chloride (5 ml.) was placed in a 20-ml. round-bottom flask along with freshly recrystallized N-bromosuccinimide (0.391 g., 0.0022 mole, m.p. 173°). The mixture was stirred and irradiated during 45 min. by means of two 200-w. tungsten lamps. At the end of the reaction, when all the succinimide floated at the surface of the mixture, the flask was cooled and the content was filtered. Succinimide was obtained (0.214 g., m.p. 122–125°), and the filtrate, after evaporation, afforded a brown oil (0.692 g., 96%). Because of the instability of this compound, it was utilized immediately without further purification (on standing, a darkening occurred accompanied by hydrogen bromide evolution).

1-(2-Iodo-4-methoxybenzyl)pyridinium Bromide (XI).—A solution of 2-iodo-4-methoxybenzyl bromide (X, 2.20 g., 0.0067 mole), dissolved in dry benzene (50 ml.) containing pyridine (5 ml.), was refluxed for 30 min. After cooling, the light brown pyridinium salt was filtered, washed with anhydrous ether, and dried (2.37 g., 87%). Recrystallization from an ethanol–ether mixture afforded an analytical sample as a tan crystalline material, m.p. 200–201°.

Anal. Calcd. for $C_{13}H_{13}BrINO$: C, 38.44; H, 3.22; N, 3.45. Found: C, 38.60; H, 3.22; N, 3.33.

2-Iodo-4-methoxyphenyl-N-*p*-dimethylaminophenylnitrone (XII).—A cold solution of 5% sodium hydroxide (5 ml.) was added dropwise at 0° to a stirred suspension of 1-(2-iodo-4-methoxybenzyl)pyridinium bromide (XI, 0.990 g., 0.00245 mole, m.p. 200–201°) and N,N-dimethylnitrosoaniline (0.365 g., 0.00245 mole, m.p. 85°) in ethanol (7.8 ml.). Stirring in the cold was allowed to proceed for 5 hr. During this period a reddish brown precipitate occurred; this material was filtered and dried (0.412 g., 43%). An analytical sample was obtained by preparative t.l.c. on silica gel $HF_{254+366}$ (2% methanol in chloroform elution), followed by recrystallization from benzene–Skellysolve B, m.p. 154–155° (yellow-green crystals).

Anal. Calcd. for $C_{16}H_{17}IN_2O_2$: C, 48.48; H, 4.32; N, 7.07. Found: C, 48.30; H, 4.20; N, 7.13.

2-Iodo-4-methoxybenzaldehyde (VI).—The nitrone XII (0.165 g., 0.00042 mole, m.p. 154–155°) was stirred vigorously into cold 6 *N* sulfuric acid to effect hydrolysis. The yellow product formed was filtered, washed with water, and dried (0.090 g., 82%). Recrystallization from Skellysolve B afforded light yellow crystals (0.073 g.), m.p. 112–113°, $\lambda_{max}^{CHCl_3}$ 5.95 μ (lit.[8] m.p. 115°).

2-Carbomethoxy-4,5-methylenedioxy-2′-iodo-4′-methoxy-α-nitro-*cis*-stilbene (XV).—In a 5-ml. erlenmeyer flask was placed a mixture of 2-carbomethoxy-4,5-methylenedioxyphenylnitromethane (XIV, 0.075 g., 0.000314 mole, m.p. 130–130.5°), *n*-propylidene base of 2-iodo-4-methoxybenzaldehyde (XIII, 0.104 g., 0.000343 mole), and glacial acetic acid (5 ml.). This mixture was heated to boiling on a hot plate and the acetic acid was allowed to evaporate almost to dryness. The resulting dark brown oil was subjected to preparative t.l.c. on silica gel $HF_{254+366}$ (chloroform elution) and the major yellow band afforded a viscous yellow oil. Crystallization was accomplished by the addition of a few drops of ethanol (0.087 g., 57%). The yellow product was recrystallized from ethanol and gave shiny yellow prisms (0.076 g.): m.p. 172–173°; $\lambda_{max}^{CHCl_3}$ 5.85, 6.60, 7.55, 8.0 μ; λ_{max}^{EtOH} 260 mμ (ϵ 12,950) (plateau), 308 (9600), 345 (12,000).

Anal. Calcd. for $C_{18}H_{14}INO_7$: C, 44.74; H, 2.92; N, 2.90. Found: C, 44.60; H, 2.87; N, 2.94.

