, I. R.; Zieserl, J. F. *Biochemistry* **1967**, *6*, 165. (b) Iwasaki, T.; Urabe, Y.; Ozaki, Y.; Miyoshi, M.; Matsumoto, K. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1019.

(22) For a review, see: Hashimoto, H. *Yuki Gosei Kagaku Kyokaishi* **1981**, *39*, 836.

Chart I



trans	trans-"syn"-trans head-to-tail	trans-"anti"-trans head-to-tail	trans-"anti"-trans head-to-head
R=$COCH_3$: 5(X=Cl)	6a(X=Cl)	6b(X=OH)	6c(X=Cl)
R=COPh : 8(X=Cl)	9a(X=Cl)	9b(X=Cl)	
X=OCH_3 : 19(R=H)	20a(R=COPh)	20b(R=COPh)	

3-Isobutyryl-2-oxazolone Telomers. The isobutyryl derivative (**10**, 2.0 g) was heated in CCl_4 (20 g, 10 equiv) at 80 °C under telomerization conditions as above to give the 1:1 adduct **11** as colorless needles (from *n*-hexane): mp 39–41 °C; 1.45 g (36.4%); IR (Nujol) 1810, 1730 cm^{-1}; ^1H NMR δ 6.55 (d, J = 1.6 Hz, 1 H), 5.35 (d, J = 1.6 Hz, 1 H), 3.83 (septet, J = 7.0 Hz, 1 H), 1.38 (d, J = 7.0 Hz, 6 H). Anal. Calcd for $C_8H_9NO_3Cl_4$: C, 31.07; H, 2.91; N, 4.53. Found: C, 30.96; H, 2.80; N, 4.56.

In addition, n = 2 and higher telomer fractions were obtained as complex mixtures by further elution of the column with CH_2Cl_2 and acetone in yields of 9.0% (0.27 g) and 15 wt % (0.3 g), respectively.

3-(*tert*-Butoxycarbonyl)-2-oxazolone Telomer. In the same way as above, free radical reaction of 3-(*tert*-butoxycarbonyl)-oxazolone (**12**,[9a] 2.0 g) with CCl_4 (18.5 g, 10 equiv) gave the 1:1 adduct **13** as the sole characterizable product in only 5% yield in addition to negligible amounts of higher telomers. The product **13** showed the following: mp 84 °C (from *n*-hexane); IR (KBr) 1850, 1746 cm^{-1}; ^1H NMR δ 6.18 (d, J = 1.9 Hz, 1 H), 5.07 (d, J = 1.9 Hz, 1 H), 1.60 (s, 9 H). Anal. Calcd for $C_9H_{11}NO_4Cl_4$: C, 31.89; H, 3.27; N, 4.13. Found: C, 31.97; H, 3.26; N, 4.15.

Telomerization Catalyzed by $RuCl_2(PPh_3)_3$. (a) The ruthenium complex (0.1 g) was added to a solution of the oxazolone **4** (1.0 g) in CCl_4 (12 g, 10 equiv) under an N_2 atmosphere, and the resulting solution was gently refluxed for 70 h, by which time the oxazolone **4** was almost completely consumed. Purification by chromatography on silica gel gave the 1:1 adduct (mp 55 °C; 2.05 g, 92.7%) which was identical with **5**.

(b) Similar reaction of **4** (2.6 g) with bromotrichloromethane (12 g, 3 equiv) in the presence of the ruthenium(II) complex (0.1 g) gave, after 18 h under reflux (in addition to unchanged **4**, 0.75 g), 4-bromo-5-(trichloromethyl)-2-oxazolidinone as colorless prisms: mp 71–73 °C (from *n*-hexane); 4.0 g (60%); IR (KBr) 1805, 1728 cm^{-1}; ^1H NMR δ 6.40 (d, J = 1.7 Hz, 1 H), 5.30 (d, J = 1.7 Hz, 1 H), 2.55 (s, 3 H). Anal. Calcd for $C_6H_5NO_3BrCl_3$: C, 22.12; H, 1.54; N, 4.30. Found: C, 22.38; H, 1.56; N, 4.36.

