Aziridines. XII. The Isomerization of Some *cis*- and *trans*-1-*p*-Nitrobenzoyl-2,3-Substituted Aziridines

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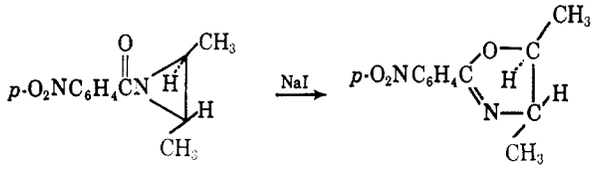
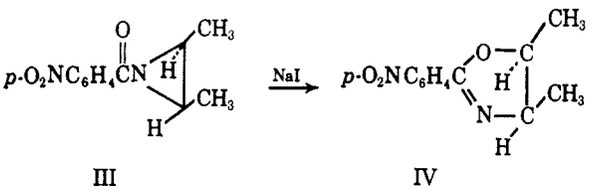
Iodide ion catalyzes the isomerization of *cis*- and *trans*-1-*p*-nitrobenzoyl-2,3-dimethylaziridines and *trans*-1-*p*-nitrobenzoyl-2,3-diphenylaziridine into *cis*- and *trans*-2-*p*-nitrophenyl-4,5-dimethyl-2-oxazolines and *trans*-2-*p*-nitrophenyl-4,5-diphenyl-2-oxazoline respectively. With the same catalyst *cis*-1-*p*-nitrobenzoyl-2,3-diphenylaziridine rearranges into *trans*-2-*p*-nitrophenyl-4,5-diphenyl-2-oxazoline. Alkaline ethanolysis of *erythro*-N-1,2-diphenyl-2-haloethyl-*p*-nitrobenzamides give *trans*-2-*p*-nitrophenyl-4,5-diphenyl-2-oxazoline but alkaline ethanolysis of *threo*-N-1,2-diphenyl-2-chloroethyl-*p*-nitrobenzamide gives only *cis*-1-*p*-nitrobenzoyl-2,3-diphenylaziridine. Acidolysis of *erythro*- and *threo*-N-1,2-diphenyl-2-hydroxyethyl-*p*-nitrobenzamide forms only *trans*-2-*p*-nitrophenyl-4,5-diphenyl-2-oxazoline.

The isomerization of 1-acylaziridines into 2-aryl- or 2-alkyl-2-oxazolines by nucleophiles such as iodide ion, thiocyanate ion, azide ion, or tributylamine is well known.[1-8] Selective rearrangement of 1-aroyl-2-alkyl substituted aziridines into 2-aryl-4-alkyl-2-oxazolines by iodide ion has also been shown to occur.[1,2] A stereochemical study of the rearrangement is now reported in this paper.

trans-1-*p*-Nitrobenzoyl-2,3-dimethylaziridine (I) was isomerized by iodide ion in acetone into *trans*-2-*p*-nitrophenyl-4,5-dimethyl-2-oxazoline (II) in 96% yield and *cis*-1-*p*-nitrobenzoyl-2,3-dimethylaziridine (III) was isomerized solely into *cis*-2-*p*-nitrophenyl-4,5-dimethyl-2-oxazoline (IV). *trans*-1-*p*-Nitrobenzoyl-2,3-diphenylaziridine (V) rearranged into *trans*-2-*p*-nitrophenyl-4,5-diphenyl-2-oxazoline (VI) but quite unexpectedly *cis*-1-*p*-nitrobenzoyl-2,3-diphenylaziridine (VII) also rearranged quantitatively into VI.



