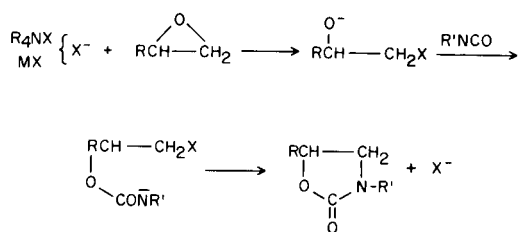# Bis-2-Oxazolidones-Preparation and Characterization

John E. Herweh

Research and Development Center, Armstrong Cork Company

A number of workers have described the preparation of simple monofunctional and polymeric 2-oxazolidones from isocyanates and epoxides (1), utilizing a variety of reaction conditions (mode of addition, catalysts and solvents). Several mechanisms have been postulated for the reaction, the nature of which is dependent on the type of catalysis employed (1a,2). The proposed reaction path, when quaternary ammonium salts or Lewis acids, such as potassium iodide and lithium chloride, are used as catalysts, involves opening of the oxirane ring followed by addition of isocyanates to the resulting anion as shown below.

$$R_4NX \atop MX \Big\{ X^- \ + \ \underset{RCH-CH_2}{\overset{O}{\triangle}} \ \longrightarrow \ R\overset{|}{C}H\overset{O^-}{\underset{|}{}}-CH_2X \ \xrightarrow{R'NCO}$$

$$\underset{O \diagdown_{CONR'}}{\overset{RCH-CH_2X}{\underset{|}{}}} \ \longrightarrow \ \underset{O \diagdown_{C} \diagup^{N-R'}}{\overset{RCH-CH_2}{\underset{||}{O}}} \ + \ X^-$$

Previously (1b) we confirmed the use of lithium chloride and dimethylformamide as satisfactory catalyst and solvent, respectively, for the preparation of N-substituted 2-oxazolidones in good yields. It was also found that addition of isocyanate to a solution of epoxide and catalyst in refluxing dimethylformamide was best for optimizing yields of N-substituted 2-oxazolidones and minimizing those of formamidines (3).

Using the reported procedure for the preparation of simple N-substituted 2-oxazolidones we have now prepared a number of bis-2-oxazolidones of two types, 1 obtained from diisocyanates and monofunctional epoxides (Table I) and II from monoisocyanates and bisepoxides (Table II). The bis-2-oxazolidones (I and II) were characterized by elemental analysis, molecular weight and pmr and have therefore been formulated as 5-substituted-2-oxazolidones. In some cases the modest yields obtained and the isolation of the desired bis-2-oxazolidone as an oil may reflect the presence of isomers. The formation of the predominant 5-isomer (III) along with the 4-isomer

(IV) has been shown in several earlier cases in the preparation of simple monofunctional 2-oxazolidones (1b).

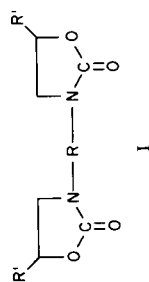| III | IV |
| 5-substituted-2-oxazolidone | 4-substituted-2-oxazolidone |
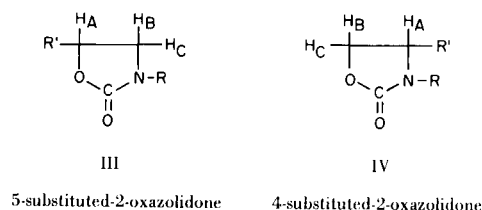
The 4-isomers were not isolable reaction products in the preparation of bis-2-oxazolidones (I and II). The pmr spectra of a number of the bis-2-oxazolidones (4) (I and II, Table III) indicated that they are in fact 5-isomers. This conclusion is based upon the chemical shifts of H_A, H_B and H_C (Table III). It has been established with monofunctional 2-oxazolidones that H_A of 5-isomers is farther downfield than the corresponding proton of the 4-isomers. This is attributed to the fact that in the 5-isomer H_A is adjacent to an oxygen atom while in the 4-isomer H_A is adjacent to nitrogen, a less electronegative atom. Conversely, the methylene protons, H_B and H_C in the 5-isomers, are farther upfield than H_B and H_C in the 4-isomers. Thus, in 5-substituted-2-oxazolidones, the chemical shift difference between H_A and $H_{B,C}$ is greater than in the isomeric 4-substituted-2-oxazolidones.

The difference in chemical shifts between H_A and $H_{B,C}$ in the bis-2-oxazolidones (I and II, Table III) conformed to that previously reported for their monofunctional 5-substituted analogs (III), and the chemical shifts also correspond very closely (< 0.1 ppm).

