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THE THERMAL INTERCONVERSION OF QUINOLINE AND ISOQUINOLINE

John M. Patterson, C. H. Issidorides, E. P. Papadopoulos and W. T. Smith, Jr.

Department of Chemistry, University of Kentucky

Lexington, Kentucky 40506

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During a study of the pyrolytic behavior of phenylalanine (1) it was found that the ratio of yields of quinoline to isoquinoline increased with increasing pyrolytic temperatures. Thus the yield-ratios (quinoline/isoquinoline) obtained from pyrolyzates of phenylalanine produced at 650, 850, and 950° were 0.5, 1.1, and 1.7 respectively. The bases were the major constituents of the basic fraction of the phenylalanine pyrolyzates and were obtained in a maximum combined yield of 3%. In order to evaluate the relative stabilities of quinoline and isoquinoline and to investigate their possible interconversion, the pyrolyzates obtained from quinoline at 850° and from isoquinoline at 650, 850 and 950° using ca. 13 sec contact times were examined. Pyrolyses and separations of the pyrolyzates were carried out as previously described (2). Identification of "volatile" constituents is based upon comparisons of g.l.p.c. retention times, ultraviolet and infrared spectra with those obtained from authentic samples (Table). The only gases observed at 850° were hydrogen cyanide and acetylene.

At 850°, quinoline is converted into isoquinoline (0.7% conversion) and isoquinoline is isomerized into quinoline (2.3% conversion).

Isoquinoline, although quite stable under the pyrolytic conditions at 650°, is less stable than quinoline at 850° both regarding the extent to which it is isomerized to quinoline and the extent to which it is converted into neutral products and basic tars. This observation corroborates previous reports that, of the two bases, isoquinoline has the lower decomposition temperature (3) and the higher decomposition rate when heated in sealed glass capillary ampoules (4).

A reasonable reaction sequence based upon the most probable bond cleavages of the heterocyclic rings can be postulated for the interconversion of quinoline and isoquinoline (Figure). The parallelism of electron impact and pyrolysis in the production of similar molecular fragments is well known (5). The mass spectra of quinoline and isoquinoline (6) as well as the

Pyrolysis Products of Quinoline and Isoquinoline

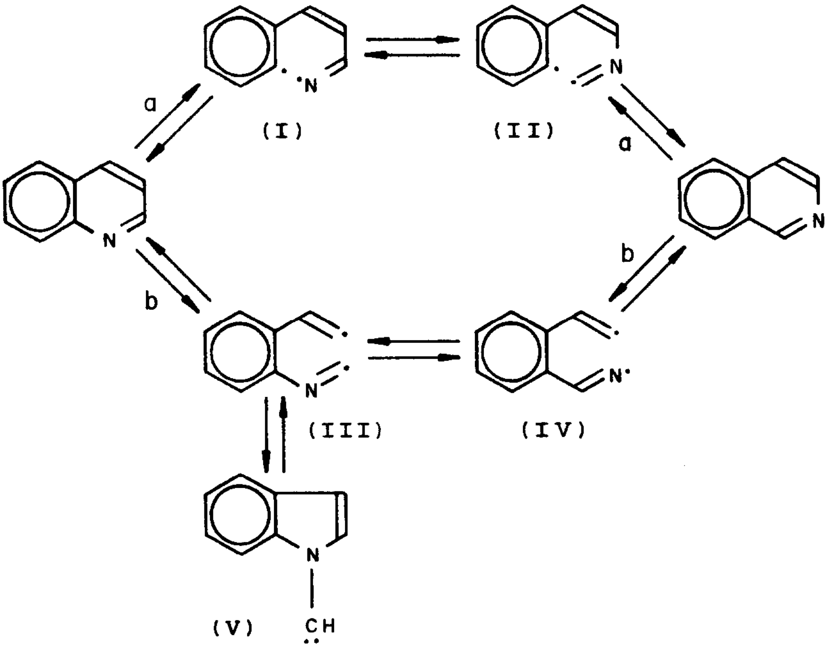
Pyrolysis Product[a]	Quinoline 850°	Isoquinoline 850°	Isoquinoline[c] 950°
Quinoline	102.8	3.0	2.5
Isoquinoline	0.9	75.2	2.5
Benzene	trace	0.03	0.2
Toluene	trace	0.02	0.02
Phenylacetylene	0.03	0.06	0.01
Styrene	0.03	0.13	0.08
Benzonitrile	0.13	0.57	2.42
o-Tolunitrile	0.02	0.16	0.04
Indene	0.01	0.06	0.08
o-Cyanostyrene	0.13	1.10	0.06
Phenylpropiolonitrile[b]	0.16	0.14	-
Naphthalene	0.15	0.16	2.1
Indole	0.26	0.07	-
Cinnamonitrile	0.33	0.17	-
2- and 3-Methylindole	0.10	-	-
1-Naphthonitrile	0.01	0.06	0.36
2-Naphthonitrile	0.02	0.07	0.29
Phenanthrene-anthracene	-	0.08	1.25

a. Grams produced per mole pyrolyzed.

b. Probable components of a mixture based upon infrared spectrum

c. The following were found in the 950° isoquinoline pyrolyzate but not in the 850° pyrolyzate 2-vinylnaphthalene (0.01), fluorene (0.07), fluoranthene (0.15), biphenyl (0.50), and 2-phenylnaphthalene (0.11).

observations of Hurd (7) in the pyridine series suggest that bond rupture by paths a and/or b represent the initial reactions involved. That these cleavages occur is substantiated by the isolation of the spontaneously isomerized forms (hydrogen shifts) of the intermediates postulated. Thus quinoline produced intermediate (I) on cleavage by path a which in turn is con-



verted into cinnamonitrile, and isoquinoline produces o-cyanostyrene by way of (IV). Intermediates (I) and (IV) possess diradical nitrene character and undergo C-to-N migration to form the precursors of isoquinoline and quinoline respectively. The N-to-C migration postulated for intermediates (II) and (III) may be similar to the previously reported thermal isomerization of isocyanides to cyanides (8). Intermediate (V) is the precursor of indole and the methylindoles.

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