# The Preparation and Attempted Polymerization of Some 3-(Substituted amino)-2-oxazolidinones[1]

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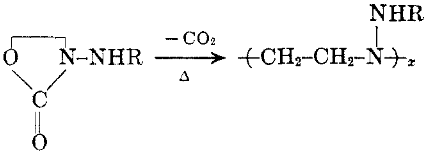
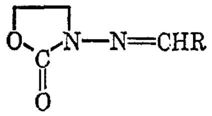
The thermal decarboxylation of 2-oxazolidinone and its 3-substituted derivatives to poly(ethyleneimine) and poly(N-substituted ethyleneimines) is a well-documented process.[2] In 1963, Evans and Jones[3] prepared poly(ethylenehydrazine) (II) by thermal decarboxylation of 3-amino-2-oxazolidinone[4] (I). We have found that 3-(monosubstituted amino)-2-oxazolidinones (III) undergo similar reactions to give low molecular weight polymers. On the other hand, 3-(disubstituted amino)-2-oxazolidinones could not be decarboxylated below their degradation temperatures.



3-Acetamido-2-oxazolidinone[5] (IIIa), 3-diacetamido-2-oxazolidinone (IIIb), and 3-benzamido-2-oxazolidinone (IIIc) were prepared by standard techniques. The monoalkylated compounds, 3-methylamino-2-oxazolidinone (IIId) and 3-ethylamino-2-oxazolidinone (IIIe), were obtained by catalytic hydrogenation of 3-methylideneamino-2-oxazolidinone[6] (IVa) and 3-ethylideneamino-2-oxazolidinone (IVb). Properties and yields of compounds III are given in Table I. 3-Dimethylamino-2-oxazolidinone (IIIf) was prepared by cyclization of (2-chloroethyl)-3,3-dimethylcarbazate.[7]

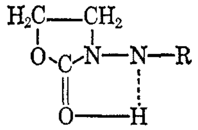


IVa, $R = CH_3$
b, $R = C_2H_5$

The acetamido (IIIa) and benzamido (IIIc) compounds both decarboxylated readily at a temperature of about 230°, and carbon dioxide evolution was completed very rapidly (5 and 12 min, respectively). Both reactions gave hard, brittle products whose microanalyses and infrared spectra were consistent with poly(N-substituted ethylenehydrazines) (V, properties given in Table II). However, molecular weight determinations[8] indicated that the average degree of polymerization of the acetamido derivative (Va) was only about 2 and that of the benzamido derivative (Vb) about 3. Attempted polymerization at higher temperatures resulted in monomer degradation, while at lower temperatures the products obtained were essentially the same.

As an intermediate case, the methylamino compound (IIId) required 1 hr at 230° for complete decarboxylation. The product polymer was a highly viscous, brown liquid. Microanalysis and infrared were in agreement with structure Vc. Molecular weight was consistent with a pentamer.[8] The ethylamino compound IIIe required a temperature of about 250° for decarboxylation, and at this temperature the monomer degraded rapidly. Under these conditions, the desired polymer could not be isolated free of monomer degradation products. The diacetamido (IIIb) and dimethylamino (IIIf) analogs did not decarboxylate under similar conditions.

The failure of IIIb and IIIf to decarboxylate, coupled with the more ready decarboxylation of IIIa and IIIe compared with IIId and IIIc, suggests involvement of the amino hydrogen in the reaction. One possibility is that this hydrogen participates in formation of a five-membered hydrogen-bonded ring (VI). This, in turn, would polarize the carbonyl carbon and facilitate decarboxylation. The electron-attracting acetamido (IIIa) and benzamido (IIIc) substituents should be more favorable for ring formation than the electron-donating methyl (IIId) and ethyl (IIIe) substituents. The disubstituted-amino compounds IIIb and IIIf would be unable to form the ring. However, insufficient evidence exists to distinguish between this and other plausible mechanisms.



VI

Despite its very low molecular weight, poly(N-methylethylenehydrazine) (Vc), interestingly, had some elastomeric properties. The polymer showed great extensibility and slight but definite retractability. For comparison, poly(ethylenehydrazine) (II) was prepared by a modification of the Evans and Jones[3] procedure. The polymer was a solid elastomer of mol wt 960. Possession of elastomeric properties in materials of such low molecular weight is highly unusual and could arise from very strong interchain hydrogen bonding.

## Experimental Section[9]

**3-Amino-2-oxazolidinone** (I).—Compound I was prepared in 43% yield from 2-hydroxyethylhydrazine and diethylcarbonate by the method of Gever:[4] mp 68–70°.