In the pmr spectra of the various compounds examined (Table III) the signal attributed to H_A appears, in most cases, as a complex multiplet due to splitting by H_B and H_C and by protons on the adjacent carbon atom associated with the R' group. In one case, namely that of N,N'-hexamethylene bis(5-phenyl-2-oxazolidone) (I-3), splitting of H_A was due solely to H_B and H_C, and an anticipated double doublet was observed. Similarly in I-3 the splitting patterns for H_B and H_C were readily

TABLE I

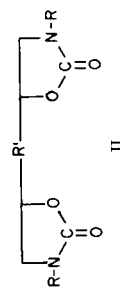### Bis-2-oxazolidones (I) From Diisocyanates and Monoepoxides

I

No.	R	R'	M.P., °C	Yield, %	Formula	Calcd. % C	Calcd. % H	Calcd. % N	Found % C	Found % H	Found % N	Mol. Wt. Calcd	Mol. Wt. Found(a)
I-1	2,4-CH$_3$C$_6$H$_3$-	C$_6$H$_5$-	77-90	100 (b,c)	C$_{25}$H$_{22}$N$_2$O$_4$	72.45	5.35	6.76	72.45	5.29	6.90	414.5	376.8
I-2a	(-CH$_2$-)$_6$	C$_6$H$_5$OCH$_2$-	130-131.5	(20)	C$_{26}$H$_{32}$N$_2$O$_6$	66.65	6.89	5.98	66.42	5.78	5.98	468.5	454.7
I-2b	"	"	91-96	(29)	C$_{26}$H$_{32}$N$_2$O$_6$	66.65	6.89	5.98	66.72	7.06	6.27	468.4	464.3
I-3	"	C$_6$H$_5$	114-115.5	(25)(d)	C$_{24}$H$_{28}$N$_2$O$_4$	70.56	6.91	6.86	70.75	6.92	6.95	408.5	428.4
I-4	"	CH$_3$(CH$_2$)$_3$OCH$_2$-	oil	91 (c)(67.5)(e)	C$_{22}$H$_{40}$N$_2$O$_6$	61.65	9.41	6.54	61.49	9.73	6.47	428.6	445.6
I-5	4,4'-C$_6$H$_4$CH$_2$C$_6$H$_4$-	C$_6$H$_5$-	248-250	(53.5)(f)	C$_{31}$H$_{26}$N$_2$O$_4$	75.90	5.34	5.71	75.92	5.31	5.35	490.6	-(h)
I-6	"	C$_6$H$_5$OCH$_2$-	204.5-207	(82)(f)	C$_{33}$H$_{30}$N$_2$O$_6$	71.98	5.49	5.09	72.07	5.46	5.05	550.6	-(h)
I-7	"	CH$_3$(CH$_2$)$_3$OCH$_2$-	150-153	(56)(g)	C$_{29}$H$_{38}$N$_2$O$_6$	68.21	7.50	5.49	67.91	7.37	5.64	510.6	502.1

(a) Determined in THF by vapor pressure osmometry. (b) Purified by recrystallization from a mixture of benzene and hexane. (c) Yield of crude product. (d) Recrystallized twice from 95% ethyl alcohol and twice from carbon tetrachloride. (e) Purified by addition of its carbon tetrachloride solution to petroleum ether. (f) DMF was used as the solvent. (g) Analytically pure material was obtained after two recrystallizations from a chloroform-carbon tetrachloride mixture. (h) Insoluble.

TABLE II

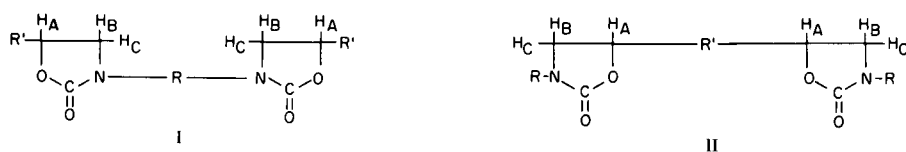### Bis-2-oxazolidones (II) From Monoisocyanates and Bisepoxides

II

No.	R	R'	M.P., °C	Yield, %	Formula	Calcd. % C	Calcd. % H	Calcd. % N	Found % C	Found % H	Found % N	Mol. Wt. Calcd	Mol. Wt. Found(a)
II-8	p-CH$_3$C$_6$H$_4$-	-CH$_2$O(-CH$_2$-)$_4$OCH$_2$-	94-97	93(c)(74)(b)	C$_{26}$H$_{32}$N$_2$O$_6$	66.65	6.89	5.98	66.50	6.98	6.12	468.5	457.7
II-9	n-CH$_3$(CH$_2$)$_3$-	"	pale yellow oil	100 (c,d)	C$_{20}$H$_{36}$N$_2$O$_6$	59.97	9.06	7.00	59.74	9.07	7.11	400.5	392.0
II-10	p-CH$_3$C$_6$H$_4$-	(4,4'-CH$_2$OC$_6$H$_4$)$_2$CMe$_2$	187-189	(79.4)(e)	C$_{37}$H$_{38}$N$_2$O$_6$	73.24	6.31	4.62	72.94	6.18	4.47	606.7	(g)
II-11	n-CH$_3$(CH$_2$)$_3$-	"	oil	99 (f)	C$_{31}$H$_{42}$N$_2$O$_6$	69.12	7.87	5.20	69.34	8.00	5.20 / 5.07	538.7	519.4