4-Methoxy-5-(trichloromethyl)-2-oxazolidinone (19). (a) From 5. The adduct **5** (0.53 g) was refluxed in methanol (25 mL) for 5 h. Removal of the solvent followed by chromatography on silica gel gave **19** as a viscous oil: yield 0.45 g (95%); IR (film) 3280, 1760 cm^{-1}; ^1H NMR δ 8.09 (br s, NH), 5.12 (br d, J = 2.0 Hz, 2 H), 4.81 (d, J = 2.0 Hz, 1 H), 3.47 (s, 3 H).

(b) From 8. Compound **8** (0.3 g) was similarly treated in MeOH (20 mL) for 5 h to give **19** (0.17 g, 96%) and methyl benzoate (0.13 g) as methanolysis products.

(–)-4-Methoxy-5-(trichloromethyl)-2-oxazolidinone ((–)-19). A solution of 3-[*N*-(*tert*-butoxycarbonyl)-L-prolyl)-2-oxazolone (**14**,[9b] 1.17 g) and $RuCl_2(PPh_3)_3$ (0.8 g) in CCl_4 (30 g) and benzene (5 mL) was refluxed under an argon atmosphere for 60 h. Purification by chromatography on silica gel (CH_2Cl_2) gave the 1:1 adduct **15** as a viscous oil [1.22 g (68%); IR (film) 1830, 1750, 1705 cm^{-1}], which was treated with MeOH to afford (–)-19: $[\alpha]_D$ –11.6° (*c* 19, acetone); 88% yield. The ^1H NMR spectrum in the presence of chiral shift reagent [Eu(tfc)$_3$] showed 28% ee.

3,3′-Dibenzoyl-4′-methoxy-5-(trichloromethyl)[4,5′-bioxazolidinyl]-2,2′-dione (20a). (a) From 6a. A solution of the acetyl telomer **6a** (50 mg) in MeOH (6 mL) was refluxed in the presence of catalytic amounts of TsOH for 5 h. Removal of the solvent gave a colorless solid (mp 140 °C) which was then treated with benzoyl chloride (0.2 g) in pyridine (0.5 mL). Purification of the product by preparative TLC gave **20a** as colorless crystals: mp 73–77 °C (from *n*-hexane–CH_2Cl_2); yield 52 mg (80%); IR (KBr) 1804, 1700 cm^{-1}. Anal. Calcd for $C_{22}H_{17}NO_7Cl_3$: C, 50.05; H, 3.22; N, 5.31. Found: C, 50.31; H, 3.52; N, 5.04.

(b) From 9a. Similar treatment of **9a** gave the same dibenzoyl derivative **20a**: mp 76 °C; 61% yield.

3,3′-Dibenzoyl-4′-methoxy-5-(trichloromethyl)[4,5′-bioxazolidinyl]-2,2′-dione (Trans-"Anti"-Trans) (20b). (a) From 6b. A solution of **6b** (0.3 g) in MeOH (12 mL) was refluxed with addition of 1 drop of hydrochloric acid for 7 h. After complete removal of the methanol, the residue was treated with benzoyl chloride (0.7 g) in pyridine (1.5 mL) to give the benzoate as colorless leaflets: mp 157–158 °C (from *n*-hexane–CH_2Cl_2); 0.24 g (61%); IR (KBr) 1804, 1695 cm^{-1}. Anal. Calcd for $C_{22}H_{17}N_2O_7Cl_3$: C, 50.05; H, 3.22; N, 5.31. Found: C, 50.10; H, 3.33; N, 5.26.

(b) From 9b. In the same manner as above, **9b** was converted to the dibenzoate (**20b**) in 68% yield; this product was identical with the above **20b**.

