tive of acetoacetic ester with β-carbalkoxypropionyl chloride with subsequent removal of the acetyl group by ammonolysis;[4] (b) Acylation of the magnesium enolate of malonic ester with the same acid chloride, followed by decarbalkoxylation by thermal decomposition in the presence of β-naphthalenesulfonic acid;[5,6] and (c) Saponification and decarboxylation or cleavage of the acylated intermediate (prepared by any method above) to the β-ketoadipic acid, followed by esterification.[3]

While the magnesium enolate method (b) appears to be the most facile, this laboratory has never been able to realize the yields reported, nor were the results consistent. Successful decomposition of the tricarboxylic ester intermediate presented the most difficulty and in many cases only tar resulted.

It has been found that the desired compound can be readily prepared in quantity by employing the procedure for the synthesis of ethyl diacetylacetate.[7] In this particular case, the magnesium enolate of methyl acetoacetate and β-carbomethoxypropionyl chloride were used. The resulting intermediate was treated with gaseous ammonia as in method (a). In spite of the relatively low yield (38% over-all) the procedure has certain merits. No isolation of intermediate is required, and except for the final distillation, the preparation can easily be completed in one day. The method is quite satisfactory for the methyl ester; in one experiment using the corresponding ethyl esters only a 25% over-all yield of diethyl β-ketoadipate was obtained. This was not investigated further.

EXPERIMENTAL[8]

Dimethyl β-ketoadipate. To 30 g. (1.23 moles) of magnesium metal turnings and 287 g. (2.47 moles) of methyl acetoacetate in 800 ml. of dry benzene was added all at once 565.8 g. (3.76 moles) of β-carbomethoxypropionyl chloride[9] and the mixture refluxed for 3.5 hr. on the steam bath. Provision was made for the removal of hydrogen chloride, which was evolved. During this time additions of fresh magnesium metal were made as follows: 7.5 g. after 1.5 hr. and 15 g. after 2.5 hr. After cooling, as much of the benzene solution as possible was decanted, and the residue treated with water and ether. The solutions were combined after filtering from unused magnesium. The separated organic layer was washed with water, 5% sodium bicarbonate solution, and finally with water, and dried over anhydrous sodium sulfate. The filtered solution was cooled to 0° and dry ammonia passed in for 40 min. After standing at room temperature for 30 min., the reaction mixture was washed with water until neutral and dried over anhydrous sodium sulfate. Removal of the solvent and distillation through a 30-cm. Vigreux column gave 174.5 g. (37.8%) of product boiling at 114–126°/0.8 mm. with most of the material distilling at 119–120° (reported 122° at 0.5 mm.[1]); n_D^{25} 1.4414. It gave a reddish-brown color with ferric chloride solution.

Anal. Calcd. for $C_8H_{12}O_5$: C, 51.06; H, 6.43. Found: C, 51.03; H, 6.45.

The *1-phenyl-3-(β-carbomethoxyethyl)-pyrazolone* was obtained in 70% yield upon heating an equimolar mixture of the adipic ester and phenylhydrazine on the steam bath for 2 hr. After recrystallization from a mixture of ethyl acetate and petroleum ether, it melted at 79–80°.

Anal. Calcd. for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.50; H, 5.79; N, 11.60.

Saponification and decarboxylation of a sample, and treatment of the resulting oil with semicarbazide hydrochloride, gave the semicarbazone of levulinic acid, m.p. 183–184.5° (reported 184–185°[1]).

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(4) *Cf.* ref. 1,3: P. Ruggli and A. Maeder, *Helv. Chim. Acta*, **25**, 936 (1942); J. R. Stevens and R. H. Beutel, *J. Am. Chem. Soc.*, **65**, 449 (1943); R. Robinson and J. S. Watt, *J. Chem. Soc.*, 1536 (1934).

(5) B. Riegel and W. M. Lilienfeld, *J. Am. Chem. Soc.* **67**, 1273 (1945).

(6) Presumably acylation of *t*-butyl malonate and thermal decomposition in the presence of *p*-toluenesulfonic acid according to the method of D. S. Breslow, E. Baumgarten, and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1286 (1944) would be a source of product.

(7) A. Spassow, *Org. Syntheses*, **Coll. Vol. III**, 390 (1955).

(8) Melting points are uncorrected.

(9) J. Cason, *Org. Syntheses*, **Coll. Vol. III**, 169 (1955).