(a) Determined in THF by vapor pressure osmometry. (b) Purified by recrystallization from 95% ethyl alcohol. (c) Yield of crude product. (d) Analytical sample was prepared by precipitation from a mixture of carbon tetrachloride and hexane. (e) DMF was used as the solvent. (f) The oil was purified by addition of its benzene solution to hexane. (g) Insoluble.

TABLE III

Pmr Data for Some Bis-2-oxazolidones

|			Chemical Shifts, ppm (TMS=O) (a)			
Compd	R	R'	H_A	H_B, H_C	H_D	H_E
I-2a	$-CH_{2_D}(-CH_2-)_4CH_{2_D}$	$C_6H_5OCH_{2_E}$	4.5(m)	3.4(t,J_{BA},J_{BC}= 8cps)3.23(d,d, J_{CA}=6cps,J_{CB}=8	3.03(t, J=6cps	3.83(d, J=4.5 cps)
I-2b	"	"	"	"	"	"
I-3	"	C_6H_5-	5.50(d,d,J_{AB}= 8.5,J_{AC}=7.5 cps)	3.93(t,J_{BA}= J_{BC}=8.5cps) 3.40(d,d,J_{CA}= 7.5,J_{CB}=8.5cps)	3.30(t,J= 7.0 cps)	
I-4 (b)	$-CH_{2_D}(-CH_2-)_4CH_{2_D}$	$CH_3(-CH_2-)_{2_E}OCH_{2_E}$	4.55 (m)	3.35 (m)	3.23(t,J= 6.3cps)	3.35(m)
II-8	$p-CH_3C_6H_4-$	$-CH_{2_E}OCH_2(-CH_2-)_2CH_{2_E}OCH_{2_E}$	4.70 (m)	3.79 (m)		3.79(m)
II-9 (b)	$CH_3CH_2CH_2CH_{2_D}$	"	4.58 (m)	3.36 (m)	3.23(t, J=6.3cps)	3.36(m)

(a) d = doublet, d,d = double doublet, t = triplet, m = multiplet. (b) Determined on a JEOL 4H-100 Spectrometer.

discernible; the signals for these protons appeared as a triplet and double doublet, respectively. The triplet for H_B results because J_{BA} and J_{BC}, cis and geminal coupling constants, are equivalent. The double doublet for H_C arises because trans coupling (J_{CA}) and geminal coupling (J_{CB}) are different. Signals for H_B and H_C of the other oxazolidones (I and II) were complex because protons adjacent to oxygen and/or nitrogen have similar field positions.

The chemical shifts for other protons associated with the oxazolidones conformed to expected values. In addition, the integrated values of the various signals were in complete agreement with the number of protons associated with the assigned structure.

In the reaction of 1,6-hexamethylene diisocyanate with phenyl glycidyl ether, two reaction products were isolated in approximately equivalent amounts (Table 1, I-2a and I-2b). Elemental analyses and molecular weights for

I-2a and I-2b agreed with calculated values for the desired bis-2-oxazolidone and the pmr spectra (Table III) were identical. As mentioned earlier, the chemical shifts of H_A, H_B and H_C of I-2a and I-2b were consistent for a 5-substituted-2-oxazolidone (Table III, I-2a and I-2b). The possibility that I-2a and I-2b are polymorphs was judged unlikely, since attempts to effect an interconversion were unsuccessful. In view of these results it is postulated that I-2a and I-2b are meso and dl forms. The planar projection formulas (V and VI) have been used to depict the postulated meso and dl forms respectively. No direct evidence was obtained, however, to confirm this. Oda and coworkers (5) rationalized some of their results obtained with polyoxazolidones by attributing them to the presence of meso and dl configurations and the consequence of these configurations on the arrangements of the oxazolidone rings.

