known reductive cleavage of 2-hydroxy-3-naphthoic acid to *o*-phenylene acetic propionic acid. This is converted to a dinitrile which is cyclized by the Ziegler process; the resulting isomeric imino nitriles, whose probable structures are indicated by certain transformations, both yield benzocycloöctanone-3 on exhaustive acid hydrolysis.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS. RECEIVED OCTOBER 16, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE, THE COLLEGE OF THE CITY OF NEW YORK]

The Preparation of Aromatic Oxazolidines

BY M. MELTSNER, E. WALDMAN AND CHESTER B. KREMER

The establishment of aminophenyl oxazolines as local anesthetics[1] leads to the belief that compounds of closely related structure might possess interesting physiological properties. Some of these related compounds have already been studied, mainly by Adams and his co-workers.[2] These include the aminophenyl pentoxazolines, the aminophenyl thiazolines and thiazines and the aminophenyl oxazoles and thiazoles. The aminophenyl oxazolidines have not been similarly investigated. Such a study should be of interest.

TABLE I

OXAZOLIDINES

Oxazolidine	Color	B. p. °C.	B. p. Mm.	M. p., °C.	Mol. formula	Nitrogen analyses, % Theory	Found
2-Phenyl	Yellow	157	(24 mm.)		$C_9H_{11}ON$	9.39	9.56
2-(*m*-Tolyl)-	Yellow	159	(14 mm.)		$C_{10}H_{13}ON$	8.58	8.71
2-(*p*-Tolyl)-	Yellow	153	(15 mm.)		$C_{10}H_{13}ON$	8.58	8.78
2-(*o*-Methoxyphenyl)-	Yellow	195	(27 mm.)		$C_{10}H_{13}O_2N$	7.81	7.87
2-(*p*-Methoxyphenyl)-	Yellow	180	(12 mm.)		$C_{10}H_{13}O_2N$	7.81	7.87
2-(*p*-Hydroxyphenyl)-	Cream			169	$C_9H_{11}O_2N$	8.48	8.56
2-(*m*-Nitrophenyl)-	White			73	$C_9H_{10}O_3N_2$	14.28	14.12
2-(*o*-Nitrophenyl)-	White			58	$C_9H_{10}O_3N_2$	14.28	14.22
ADDITION COMPOUNDS							
From							
Salicylic aldehyde	Yellow	180	(13 mm.)		$C_9H_{13}O_3N$	7.64	7.50
o-Chlorobenzaldehyde	Yellow	178	(22 mm.)		$C_9H_{12}O_2NCl$	7.00	7.04

While much work is reported in the literature dealing with the preparation of aliphatic oxazolidines, there is surprisingly little on the aromatic analogs, the only compound of this type reported being phenyl oxazolidine.[3] The method of preparation for the latter was found impractical in attempting to synthesize others of the aromatic series. This paper deals with an improved method for preparing substituted phenyl oxazolidines and reports the synthesis of seven new ones. A report upon the physiological possibilities of the aminophenyl derivatives will follow at a later date.

In the course of this work, it was found that *o*-chlorobenzaldehyde and salicylic aldehyde yielded only addition compounds. This may be due to the existence of these compounds in a chelated form. All other aldehydes investigated proceeded to the oxazolidine stage by dehydration.

The oxazolidines are in general yellow, or slightly yellow, liquids or solids of a basic nature, easily hydrolyzed by water or alcohol. They are insoluble (or hydrolyzed) in water; soluble in benzene and chloroform. Due to hydrolysis, positive reactions for monoethanolamine and the aldehydes are obtained with bromine water, potassium permanganate, silver nitrate and Schiff reagent. Hydrolysis also accounts for the fact that the oxazolidines yield, in general, the picrate of monoethanolamine and the phenylhydrazone of the aldehyde.

Experimental

***p*-Hydroxyphenyl oxazolidine.**—*p*-Hydroxybenzaldehyde was dissolved in butanol and an equivalent quantity of

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[1] M. T. Leffler and Roger Adams, THIS JOURNAL, **59**, 2252 (1937).

[2] A. Novelli and Roger Adams, *ibid.*, **59**, 2259 (1937); S. H. Babcock and Roger Adams, *ibid.*, **59**, 2260 (1937); B. S. Friedman, Meredith Sparks and Roger Adams, *ibid.*, **59**, 2262 (1937).

[3] L. Knorr and H. Matthes, *Ber.*, **34**, 3487 (1901).

monoethanolamine slowly added. The mixture was refluxed for four hours and on cooling deposited yellow crystals. Recrystallizations from butanol yielded the oxazolidine, m. p. 169°.

The other oxazolidines were made in a similar manner and are reported in Table I. Butyl ether or a mixture of butyl ether and butanol may be used as solvents and after refluxing, removed under vacuum.

