58207-39-9; (±)-**8**, 75420-51-8; (±)-**9**, 75420-50-7; **10**, 2938-53-6; **11**, 57194-67-9; **11** (*N*-oxide), 89959-62-6; **12**, 57147-57-6; (±)-**13**, 75509-50-1; (±)-**14**, 89959-61-5; (±)-**14**-picrate, 89959-63-7; **15**, 57147-55-4; **16**, 57147-56-5; **17**, 90025-88-0; **18**, 57147-60-1; (±)-**19**, 90025-89-1; (±)-**20**, 90027-00-2; (±)-**22**, 90025-90-4; **23**, 61714-12-3; **24**, 17508-17-7; (±)-**26**, 75556-10-4; (±)-**27**, 75556-08-0; (±)-**28**, 75556-09-1; (±)-**31**, 75509-51-2; (±)-**32**, 89959-64-8; (±)-**33**, 75543-75-8; (±)-**33** (thioketal), 89959-65-9; (±)-**33** (tosylhydrazone), 75509-49-8; (±)-**33** (hydrazone), 89959-66-0; (±)-**35**, 75375-41-6; (±)-**36**, 75375-42-7; (±)-**39**·FSO_3, 90025-92-6; (±)-**40**·FSO_3, 90025-94-8; (±)-**41**, 90025-95-9; (±)-**47**, 90025-96-0; **48**, 72362-35-7; **49**, 72473-11-1; **50**, 72473-13-3; (±)-**52**, 90025-97-1; (±)-**53**, 90025-98-2; (±)-**54**, 90025-99-3; (±)-**55**, 89959-68-2; (±)-**56**, 89959-67-1; **57**, 89959-69-3; **57** (*C*-2 epimer), 90026-00-9; **58**, 89959-70-6; **59**, 89959-71-7; 1,5,9-cyclododecatriene, 4904-61-4; ethyl *O*-(2,4-dinitrophenyl)acetohydroxamate, 54322-32-6.

Supplementary Material Available: A description of the treatment of the disorder between C2 and C4, tables of bond lengths, bond angles, and atomic positional and thermal parameters for the chloride salt of **40** (7 pages). Ordering information is given on any current masthead page.

Synthesis of α,β-Epoxyacyl Azides and Their Rearrangement to Epoxy Isocyanates and 3- and 4-Oxazolin-2-ones

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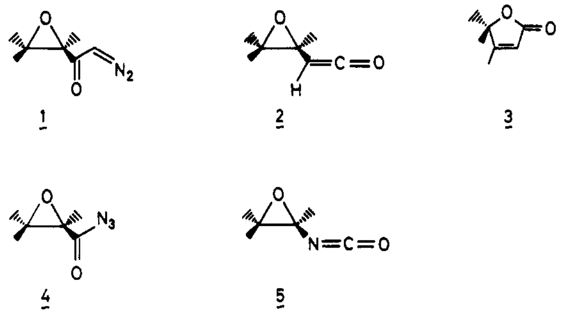
Received October 28, 1983

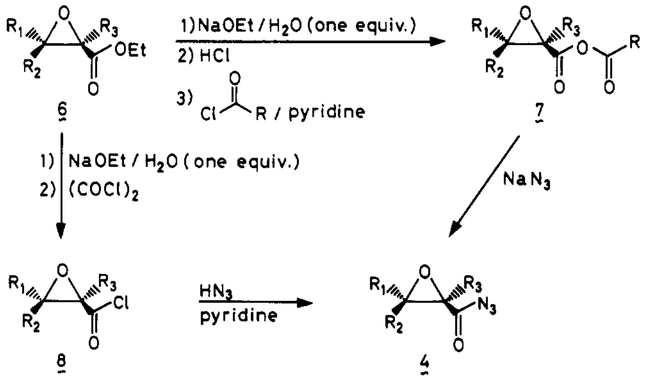
The conversion of α,β-epoxy carboxylates **6** into α,β-epoxyacyl azides **4** proceeds either via reaction of the mixed anhydrides **7** with sodium azide or via reaction of epoxyacyl chlorides **8** with hydrazoic acid–pyridine. The latter method is preferred. The azides **4** undergo a smooth thermal Curtius rearrangement to give 4-oxazolin-2-ones **10** for the substrates **4a–h** having a hydrogen atom at C_β. Monitoring this reaction by means of IR shows that the epoxy isocyanates **5** are intermediates. Intramolecular ring expansion of **5** then leads to 3-oxazolin-2-ones **9** that tautomerize to the 4-isomers **10a–h**. Epoxyacyl azides **4i,n–q**, having no hydrogen atom at C_β, producing 3-oxazolin-2-ones **9i,n–q** by a proton shift is not possible. The products **9i** and **9q** rapidly add water at the imine bond to give oxazolidin-2-ones **11**. Epoxy isocyanate **5k** is reasonably stable in solution; reaction with methanol affords urethane **12**.