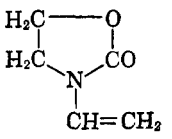
N-Vinyl-2-oxazolidone

ERHART K. DRECHSEL

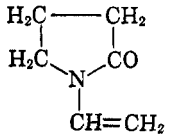
Received December 19, 1956

Widespread attention has been focused upon the rapid growth of the synthetic water-soluble polymer field.[1] In this connection, polyvinylpyrrolidone (PVP) has been given special recognition because of its original use as a blood plasma extender and because of its versatility in many industrial applications. Structurally related compounds are thus of considerable interest.

A recent German patent application[2] describes a process for the preparation of *N*-vinyl-2-oxazolidone and prompts a preliminary disclosure of our own research with this material. The structural similarity between this compound and *N*-vinyl-2-pyrrolidone is shown below:



N-vinyl-2-oxazolidone
(cyclic carbamate)



N-vinyl-2-pyrrolidone
(cyclic amide)

In spite of the structural similarity, these compounds and their polymers belong to different chemical families. The substitution of an oxygen atom for a methylene group within the heterocyclic ring (see formulas above) contributes an additional

(1) Symposia on Water-Soluble Polymers, Polymer and Cellulose Divisions, American Chemical Society, Dallas Meeting, April 8–13, 1956.

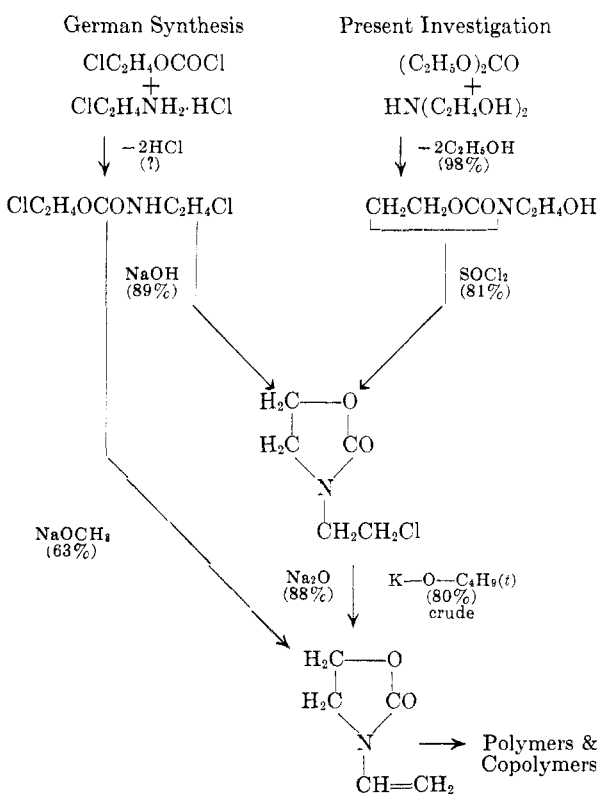
(2) W. Arend and H-G. Trieschmann, German Patent application Klasse 12p Gruppe 3, B340321Vb/12p; Filed 1/8/55, Published 3/29/56.

TABLE I

Compound (Where R Is)	2-Oxazolidone $CH_2CH_2OCON—R$ B.p.	Mm.	n_D^{25}	Ref.	2-Pyrrolidone $CH_2CH_2CH_2CON—R$ B.p.	Mm.	n_D^{25}	Ref.
—H	200°	21		(4)	245°	760	1.486	(5)
	(M.p. 90–91°)			(3)	(M.p. 25°)			(5)
$—C_2H_4OH$	162°	1.0	1.482		142–143°	2.3		(6)
$—C_2H_4Cl$	100°	0.1	1.490		118–119.5°	7.0		(6)
$—CH=CH_2$	70°	0.1	1.494		94–96°	13–14	1.510	(7)
	100–105°	1.3		(2)	148°	100		(7)
	(M.p. *ca.* −15°)				(M.p. 13.5°)			(7)
$[—CH(—)—CH_2—]_n$	Polymers and copolymers are readily formed. Homopolymers are water-soluble. Homopolymers are complexing agents.							

pair of unshared electrons to the molecular structure and provides a basis for differences in chemical and physical properties. Moreover, hydrolysis of the polymers leads to entirely dissimilar products; *e.g.*, polyvinyloxazolidone (PVO) yields an ethanolamine derivative while PVP yields a γ-aminobutyric acid derivative. The properties of both monomers and their key intermediates, together with qualitative polymer characteristics, are shown in Table I; infrared data on the oxazolidone derivatives are shown in Fig. 2.