Summary

1. An improved method for making substituted phenyl oxazolidines is reported.

2. Salicylic aldehyde and *o*-chlorobenzaldehyde, due to chelation, form addition compounds instead of oxazolidines.

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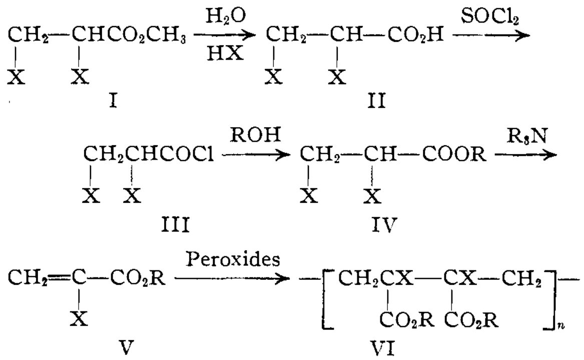
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polymers of the α-Haloacrylic Acids and their Derivatives[1]

BY C. S. MARVEL, JOSEPH DEC, H. G. COOKE, JR.,[2] AND JOHN CHARLES COWAN[3]

Despite general recognition of the fact that substitution of halogen for hydrogen in a vinyl group usually accelerates the speed of polymerization, interest in the poly-α-haloacrylates has been dormant until recently. The discovery[4] that the polymers of methyl α-chloro- and α-bromoacrylates have the "head to head, tail to tail" structure has stimulated further work on the haloacrylic acids and their acid chlorides and esters in order to learn their propensity to polymerize and the nature of the polymers.

The starting materials used in our work were methyl α,β-dichloropropionate and methyl α,β-dibromopropionate which were conveniently prepared by the addition of halogen to technical methyl acrylate. These esters have long been known[5,6] but the present preparative procedures have apparently not been described before. The alkyl haloacrylates (V) were prepared from the methyl dihalopropionates (I) by the following steps



$$\underset{\mathrm{I}}{\underset{\mathrm{X}}{\mathrm{CH_2}}\text{—}\underset{\mathrm{X}}{\mathrm{C}}\mathrm{HCO_2CH_3}} \xrightarrow[\mathrm{HX}]{\mathrm{H_2O}} \underset{\mathrm{II}}{\underset{\mathrm{X}}{\mathrm{CH_2}}\text{—}\underset{\mathrm{X}}{\mathrm{CH}}\text{—}\mathrm{CO_2H}} \xrightarrow{\mathrm{SOCl_2}}$$

$$\underset{\mathrm{III}}{\underset{\mathrm{X}}{\mathrm{CH_2}}\underset{\mathrm{X}}{\mathrm{C}}\mathrm{HCOCl}} \xrightarrow{\mathrm{ROH}} \underset{\mathrm{IV}}{\underset{\mathrm{X}}{\mathrm{CH_2}}\text{—}\underset{\mathrm{X}}{\mathrm{CH}}\text{—}\mathrm{COOR}} \xrightarrow{\mathrm{R_3N}}$$

$$\underset{\mathrm{V}}{\mathrm{CH_2{=}}\underset{\mathrm{X}}{\mathrm{C}}\text{—}\mathrm{CO_2R}} \xrightarrow{\text{Peroxides}} \underset{\mathrm{VI}}{\text{—}\left[\mathrm{CH_2}\underset{\mathrm{CO_2R}}{\mathrm{CX}}\text{—}\underset{\mathrm{CO_2R}}{\mathrm{CX}}\text{—}\mathrm{CH_2}\right]_n\text{—}}$$

To obtain the phenyl ester (IV, R = C_6H_5) the acid chloride (III) was treated with phenol and pyridine. Removal of halogen acid from the dihaloesters (IV) was conveniently accomplished with such amines as quinoline, quinaldine or dimethylaniline. α-Chloroacrylyl chloride was obtained from α,β-dichloropropionyl chloride by heating with dimethylaniline.

The esters of the α-haloacrylates studied were the ethyl, *s*-butyl, cyclohexyl, phenyl and β-chloroethyl. When carefully purified, all of these esters polymerized with comparative ease either as pure liquids or in solution. Ultraviolet light, heat and benzoyl peroxide generally accelerated the rate of polymerization. The polymers formed by bulk polymerization were clear, hard, glassy products which were highly resistant toward scratching. These polymers have indices of refraction in the range of 1.5 to 1.6. The polymers formed in dioxane solution were precipitated by the addition of either alcohol or ether.

The polymers of the esters sometimes contained less halogen than the corresponding monomer. This may be the result of lactone formation along the chain by the loss of alkyl halide or it may have been due to loss of hydrogen halide to give unsaturation in the chain. The polymers formed slowly in solution in dioxane were generally lower in halogen than those formed rapidly by bulk polymerization under ultraviolet light.

The polymeric esters usually remained clear for long periods of time. Some samples darkened after standing for several months. In general, the polymeric bromo esters were less stable toward light than the chloro esters.

The polymeric α-bromoacrylic acid decomposed rather rapidly and gave a halogen free product. The polymer of α-chloroacrylic acid was water-

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(1) This is the tenth communication on vinyl polymers. For the ninth see THIS JOURNAL, **62**, 2666 (1940).

(2) Du Pont Special Research Assistant in Chemistry, 1940.

(3) Du Pont Special Research Assistant in Chemistry, 1938–1939.

(4) Marvel and Cowan, THIS JOURNAL, **61**, 3156 (1939).

(5) Franklin and Turnbull, *J. Chem. Soc.*, **105**, 459 (1914).

(6) Moureu, Murat and Tampier, *Ann. chim.*, **15**, 221 (1921).