3-Acetyl-4-chloro-5-(dichloromethyl)-2-oxazolidinone (25). A solution of **5** (2.8 g) in dry THF (100 mL) was irradiated in a quartz vessel with a high-pressure Hg lamp (400 W) at room temperature for 4 h. Chromatographic purification gave the dichloromethyl compound as a viscous liquid: 2.32 g (95%); IR (film) 1810, 1722 cm^{-1}; ^1H NMR δ 6.40 (d, J = 1.3 Hz, 1 H), 5.94 (d, J = 3.8 Hz, 1 H), 5.00 (dd, J = 3.8 Hz, J' = 1.3 Hz, 1 H), 2.56 (s, 3 H).

3,3′-Diacetyl-5-(dichloromethyl)-5′-chloro[4,4′-bioxazolidinyl]-2,2′-dione (26c). In the same way as above, **6c** (0.2 g) was irradiated in THF (100 mL) to give the dichloromethyl compound **26c**: 0.14 g (79%); mp 146–149 °C (from CCl_4–*n*-hexane); IR (KBr) 1805, 1709 cm^{-1}; ^1H NMR δ 6.28 (d, J = 0.8 Hz, 1 H), 5.95 (d, J = 4.0 Hz, 1 H), 5.07 (m, 2 H), 4.60 (dd, J = 1.2 Hz, J' = 4.0 Hz, 1 H), 2.61 (s, 3 H), 2.56 (s, 3 H). Anal. Calcd for $C_{11}H_{11}N_2O_6Cl_3$: C, 35.34; H, 2.95; N, 7.50. Found: C, 35.57; H, 3.03; N, 7.34.

5-(Dichloromethyl)-2-oxazolidinone (27, R = H). A solution of **25** (2.5 g) in THF (20 mL) was treated with $NaBH_4$ (1.0 g) at 60 °C for 5 h to give the reduced product **27**: 1.05 g (63%); mp 88–89 °C (from CH_2Cl_2–*n*-hexane); IR (KBr) 3290, 1750 cm^{-1}; ^1H NMR δ 6.45 (NH), 5.90 (d, J = 4.0 Hz, 1 H), 4.92 (td, J = 7.0 Hz, J' = 4.0 Hz, 1 H), 3.77 (d, J = 7.0 Hz, 2 H). Anal. Calcd for $C_4H_5NO_2Cl_2$: C, 28.24; H, 2.86; N, 8.24. Found: C, 28.50; H, 2.95; N, 8.26.

3,3′-Diacetyl-5-(dichloromethyl)[4,5′-bioxazolidinyl]-2,2′-dione (28a, R = Ac). Compound **30a** (R = Ac, 85 mg) was UV irradiated in THF (5 mL) for 4.5 h to afford the photoproduct (**28a**, which was purified by chromatography on silica gel: 70 mg (91%), mp 60–62 °C (from CH_2Cl_2–*n*-hexane); IR (KBr) 1800, 1706 cm^{-1}; ^1H NMR δ 5.98 (d, J = 2.8 Hz, 1 H), 5.07 (ddd, J = 9.3 Hz, J' = 8.7 Hz, J'' = 2.8 Hz, 1 H), 4.79 (d, J = 2.8 Hz, 1 H), 4.23 (dd, J = 12.0 Hz, J' = 9.3 Hz, 1 H), 3.92 (dd, J = 12.0 Hz, J' = 8.7 Hz, 1 H), 2.57 (s, 3 H), 2.53 (s, 3 H). Anal. Calcd for $C_{11}H_{12}N_2O_6Cl_2$: C, 38.94; H, 3.54; N, 8.26. Found: C, 38.91; H,

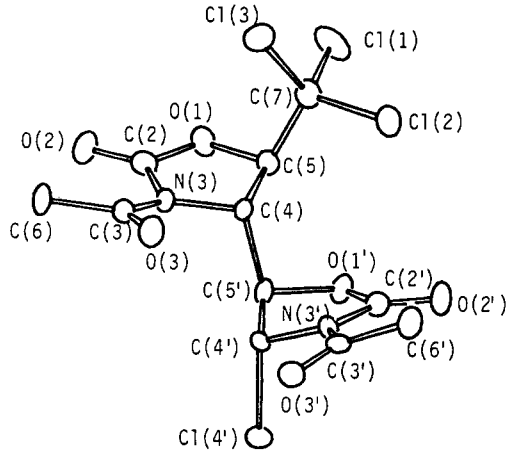


Figure 1. Computer-generated perspective drawing of the X-ray model of telomer **6a**. Hydrogens are omitted for clarity.

