The product was recrystallized from 1:5 water–dimethylformamide giving 341 mg., m.p. 295–303° (dec.), of 7-hydroxy-8-methyl-2-methyloxazolo(4′,5′-3,4)coumarin (I). An analytical sample was prepared by recrystallization of a small sample from 1:3 water–dimethylformamide and 1:1 water–dimethylformamide successively.

Anal. Calcd. for $C_{21}H_9NO_4$: C, 62.34; H, 3.92; N, 6.06. Found: C, 62.22; H, 3.89; N, 6.51.

Other physical properties of I were: $\lambda_{max}^{CH_3OH}$ 316 mμ (ε, 18,500), shoulder 295 (ε, 9450), shoulder 249 (ε, 10,150), 2440 (ε, 10,500); pK_a'[8] 9.6; λ_{max}^{Nujol} 5.72 (C=O), 6.03.

(8) All pK_a' values are $pH\ ^1/_2$ values obtained by potentiometric titration of the compounds in 70% acetone-water mixtures.

4-Carboxy-5-(2,4-dihydroxy-3-methylphenyl)-2-methyloxazole (III). To a slurry of 231 mg. (1 mmole) of 7-hydroxy-8-methyl-2-methyloxazolo(4′,5′-3,4)coumarin (I) in 5 ml. of ethanol was added 10 ml. of 0.6*N* sodium hydroxide. The yellow-green solution was allowed to stand overnight at room temperature and then evaporated *in vacuo* to about 3 ml. The solution was diluted to about 8 ml. with water and acidified with 2.5*N* hydrochloric acid. The precipitate weighed 273 mg. When this material was heated on the Micro Hot Stage, it changed crystal form at 115–125°, sublimed at 180°, and decomposed at 290–300°. Two crystallizations of this product from water gave 88 mg. of 4-carboxy-5-(2,4-dihydroxy-3-methylphenyl)-2-methyloxazole, transition 228–233°, 290–300° (dec.).

Anal. Calcd. for $C_{12}H_{11}NO_5$: C, 57.83; H, 4.45; N, 5.62. Found: C, 57.59; H, 4.40; N, 6.17.

Other physical properties were $\lambda_{max}^{CH_3OH}$ 300 mμ (ε, 13,200), 222 (ε, 20,400); pK_a' 4.2; λ_{max}^{Nujol} 5.89 (C=O), 6.17.

For comparison with II, we here record our physical data on 3-acetamido-4,7-dihydroxy-8-methylcoumarin (II): m.p. 280–281°; λ_{max}^{MeOH} 316 mμ (ε, 5270), 292 (ε, 2660), shoulder 249 (ε, 3160), 245 (ε, 3210); pK_a' 5.3; λ_{max}^{Nujol} 6.09, 6.18.

When III was sublimed at 200–220° and *ca.* 0.1 mm., the crystalline sublimate melted at 315–325° (dec.) with a transition 220–230°. Apparently no lactonization to I had occurred. Refluxing acetic anhydride, however, converted III into *O*-acetyl I in 40 min. The crude product obtained melted at 200–204° and its mixture with authentic *O*-acetyl I melted at 204–209°.

4-Carboxy-5-(2-hydroxyphenyl)-2-methyloxazole (VII). A slurry of 380 mg. (2 mmoles) of the 2-methyloxazolo(4′,5′-3,4)coumarin[6] V (m.p. 195–196°) in 10 ml. of ethanol was treated with 20 ml. of 0.6*N* sodium hydroxide. A yellow-green color formed in the solution and the oxazole slowly dissolved. After 16 hr. at room temperature, the solution was evaporated *in vacuo* to a volume of about 2 ml. and acidified with concentrated hydrochloric acid. The crude product, 380 mg. (92%), melted at 165–170°. After one recrystallization from ethyl acetate, the 4-carboxy-5-(2-hydroxyphenyl)-2-methyloxazole (VII), 175 mg., melted at 170–173°. After one further recrystallization from ethyl acetate, the product had m.p. 171–174°; $\lambda_{max}^{CH_3OH}$ 295 mμ (ε, 5400), 262 (ε, 8240), pK_a' 4.4; λ_{max}^{Nujol} 6.01, 6.18.