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[1] This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, under Contract NOrd 18728, and was monitored by the Bureau of Naval Weapons, RMMP, under Contract NOw 65–0277-c.

[2] J. I. Jones, *Chem. Ind.*, (London), 1454 (1956); M. Crowther and W. R. Nummy, U. S. Patent 2,860,839 (1957), *Chem. Abstr.*, **52**, 3405 (1958); R. Oda, M. Miyanoki, and M. Okano, *Bull. Chem. Soc. Japan*, **35**, 1910, 1915 (1962).

[3] R. F. Evans and J. I. Jones, *J. Chem. Soc.*, 3523 (1963).

[4] G. Gever, U. S. Patent 2,742,462 (1956); *Chem. Abstr.*, **50**, 10787 (1956).

[5] G. Gever and C. J. O'Keefe, U. S. Patent 2,927,110 (1960); *Chem. Abstr.*, **54**, 12158 (1960).

[6] B. Hellinghuizer-Gerriesen, British Patent 862,206 (1961); *Chem. Abstr.*, **55**, 1511 (1961).

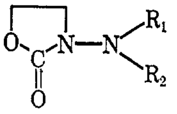
[7] R. Delaby, F. Brustlein, C. Warolin, and P. Chabrier, *Bull. Soc. Chim. France*, 2056 (1961).

[8] Number-average molecular weight determined by thermistor micromethod: A. Wilson, L. Bini, and R. Hofstader, *Anal. Chem.*, **33**, 135 (1961).

[9] Melting points were taken on a Fisher-Johns apparatus and are corrected. Infrared spectra were taken on a Perkin-Elmer Model 137 Infracord spectrophotometer. Microanalyses and molecular weights were by Research Service Department, Central Research Division, American Cyanamid Co.

TABLE I

3-(SUBSTITUTED AMINO)-2-OXAZOLIDINONES

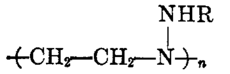


III

| Compound | $R_1$ | $R_2$ | Bp (mm) or mp, °C | Yield, % | Calcd, % C | Calcd, % H | Calcd, % N | Found, % C | Found, % H | Found, % N |
|---|---|---|---|---|---|---|---|---|---|---|
| IIIa | $COCH_3$ | H | 120–122 | 80 | ... | ... | ... | ... | ... | ... |
| IIIb | $COCH_3$ | $COCH_3$ | 91–92 | 68 | 45.16 | 5.38 | 15.05 | 45.28 | 5.57 | 15.40 |
| IIIc | $COC_6H_5$ | H | 178–180 | 65 | 58.25 | 4.85 | 13.59 | 58.25 | 5.17 | 13.49 |
| IIId | $CH_3$ | H | 185–187 (1.7) | 67 | 41.38 | 6.89 | 24.14 | 41.29 | 6.83 | 24.39 |
| IIIe | $C_2H_5$ | H | 77–79 (0.7) | 68 | 46.16 | 7.69 | 21.54 | 46.06 | 7.38 | 21.60 |
| IIIf | $CH_3$ | $CH_3$ | 71–73 | 79 | ... | ... | ... | ... | ... | ... |

TABLE II

POLY(SUBSTITUTED AMINOETHYLENEHYDRAZINE)



$$\left(CH_2-CH_2-\overset{NHR}{\overset{|}{N}}\right)_n$$

V

| Polymer | R | Physical state | Calcd, % C | Calcd, % H | Calcd, % N | Found, % C | Found, % H | Found, % N | Mol wt Calcd | Mol wt Found |
|---|---|---|---|---|---|---|---|---|---|---|
| Va | $COCH_3$ | Hard, brittle solid | 47.98 | 8.05 | 27.99 | 45.89 | 7.70 | 25.84 | $(100.1)_x$ | 206 |
| Vb | $COC_6H_5$ | Hard, brittle solid | 66.65 | 6.21 | 17.27 | 66.40 | 6.47 | 17.48 | $(162.2)_x$ | 467 |
| Vc | $CH_3$ | Highly viscous liquid | 50.00 | 11.11 | 38.88 | 49.82 | 9.74 | 37.03 | $(72.1)_x$ | 350 |

**Poly(ethylenehydrazine) (II).**—Polymer II was prepared by the following modification of the method of Evans and Jones.[3] Eighteen grams (0.176 mole) of I was heated at 210° in a nitrogen atmosphere. Gas evolution commenced after 5 min and continued for about 15 min. The reaction product was then heated at 100° *in vacuo* for 18 hr to sublime unreacted monomer. The residue was a yellow elastomer (9.0 g, 88%) and showed no carbonyl absorption in the infrared.