Methyl Ester of Aristolochic Acid-C Methyl Ether (XVI).—A solution of XV (0.009 g., 0.00002 mole, m.p. 172–173°) in purified cyclohexane (75 ml.) was photolyzed in a Vycor tube utilizing a Rayonet photochemical reactor as the light source. The photolysis required 25 min. A noticeable color of iodine was observed as usual. Evaporation of the solvent afforded a yellow-orange oily solid (0.009 g.). This product was purified by preparative t.l.c. on silica gel $HF_{254+366}$ (chloroform elution). Starting material was isolated from a deep yellow band having a slightly higher R_f value than the desired product (2.3 mg.). The yellow band with the lower R_f value afforded shiny microcrystals (2.2 mg., 45% based on unrecovered starting material), m.p. 256–260°. Recrystallization from ethanol gave shiny yellow microcrystals (2.15 mg.), m.p. 258–260°, melting point undepressed upon admixture with an authentic sample.[12] The thin layer chromatographic behavior was identical with that of the reference sample in four different solvent systems (chloroform and 1, 2, and 3% methanol in chloroform). The infrared spectrum (KBr) was superimposable upon that of the authentic sample: λ_{max}^{EtOH} 255 mμ (ϵ 41,300), 281 (16,600), 302 (13,060).

An Improved Technique for the Hydroxylation of 4,5-Diphenyl-2-imidazolones

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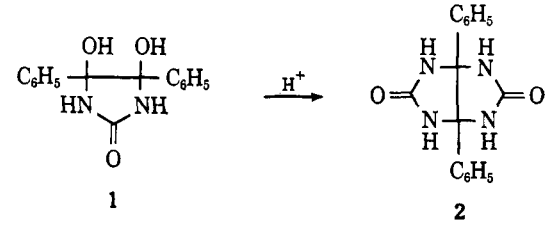
Biltz[2] has shown that 4,5-diphenyl-2-imidazolone can be hydroxylated to 4,5-dihydroxy-4,5-diphenyl-2-imidazolidinone (1) with concentrated nitric acid. His method omitted some critical experimental details and was later modified by Dunnavant.[3] The modified procedure still proved unsatisfactory in our hands, giving either benzil or N,N′-dibenzoylurea as the sole products.

It was shown that treatment of the imidazolone with bromine in acetic acid buffered with sodium acetate gave the glycol. This method was also used to prepare the glycol of 4,5-di(*p*-bromophenyl)-2-imidazolone. In both cases the glycols were quantitatively oxidized with periodate to the corresponding N,N′-dibenzoylurea.

In the presence of aqueous acid the glycol gave the benzil and the corresponding 3a,6a-diphenylglycoluril (2). These results are in conflict with those reported by Dunnavant and James[4] who claimed that the glycol rearranged to the 5,5′-diphenylhydantoin in acid solution; this rearrangement does occur, but only under alkaline conditions.[5] The glycols and urea in the presence of acid gave the corresponding glycolurils quantitatively.[6]



1 2

Experimental Section[7]

4,5-Dihydroxy-4,5-diphenyl-2-imidazolidinone.—4,5-Diphenyl-2-imidazolone[8] (2.36 g., 0.01 mole), glacial acetic acid (25 ml.), and anhydrous sodium acetate (3 g.) were heated to boiling. The external heating was removed and a solution of bromine in acetic acid (160 g. of Br_2/l. of acetic acid, 10 ml., 0.01 mole) was added rapidly. The reaction mixture was allowed to stand until all the bromine had been consumed (about 10 min.) and then ice–water (70 ml.) was added dropwise with stirring. The reaction mixture set to a jelly-like mass which on continued stirring became granular. The solid was removed by filtration and washed with saturated sodium bicarbonate solution with water, and finally twice with ethanol–ether (1:3, 20 ml.). After drying in a vacuum desiccator, the glycol was crystallized from methanol, yielding 1.99 g. (74%), m.p. 153–155° (lit.[3] m.p. 158–161°).

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4,5-Dihydroxy-4,5-di(*p*-bromophenyl)-2-imidazolidinone.—4,5-Di(*p*-bromophenyl)-2-imidazolone[9] (3.94 g., 0.01 mole) as above gave the glycol which crystallized poorly from acetone–ether, m.p. 305–310° (with slow heating), lit.[10] m.p. 320–325°, yield 3.95 g. (92%).

Periodate Oxidation of the Glycols.—Periodic acid (0.40 g.), water (10 ml.), ethanol (50 ml.), and the appropriate glycol (0.002 mole) were allowed to stand overnight. N,N'-Dibenzoylurea or N,N'-di(*p*-bromobenzoyl)urea separated out; the identity of these compounds was confirmed by mixture melting point.