In the context of our interest in the selective transformation of functionalized epoxides, we previously investigated the synthesis and chemical behavior of α,β-epoxy diazomethyl ketones[1] **1**. We showed that in these substrates a selective Wolff rearrangement of the diazo ketone moiety can be accomplished upon irradiation in an inert solvent.[1b] The initially formed epoxy ketenes **2** undergo a further intramolecular ring expansion reaction to give the butenolides[1b] **3** (Scheme I). This paper deals with the preparation and reactions of α,β-epoxyacyl azides **4** that are isoelectronic analogues of the diazo ketones **1**. The prime objective of this study is to learn whether a selective Curtius rearrangement of these acyl azides to epoxy isocyanates **5** can be realized. Species of this kind have previously been reported only once during the photochemical rearrangement of 2-oxazolin-4-ones.[2] The epoxides **5** are expected to be reactive compounds that are prone to undergo further reactions, e.g., intramolecular ring expansion reaction similar to that of epoxy ketenes **2**.

Scheme I



Scheme II



Results and Discussion

The epoxy carboxylic esters **6** serve as starting materials. They can either be prepared[1d] by a Darzens condensation of an appropriate carbonyl compound and an α-halo ester or by epoxidation of α,β-unsaturated carboxylic ester using *m*-chloroperbenzoic acid. The synthesis of the epoxyacyl azides was accomplished by using two related procedures. In the first one, saponification of the epoxy esters using the Claisen method[3] gave, after acidification, the free acids

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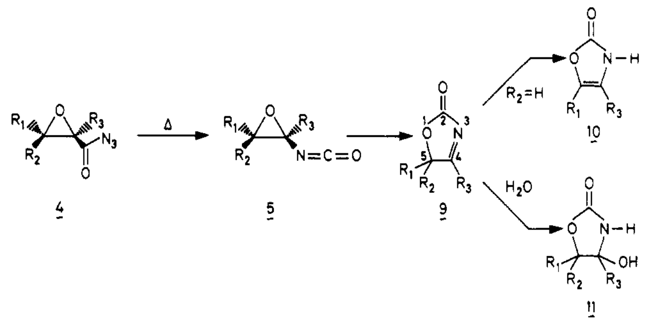
[1] (a) Zwanenburg, B.; Thijs, L. *Tetrahedron Lett.* **1974**, 2459. (b) van Haard, P. M. M.; Thijs, L.; Zwanenburg, B. *Ibid.* **1975**, 803. (c) Brouwer, A. C.; Thijs, L.; Zwanenburg, B. *Ibid.* **1975**, 807. (d) Thijs, L.; Smeets, F. L. M.; Cillissen, P. J. M.; Harmsen, J.; Zwanenburg, B. *Tetrahedron* **1980**, *36*, 2141. (e) Smeets, F. L. M.; Thijs, L.; Zwanenburg, B. *Ibid.* **1980**, *36*, 3269.

[2] (a) Koch, T. H.; Rodehorst, R. M. *Tetrahedron Lett.* **1972**, 4039. (b) Rodehorst, R. M.; Koch, T. H. *J. Am. Chem. Soc.* **1975**, *97*, 7298.

0022-3263/84/1949-2231$01.50/0

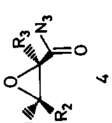
Scheme III



that then were converted into the mixed anhydrides 7 (R = *t*-Bu).[4] Subsequent treatment of these, in situ prepared, anhydrides with sodium azide in a heterogeneous manner resulted in the azides 4 in moderate yields. The second, better method, involves the treatment of the carefully dried sodium epoxy carboxylates (again obtained by Claisen saponification of 6) with a slight excess of oxalyl chloride in the presence of a catalytic amount of pyridine giving the epoxyacyl chlorides[5] 8. These, in situ prepared, chlorides 8 were then treated with hydrazoic acid and pyridine according to the homogeneous procedure described by Van Reyendam and Baardman[6] (Scheme II). Most of the azides 4 were obtained as oils, only three of them were isolated as crystalline compounds. At room temperature most of the prepared azides can be kept for a few days; however, some of them (**4n–p**) decompose spontaneously. The azides are characterized by their ^1H NMR spectra and the typical infrared absorptions at ca. 1700 cm^{-1} (ν_{CO}) and ca. 2140 cm^{-1} (ν_{N_3}). Yields and NMR spectra are collected in Table I.