3.63; N, 7.97.

5-(Trichloromethyl)-2-oxazolidinone (29). $NaBH_4$ (0.08 g) was added to a solution of **8** (0.3 g) in THF (25 mL), and the mixture was heated at 65 °C for 4 h. The products were chromatographed on silica gel (CH_2Cl_2) to give colorless prisms of **29** in addition to benzyl alcohol (47%). Recrystallization from CH_2Cl_2 gave an analytical sample: 0.15 g (84%); mp 113 °C; IR (KBr) 3300, 1750 cm^{-1}; ^1H NMR δ 6.58 (NH), 5.09 (dd, J = 6.0 Hz, J' = 7.6 Hz, 1 H), 3.6–4.1 (m, 2 H). Anal. Calcd for $C_4H_4NO_2Cl_3$: C, 23.47; H, 1.96; N, 6.85. Found: C, 23.62; H, 1.97; N, 6.74.

3,3'-Diacetyl-5-(trichloromethyl)[4,5'-bioxazolidinyl]-2,2'-dione (30, R = Ac). The head-to-tail telomer **6a** (1.58 g) was treated under reflux with $NaBH_4$ (0.55 g) in THF (25 mL) for 5 h. The resulting product was acetylated with Ac_2O–pyridine followed by chromatographic purification to give **30**: 0.71 g (64%); mp 54–56 °C (CH_2Cl_2–*n*-hexane); IR (KBr) 1805, 1709 cm^{-1}; ^1H NMR δ 5.2–4.6 (m, 3 H), 4.4–3.9 (m, 2 H), 2.52 (s, 3 H), 2.48 (s, 3 H). Anal. Calcd for $C_{11}H_{11}N_2O_6Cl_3$: C, 35.34; H, 2.95; N, 7.50. Found: C, 35.65; H, 3.00; N, 7.78.

4-(Benzylthio)-5-(trichloromethyl)-2-oxazolidinone (31). Treatment of **5** (0.45 g) with benzenemethanethiol (3 mL) at 45 °C for 4.5 h gave 67.3% of **31** (X = $PhCH_2S$): mp 130–131 °C (from *n*-hexane–CH_2Cl_2); IR (KBr) 3386, 1770 cm^{-1}; ^1H NMR δ 7.30 (s, 5 H), 7.10 (NH), 4.73 (s, 2 H), 3.92 (s, 2 H). Anal. Calcd for $C_{11}H_{10}NO_2Cl_3S$: C, 40.45; H, 3.09; N, 4.29. Found: C, 40.45; H, 3.12; N, 4.10.

4-Phenyl-5-(trichloromethyl)-2-oxazolidinone (32). Powdered $AlCl_3$ (0.45 g) was added to a solution of **5** (0.6 g) in benzene (20 mL), and the mixture was refluxed for 12 h and then cooled. Hydrated sodium sulfate was added to decompose the complexes and filtered off. Removal of the benzene followed by recrystallization from *n*-hexane–CH_2Cl_2 gave the phenylation product **32** [R = H; 0.37 g (62%); mp 165–167 °C (lit.[21] mp 167 °C)] which was identical with an authentic sample with regard to the IR spectrum. Chromatography of the mother liquor gave 3-acetyl-4-phenyl-5-(trichloromethyl)-2-oxazolidinone [**32** (R = Ac): 0.17 g (27%); ^1H NMR δ 7.31 (s, 5 H), 5.47 (d, J = 2.4 Hz, 1 H), 4.75 (d, J = 2.4 Hz, 1 H), 2.50 (s, 3 H)] in addition to acetophenone (0.14 g, 54.6%). The former compound was deacylated with aqueous Et_3N to **32** (R = H).