Anal. Calcd. for $C_{11}H_9NO_4$: C, 60.27; H, 4.14; N, 6.39. Found: C, 60.44; H, 4.38; N, 6.47.

We obtained the following physical data on 3-acetamido-4-hydroxycoumarin (VI) in order to compare it with the acid VII obtained above: m.p. 229–230°, $\lambda_{max}^{CH_3OH}$ 316 mμ (ε, 11,700), shoulder 295 (ε, 9450), 282 (ε, 8320); pK_a' 5.0; λ_{max}^{Nujol} 5.93 (C=O), 6.13.

When the acid VII was sublimed at 150–160° and *ca.* 0.05 mm., the sublimate melted at 175–178°. Apparently no lactonization to V, m.p. 195–196°, had occurred. However, when VII was treated with refluxing acetic anhydride for 30 min., a 64% yield of oxazole V crystallized from the solution.

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The Isomerization of Some Aziridine Derivatives. III. A New Synthesis of 2-Imidazolines

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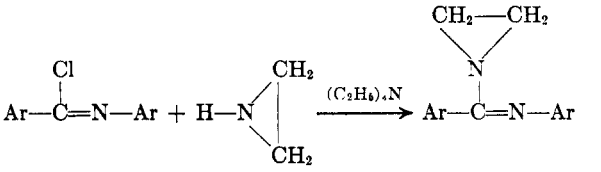
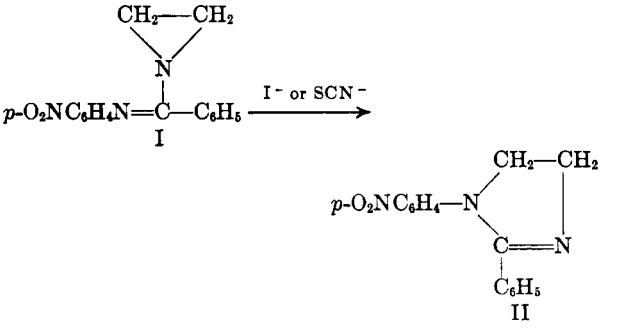
Previous work in this laboratory has been concerned with the isomerization of 1-aroylaziridines.[1,2] For example, 1-*p*-nitrobenzoyl-2,2-dimethylaziridine has been selectively isomerized to 2-*p*-nitrophenyl-4,4-dimethyl-2-oxazoline, 2-*p*-nitrophenyl-5,5-dimethyl-2-oxazoline, or *N*-(β-methallyl)-*p*-nitrobenzamide by sodium iodide in acetone, concentrated sulfuric acid, or refluxing heptane respectively. We now wish to report the synthesis and isomerization of a new class of aziridine derivatives, the 1-(*N*-arylbenzimidoyl)aziridines.

The 1-(*N*-*p*-nitrophenylbenzimidoyl)aziridine (I) and the 1-(*N*-phenyl-*p*-nitrobenzimidoyl)aziridine used in the present study were prepared by reaction of the corresponding *N*-arylbenzimidoyl chloride with aziridine in benzene containing triethylamine:



The *N*-*p*-nitrophenylbenzimidoyl chloride reacted much faster with aziridine than did *N*-phenyl-*p*-nitrobenzimidoyl chloride. Evidently *N*-arylbenzimidoyl chlorides are much less susceptible to nucleophilic attack when a strong electron-withdrawing group is attached to the benzimidoyl moiety than when it is attached to the *N*-aryl moiety.

The 1-(*N*-arylbenzimidoyl)aziridines in acetone solutions containing iodide ion or thiocyanate ion smoothly undergo isomerization to 2-imidazolines. Thus I was converted in over 90% yield to 1-*p*-nitrophenyl-2-phenyl-2-imidazoline (II):



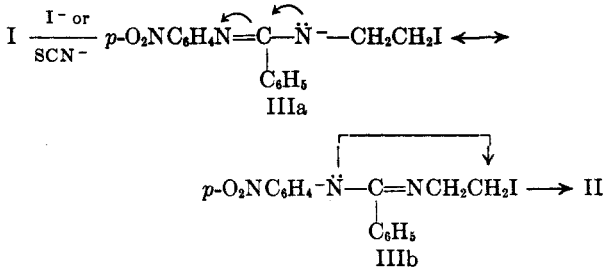
The structure of II was confirmed by comparison of infrared spectra and by mixed melting point

(1) H. W. Heine and Z. Proctor, *J. Org. Chem.*, **23**, 1554 (1958).