The epoxyacyl azides undergo a smooth rearrangement reaction on gentle heating in an inert dry solvent such as carbon tetrachloride or benzene. For the substrates **4a–h** having in common that R_2 is H, the isolated products were identified as 4-oxazolin-2-ones **10a–h** (Scheme III, Table II). The formation of these products is readily rationalized as outlined in Scheme III. Curtius rearrangement of the acyl azides 4 leads to epoxy isocyanates 5 that undergo ring expansion to give 3-oxazolin-2-ones 9 (cf. the conversion of 2 to 3).[1b] These heterocyclic compounds rapidly tautomerize to the Δ^4-isomers 10 by a 1,3-proton shift. Support for this sequence of events was obtained by monitoring the rearrangement of 4 by means of infrared spectroscopy. The characteristic azide absorption at 2140 cm^{-1} diminished upon heating 4 in refluxing carbon tetrachloride while at the same time an absorption at 2250 cm^{-1} due to the isocyanate function showed up. Soon thereafter an absorption appeared at 1750 cm^{-1}, attributed to the 4-oxazolin-2-ones 10, with a concomitant reduction of the intensity of the isocyanate band.

Table I. Physical and Spectral Properties of α,β-Epoxyacyl Azides 4



compd	yield,[a] %	mp, °C (solv)	^1H NMR ($CDCl_3$)					
			R_1	δ	R_2	δ	R_3	δ
4a	77 (44)	69–70 (diethyl ether)	Ph	7.32 (m)	H	4.11 (d, *J* = 2 Hz)	H	3.45 (d, *J* = 2 Hz)
4b	85	100–102 (diethyl ether)	*p*-$NO_2C_6H_4$	7.49 (AB, 2 H), 8.26 (AB, 2 H)	H	4.25 (d, *J* = 2 Hz)	H	3.50 (d, *J* = 2 Hz)
4c	90	oil	Ph	7.00–7.20 (m)	H	4.57 (s)	Ph	7.00–7.20 (m)
4d[b]	80	oil	Ph	*b*	H	*b*	*p*-$CH_3C_6H_4$	*b*
4e	93	oil	*p*-$CH_3C_6H_4$	6.86–7.30 (m)	H	4.70 (s)	Ph	6.86–7.30 (m)
4f	87	>90 dec	*p*-$NO_2C_6H_4$	7.15 (AB, 2 H), 8.00 (AB, 2 H)	H	4.68 (s)	Ph	7.26 (m)
4g	80	oil	Ph	7.32 (m)	H	4.30 (s)	CH_3	1.25 (s)
4h	85	oil	R_1-R_3 = $(CH_2)_5$	1.20–2.60 (m)	H	3.30 (tr)		
4i	63 (38)	oil	R_1-C-R_2 = adamantane	1.50–2.25 (m)			H	3.18 (s)
4j	94 (50)	oil	Ph	7.20–7.50 (m)	Ph	7.20–7.50 (m)	H	3.81 (s)
4k	91 (59)	oil	R_1-R_2 = $(CH_2)_5$	1.50–2.00 (m)			H	3.25 (s)
4l	90	oil	R_1-R_2 = $(CH_2)_4$	1.79 (m)			H	2.96 (s)
4m	91	oil	Ph	7.30 (m)	CH_3	1.75 (s)	H	3.53 (s)
4n	65	oil	CH_3	1.00 (s)	CH_3	1.44 (s)	Ph	7.32 (m)
4o	85	oil	CH_3	1.00 (s)	CH_3	1.43 (s)	*p*-$CH_3C_6H_4$	2.33 (s), 6.90–7.60 (m)
4p[c]	90		CH_3		CH_3		*p*-$OCH_3C_6H_4$	
4q	89	oil	R_1-R_2 = $(CH_2)_5$)	1.50–1.78 (m, 10 H)			CH_3	1.55 (s)

[a] The yield in parentheses refers to the anhydride method. [b] Instable oil that rearranged violently at room temperature to the 4-oxazolin-2-one **10d**. [c] Not isolated, but immediately rearranged to the 3-oxazolin-2-one **9d**.

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(3) Claisen, L. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 693. See also ref 1d.

(4) Also the mixed anhydrides 7 with R = Et and *i*-Bu were prepared and subsequently treated with sodium azides. The yields of 4 were usually lower than those with R = *t*-Bu.