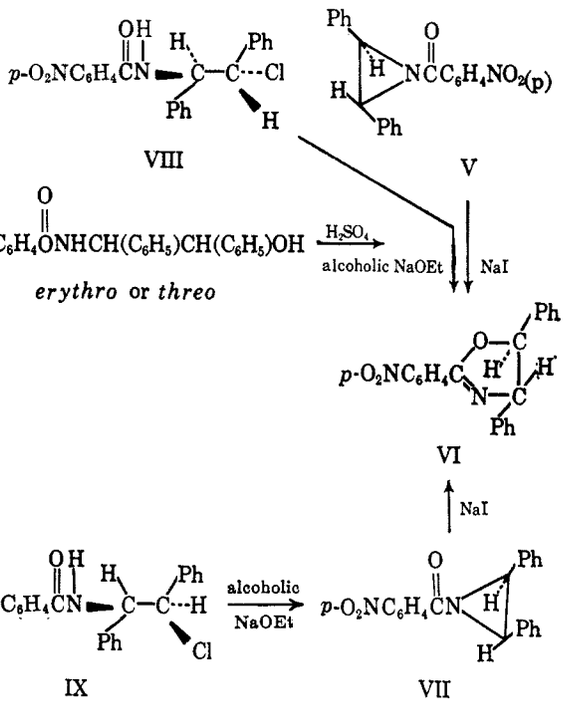
I II



III IV

Authentic samples of the *cis*- and *trans*-oxazolines were prepared by the reaction of ethyl-*p*-nitrobenzimidate with the appropriate *erythro* and *threo* amino alcohols. Imido esters are known to react with *erythro* and *threo* amino alcohols to form *cis*- and *trans*-2-oxazolines, respectively.[9-13]

Alkaline ethanolysis of *erythro*-N-1,2-diphenyl-2-chloroethyl-*p*-nitrobenzamide (VIII) or *erythro*-N-1,2-diphenyl-2-iodoethyl-*p*-nitrobenzamide (VIIIa) also gave the *trans*-oxazoline VI but similar treatment of *threo*-N-1,2-diphenyl-2-chloroethyl-*p*-nitrobenzamide (IX), interestingly, formed the *cis*-aroylaziridine VII.



The *erythro* and *threo* compounds VIII and IX and compounds V and VII were prepared by the reaction of *p*-nitrobenzoyl chloride in alkaline media with the previously characterized *erythro*- and *threo*-1,2-diphenyl-2-chloroethylamines and *trans*- and *cis*-2,3-diphenylaziridines, respectively.[14] *erythro*-1,2-Diphenyl-2-iodoethylamine hydrochloride, the precursor to *trans*-2,3-diphenylaziridine and VIIIa, was prepared by the reduction of the recently described *erythro*-1-azido-2-iodo-1,2-diphenylethane.[15]

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Dissolution of either *erythro-* or *threo*-N-1,2-diphenyl-2-hydroxyethyl-*p*-nitrobenzamide in concentrated sulfuric acid followed by neutralization gave VI.

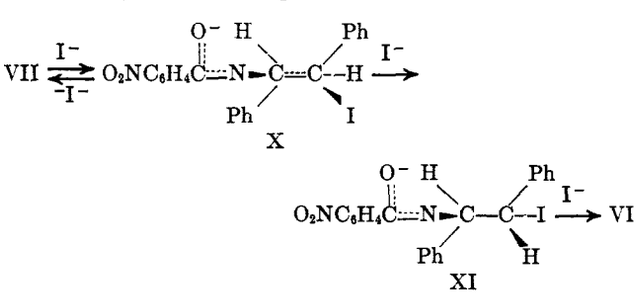
Discussion of Results

The mechanism of the iodide ion catalyzed isomerization of 1-acylaziridines has been postulated as occurring by attack of the nucleophile on the aziridinyl carbon to produce an N-2-iodoethylbenzamido ion which subsequently cyclizes to the oxazoline.[1,2,16] If this be the case, the action of iodide ion on a 1-aroyl-2,3-disubstituted aziridine would involve an inversion of configuration when the iodide ion opens the aziridine ring and another inversion when the formed N-2-iodoethylbenzamido ion is converted to the oxazoline. In other words a *cis*-1-aroyl-2,3-disubstituted aziridine should form a *threo*-N-2-iodoethylbenzamido ion which in turn should yield a *cis*-2-aryl-4, 5-disubstituted-2-oxazoline. Similarly, a *trans*-1-aroyl-2,3-disubstituted aziridine should be transformed into an *erythro*-N-2-iodoethylbenzamido ion which then cyclizes to a *trans*-2-aryl-4,5-disubstituted 2-oxazoline. In harmony with this view *cis*-1-*p*-nitrobenzoyl-2,3-dimethylaziridine rearranged to the corresponding *cis*-oxazoline IV and *trans*-1-*p*-nitrobenzoyl-2,3-dimethyl- and *trans*-1-*p*-nitrobenzoyl-2,3-diphenylaziridine rearranged to the *trans*-oxazolines II and VI, respectively.