(2) H. W. Heine, M. E. Fetter and E. M. Nicholson, *J. Am. Chem. Soc.*, **81**, 2202 (1959).

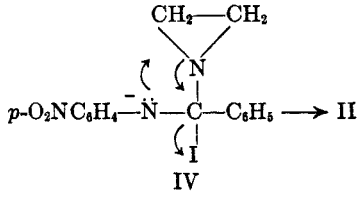
with an authentic sample of II prepared by the method of Partridge and Turner.[3] In an analogous experiment 1-(*N*-phenyl-*p*-nitrobenzimidoyl)aziridine was converted into 1-phenyl-2-nitrophenyl-2-imidazoline.

The 2-imidazoline is probably formed by a two step process involving first a nucleophilic attack of iodide or thiocyanate ion on the methylene group of the aziridine ring to form an amidino ion IIIa as an intermediate. This step is quite similar to the opening of the ethylene oxide ring by iodide ion[4,5] or thiocyanate ion[6] to form the corresponding β-substituted alkoxide ions. The second step of the process is the displacement of the iodide ion or thiocyanate ion by the negatively charged nitrogen of the resonance hybrid IIIb:



This mechanism requires the displacement of thiocyanate ion from carbon which, while unusual, is not entirely without analogy.[7,8,9]

Alternatively, the isomerization may also take place by the addition of the iodide or thiocyanate ion to the benzimidoyl carbon to give the intermediate IV which subsequently cyclizes to the imidazoline:



2-Propanol can also be used as a solvent for carrying out the isomerization. Thus I rearranged to II in over 94% yield in 2-propanol containing iodide ion. Under these same experimental conditions, 1-*p*-nitrobenzoylaziridine isomerized to 2-*p*-nitrophenyl-2-oxazoline in high yield. The latter result was contrasted with methanolic solutions containing iodide ion whereupon 1-*p*-nitrobenzoylaziridine formed methyl *p*-nitrobenzoate in 95% yield.[2]

Acid catalyzed methanolysis of 1-(*N*-*p*-nitrophenylbenzimidoyl)aziridine and 1-*p*-nitrobenzoylaziridine gave, as expected, *N*-*p*-nitrophenyl-*N'*-2-methoxyethylbenzamidine and *N*-2-methoxyethyl-*p*-nitrobenzamide respectively. The structures of these two products were confirmed by independent syntheses.

EXPERIMENTAL

1-(N-p-nitrophenylbenzimidoyl)aziridine. To a 300 ml. flask equipped with a stirrer, drying tube and dropping funnel was added 1.1 g. of aziridine, 5.05 g. triethylamine and 70 ml. of dry benzene. Over the course of 1 hr. a solution of 6.52 g. of *N*-*p*-nitrophenylbenzimidoyl chloride[10] (m.p. 113–114.5°) in 100 ml. of benzene was added. The mixture was stirred at room temperature for 12 hr., the triethylamine hydrochloride filtered, and the solvent evaporated. A crude yield of 6.6 g. melting at 116–120° was obtained. The substituted aziridine was recrystallized in small portions from 2-propanol to give material melting at 132–134°.

Anal. Calcd. for $C_{15}H_{13}N_3O_2$: N, 15.71. Found: N, 15.80.

1-(N-phenyl-p-nitrobenzimidoyl)aziridine. To a mixture of 2.2 g. of aziridine, 10.1 g. of triethylamine, and 70 ml. of benzene was added slowly (1 hr.) a solution of 13.1 g. of *N*-phenyl-*p*-nitrobenzimidoyl chloride[11] in 100 ml. of benzene. The mixture was heated to 40° and stirred for 43 hr. The triethylamine hydrochloride was filtered and the solvent evaporated to give 13.1 g. of crude product melting at 81–84°. Recrystallization twice and in small portions from cyclohexane gave product melting 94–96°.

Anal. Calcd. for $C_{15}H_{13}N_3O_2$: N, 15.71. Found: N, 15.75.