(5) (*E*)-2,3-Diphenyl-2,3-epoxypropionyl chloride was prepared previously by treatment of the corresponding acid with oxalyl chloride (Padwa, A.; Das, N. C. *J. Org. Chem.* **1969**, *34*, 816). 3,3-Pentamethylene-2,3-epoxypropionyl chloride was obtained from the corresponding sodium salt and oxalyl chloride (Speciale, A. J.; Frazier, H. W. *J. Org. Chem.* **1961**, *26*, 3176). The present method is in fact a modification of the latter procedure.

(6) Van Reyendam, J. W.; Baardman, F. *Synthesis* **1973**, 413.

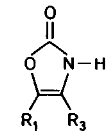
(7) Krieg, B.; Konieczny, P. *Justus Liebigs Ann. Chem.* **1976**, 1862.

(8) Hakimelaki, G. H.; Boyce, C. B.; Kasmai, H. S. *Helv. Chim. Acta* **1977**, *60*, 342.

(9) Stevens, G. de *J. Org. Chem.* **1958**, *23*, 1572.

(10) Hofmann, H.; Wagner, R.; Uhl, J. *Chem. Ber.* **1971**, *104*, 2134.

Table II. Physical and Spectral Properties of 4-Oxazolin-2-ones 10

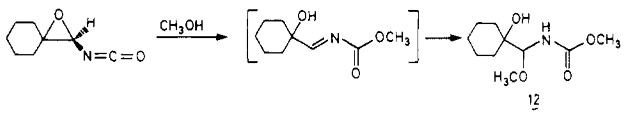


10

compd	yield, %	mp, °C (lit.)^ref	reactn time, h	solv	¹H NMR (Me₂SO-d_6) R₁	δ	R₃	δ	δ(NH)	IR, cm⁻¹ ν_{NH}, $\nu_{amide\ I}$, $\nu_{amide\ II}$	anal. found (calcd) C	H	N	formula
10a	81	212-214 (217-219)[7]	2	benzene	Ph	7.40 (m)	H	7.27 (s)	10.81 (s)	3490, 3204, 3145, 3070, 2830, 1755, 1720, 1495	66.84 (67.08)	4.43 (4.83)	8.52 (8.69)	$C_9H_7NO_2$
10b	82	>240 dec	2	benzene	p-NO$_2$Ph	7.93 (AB), 8.49 (AB)	H	8.13 (s)	11.47 (s)	3460, 3210, 3140, 3100, 2820, 1765, 1330	52.26 (52.44)	3.02 (2.93)	13.51 (13.51)	$C_9H_6N_2O_4$
10c	69	210-211 (205-209)[7]	1	benzene	Ph	7.50 (m)	Ph	7.62 (m)	11.40 (s)	3460, 3180, 3090, 3037, 2860, 2780, 1750, 1505	76.30 (75.94)	4.80 (4.67)	5.87 (5.90)	$C_{15}H_{11}NO_2$
10d	84	205-212	2	benzene	Ph	7.50 (m)	p-CH$_3$Ph	2.30 (s), 7.10-7.50 (m)	11.26 (s)	3450, 3170, 3070, 3025, 2850, 2760, 1740, 1510, 1485	76.56 (76.48)	5.50 (5.21)	5.57 (5.57)	$C_{16}H_{13}NO_2$
10e	57	209-210 (158-160)[a]	5	CCl_4	p-CH$_3$Ph	2.26 (s), 7.02 (AB), 7.19 (AB)	Ph	7.38 (m, 5 H)	11.06 (s)	3440, 3175, 3080, 3045, 2850, 2760, 1740, 1512	76.49 (76.48)	5.37 (5.21)	5.65 (5.57)	$C_{16}H_{13}NO_2$
10f	84	>250 dec	2	benzene	p-NO$_2$Ph	7.29-7.65 (m, 2 H), 8.20 (d, 2 H)	Ph	7.29-7.65 (m)	10.95 (s)	3450, 3170, 3100, 3020, 2920, 2825, 1760, 1340	63.31 (63.83)	3.73 (3.57)	9.83 (9.93)	$C_{15}H_{10}N_2O_4$
10g	66	149-151 (151-152)[7]	1	benzene	Ph	7.45 (m)	CH_3	2.27 (s)	9.50 (s)	3470, 3250, 3050, 1780, 1308	68.71 (68.56)	5.04 (5.18)	7.84 (8.00)	$C_{10}H_9NO_2$
10h	66	93-115[b]	16	CCl_4	R$_1$-R$_3$ = (CH$_2$)$_4$	1.53-1.90 (m, 4 H), 2.16-2.46 (m, 4 H)			9.76 (s)	3445, 3240, 3140, 3060, 2770, 1732, 1350	[b]			

[a] Presumably a mixture of isomers (see ref 8). [b] This compound is very hard to purify.