3-Acetyl-4-cyano-5-(trichloromethyl)-2-oxazolidinone (33, R = Ac). An aqueous solution of KCN (95 mg) was added to a mixture of **5** (0.28 g) and tetrabutylammonium bromide (0.13 g) in CH_2Cl_2 (5 mL) under vigorous stirring. The mixture was kept at room temperature for 14 h, and then the organic layer was separated and concentrated in vacuo to leave an oil, which was chromatographed on silica gel (CH_2Cl_2) to give the cyanide **33**: 93 mg (34%); mp 220–221 °C (from CH_2Cl_2–*n*-hexane); IR (KBr) 1809, 1730 cm^{-1}; ^1H NMR δ 5.22 (s, 2 H), 2.59 (s, 3 H). Anal. Calcd for $C_7H_5N_2O_3Cl_3$: C, 30.94; H, 1.84; N, 10.31. Found: C, 30.74; H, 1.74; N, 10.19.

Methyl 2-Oxo-3-benzoyl-5-(dichloromethyl)oxazolidine-4-carboxylate (34). Hydrogen chloride was gently bubbled through a cooled solution of **33** (R = Ac, 0.15 g) in MeOH (5 mL) and ether (5 mL) for 20 min. After removal of the precipitates, the solvents were removed in vacuo to leave an oily ester: ^1H NMR δ 8.68 (NH), 5.24 (d, J = 4.0 Hz, 1 H), 4.55 (d, J = 4.0 Hz, 1 H), 3.89 (s, 3 H). Photoreduction of the resulting oil in THF as described for **25** gave an 80% yield of the dichloro compound which was benzoylated to **34**: mp 114–115 °C (from CH_2Cl_2); IR (KBr) 1797, 1783, 1746, 1684 cm^{-1}; ^1H NMR δ 7.3–7.8 (m, 5 H), 5.96 (d, J = 3.1 Hz, 1 H), 5.19 (d, J = 3.3 Hz, 1 H), 4.82 (t, J = 3.3 Hz, 1 H), 3.80 (s, 3 H). Anal. Calcd for $C_{13}H_{11}NO_5Cl_2$: C, 46.99; H, 3.31; N, 4.22. Found: C, 46.70; H, 3.46; N, 4.20.

3,3-Dichloro-1-amino-2-propanol (35). The oxazolidinone **27** (R = H, 0.17 g) was hydrolyzed with 6 N HCl (8 mL) at 100 °C for 8 h to give the cleaved product **35** as an oil, which was characterized as the *N,O*-diacetyl derivative: 0.11 g (47%); IR (film) 3320, 1748, 1653 cm^{-1}; ^1H NMR δ 6.60 (NH), 5.80 (d, J = 4.0 Hz, 1 H), 5.25 (m, 1 H), 3.64 (m, 2 H), 2.12 (s, 3 H), 1.97 (s, 3 H); mass spectrum (70 eV), m/e 228 (M^+), 230 ($M^+ + 2$), 232 ($M^+ + 4$).

***threo*-2-Amino-3-hydroxy-4,4-dichlorobutyric Acid (36).** The oxazolidine ester **34** (0.09 g) was hydrolyzed in 6 N HCl (2 mL) at 100–120 °C for 32 h. The resulting amino acid was purified on an ion-exchange column (Dowex 50 H^+ form) with 5% ammonia as the eluent. The eluates were acidified with dilute HCl and lyophilized. Recrystallization from EtOH gave threonine derivative **36** as its hydrochloride: 30 mg (50%); mp 145–148 °C (lit.[21b] mp 148 °C). The IR spectrum was identical with that of an authentic sample. Anal. Calcd for $C_4H_7NO_3Cl_2$: C, 21.38; H, 3.56; N, 6.24. Found: C, 21.67; H, 3.88; N, 6.53.