Isomerization of 1-(N-p-nitrophenylbenzimidoyl)aziridine (I). One hundred milligrams of I was added to 50 ml. of acetone containing 274 mg. of sodium iodide. The mixture was refluxed 3.5 hr., the solvent evaporated, and the residue washed with water and filtered. The crude 1-*p*-nitrophenyl-2-phenyl-2-imidazoline weighed 98 mg., turned slightly amber on heating, and melted at 172–175°. A mixed melting point with an authentic sample of the 2-imidazoline[3] showed no depression of melting point. An infrared spectrum of the crude product was identical with the spectrum of the authentic sample. Other experiments using smaller quantities of sodium iodide (*e.g.* 20 mg.) and the same reaction time gave only slight conversion. However, a 93% yield of crude imidazoline was obtained using 100 mg. I, 50 ml. acetone, and 20 mg. sodium iodide with a reflux period of 76 hr.

Isomerization of I *by potassium thiocyanate.* To a solution of 50 ml. of acetone and 1 g. of potassium thiocyanate was added 100 mg. of I. The mixture was refluxed for 47 hr., the solvent evaporated, and the residue washed with water and filtered. The crude 1-*p*-nitrophenyl-2-phenyl-2-imidazoline weighed 94 mg. and melted at 169–174°.

Rearrangement of 1-(N-phenyl-p-nitrobenzimidoyl)aziridine (V). One hundred milligrams of V was added to 50 ml. of acetone containing 250 mg. of sodium iodide. The reaction mixture was refluxed 3 hr. and worked up as described above. A crude yield of 96 mg. of 1-phenyl-2-*p*-nitrophenyl-2-imidazoline melting at 102–104° was obtained. Mixed melting point determinations of the isomerized product with a sample of authentic 1-phenyl-2-*p*-nitrophenyl-2-imidazoline melted 102–108°. Infrared spectra of the two samples were identical.

1-Phenyl-2-p-nitrophenyl-2-imidazoline. To a 200 ml. round-bottom flask equipped with a condenser and drying

(3) M. W. Partridge and H. A. Turner, *J. Chem. Soc.*, 1308 (1949).

(4) L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Company, Inc., New York, 1940, pp. 301–302.

(5) J. N. Bronsted, M. Kilpatrick, and M. Kilpatrick, *J. Am. Chem. Soc.*, **51**, 428 (1929).

(6) P. L. Nichols, Jr., and J. D. Ingham, *J. Am. Chem. Soc.*, **77**, 6547 (1955).

(7) L. Hagelberg, *Ber.*, **23**, 1083 (1890).

(8) H. P. Kaufmann, E. Gindsberg, W. Rottig, and R. Salchow, *Ber.*, **70**, 2519 (1937).

(9) J. R. Siegel and D. H. Rosenblatt, *J. Am. Chem. Soc.*, **80**, 1753 (1958).

(10) O. Mumm, *Ber.*, **43**, 892 (1910).

(11) R. C. Shah and J. S. Chanbal, *J. Chem. Soc.*, 651 (1932).

tube were added 5.75 g. of phosphorus pentachloride and 6.85 g. of *N*-2-bromoethyl-*p*-nitrobenzamide.[12] The mixture was heated for 120 hr. To this mixture was added 2.33 g. of aniline dissolved in 70 ml. of benzene. After an additional 24 hr. of refluxing, the phosphorus oxychloride which was formed and benzene were evaporated by means of a water aspirator and water bath. The resulting brown oil was poured into 250 ml. of hot water, the solution neutralized with ammonium hydroxide, and the organic material extracted with chloroform. The chloroform extracts were filtered through a norit pad and evaporated. The yellow crystalline residue was recrystallized twice from 50% aqueous ethanol and melted at 109–111°. A crude yield of 3.1 g. was obtained.

Anal. Calcd. for $C_{15}H_{13}N_3O_2$: N, 15.71. Found 15.71.

Acid methanolysis of I. To a mixture of 50 ml. of methanol and 36 mg. of concentrated sulfuric acid was added 100 mg. of I. The mixture was refluxed 3 hr., neutralized with several drops of 30% sodium hydroxide, the solvent evaporated, and the residue washed with water and filtered. A yield of 98.9 mg. of crude *N p*-nitrophenyl-N'-2-methoxyethylbenzamidine melting at 87–89° was obtained. An infrared spectrum of the crude product was identical with spectrum of an authentic sample of the amidine. Recrystallization of the crude product from cyclohexane gave crystals melting 95–97°.