Scheme IV



The prototopic shift of **9** to give **10** will be impossible for substrates **4** having no hydrogen atom at the β-carbon atoms. Accordingly, the epoxyacyl azide **4i** gave on heating in refluxing super dry benzene (or carbon tetrachloride) the 3-oxazolin-2-one **9i**. Similarly, the azides **4n–q** thermally rearranged to the corresponding 3-oxazolin-2-ones **9n–q** (Table III). The compounds **9** are characterized by a carbonyl absorption at 1740–1760 cm^{-1} and an imine band 1540–1630 cm^{-1}. They are all sensitive to moisture, particularly **9i** and **9q**. Reaction with water in these latter cases leads to hydration of the imine band to give the corresponding 4-hydroxy-oxazolidin-2-ones **11**. This property forms additional evidence for the structure of the 3-oxazolin-2-ones **9**.

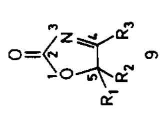
The epoxyacyl azides **4j–m** showed a deviant behavior. On heating in benzene no 3-oxazolin-2-ones were obtained but instead a polymeric material was formed. By means of IR it was shown that the Curtius rearrangement to epoxy isocyanates **5** had taken place. Probably, the subsequently formed 3-oxazolin-2-ones are unstable and undergo polymerization.[11] The epoxy isocyanate **5k** was reasonably stable in benzene solution. Reaction hereof with methanol leads to the hydroxy carbamate **12** arising from initial reaction of the isocyanate function with concomitant opening of the epoxide ring (Scheme IV) (cf. the reaction of epoxy ketenes **2** in methanol that leads to γ-hydroxy-α,β-unsaturated esters).[1b] It should be noted that reaction of epoxy azide **4k** in refluxing methanol leads, as expected, to the corresponding methyl epoxy carboxylate.

In the literature several good syntheses for 4-oxazolin-2-ones have been described.[12] The new method presented here is attractive as it is simple and moreover is based on a concept entirely different from previous ones. So far, the synthesis of 3-oxazolin-2-ones received only little attention. Reaction of tertiary α-hydroxy ketones with chlorosulfonyl isocyanate followed by hydrolysis and subsequent thermal cyclization is virtually[10] the only synthesis reported.[13] Our method is experimentally much simpler, and it also has promising prospects.

Experimental Section

Melting points were determined on a Reichert hot-stage microscope and are uncorrected. ^{1}H NMR spectra were recorded on a Varian EM-390 spectrometer using Me_4Si as internal standard. IR spectra were run on a Perkin-Elmer 257 grating spectrophotometer. Mass spectra were obtained with a Varian MAT SM_2B mass spectrometer. Elemental analyses were performed by Mr. J. Diersmann (University of Nijmegen). All

Table III. Physical and Spectral Properties of 3-Oxazolin-2-ones 9



9

compd	yield, %	mp, °C (lit.)^{ref}	reactn time	solv	^{1}H NMR (CDCl$_3$) R$_1$	δ	R$_2$	δ	R$_3$	δ	IR, cm^{-1} $\nu_{C=O}$, $\nu_{C=N}$	anal. found (calcd) C	H	N	formula
9i	85	162–164	3 days	benzene	R_1–C–R_2 = adamantane	1.10–2.50 (m)			H	7.29 (s)	1790, 1600	68.35 (70.22)	7.42 (7.37)	6.59 (6.82)	$C_{12}H_{15}NO_2$
9n	69	111–112 (111–111.5)[10]	5 days[a]	none	CH_3	1.76 (s)	CH_3	1.76 (s)	Ph	7.26–7.79 (m, 3 H), 8.03–8.20 (m, 2 H)	1765, 1560	69.14 (69.83)	6.03 (5.86)	7.41 (7.40)	$C_{11}H_{11}NO_2$
9o	69	124–128	5 days	none	CH_3	1.76 (s)	CH_3	1.76 (s)	p-CH_3Ph	2.46 (s, 3 H), 7.33 (AB, 2 H), 8.00 (AB, 2 H)	1760, 1545	70.86 (70.92)	6.58 (6.45)	6.82 (6.89)	$C_{12}H_{13}NO_2$
9p	72	141–148	5 days	none	CH_3	1.76 (s)	CH_3	1.76 (s)	p-OCH_3Ph	3.90 (s, 3 H), 7.00 (AB, 2 H), 8.06 (AB, 2 H)	1755, 1545	65.29 (65.74)	6.10 (5.98)	5.92 (6.39)	$C_{12}H_{13}NO_3$
9q	74	b	4 h	benzene	R_1–R_2 = $(CH_2)_5$	b			CH_3	b	b	b			

[a] After 5 days at room temperature the reaction mixture was kept at 80 °C for 4 h. [b] Not isolated as the 3-oxazolin-2-one but analyzed as its hydroxyoxazolidine **11q**, see Experimental Section.