The rearrangement of *cis*-1-*p*-nitrobenzoyl-2,3-diphenylaziridine into *trans*-2-*p*-nitrophenyl-4,5-diphenyl-2-oxazoline represents an anomaly to the proposed mechanism. The intermediate *threo*-N-1,2-diphenyl-2-iodoethyl-*p*-nitrobenzamido ion (X) would be expected to yield the corresponding *cis*-oxazoline. However, examination of Fischer–Hirschfelder–Taylor models of X and of *erythro*-N-1,2-diphenyl-2-iodoethylbenzamido ion (XI) revealed considerable steric hindrance toward oxazoline formation for X due to close approach of the phenyl groups. This is not the case for XI.

The alkaline ethanolysis of *threo*-N-1,2-diphenyl-2-chloroethyl-*p*-nitrobenzamide (IX) demonstrated convincingly that steric factors prevent oxazoline formation. Only the *cis* aziridine VII is produced in 94% yield. *threo*-N-1,2-Diphenyl-2-chloroethylbenzamide has also been shown to undergo alkaline ethanolysis to form *cis*-1-benzoyl-2,3-diphenylaziridine.[17] The *erythro* isomer VIII, on the other hand, formed only the *trans*-oxazoline VI.

On the basis of these observations the rearrangement of *cis*-1-*p*-nitrobenzoyl-2,3-diphenylaziridine (VII) by iodide ion into the *trans*-2-*p*-nitrophenyl-4,5-diphenyl-2-oxazoline (VI) can be explained. The *cis*-aziridine VII



reacts with iodide ion to yield the *threo*-N-1,2-diphenyl-2-iodoethyl-*p*-nitrobenzamido ion (X) which is in equilibrium with the aziridine VII and which is prevented sterically from forming the *cis*-oxazoline. The iodide ion can convert X*via* a Finkelstein reaction to the *erythro*-N-1,2-diphenyl-2-iodoethyl-*p*-nitrobenzamido ion XI which then ring closes to the *trans*-oxazoline VI.

For the sake of completeness a control run with authentic *cis*-2-*p*-nitrophenyl-4,5-diphenyl-2-oxazoline and sodium iodide was carried out under the conditions of the isomerization of the 1-aroylaziridines. The *cis*-oxazoline was recovered unchanged—indicative that if formed from X it would have been isolable.

The present study is an example of steric factors governing effectively the course of reaction of ambident N-2-haloethylbenzamido ions. Previous work, especially with carbohydrate derivatives, has shown that the ratio of aziridine to oxazoline formation is dependent on both steric and electronic factors.[18,19] Competitive three-membered and five-membered ring closure has also been observed in the alkaline ethanolysis of *trans*-2-benzamidocyclohexyl toluene-*p*-sulfonate.[20] Various cyclic *trans*-2-iodocarbamates have been found, too, which ring close in the presence of base to an aziridine[21,22] when a five-membered oxazoline could have resulted.[23,24]

Competitive aziridine and thiazoline formation with carbohydrate derivatives has also been observed[25] and a comprehensive group of papers has appeared on the subject.[26,27]

The conversion of both *erythro-* and *threo*-N-2,3-diphenyl-2-hydroxyethyl-*p*-nitrobenzamide in concentrated sulfuric acid to *trans*-2-*p*-nitrophenyl-4,5-diphenyl-2-oxazoline indicates the formation of a common carbonium ion intermediate which subsequently ring closes to the sterically preferable *trans*-oxazoline.