N-p-nitrophenyl-N'-2-methoxyethylbenzamidine. To 3.25 g. of *N*-*p*-nitrophenylbenzimidoyl chloride was added 1.60 g. of 60% aqueous 2-methoxyethylamine. After the reaction subsided, the mixture was allowed to cool to room temperature and 40 ml. of water was added. The mixture after standing overnight gave 3.4 g. of material melting at 80–85°. Recrystallization from cyclohexane gave crystals melting at 95–97°.

Anal. Calcd. for $C_{16}H_{17}N_3O_3$: N, 14.04. Found 14.51.

Acid methanolysis of 1-p-nitrobenzoylaziridine. To a solution of 14 mg. of 98% sulfuric acid in 60 ml. of methanol was added 384 mg. of 1-*p*-nitrobenzoylaziridine. The reaction mixture was allowed to stand 13 hr. at room temperature, the solvent was then evaporated, and the residue was washed and filtered. A yield of 422 mg. of *N*-2-methoxyethyl-*p*-nitrobenzamide melting at 109–113° and having an infrared identical with an authentic sample[13] was obtained.

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(13) H. W. Heine, *J. Am. Chem. Soc.*, **79**, 907 (1957).

"1-Phenylazetidine" and an Unusual Hofmann-Martius Reaction

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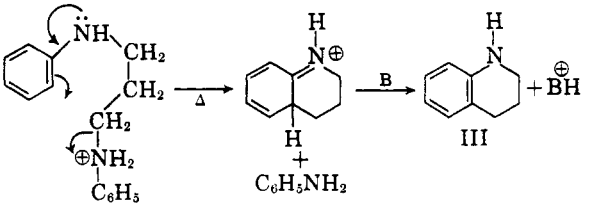
In 1899 Scholtz[1] claimed to have prepared 1-phenylazetidine [*N*-phenyltrimethyleneimine (I)] by the reaction of 1,3-dibromopropane with aniline. Not only is this the sole recorded preparation of an azetidine from the reaction of a dihalide with an amine,[2] but on no other occasion has the isolation of any *N*-aryl derivative of this ring been claimed. Scholtz obtained the compound, in small yield, as a low-boiling fraction when distilling his main reaction product, which was *N,N'*-diphenyltrimethylenediamine (II). Hanssen[3] had previously prepared the diamine (II) by this method but failed to distill it owing to extensive decomposition. Veer[4] later carried out the same preparation. He differed from Hanssen in distilling the diamine (II) quite readily, and differed from Scholtz in obtaining only aniline, and no trace of the cyclic compound (I), in the very small first runnings of his distillation.

In repeating Scholtz's preparation, we found that during the distillation of diamine (II), the "low-boiling" fraction could be separated into aniline, and a material answering to Scholtz's description of the azetidine (I). This description, however, also fits the secondary amine 1,2,3,4-tetrahydroquinoline (III), with which the compound was readily identified.

When the diamine (II) was carefully freed from acid (following Veer's[4] procedure of repeated water and ether extractions) it could, indeed, be distilled unchanged, but the monohydrobromide of II was found to break down smoothly at 230–250° into aniline and the reduced quinoline (III). With smaller amounts of hydrobromic acid present, decomposition of II was less rapid and although breakdown was still perceptible with "catalytic" quantities, it was found convenient to use 0.1 mol. hydrobromic acid. Under these conditions the yield of purified III, over several runs, was 50% of theory (on scheme below), with an apparently quantitative yield of aniline.

It seems likely that formation of the compound (III) is the result of an interesting Hofmann-Martius reaction:



On this scheme, the results obtained by Hanssen, Scholtz, and Veer are understandable, because incomplete removal of acid from the diamine (II) should result, at distillation temperature, in reaction of the type postulated. It is of interest that Scholtz prepared the *o*-tolyl analog of II. His predistillation treatment of this compound resembled that of Veer and consequently no breakdown products of distillation were reported. We find that addition of 0.1 mol. hydrobromic acid to this

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