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[11] A tentative explanation is that the 3-oxazolin-2-ones **4j–m** react with a trace of water present in the reaction medium to give the corresponding hydroxy compounds **11j–m**; ring opening then leads to aldehyde urethanes $O{=}CHCR_1R_2OC({=}O)NH_2$, which may undergo linear polymerization. In the case of **9i** (also having R_3 = H) the adamantane substituent apparently has a stabilizing effect on the covalently hydrated compound **11i**. The properties of the heterocyclic compounds **9** and **11** are currently under investigation.

[12] Cornforth, J. W. *Heterocycl. Compd.* **1957**, *5*, 336. Filler, R. *Adv. Heterocycl. Chem.* **1965**, *4*, 75. Filler, R.; Rao, Y. S. *Ibid.* **1977**, *21*, 176.

[13] Special types of 3-oxazolin-2-ones are reported by: Davies, J. S. H.; Hook, W. H. *J. Chem. Soc.* **1950**, *30* (cf. Spielman, M. A. *J. Am. Chem. Soc.* **1944**, *66*, 1244). Schreiber, J.; Leimgruber, W.; Pesaro, M.; Schudel, P.; Threlfall, T.; Eschenmoser, A. *Helv. Chim. Acta* **1961**, *44*, 540, i.e., 581. Baxter, J.; Cameron, D. W.; Thoseby, M. R. *J. Chem. Soc. C* **1970**, 850. Caillaux, B.; George, P.; Tataruch, F.; Janousek, Z.; Viehe, H. G. *Chimia* **1976**, *30*, 387.

solvents were carefully dried and distilled before use.

Unless indicated otherwise the spectral and analytical data are collected in the Tables I–III.

Sodium α,β-Epoxy Carboxylates (General Procedure). A solution of ethyl (or methyl) α,β-epoxy carboxylate in ethanol (or methanol) was added to a solution of exactly 1 equiv of NaOEt (or NaOMe) in ethanol (or methanol) at room temperature. After homogenation exactly 1 equiv of water was added. In most cases the sodium salts had precipitated after the mixture was left standing for 24 h. When no precipitation took place, the solvent was removed in vacuo and the remaining solid carefully washed with ether (in some cases this washing was performed by using the centrifuge). The sodium salts thus obtained were dried in an oven (110 °C) under vacuum (200 torr) using IR spectra to check the complete removal of water and alcohol.

α,β-Epoxyacyl Azides 4 via Mixed Anhydrides 7 (General Procedure). A slight excess of 4 N hydrochloric acid was added to an ice-cooled solution of sodium epoxy carboxylate (15 mmol) in water (50 mL). The free acid, which precipitated in most cases, was extracted with ether (3 × 20 mL). After the mixture was dried over $MgSO_4$ at 4 °C, a slight excess of triethylamine (16 mmol) in ether (10 mL) was added in one portion to the ice-cooled solution of the acid. Then 1 equiv of pivaloyl chloride in ether (10 mL) was added under efficient stirring. In some cases it was found advantageous to reverse the order of the addition of acyl chloride and amine to avoid precipitation of triethylammonium carboxylate. After 2 h of stirring a solution of NaN_3 (20 mmol) in water (20 mL) was added. Stirring was continued for 16 h at room temperature. Then the ether layer was separated and the aqueous layer extracted with ether. The combined ether solutions were washed with saturated aqueous ammonium chloride, dried over $MgSO_4$, and concentrated at reduced pressure (0 °C) to afford the epoxy acyl azides 4. Due to their thermal instability elemental analyses cannot be carried out.

α,β-Epoxyacyl Azides 4 via Acyl Chlorides 8 (General Procedure). A few drops of pyridine were added to a suspension of dry sodium epoxy carboxylate (10.7 mmol) in super dry THF (100 mL). (THF is the recommended solvent; however, carbon tetrachloride, benzene, and toluene can be used as well). Under constant stirring oxalyl chloride (16 mmol) was gradually added at −20 °C. After 1 h of stirring at room temperature the excess of oxalyl chloride and other volatiles were removed at reduced pressure first with an aspirator and then an oil vacuum pump. The residue was dissolved in ether (150 mL), and at −20 °C pyridine (10.7 mmol) was added, followed by hydrazoic acid (16 mmol) in benzene (50 mL).[6] Stirring was continued for 1 h while the temperature was raised to 10 °C. The precipitated solid was filtered off and the filtrate concentrated at reduced pressure (first with an aspirator and then an oil vacuum pump), keeping the temperature below 5 °C. The remaining product consisted of pure epoxyacyl azide 4 according to the ^1H NMR spectrum.

