

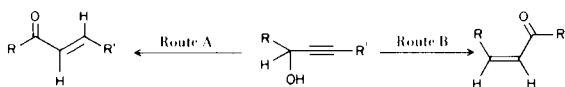
Chemistry of Heterocyclic Compounds. 16. Isomerization of Acetylenic Diols:  
1,4-Di(2'-pyridyl)-2-butyne-1,4-diol (1)

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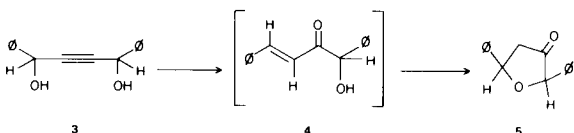
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It has been proposed (2) that 1,4-diphenyl-1,4-di(2'-pyridyl)-2-butyne-1,4-diol (1) underwent an acid-catalyzed rearrangement to afford 1,4-diphenyl-1,4-di(2'-pyridyl)-1-buten-3-ol (2), as the major product. We recently reported (3) that the proposed structure (2) is *not* the major product of this reaction, but rather 3-hydroxy-4,9a-diphenyl-4*r*-(2-pyridyl)-4*H*-quinolizin-1(9*aH*)one, as based upon analytical and extensive spectral data. In less complicated systems, secondary ethynylcarbinols are well documented (4) to undergo acid- and base-catalyzed reactions to give products which are derived through either a prototropic (Route A) or an anionotropic (Route B) propargylic rearrangement. Under acidic conditions, 1,4-diphenyl-2-

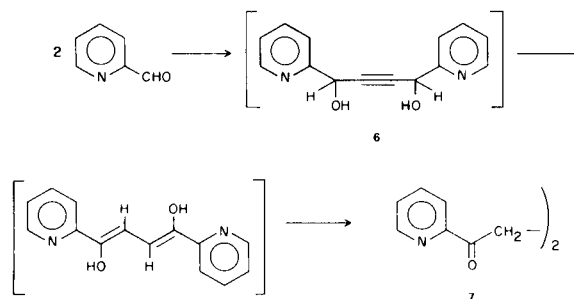


butyne-1,4-diol (3) underwent an anionotropic rearrangement (5) *via* intermediate 4 to generate the furanone 5. Dianionotropic rearrangement of 3 has not yet been experienced, but tetrasubstituted 2-butyne-1,4-diols have been shown (6) to isomerize to  $\alpha$ -diketones (e.g. 2,3-butanediones). Under varied basic conditions [acetylene *bis*-magnesium bromide (during preparation) or refluxing pyridine], 3 does not undergo an easy prototropic rearrangement; however, 1,3-diaryl-2-propyn-1-ols have been shown (7) to isomerize *via* a simple prototropic rearrangement in unspecified yields. In this note, we describe the first example in these systems of a *double* prototropic rearrangement, which was encountered during our attempted preparation of 1,4-di(2'-pyridyl)-2-butyne-1,4-diol (6).



Reaction of redistilled 2-pyridinecarboxaldehyde with ethereal acetylene *bis*-magnesium bromide (8), prepared by bubbling acetylene through ethereal ethylmagnesium bromide, afforded predominately, 1,4-di(2'-pyridyl)butane-1,4-dione (7). To further substantiate the structure, Bayer-

Villiger oxidation [*m*-chloroperbenzoic acid and sodium bicarbonate in dichloromethane] of 7 afforded, after hydrolysis, succinic acid and 2-hydroxypyridine. In our hands, 6 was neither isolated nor detected under the reaction conditions; however, 1-(2'-pyridyl)-1-propanol, the major side product, was isolated along with several presently unidentified trace compounds.



Formation of 7 can be rationalized by a *double* prototropic rearrangement followed by tautomerization. The enhanced facility of this rearrangement is best explained by the initial ease of proton abstraction from the reactive site(s) caused by the electron-withdrawing properties of the pyridyl group. The possibility of a double [1,2] or [1,3] sigmatropic process (9) or a dyotropic rearrangement (10) can also be considered; however, conceivable catalytic action of the integral base may negate such concerted processes.

#### EXPERIMENTAL

##### Attempted Preparation of 1,4-Di(2'-pyridyl)-2-butyne-1,4-diol.

Purified acetylene (dry-ice, concentrated sulfuric acid, and soda-lime traps) was slowly bubbled through ethylmagnesium bromide [from ethyl bromide (43.6 g., 0.4 mole) and magnesium (9.22 g., 0.4 mole)] in ether solution (200 ml.) with vigorous stirring for 20 hours at room temperature. 2-Pyridinecarboxaldehyde (10.7 g., 0.1 mole) in ether (30 ml.) was slowly added and stirring was maintained for an additional 3 hours. The reaction mixture was cooled and saturated aqueous ammonium chloride was added. The aqueous layer was separated, washed twice with chloroform and

the combined organic extracts were dried with magnesium sulfate and evaporated. The crude concentrate was distilled *in vacuo* affording unreacted starting material and 1.45 g. of 1-(2'-pyridyl)-1-propanol: b.p. 80-84° (0.15 mm) [lit (11) g.p. 94-98°/1 mm].

The residue was chromatographed on silica gel with ethyl acetate-ether (1:1) affording tan crystals. Two recrystallizations from chloroform-ether gave 2.9-3.5 g. of 1,4-di(2'-pyridyl)-1,4-butanedione. Sublimation at 140-145° (6 mm) afforded an analytical sample of white needles, m.p. 139-140°; nmr (deuteriochloroform):  $\delta$  8.72 (COCH<sub>2</sub>, s, 4H), 8.2-7.2 (pyr-H, m, 6H), and 8.75 (6-pyr-H, d, 2H); ir (chloroform): 1695 cm<sup>-1</sup> (>C=O).

Anal. Calcd. for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: C, 69.99; H, 5.03; N, 11.69. Found: C, 70.05; H, 4.91; N, 11.66.

Oxidation of 1,4-Di(2'-pyridyl)-1,4-butanedione.

A mixture of **7** (120 mg., 0.5 mmole), *m*-chloroperbenzoic acid (85%, 530 mg., 3.06 mmoles) and excess sodium bicarbonate in 20 ml. of dichloromethane was refluxed with stirring for 4 hours. The solution was cooled, poured into a cold dilute sodium hydroxide solution and extracted with dichloromethane. The combined organic extracts were washed with saturated salt solution, dried with magnesium sulfate, and concentrated. To the residue was added solid potassium hydroxide (60 mg.) in 50% ethanol-water (10 ml.). The mixture was refluxed for two hours, cooled, carefully acidified, and extracted twice with chloroform (20 ml.). The organic layer was concentrated *in vacuo* affording  $\alpha$ -pyridone: m.p. 105-107°. The aqueous layer afforded, after further acidification, succinic acid, m.p. 187-190°.

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