Experimental Section

***trans*-1-p-Nitrobenzoyl-2,3-dimethylaziridine** (I).—To a solution of 2.13 g (0.03 mole) of *trans*-2,3-dimethylaziridine[28] and 3.03 g (0.03 mole) of triethylamine in 50 ml of anhydrous benzene was added portionwise a solution containing 5.57 g (0.03 mole) of *p*-nitrobenzoyl chloride in 50 ml of benzene. The reaction mixture was kept at room temperature for several hours and then the triethylamine hydrochloride was filtered and the benzene filtrate evaporated. The yield of crude I was 6.5 g (98%). Several recrystallizations from hexane gave I melting at 79–81°.

Anal. Calcd for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49; N, 12.72. Found: C, 60.40; H, 5.62; N, 12.51.

***cis*-1-*p*-Nitrobenzoyl-2,3-dimethylaziridine** (III) was prepared analogously as I in quantitative yield using *cis*-2,3-dimethyl-

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(28) The authors thank Professor George K. Helmkamp for samples of these materials.

aziridine.[28] Recrystallization from methanol gave III melting at 143–145°.

Anal. Calcd for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49; N, 12.72. Found: C, 59.87; H, 5.52; N, 13.02.

***cis*-1-*p*-Nitrobenzoyl-2,3-diphenylaziridine (VII)** was synthesized in the same manner as I and III using 5.00 g of *cis*-2,3-diphenylaziridine[14] and 2.56 g (0.025 mole) of triethylamine and a solution of 4.74 g (0.025 mole) of *p*-nitrobenzoyl chloride in 160 ml of benzene. A 68% yield of VII, mp 153–156°, was obtained after recrystallization from petroleum ether (bp 60–110°).

Anal. Calcd for $C_{21}H_{16}N_2O_3$: C, 73.24; H, 4.68; N, 8.13. Found: C, 73.32; H, 4.72; N, 8.01.

***trans*-1-*p*-Nitrobenzoyl-2,3-diphenylaziridine (V)** was similarly synthesized using 0.391 g (0.002 mole) of *trans*-2,3-diphenylaziridine and 0.202 g (0.002 mole) of triethylamine in 20 ml of dry ether. To this mixture was added a solution of 0.371 g (0.002 mole) of *p*-nitrobenzoyl chloride in 30 ml of dry ether. After standing for 2 hr the triethylamine hydrochloride was filtered and the ether evaporated. The crude V weighed 0.575 g (83%) and was recrystallized from 95% ethanol forming crystals melting at 121–122°.

Anal. Calcd for $C_{21}H_{16}N_2O_3$: C, 73.24; H, 4.68; N, 8.13. Found: C, 73.60; H, 4.90; N, 7.90.

***trans*-2-*p*-Nitrophenyl-4,5-dimethyl-2-oxazoline (II).**—A mixture of 0.44 g (0.0049 mole) of *threo*-3-amino-2-butanol[29] and 0.97 g (0.0050 mole) of ethyl-*p*-nitrobenzimidate[30] was heated at 140° for 3.5 hr. The crude II that was obtained weighed 1.0 g (91%). Several recrystallizations from small quantities of methanol provided material melting 106.5–108.5°.

Anal. Calcd for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49; N, 12.72. Found: C, 59.95; H, 5.54; N, 12.76.

***cis*-2-*p*-Nitrophenyl-4,5-dimethyl-2-oxazoline (IV)** was prepared analogously as II using 0.44 g of *erythro*-3-amino-2-butanol[28] and 0.97 g of ethyl-*p*-nitrobenzimidate except that reaction time was 2.5 hr and the crude IV was slurried with 3 ml of cold methanol and filtered. Recrystallization from water–ethanol (1:1) gave 0.5 g of IV, mp 146–147°.

Anal. Calcd for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.45; N, 12.72. Found: C, 59.79; H, 5.51; N, 12.80.

***trans*-1-*p*-Nitrophenyl-4,5-diphenyl-2-oxazoline (VI).**—A mixture of 1.65 g (0.00773 mole) of *threo*-1,2-diphenyl-2-hydroxyethylamine[31] and 1.50 g (0.00772 mole) of ethyl-*p*-nitrobenzimidate was heated at 140° for 2.5 hr. The cooled mixture was slurried with 10 ml of methanol, warmed slightly, and filtered. The crude VI weighed 2.5 (94%). Recrystallization from methanol gave VI, mp 122–124°.