2-Oxo-4-oxazoline-5-carbonyl Chloride (37). Compound **19** (1.0 g) was gently refluxed in trifluoroacetic acid for 7 h, and removal of the TFA left the acid chloride **37**: 0.56 g (90%); mp 300 °C. Successive treatment with MeOH (20 mL) gave the methyl ester which was recrystallized from CH_2Cl_2–MeOH: mp 203–205 °C (lit.[20] mp 210 °C); yield 0.48 g (76%). The ester was identified by direct comparison with an authentic specimen.[20]

X-ray Analysis of Telomer 6a. Recrystallization of **6a** from *n*-hexane–CH_2Cl_2 gave colorless crystals, among which a rhombic thin plate of about 0.4 × 0.3 × 0.02 cm in size was used for this work. The crystal data were as follows: $C_{11}H_{10}N_2O_6Cl_4$, mol wt 408.0, triclinic, space group $P\bar{1}$ a = 14.510 (7) Å, b = 10.748 (6) Å, c = 10.575 (6) Å, α = 99.82 (5)°, β = 98.12 (5)°, γ = 82.82 (4)°, V = 1600.2 Å^3, Z = 4, d_{calcd} = 1.693 g cm^{-3}. The intensities of 4892 reflections, corresponding to about 85% of the theoretically possible ones within a 2θ angle of 150°, were measured on a Philips PW 1100 diffractometer by using graphite-monochromated Cu Kα radiation. The positions of eight chlorine atoms were determined by the direct method, which revealed the locations of almost all the heavier atoms on the electron-density map. The structure was refined by the block-diagonal matrix least-squares method to an R value of 0.107, including anisotropic thermal parameters. Hydrogen atoms were not included. The atomic coordinates, temperature factors, bond lengths and bond angles are listed in the supplementary material. Figure 1 illustrates the stereostructure of the molecule.

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Registry No. 2 (R = $COCH_3$), 74190-75-3; **4**, 60759-49-1; **5**, 82918-34-1; **6a**, 82950-37-6; **6b**, 82918-35-2; **6c**, 82950-38-7; **7**, 60759-50-4; **8**, 82918-36-3; **9a**, 82918-37-4; **9b**, 82918-38-5; **10**, 82918-39-6; **11**, 82918-40-9; **12**, 75844-68-7; **13**, 82918-41-0; **14**, 78605-46-6; **15**, 82918-42-1; **16**·HCl, 82918-55-6; **17**·HCl, 82918-56-7; **19**, 82918-43-2; (−)-**19**, 82918-44-3; **20a**, 82918-45-4; **20b**, 82950-39-8; **25**, 82918-46-5; **26c**, 82918-47-6; **27**, 82918-48-7; **28**, 82918-49-8; **29**, 22901-35-5; **30**, 82918-50-1; **31**, 82918-51-2; **32**, 82918-52-3; **33** (R = Ac), 82918-53-4; **34**, 82918-54-5; **35**, 52239-36-8; **36**·HCl, 60191-68-6; **37**, 64843-26-1; $RuCl_2(PPh_3)_3$, 15529-49-4; KCN, 151-50-8; 3-acetyl-2-oxazolidinone, 1432-43-5; diphenyl 2-oxo-3-oxazolinylphosphonate, 78605-38-6; 4-chloro-5-benzoxy-2-oxazolidinone, 82918-57-8; bromotrichloromethane, 75-62-7; 4-bromo-5-(trichloromethyl)-2-oxazolidinone, 82918-58-9; benzylthiol, 100-53-8; benzene, 71-43-2; carbon tetrachloride, 56-23-5.

Supplementary Material Available: Tables of fractional coordinates, temperature factors, bond lengths, and bond angles for **6a** (4 pages). Ordering information is given on any current masthead page.