sodium acetate solution are added; the appearance of a blue color indicates a positive test.

A platinum spoon can be advantageously substituted for the loop, using a short heavy piece of platinum wire fused in a glass rod as a handle. After use of the spoon, any fused mixture remaining within is dissolved in dilute hydrochloric acid, and the spoon is then rinsed with distilled water. The spoon is dried, amost filled with sodium potassium carbonate and again fused. After dissolving the carbonate mixture as described above, the spoon is again ready for use.

Instead of sodium acetate, ammonia vapor can be used to neutralize the free mineral acid. The advantages of employing sodium acetate for this purpose are enumerated in the introductory section of this article; however, the use of ammonia vapor does somewhat increase the sensitivity of the test.

If a blue color is obtained upon addition of the solution containing the fused carbonate mixture to the ammonium molybdate, one of the elements has not been completely oxidized and the test should be repeated using a larger excess of sodium peroxide. It is advisable to run a blank test with the wire (or spoon) and the reagents to assure the initial absence of silicates. A saturated sodium acetate solution on standing will dissolve sufficient silica from a glass container to give a weakly positive test; therefore, the sodium acetate reagent should either be stored in a polyethylene bottle or be freshly prepared.

Concentrated sulfuric acid may be employed (with a platinum spoon) to decompose the organosilicon compound to silica,[9] the sensitivity might be slightly increased; however, the use of sodium peroxide is much more convenient.

Other reagents[13] have been suggested as replacements for benzidine to reduce the molybdenum compound and include pyrrole, 2,4-diaminophenol hydrochloride, hydroquinone, *p*-hydroxyphenylglycine, 1-amino-2-naphthol-4-sulfonic acid, 3,7-diaminodibenzofuran and stannous chloride.

In connection with obtaining some idea of the sensitivity of the test under the above-described conditions, 0.1 g. of tetraphenylsilane (and tetraphenylgermane) was fused with sodium potassium carbonate and the fusion mixture was diluted with water to a volume of 10 ml. Aliquots of this solution were then diluted to various concentrations and a test made of these solutions. With the tetraphenylsilane using sodium acetate for neutralization, solutions as dilute as 0.0125 g. of the original sample in 10 ml. gave a positive test; using ammonia vapor for neutralization, solutions diluted to 0.0063 g./10 ml. still gave a positive test. With tetraphenylgermane using sodium acetate, solutions as dilute as 0.0031 g./10 ml. gave a positive test; using ammonia vapor, solutions diluted to 0.0016 g./10 ml. gave a positive test.

TABLE I

ORGANOSILICON COMPOUNDS TESTED[a]

Tetraphenylsilane	Diphenyldi-*n*-dodecylsilane
Triethylsilane	Trimethylphenylsilane
Triethylchlorosilane	Tri-*n*-hexadecylphenylsilane
Diphenyldichlorosilane	2-Trimethylsilyldibenzothiophene-5-dioxide
Triphenylchlorosilane	3-Trimethylsilyldibenzothiophene-5-dioxide
Ethyl silicate	4-Trimethylsilyldibenzothiophene-5-dioxide
Tri-1-naphthyl-*p*-tolylsilane	3-Nitro-4-trimethylsilyldibenzothiophene-5-dioxide
Tri-*o*-tolyl-*p*-anisylsilane	N-(*p*-Triphenylsilylphenyl)-α,α'-dimethylpyrrole
Triphenylphenoxysilane	Triphenyl-(phenylethynyl)-silane
Triphenylbenzyloxysilane	Tetra-(phenylmercaptomethyl)-silane
Triphenyl-*n*-tetradecylsilane	Hexaphenyldisilazane
Triphenyl-*n*-hexadecylsilane	Hexabenzyldisiloxane
Tetra-β-phenylethylsilane	*p,p'*-Di-(trimethylsilyl)-biphenyl
Diphenyldibenzylsilane	Trimethyltriphenylmethylsilane
Tri-γ-phenylpropylphenylsilane	
Diphenyldi-*n*-tetradecylsilane	
Hexaphenyldisilane	
Decaphenyltetrasilane	
Octaphenyltrisilane	
1,1,1-Trimethyl-1,1,1-tri-*o*-tolyldisiloxane	

[a] All of the compounds listed gave a positive test for silicon. Tetraphenyltin and tetraphenyllead were tested and did not give a positive test.

(13) F. J. Welcher, "Organic Analytical Reagents," D. Van Nostrand and Co., Inc., New York, N. Y., 1947, 4 vols.