Rearrangement to 4-Oxazolin-2-ones 10 (General Procedure). A solution of azide **4a–h** (3 mmol) in an inert solvent (150 mL) was heated under reflux for the time indicated in Table II. The completeness of the reaction was checked by means of IR. The solvent was removed in vacuo and the crude product crystallized from methanol. For **10h** the initially obtained yellow product was crystallized from benzene–hexane to give a colorless crystalline material that rapidly darkened and liquefied on standing. Purification was then performed by sublimation in vacuo (120 °C (6 torr)): yield 66%, melting range 93–115 °C.

Adamantanespiro-5-(3-oxazolin-2-one) (9i). A solution of azide **4i** (1.10 g, 4.7 mmol) in dry benzene (150 mL) was heated under reflux for 3 days. After removal of the solvent in vacuo, the residue was crystallized from benzene–hexane, affording white crystals that were dried over P_2O_5 in a drying pistol at 50 °C; yield 0.81 g (85%). This product **9i** picked up water spontaneously on standing in an open flask, yielding **adamantanespiro-5-(4-hydroxy-oxazolidin-2-one) (11i)** almost quantitatively: mp 202–206 °C (from methanol); ^1H NMR (Me_2SO-d_6 + $CDCl_3$) δ 1.36–2.38 (m, 14 H, adamantane H), 5.00 (d, 1 H, J = 8.4 Hz, C_4H), 5.85 (d, 1 H, J = 8.4 Hz, OH), 7.94 (s, 1 H, NH), the signals at δ 5.85 and 7.94 disappeared on shaking with D_2O; IR (KBr) 3480, 3400 (NH, OH), 1720, 1680 (C=O) cm^{-1}. Anal. Calcd for $C_{12}H_{17}NO_3$ (223.27): C, 64.57; H, 7.62; N, 6.28. Found: C, 65.14; H, 7.83; N, 6.27.

5,5-Dimethyl-4-phenyl-3-oxazolin-2-one (9n). In a sublimation flask that was rinsed with diluted ammonia and then dried at 150 °C, azide **4n** (1.95 g, 8.9 mmol) was kept for 5 days and subsequently heated at 80 °C for 4 h. The initially formed light brown oil slowly solidified. After being washed with ether–petroleum ether (1:1; 5 mL) the product was sublimied (80 °C, 12 torr), affording **9n** (1.31 g). On standing in air water was picked up as was indicated by the appearance of IR absorptions at 3348 (NH) and 3225 (OH) cm^{-1}. **3-Oxazolin-2-ones 9o** and **9p** were obtained following the procedure described for **9n**.

Cyclohexanespiro-5-(4-methyl-3-oxazolin-2-one) (9q). A solution of azide **4q** (1.90 g, 11.37 mmol) in dry benzene (250 mL) was heated at reflux for 4 h. After removal of the solvent the residual colorless solid was washed with ether–petroleum ether (1:1, 5 mL) and then sublimed (140 °C (5 torr)), yielding **9q** (1.40 g). This material was very hygroscopic and therefore analyzed as its hydrate obtained by crystallization from slightly wet ether, yielding **Cyclohexanespiro-5-(4-hydroxy-4-methyl-oxazolidin-2-one) (11q)**: 1.56 g (74%); mp 115–118 °C; IR (KBr) 3400 (OH), 3280 (NH), 1770 (C=O) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 1.23 (s, 3 H, CH_3), 1.23–1.90 (m, 10 H, $(CH_2)_5$), 5.64 (s, 1 H, OH), 7.90 (s, 1 H, NH). Anal. Calcd for $C_9H_{15}NO_3$ (185.22): C, 58.36; H, 8.16; N, 7.56. Found: C, 58.08; H, 8.08; N, 7.39.