The Effect of Acid on the Glycols.—The appropriate glycol (0.50 g.), ethanol (15 ml.), and concentrated sulfuric acid (1 ml.) were refluxed for 2 hr., diluted with water, and filtered. In the one case the solid was washed with methanol (75 ml.) to give 3a,6a-diphenylglycoluril,[11] m.p. 354–356°, 0.17 g. (31%). Evaporation of the methanolic filtrate gave benzil, 0.24 g. (62%). In the other case the solid was extracted with boiling benzene to give 3a,6a-di(*p*-bromophenyl)glycoluril,[12] m.p. 360–362°, 0.15 g. (28%). Evaporation of the benzene gave 4,4'-dibromobenzil, 0.25 g. (58%).

Effect of Urea on the Glycols.—The appropriate glycol (0.50 g.), ethanol (15 ml.), urea (0.5 g.), and concentrated hydrochloric acid (1 ml.) were allowed to stand overnight. The corresponding glycolurils were obtained in quantitative yields.

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Reaction of Butyramidine with Epoxides. Preparation of 2-Propyl-2-oxazolines

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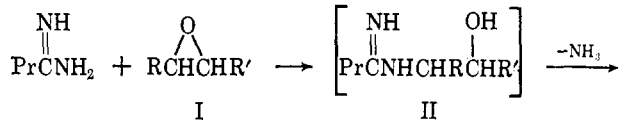
It has been postulated[2] that N-(2-hydroxyethyl)-amidine salts, or closely related structures, are intermediates in the formation of 2-oxazolines from N-alkylamidines and salts of 2-aminoethanol. Likewise, the formation of 2-oxazolines from 2-amino alcohols and imino esters has been shown to involve N-(2-hydroxyalkyl)amidine intermediates.[3]

It therefore might be expected that reaction of amidines with epoxides would also produce 2-oxazolines through the intermediate formation of N-(2-hydroxyalkyl)amidines. This latter method would be advantageous in that epoxides are often more readily available than the amino alcohols required for most other methods of oxazoline preparation. Preparations of 2-oxazolines from epoxides and nitriles[4] and from epoxides and cyanamide[5] apparently are useful only in special cases.

As expected, we have found that 2-propyl-2-oxazolines can be readily obtained from the reaction of butyramidine with various epoxides. Butyramidine reacted at room temperature with each of the first three epoxides listed, Ia–c, to form the corresponding intermediates (IIa–c) which, on heating, evolved ammonia to give the oxazolines (IIIa–c). Reaction of both *cis* and *trans* Id with butyramidine required somewhat higher temperatures. At these higher temperatures, the intermediates were unstable and the oxazolines (*trans* and *cis* IIId) were obtained directly.



I II III

a, R = R' = H
b, R = H, R' = CH_3
c, R = H; R' = CH_2CH_3
d, R = R' = CH_3 (*cis* I → *trans* III, *trans* I → *cis* III)

Both of the unsymmetrical epoxides, Ib and Ic, reacted at the unsubstituted epoxide ring position to give 5-substituted oxazolines. 2-Propyl-5-methyl-2-oxazoline (IIIb) was identified by comparison with an authentic sample,[6] and analysis by gas chromatography showed that it contained no more than a trace of the isomeric 4-methyl compound. 2-Propyl-5-ethyl-2-oxazoline (IIIc) also appeared homogeneous by gas chromatography, although an authentic sample was not available for comparison.

In the n.m.r. spectrum of each of these two oxazolines, the tertiary ring proton appeared at lower τ values than the methylene ring protons. This confirms that the single proton, and thus the ring substituent, is in the 5-position adjacent to O rather than the 4-position adjacent to N. For IIIb and IIIc, the single C-5 protons appeared as complex multiplets at τ 5.35 and 5.52, respectively, and the C-4 methylene protons appeared as complex multiplets at τ 6.35 for both compounds. The multiplets assigned to the C-4 protons correspond to the AB part of ABC spectra, and, in both cases, there is additional fine structure arising from long-range coupling (~2 c.p.s.) with the α-methylene protons of the *n*-propyl substituent.[7]

Intermediates IIa–c were not stable enough for purification but were identified by the infrared spectra of samples taken from the reaction mixtures before heating. IIb and IIc are apparently not completely stable even at room temperature since their spectra before heating showed the presence of some oxazoline.

Inversion occurs during the epoxide ring opening as evidenced by the fact that *cis* Id gives *trans* 2-propyl-4,5-dimethyl-2-oxazoline (*trans* IIId), and *trans* Id gives *cis* IIId. The stereochemical assignments were made on the basis of the n.m.r. spectra. The n.m.r. spectrum of *trans* IIId includes a quartet at τ 5.95 assignable to the C-5 proton and indicating no appreciable coupling with the C-4 proton. This agrees with the expected dihedral angle between these

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