TABLE II

ORGANOGERMANIUM COMPOUNDS TESTED

Tetraphenylgermane	Triphenyl-β-phenylethylgermane
Hexaphenyldigermane	Triphenyl-*n*-octadecylgermane
Triphenylgermane	Tetra-*n*-dodecylgermane
Triphenylchlorogermane	Tetra-*n*-tetradecylgermane
Triphenylbromogermane	Triphenyl-(triethylsilyl)-germane
Triphenyliodogermane	Triphenyl-(triphenylsilyl)-germane
Triphenylbenzylgermane	Hexaphenyldigermoxane

The organosilicon and organogermanium compounds which have been tested are listed in Tables I and II.

Reagents.[14]—**Ammonium Molybdate Solution.**—Five grams of ammonium molybdate is dissolved in 100 ml. of cold water and poured into 35 ml. of nitric acid (sp. gr. 1.42).

Benzidine Solution.—Five-hundredths of a gram of benzidine or benzidine hydrochloride is dissolved in 10 ml. of glacial acetic and diluted with water to 100 ml.

Sodium Acetate Solution.—A saturated solution is used.

(14) F. Feigl, "Qualitative Analysis by Spot Tests," Elsevier Publishing Co., Inc., Houston, Texas, 1946, p. 252.

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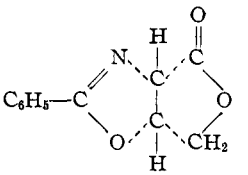
Mutarotation of *cis*-2-Phenyl-4-carboxy-5-hydroxymethyl-2-oxazolines

BY EDWARD E. HAMEL AND EDGAR PAGE PAINTER

RECEIVED JULY 20, 1953

Lactones of two *cis*-2-phenyl-4-carboxy-5-hydroxymethyl-2-oxazolines recently were described.[1] One (αD +254°) was assigned the L-configuration and the other (II, αD −251°) the D-configuration.[2] When I reacted with a base and was then hydro-



L-*cis*-oxazoline (I)

lyzed by acid the amino acid D-*threo*-α-amino-β,γ-dihydroxybutyric (where C_α is used to indicate configuration and not C_β as used formerly[1]) was obtained. If our assignment of the configuration of I is correct, inversion occurred at C_α. Elliott[4] has reported that bases invert C_α of oxazolines prepared from threonine and allothreonine and that the equilibrium favors the trans (*threo*) compound. If the reaction by bases is a mutarotation and I and II are indeed enantiomers, the rate of the reversible reaction

$$\text{L}[C\alpha] \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{D}[C\alpha]$$

is given by

$$k_1 + k_2 = \frac{2.3}{t} \log \frac{a_0 - a_\infty}{a_t - a_\infty}$$

This is the well-known expression describing the mutarotation of sugars.

(1) E. E. Hamel and E. P. Painter, THIS JOURNAL, **75**, 1362 (1953).

(2) In drawing the projection formula of I the convention suggested in the A.C.S. report[3] was followed. While no convention exists for oxazolines I is intended to show the configuration at both optical centers is the same as in L-glyceraldehyde. I is compound VII in a former paper.[1]

(3) *Chem. Eng. News*, **30**, 4524 (1952).

(4) D. F. Elliott, *J. Chem. Soc.*, 62 (1950); 589 (1949).

Rotation changes when I and II were dissolved in 0.526 *M* sodium hydroxide are shown in Fig. 1. The curves are those predicted for enantiomers. The average rate constant ($k_1 + k_2$) for I was 2.50×10^{-3} min.$^{-1}$ and for II 2.53×10^{-3} min.$^{-1}$. The initial three readings gave somewhat high constants, then the individual values were close to the average throughout the run.

To learn whether the mutarotation is a reaction of the anions of I and II and not the lactones aliquots of the solution of I in base were titrated with acid. The volume of acid required to neutralize the solution (phenolphthalein end-point) was the same after 4 minutes as after one hour. The amount of sodium hydroxide consumed in a 10-cc. aliquot at 4 minutes was 0.00098 mole which is close to the calculated 0.00099 mole of oxazoline present. Additional evidence that the lactone ring opened rapidly may be adduced from the rotation. The rotation of I was +254° and of II −251°. The initial readings in Fig. 1 were at 5 and 6 minutes after addition of base.