FIG. 1



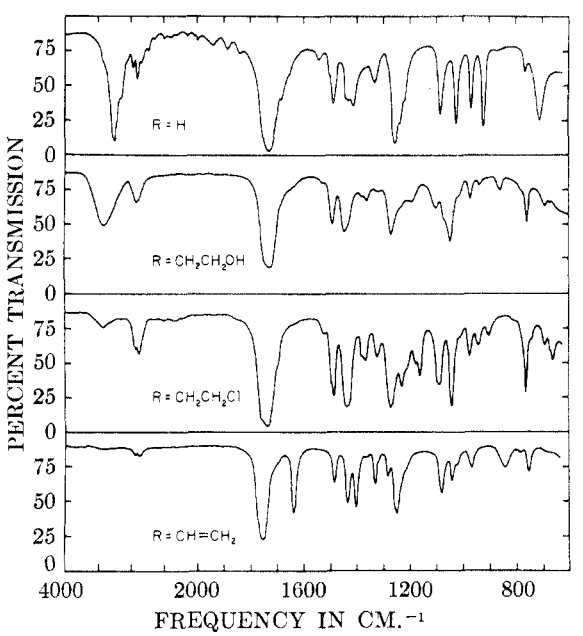


FIG. 2. INFRARED SPECTRA OF KEY OXAZOLIDONE INTERMEDIATES, $CH_2CH_2OCON—R$

Inspection of the vinyloxazolidone structure indicates several possible synthetic routes based upon readily available raw materials. Unfortunately, several attempts at direct vinylation of the parent oxazolidone heterocycle with acetylene were unsuccessful. This observation is confirmed by the German application.

The synthesis of *N*-vinyl-2-oxazolidone herein reported was developed some time ago and in some respects parallels a laboratory synthesis for *N*-vinyl-2-pyrrolidone.[6] The relationship between our method for preparing *N*-vinyl-2-oxazolidone and the German one is shown in Figure 1.

(3) S., Gabriel, *Ber.*, **21**, 568 (1888); *Beilstein* **27**, 135 (259).
(4) L. Knorr, and P. Rössler, *Ber.*, **36**, 1281 (1903).
(5) General Aniline & Film Data Sheet B-105 (August 1953).
(6) B. Puetzer, *et al.*, *J. Am. Chem. Soc.*, **74**, 4959 (1952).
(7) General Aniline & Film Data Sheet B-104 (August 1954).

EXPERIMENTAL

N-(2'-Hydroxyethyl)-2-oxazolidone. To 472 g. (4.0 moles) of diethyl carbonate under agitation 420 g. (4.0 moles) diethanolamine was slowly added. The resulting reaction mixture was then heated to reflux and ethanol taken off using a 10-in. column packed with refractory material and fitted with a variable take-off head. In this way, 84% of the ethanol was stripped out with a pot temperature mainly between 110°–120°, and gradually rising to 135°. The remaining ethanol was separated using reduced (aspirator) pressure. The crude product was treated with finely divided decolorizing carbon and filtered hot to yield 513 g. (98.0%) of clear, light-colored *N*-(2'-hydroxyethyl)-2-oxazolidone.

This product was quite suitable for use in subsequent reactions. Initial batches readily distilled at 162°/1.0 mm., n_D^{25} 1.4823; but later runs demonstrated a tendency to decompose during distillation. These data compare favorably with those reported in the patent literature.[8,9]

Anal. Calcd. for $C_5H_9O_3N$: C, 45.79; H, 6.92; N, 10.68; Hydroxyl value, 429. Found: C, 45.81; H, 6.89; N, 10.84; Hydroxyl value 428.7.

N-(2'-Chloroethyl)-2-Oxazolidone. A total of 238 g. (2.0 moles) thionyl chloride was gradually added to 262 g. (2.0 moles) *N*-(2'-hydroxyethyl)-2-oxazolidone in 200 ml. dry benzene over a 3-hr. period at 30 ± 5°. The use of an efficient Friedrichs condenser throughout the reaction period is strongly recommended since any thionyl chloride losses give an incomplete reaction and amplify isolation problems. The clear, amber-colored solution resulting from an originally cloudy dispersion was strongly acidic. Even though a slow stream of nitrogen was passed through the reaction mixture overnight, almost a full equivalent of sodium bicarbonate was required for complete neutralization (HCl complex with oxazolidone heterocycle?). The filtrate resulting from the products of this neutralization was combined with additional benzene washings of the sodium chloride salt, clarified with finely divided decolorizing carbon, and stripped of solvent to yield 241 g. (80.6%) of a light amber-colored liquid *N*-(2'-chloroethyl)-2-oxazolidone. This material was readily distilled, b.p. 100°/0.1 mm., n_D^{25} 1.4900.

Anal. Calcd. for $C_5H_8O_2NCl$: C, 40.15; H, 5.39; N, 9.37; Cl, 23.70. Found: C, 39.48; H, 5.45; N, 9.46; Cl, 24.65. Excess Cl equivalent to 1.39% (combined?) HCl.