Anal. Calcd for $C_{21}H_{16}N_2O_3$: C, 73.24; H, 4.69; N, 8.13. Found: C, 73.16; H, 4.74; N, 7.89.

***cis*-1-*p*-Nitrophenyl-4,5-diphenyl-2-oxazoline** was prepared in exactly the same way as VI using *erythro*-1,2-hydroxyethylamine.[31] The *cis*-oxazoline was isolated in 76% yield and after recrystallization from methanol melted at 163–165°.

Anal. Calcd for $C_{21}H_{16}N_2O_3$: C, 73.24; H, 4.68; N, 8.13. Found: C, 73.36; H, 4.63; N, 8.23.

Isomerization of I into II.—A mixture of 350 mg of I and 1.0 g of sodium iodide in 60 ml of acetone was refluxed for 12 hr. The solvent was evaporated and the residue washed several times with water and filtered. The II obtained weighed 335 mg (96%) and melted at 106°. The spectra of II obtained by the isomerization of I and by the reaction of *threo*-3-amino-2-butanol and ethyl-*p*-nitrobenzimidate were identical.

Isomerization of III into IV was accomplished in the same manner as the isomerization of I. A crude yield of 89% of IV was obtained. The spectrum of IV corresponded exactly to the spectrum of IV that was synthesized by heating *erythro*-3-amino-2-butanol with ethyl-*p*-nitrobenzimidate.

Isomerization of VII into VI.—A mixture of 1.02 g of VII and 440 mg of sodium iodide in 12 ml of butanone was refluxed for 2 hr. The solvent was evaporated and the residue washed with water and filtered. The crude VI weighed 1.0 g (98%) and melted at 118–122°. Recrystallization of VI gave product melting 122–124° and having the same spectrum as VI prepared by reaction of *threo*-1,2-diphenyl-2-hydroxyethylamine and ethyl *p*-nitrobenzimidate.

Isomerization of V into VI.—A mixture of 135 mg of V and 50 mg of sodium iodide in 16 ml of butanone was refluxed for 2.5 hr. The solvent was evaporated and the residue slurried with 1 ml of cold methanol and filtered. The crude VI, mp 120–122°, weighed 115 mg (85%) and the spectrum was identical with that of authentic VI.

Preparation of IX.—In a separatory funnel containing 150 ml of water was added 13.41 g (0.05 mole) of *threo*-2,3-diphenyl-2-chloroethylamine hydrochloride.[14] A solution of 2 g (0.05 mole) of sodium hydroxide in 50 ml of water was added and the mixture immediately extracted three times with 150-ml portions of ether. The ether extracts were pooled and dried over anhydrous magnesium sulfate. Following filtration the ether was evaporated and 8.7 g (0.037 mole) of *threo*-1,2-diphenyl-2-chloroethylamine was obtained. The amine was dissolved in 60 ml of dry benzene and then 3.8 g (0.037 mole) of triethylamine was added. To this mixture was added in portions a solution containing 7.0 g (0.037 mole) of *p*-nitrobenzoyl chloride in 100 ml of benzene. After standing overnight the precipitate was filtered and then it was mixed with water to dissolve the triethylamine hydrochloride and again filtered. The crude IX weighed 14.0 g and melted 152–157°. Two recrystallizations from 95% ethanol gave IX, mp 165–167°.

Anal. Calcd for $C_{21}H_{17}ClN_2O_3$: C, 66.22; H, 4.50; N, 7.33. Found: C, 66.51; H, 4.61; N, 7.26.

Conversion of IX to VII.—A mixture of 1.45 g. (0.0038 mole) of IX in 80 ml of anhydrous ethanol was heated until boiling commenced. To the boiling mixture was added slowly and portionwise over a 5-min period 10 ml of a 0.38 *M* sodium ethoxide solution. Each increment of sodium ethoxide colored the reaction mixture a deep yellow and the next increment was not added until the color had disappeared. After a period of 20 min the reaction was stopped, the solvent evaporated, and the residue washed with water and filtered. The crude VII weighed 1.22 g (93%) and had the same spectrum as VII prepared from *cis*-2,3-diphenylaziridine and *p*-nitrobenzoyl chloride. Recrystallization gave 1.0 g of VII, mp 155°.