*Anal.* Calcd for $(C_2H_6N_2)_x$: C, 41.38; H, 10.34; N, 48.28. Found: C, 41.51; H, 9.72; N, 47.75.

**3-Acetamido-2-oxazolidinone (IIIa)** was prepared from I and acetic anhydride by the method of Gever and O'Keefe.[5]

**3-Diacetamido-2-oxazolidinone (IIIb).**—Acetic anhydride (54.0 g, 0.53 mole) was added with cooling to 20.4 g (0.20 mole) of I. After 5 days, acetic acid and excess anhydride were stripped *in vacuo*. Recrystallization of the residue from absolute ethanol gave 25.2 g of white crystals.

**3-Benzamido-2-oxazolidinone (IIIc).**—Benzoyl chloride (36.6 g, 0.26 mole) was added to a solution of I (15.0 g, 0.18 mole) in water (75 ml). A precipitate immediately formed. The mixture was made alkaline with 100 ml of 5 *N* sodium hydroxide and filtered. The solid product was washed with water, dried *in vacuo*, and recrystallized from alcohol to give 24.1 g of white crystals.

**3-Methylideneamino-2-oxazolidinone (IVa)** was prepared in 47% yield from I and formaldehyde by the method of Hellinghuizer-Gerriesen:[6] mp 92–94°.

**3-Methylamino-2-oxazolidinone (IIId).**—A mixture of IVa (51 g, 0.45 mole), 5% Pd–C (20 g), and absolute methanol (600 ml) was charged to a stainless steel autoclave. The autoclave was pressured to 100 psig with hydrogen and rocked for 2 hr, repressurizing as necessary. After 2 hr, the hydrogen uptake was complete and quantitative. The catalyst was filtered, and the methanol was then stripped. Vacuum distillation of the residue gave 34.5 g of water-white, viscous liquid.

**3-Ethylideneamino-2-oxazolidinone (IVb).**—A solution of I (5.1 g, 0.050 mole) and acetaldehyde (8.8 g, 0.20 mole) in 100 ml of absolute alcohol was refluxed 20 hr. Evaporation of the alcohol gave a pale yellow solid. Recrystallization from methanol yielded 5.7 g (89%) of small, white crystals, mp 93–95°.

*Anal.* Calcd for $C_5H_8N_2O_2$: C, 46.87; H, 6.25; N, 21.87. Found: C, 46.76; H, 6.13; N, 21.77.

**3-Ethylamino-2-oxazolidinone (IIIe)** was prepared from IVb in a manner identical with the preparation of IIId above. From 12.8 g (0.10 mole) of IVb was obtained 8.8 g of IIId, a clear, viscous liquid.

**3-Dimethylamino-2-oxazolidinone (IIIf)** was prepared by sodium ethoxide cyclization of (2-chloroethyl)-3,3-dimethylcarbazate by the method of Delaby, *et al.*[7]

**Decarboxylation of IIIa and IIIb. Preparation of Va and Vb.**—A 5-g sample of the oxazolidinone was heated at 230° in a nitrogen atmosphere. The effluent carbon dioxide was passed through a trap containing barium hydroxide solution so as to follow the reaction by precipitation of barium carbonate. After gas evolution was completed, the polymeric residues were heated at 100° *in vacuo* for 48 hr to sublime unreacted monomer. Both Va and Vb were hard, brittle, amber-colored solids. Their infrared spectra showed complete absence of the $1740\text{-cm}^{-1}$ ring carbonyl band of IIIa and IIIc.

**Decarboxylation of IIId. Preparation of Vc.**—A sample of IIId was heated for 1 hr at 230° in a nitrogen atmosphere. The temperature was lowered to 100°, and the system was placed under vacuum. Two days was required for complete removal of unreacted monomer as finally indicated by the absence of a carbonyl band in the infrared spectrum of the product. Polymer Vc was a highly viscous, dark brown liquid.

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# Trimethylsilyl Derivatives of Salicylic Acid

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The preparation of trimethylsilyl derivatives of salicylic acid has been reported by Burkhard[1] and by Mehrotra and Pant.[2] The first of these workers found that stirring salicylic acid with excess trimethylchlorosilane in pyridine for several hours at room tempera-

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(1) C. A. Burkhard, *J. Org. Chem.*, **22**, 592 (1957).

(2) R. C. Mehrotra and B. C. Pant, *J. Indian Chem. Soc.*, **40**, 623 (1963).