V
meso

VI
dl
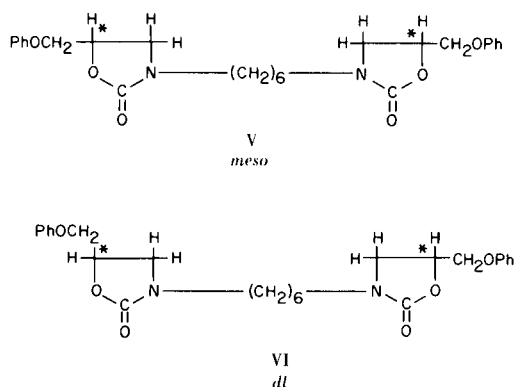
The infrared spectra of the bis-2-oxazolidones exhibited a strong band at 1725-1750 cm^{-1}. This absorption is attributed to C=O stretching vibration and its relatively high frequency, as compared to that of open chain carbamic esters, is characteristic of 2-oxazolidones (1a). In addition, most of the bis-2-oxazolidones exhibited absorption of weak to medium intensity between 980-1060 cm^{-1}. Absorption in this region reportedly is characteristic of the 2-oxazolidone ring (1a). All of the compounds showed a band of generally medium intensity at 1225-1260 cm^{-1}. This absorption may be due to C-O stretching vibration.

EXPERIMENTAL (6)

Isocyanates and epoxides, except the bisglycidyl ether of 4,4'-isopropylidene diphenol, were distilled prior to use. The bisglycidyl ether of 4,4'-isopropylidene diphenol was used as obtained from the Dow Chemical Company. Dimethylformamide (Fisher Sci. Co.) was distilled at atmospheric pressure from calcium hydride.

General Procedure for the Preparation of Bis-2-oxazolidones (I) from Diisocyanates and Epoxides.

The diisocyanate (0.1 mole) in 30 ml. of DMF was added in 1 hour to a stirred refluxing solution of the epoxide (0.21 mole) in 80 ml. of DMF containing 0.08 g. of dried lithium chloride under a nitrogen atmosphere. Upon completing the addition, the reaction mixture was stirred at reflux temperature for 6 hours. The reaction mixture was cooled and the DMF was removed by distillation *in vacuo*. The still residue, an oil in the case of I-1, I-3 and I-4, was reprecipitated from suitable solvents to yield the desired products (Table I).

In the preparation of I-5, I-6 and I-7 a major portion of the product precipitated as a solid on cooling the reaction mixture. When this occurred the solid was filtered, washed with small portions of fresh DMF and subsequently purified (Table 1). Additional product was obtained when the combined DMF washings and filtrate were distilled *in vacuo* to remove solvent.

Reaction of 1,6-Hexamethylenediisocyanate with Phenyl Glycidyl Ether.

1,6-Hexamethylenediisocyanate (0.1 mole) and phenyl glycidyl ether (0.21 mole) were allowed to react as described above. Distillation of the DMF at reduced pressures left a pale amber viscous oil (53.4 g.).

The residual oil (53.4 g.) was recrystallized twice from 95% ethyl alcohol to yield 28.4 g. of a white solid that softened at 74° and metled at 84-97°. Addition of a chloroform solution of the solid (28.4 g.) to petroleum ether precipitated 9.5 g. of crude I-2a, m.p. 114-120°. Two recrystallizations of crude I-2a from a chloroform-carbon tetrachloride mixture (1:4 by volume) gave analytically pure I-2a, m.p. 130-131.5°. Upon concentrating the chloroform-petroleum ether filtrate, 13.7 g. of crude I-2b, m.p. 90-96°, was obtained. Recrystallization from dilute ethyl alcohol and then from a chloroform-carbon tetrachloride mixture gave analytically pure I-2b, m.p. 91-96° (Table I).

General Procedure for the Preparation of Bis-2-oxazolidones (II) from Monoisocyanates and Bisepoxides.

The procedure used for the preparation of II was identical to that described above for the bis-2-oxazolidones of type I except that 0.21 mole of the monoisocyanate and 0.1 mole of the bisepoxide were used. The crude bis-2-oxazolidones (II) were purified from suitable solvents (Table II).

Crude bis-2-oxazolidones (II-8, II-9 and II-11) were obtained as viscous pale amber oils upon removal of the DMF. In the case of II-10, however, the major portion of crude product precipitated from DMF on cooling the reaction mixture to room temperature.

Acknowledgment.

REFERENCES

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(2) L. N. Grobov, A. P. Sineokov and V. S. Etlis, Russ. Chem. Rev. English Transl., 35, 671, (1966).

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(4) The pmr spectra were not obtained in all cases due to insolubility.

(5) R. Oda, S. Tokiura, A. Miyasu and M. Okano, Kobunshi Kaqaku, 17, 72 (1960); Chem. Abstr., 55, 16516a (1961).

(6) Melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 337 Spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville 21, Tenn. The pmr spectra were determined on a Varian A-60 spectrometer and where indicated on a Japan Electron Optics Lab 4H-100 spectrometer. TMS was used as an internal standard and deuteriochloroform as a solvent.