The procedure for the preparation of VIIIa was the same as that for IX, except that 2.16 g (0.006 mole) of *erythro*-1,2-diphenyl-2-iodoethylamine hydrochloride was employed and corresponding quantities of the other reagents. The yield of VIIIa was 1.78 g, mp 135–136°. It was slurried with benzene, filtered, and washed rapidly with small quantities of acetone and chloroform to give VIIIa, mp 139–140°.

Anal. Calcd for $C_{21}H_{17}IN_2O_3$: C, 53.39; H, 3.62; N, 5.93. Found: C, 53.67; H, 3.69; N, 5.90.

Conversion of VIII to VI.—To a mixture of 0.473 g (0.001 mole) of VIII in 10 ml of absolute ethanol was added 10 ml of a 0.114 molar solution of sodium ethoxide. After standing at room temp for 2.5 hr the reaction mixture was refluxed for 15 min. The solvent was evaporated and the residue washed with water. The crude VI, mp 117–119, weighed 0.338 g (98%). The spectrum of crude VI was identical with the spectrum of VI prepared from *threo*-1,2-diphenyl-2-hydroxyethylamine and ethyl *p*-nitrobenzimidate.

Preparation of *erythro*-1,2-diphenyl-2-iodoethylamine hydrochloride.[32]—A solution of 6.9 g (0.020 mole) of 1-azido-2-iodo-1,2-diphenylethane[15] was dissolved in 80 ml of tetrahydrofuran. Diborane[33] (in excess), was bubbled into this solution. After standing overnight the excess diborane was destroyed by the addition of ethanol. Gaseous hydrogen chloride was bubbled into the reaction mixture and 2.3 g (32%) of the iodoamine hydrochloride precipitated from the solution and was filtered. The hydrochloride decomposed at 170–174°.

***trans*-2,3-Diphenylaziridine.**—A solution of 200 ml of 95% ethanol containing 7.0 g of sodium hydroxide was added to 6.4 g (0.0178 mole) of *erythro*-1,2-diphenyl-2-iodoethylamine hydrochloride dissolved in 100 ml of 95% ethanol. The reaction mixture was stirred for 1 day and then poured into 300 ml of water. The mixture was placed under a hood for 2 days. The *trans*-2,3-diphenylaziridine gradually precipitated during this time. The crude material was filtered and weighed 2.64 g (75%) and melted at 45–46° (lit.[14] mp 47–48). This material was used without further purification for the preparation of V and VIII.

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Preparation of VIII.—To 10 ml of water was added 0.306 g (0.00114 mole) of *erythro*-1,2-diphenyl-2-chloroethylamine hydrochloride prepared from reaction of *trans*-2,3-diphenylaziridine and hydrogen chloride according to the procedure of Weissberger.[14] A solution of 55.9 mg of sodium hydroxide in 5 ml of water was added and the mixture extracted four times with 40-ml portions of ether. The ether extracts were dried for a few min over anhydrous magnesium sulfate and filtered. The ether filtrate was added to 0.121 g of triethylamine in 10 ml of dry ether. To this solution was added 0.212 g of *p*-nitrobenzoyl chloride dissolved in 10 ml of dry ether. The precipitate was filtered and the ether evaporated. The crude VIII weighed 0.415 g (95.6%) and melted at 159–161°. Several recrystallizations from absolute ethanol gave VIII, mp 166–168°.

Anal. Calcd for $C_{21}H_{17}ClN_2O_3$: C, 66.22; H, 4.50; N, 7.33. Found: C, 65.99; H, 4.49; N, 7.44.

Conversion of VIII to VI.—The same procedure and the same quantities of reagents were used as for the conversion of IX to VII. The *erythro* isomer VII formed VI in 95% yield and melted at 116–119°. The infrared spectrum of crude VI was identical with an authentic sample.