Thermal Rearrangement of 4k. Formation of Methyl *N*-(1-Methoxy-2-hydroxy-2,2-pentamethyleneethyl)carbamate (12). Azide **4k** (2.30 g, 13 mmol) was heated in refluxing benzene for 1 h. According to the IR spectrum the conversion of **4k** into epoxy isocyanate **5k** was complete. To this solution of **5k** was added methanol (1.28 g, 40 mmol). After the mixture was heated at reflux temperature for 3 h, the volatiles were remove in vacuo and the residue was chromatographed over silica gel (ethyl acetate), affording carbamate **12** as a yellow oil (2.72 g, 96%): IR (film) 3440 (OH), 3340 (NH), 1720 (C=O), 1500 (amide II) cm^{-1}; ^1H NMR (CCl_4) δ 1.00–1.97 (m, 10 H), 2.50 (s, OH), 3.33 (s, OCH_3), 3.66 (s, OCH_3), 4.50 (d, 1 H, J = 9.6 Hz), 4.70 (d, 1 H, J = 9.6 Hz). Anal. Calcd for $C_{10}H_{19}NO_4$ (217.26): C, 55.28; H, 8.82; N, 6.45. Found: C, 55.37; H, 8.74; N, 6.34.

Registry No. **4a**, 89848-92-0; **4b**, 89848-93-1; **4c**, 89848-94-2; **4d**, 89848-95-3; **4e**, 89848-96-4; **4f**, 89848-97-5; **4g**, 89848-98-6; **4h**, 89848-99-7; **4i**, 89849-00-3; **4j**, 89849-01-4; **4k**, 89849-02-5; **4l**, 89849-03-6; **4m**, 89849-04-7; **4n**, 89849-05-8; **4o**, 89849-06-9; **4p**, 89849-07-0; **4q**, 89849-08-1; **5k**, 89849-18-3; **6a**, 2272-55-1; **6a** (Na salt), 54885-10-8; **6a** (free acid), 1566-68-3; **6b**, 54679-39-9; **6b** (Na salt), 89848-67-9; **6b** (free acid), 56010-46-9; **6c**, 7042-27-5; **6c** (Na salt), 60727-80-2; **6c** (free acid), 53884-88-1; **6d**, 89848-60-2; **6d** (Na salt), 89848-68-0; **6d** (free acid), 89848-76-0; **6e**, 89848-61-3; **6e** (Na salt), 89848-69-1; **6e** (free acid), 89848-77-1; **6f**, 89848-62-4; **6f** (Na salt), 89848-70-4; **6f** (free acid), 89848-78-2; **6g**, 7141-24-4; **6g** (Na salt), 53635-54-4; **6g** (free acid), 82812-97-3; **6h**, 89848-63-5; **6h** (Na salt), 89848-71-5; **6h** (free acid), 89848-79-3; **6i**, 89848-64-6; **6i** (Na salt), 89848-72-6; **6i** (free acid), 76527-34-9; **6j**, 5449-40-1; **6j** (Na salt), 54934-19-9; **6j** (free acid), 53884-87-0; **6k**, 6975-17-3; **6k** (Na salt), 25957-47-5; **6k** (free acid), 6190-79-0; **6l**, 6975-15-1; **6l** (Na salt), 89848-73-7; **6l** (free acid), 5974-79-8; **6m**, 19464-92-7; **6m** (Na salt), 54984-42-8; **6m** (free acid), 76527-32-7; **6n**, 59070-02-9; **6n** (Na salt), 24568-18-1; **6n** (free acid), 76527-37-2; **6o**, 89848-65-7; **6o** (Na salt), 89848-74-8; **6o** (free acid), 76527-38-3; **6p**, 89848-66-8; **6p** (Na salt), 89848-75-9; **6p** (free acid), 76527-39-4; **6q**, 31045-09-7; **6q** (Na salt), 31045-11-1; **6q** (free acid), 76527-35-0; **8a**, 76527-41-8; **8b**, 89848-80-6; **8c**, 18521-11-4; **8d**, 89848-81-7; **8e**, 89848-82-8; **8f**, 89848-83-9; **8g**, 89848-84-0; **8h**, 89848-85-1; **8i**, 89848-86-2; **8j**, 76527-40-7; **8k**, 76527-44-1; **8l**, 89848-87-3; **8m**, 76527-42-9; **8n**, 89848-88-4; **8o**, 89848-89-5; **8p**, 89848-90-8; **8q**, 89848-91-9; **9i**, 89849-12-7; **9n**, 33664-90-3; **9o**, 89849-13-8; **9p**, 89849-14-9; **9q**, 89849-15-0; **10a**, 17107-25-4; **10b**, 27353-93-1; **10c**, 5014-83-5; **10d**, 89849-09-2; **10e**, 62762-78-1; **10f**, 89849-10-5; **10g**, 61416-45-3; **10h**, 89849-11-6; **11i**, 89849-16-1; **11q**, 33664-89-0; **12**, 89849-17-2; NaN_3, 26628-22-8; pivaloyl chloride, 3282-30-2; hydrazoic acid, 7782-79-8.