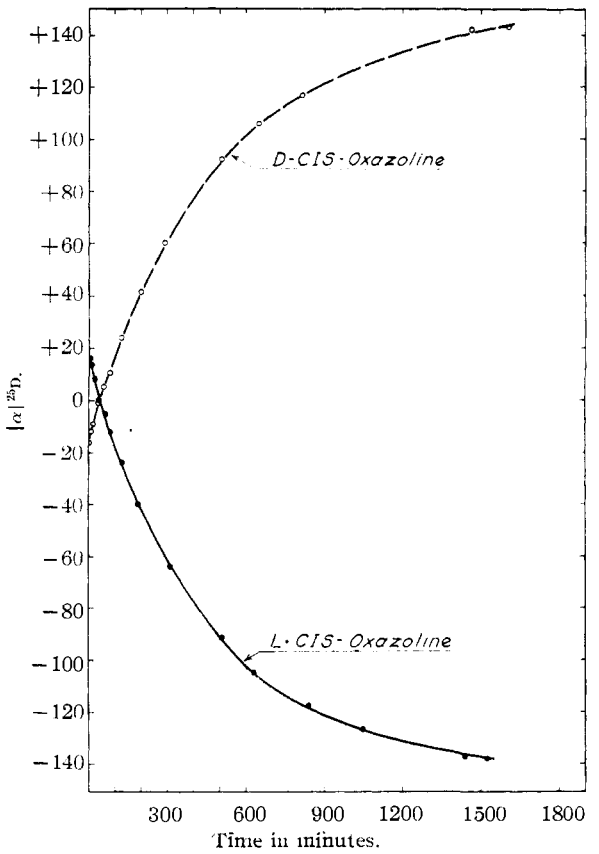
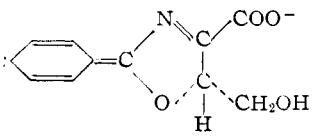


Fig. 1.—Mutarotation of oxazolines in aqueous alcoholic sodium hydroxide solution at 25°.

Whereas peptides and azlactones are racemized by bases, free amino acids and aryl or alkylamido derivatives are relatively stable. Enolization of the anion of I in the manner which appears to satisfactorily explain the racemization of azlactones would lead to a carbanion with both negative charges close together. This does not happen with benzamido derivatives of amino acids. The carbanion in which the charges are widely separated



may be a major contributing species. In view of the similarity of structure of the oxazoline of serine and I and II, it is surprising that Fry[5] reported the methyl ester of the phenyl oxazoline of L-serine did not racemize on alkaline hydrolysis.

The rotations of the anions of I and the corresponding *threo* diastereoisomer are not known so the equilibrium composition cannot be calculated. Only one amino acid (the *threo*) has been obtained from acid hydrolysis of the equilibrium mixture so apparently the equilibrium lies far in favor of the *trans* form.

Experimental

The sodium hydroxide solution contained equal volumes of water and ethanol. Zero time was taken when the solvent was added to the volumetric flask containing the oxazolines, but 2–3 minutes elapsed before the compounds completely dissolved. The solution was transferred to polarimeter tubes and the rotation change followed at 25 ± 0.1°.

(5) E. M. Fry, *J. Org. Chem.*, **15**, 438 (1950).

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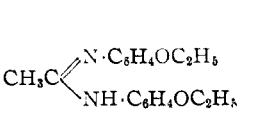
Amidines Derived from Ethylenediamine. I. Diamidines[1]

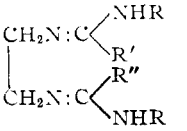
BY ARTHUR J. HILL AND JEAN V. JOHNSTON[2]

RECEIVED AUGUST 12, 1953

The objective of the work described in this paper was to prepare a series of compounds represented by II which might be more useful than phenacaine, the hydrochloride of I as a local anesthetic because, by doubling the number of amidine groups and separating them by a non-toxic bridge, a high activity at a lower and thereby less toxic dosage might result. In choosing the substituent R it seemed desirable to include phenyl and *p*-ethoxy-



I



II

phenyl which are effective in simpler amidines and *p*-carbethoxyphenyl. The effect of aromaticity was studied in regard to R′ and R″ by attaching a phenyl group directly to the amidine carbon and by allowing one and two methylene groups as well as an ether linkage to intervene. The effect of chain branching was studied in the aliphatic series. In only one compound was R′ different from R″. Utilizing the conventional conversion of an amide *via* the chloroimide to an amidine the method of preparation is unique for the synthesis of diamidines from an aliphatic diamine. While this work was in progress, Rao and Wheeler[3] prepared diamidines

(1) From the dissertation presented by Jean V. Johnston for the degree of Doctor of Philosophy, Yale University.

(2) Connecticut College, New London, Connecticut.

(3) H. K. S. Rao and T. S. Wheeler, *J. Chem. Soc.*, 1743 (1937).