***erythro*-N-1,2-Diphenyl-2-hydroxyethyl-*p*-nitrobenzamide.**—A solution of 11.13 (0.0599 mole) of *p*-nitrobenzoyl chloride dissolved in 100 ml of benzene was added portionwise to a solution of 12.80 g (0.0600 mole) of ***erythro*-1,2-diphenyl-2-hydroxyethylamine** and 6.06 g (0.0600 mole) of triethylamine in 250 ml of benzene. The reaction mixture was allowed to stand overnight and then filtered. The solid residue was treated with water and filtered again. The crude product weighed 15.0 g (69%) and was recrystallized from ethanol. The recrystallized material melted at 212–213°.

Anal. Calcd for $C_{21}H_{18}N_2O_4$: C, 69.60; H, 5.00; N, 7.73. Found: C, 69.78; H, 5.03; N, 7.73.

***threo*-N-1,2-Diphenyl-2-hydroxyethyl-*p*-nitrobenzamide** was prepared in the same manner as the *erythro* isomer in 68% yield. Recrystallization from absolute ethanol gave material melting at 217.5–219.5°.

Anal. Calcd for $C_{21}H_{18}N_2O_4$: C, 69.60; H, 5.00; N, 7.73. Found: C, 69.11; H, 5.08; N, 7.68.

Conversion of *threo*-N-1,2-Diphenyl-2-hydroxyethyl-*p*-nitrobenzamide to VI.—To 20 ml of cooled concentrated sulfuric acid was added gradually over 0.5 hr with stirring 4.0 g (0.011 mole) of the *threo* amide. After another 10 min at room temperature the reaction mixture was poured over 300 g of ice; the mixture was stirred vigorously and neutralized with 30% sodium hydroxide solution. The mixture was filtered and the solid residue stirred with water and filtered again. Recrystallization from methanol gave 3.0 g (79%) of VI, mp 122–124°.

Conversion of *erythro*-N-1,2-diphenyl-2-hydroxyethyl-*p*-nitrobenzamide to VI was carried out in the same manner as the acidolysis of the *threo* isomer. The yield of recrystallized VI, mp 122–124°, was 40%.

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Notes

Acetal Formation for Cyclic Ketones[1]

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A previous study of neat cyclohexanone–methanol mixtures demonstrated that in acidic media the predominant reaction is acetal formation.[3] Recently it has been shown that cyclohexanone and 3- and 4-alkyl substituted cyclohexanones form a small amount of hemiacetal (about 10–12%) along with a large amount of acetal in dilute methanol solutions. Other cyclic and acyclic ketones and some aromatic aldehydes do not form significant amounts of hemiacetals.[4]

During earlier studies on the acetal equilibrium we evaluated the use of short-path quartz cells (down to 0.025 mm) to measure the absorbances of carbonyl compounds in neat mixtures with methanol. This permitted us to study more concentrated solutions than have been previously reported for such systems. Thus we could decide whether hemiacetal or acetal equilibrium was predominant since in concentrated solutions both equilibria are quite sensitive to concentration changes, while in very dilute solutions the values tend to be constant whether calculated for hemiacetal or acetal. Furthermore, in dilute solutions, errors for acetal formation are magnified in the absence of accurate analyses for water content in the reactants. Although the short-path measurements lacked versatility, we did complete a study of the effect of ring size of ketones upon the extent of formation of methyl acetals and these results are reported.

The solutions of ketones in neutral methanol were found to follow Beer's law for fairly wide concentration ranges. Generally we used from 0.3 to 1.5 *M* ketone in methanol. From the known weight of reactants, from the measured concentration of the ketone by ultraviolet analysis, and from the stoichiometry for acetal formation, the mole fraction equilibrium constants were calculated. The results are summarized in Table I. We have also calculated mole-fraction equilibrium constants for hemiacetal formation which are shown in the last column of Table I.

The calculated K_x values for acetal formation are sensibly constant for all of the ketones studied while K_x for hemiacetal change significantly, and we conclude that the predominant reaction is acetal formation. There have been reports that ketones form only hemiacetals[5–7] and other reports that ketones form

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