N-Vinyl-2-oxazolidone. To a previously* prepared solution of potassium *tert*-butoxide[10] in *tert*-butanol, made by reacting 40 g. (1.02 moles) potassium metal with 700 ml. dry *tert*-butanol, 150 g. (1.002 moles) *N*-(2'-chloroethyl)-oxazolidone was added slowly over a 2.5-hr. period. The initial exothermic reaction carried the temperature from 60° to 85° (reflux), and this latter temperature was maintained during most of the addition period. Reflux was then continued for an additional 20 hr. when a titration indicated the reaction to be 88% complete. The reaction slurry was then filtered and the solid potassium chloride thoroughly washed with additional solvent. Combined washings and filtrate were then treated with finely divided decolorizing carbon, and stripped of solvent to yield 90 g. (79.6%) of crude, amber-colored *N*-vinyl-2-oxazolidone. This liquid readily distilled at 70°/0.1 mm., n_D^{25} 1.4939. A cooling bath indicated the m.p. of this distilled product to be approximately −15°. An infrared curve showed strong absorption at 1620 cm.$^{-1}$ characteristic of the CH_2=CH— group.

Anal. Calcd. for $C_5H_7O_2N$: C, 53.09; H, 6.24; N, 12.38. Found: C, 52.54; H, 6.46; N, 12.42.

Homopolymerization of N-vinyl-2-oxazolidone. To a solution of 20 g. of *N*-vinyl-2-oxazolidone in 80 g. of xylene was added 0.60 g. (3% on weight of monomer) of α,α'-azobisisobutyronitrile (catalyst). The resulting clear solution was heated on a steam bath (95°) under a reflux condenser for 3 hr. The white solid polymer which precipitated from solution during the heating period was filtered and washed thoroughly with fresh xylene. After drying under reduced pressure, the poly(*N*-vinyl-2-oxazolidone) weighed 14.1 g. (70.5%). The dried material was found to be water soluble. The molecular weight of this polymer was about 1250 by microisopiestic measurements. Infrared confirmed the structure as that of poly(*N*-vinyl-2-oxazolidone).

Additional *N*-vinyl-2-oxazolidone polymerizations have indicated that homopolymers with molecular weights ranging from 450 to over 100,000 can be formed. All of the products were water soluble, white solids.

Additional polymerization characteristics of N-vinyl-2-oxazolidone. Exposure of N-vinyl-2-oxazolidone monomer droplets to air gave clear, solid, orange-colored beads after several days' exposure. *N*-vinyl-2-oxazolidone when heated to 80° in the presence of benzoyl peroxide gave dark viscous liquids. Using the same conditions, α,α'-azobisisobutyronitrile gave clear, tough, orange-colored, water soluble glasses.

When a solution of one part *N*-vinyl-2-oxazolidone in four parts acrylonitrile was heated to 80° in the presence of α,α'-azobisisobutyronitrile, a vigorous evolution of heat resulted. The product, in part, was a rubbery, colorless, translucent mass which was water insoluble.

NEW PRODUCT DEVELOPMENT DEPARTMENT
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(8) J. R. Caldwell, U. S. Patent **2,656,328** Ex. 3 (1953); *Chem. Abstr.*, **48**, 2415 (1954).

(9) J. B. Bell, and J. D. Malkemus, U. S. Patent **2,755,286** Ex. IV & V (1956).

(10) S. M. McElvain and A. N. Bolstad, *J. Am. Chem Soc.*, **73**, 1988 (1951).

Lithium Cleavages of Some Heterocycles in Tetrahydrofuran

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Cleavages of heterocycles using various media and cleaving agents has often proved to be a valuable tool in synthesis and structure proof.

Using lithium in refluxing ether over a period of 22 hr., there were obtained excellent yields of 3,4-benzocoumarin from dibenzofuran when the reaction was terminated by carbonation. When refluxing dioxane was used as the solvent, only 2-hydroxybiphenyl was obtained upon hydrolysis or carbonation after 12 hr.[1]

Dibenzo-*p*-dioxin has been cleaved by lithium in refluxing ether after 24 hr. to yield upon carbonation 23% of 2-hydroxy-2'-carboxydiphenyl ether.[2] This molecule could presumably be cleaved in refluxing dioxane.

In refluxing ether lithium does not cause the cleavage of dibenzothiophene even after 36 hr. However, dibenzothiophene can be cleaved by lithium in refluxing dioxane over a period of 12 hr. to yield biphenyl and 2-mercaptobiphenyl

(1) H. Gilman and D. Esmay, *J. Am. Chem. Soc.*, **75**, 2947 (1953).

(2) Unpublished studies.