Aqueous high-temperature chemistry of carbo- and heterocycles. 18.1 Six-membered heterocycles with one nitrogen atom. Pyridine, quinoline, acridine, and phenanthridine systems

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Aqueous High-Temperature Chemistry of Carbo- and Heterocycles. 18.[1] Six-Membered Heterocycles with One Nitrogen Atom: Pyridine, Quinoline, Acridine, and Phenanthridine Systems

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Seven nitrogen-containing heterocycles were chosen as model compounds: pyridine, 2-picoline, acridine, phenanthridine, quinoline, isoquinoline, and 2-methylquinoline. They were heated in eight different sets of conditions: (i) cyclohexane, (ii) water alone, (iii) aqueous formic acid, (iv) aqueous phosphoric acid (v) aqueous sulfuric acid, (vi) water and nontronite clay, (vii) water and Al-pillared clay, and (viii) water and calcium montmorillonite clay. Aquathermolyses under conditions (ii)–(viii) could thus be compared with purely thermal reactions under condition (i). Pyridine is almost unreactive under both thermolysis and aquathermolysis conditions, but in the presence of 10% H_3PO_4 almost 10% conversion was observed. 2-Picoline is more reactive toward heteroatom removal affording phenol (5.2%) as the major product. Acridine showed much higher conversions than phenanthridine; however, no nitrogen removal was observed and both compounds showed only hydrogenation and/or oxidation products. Quinoline, isoquinoline, and 2-methylquinoline are much more reactive than pyridine and 2-picoline, especially in the presence of 10% HCO_2H, H_3PO_4, or H_2SO_4, and yield a large variety of products including phenol and aniline. Structures of the products have been elucidated and reaction sequences for their formation suggested.

Introduction

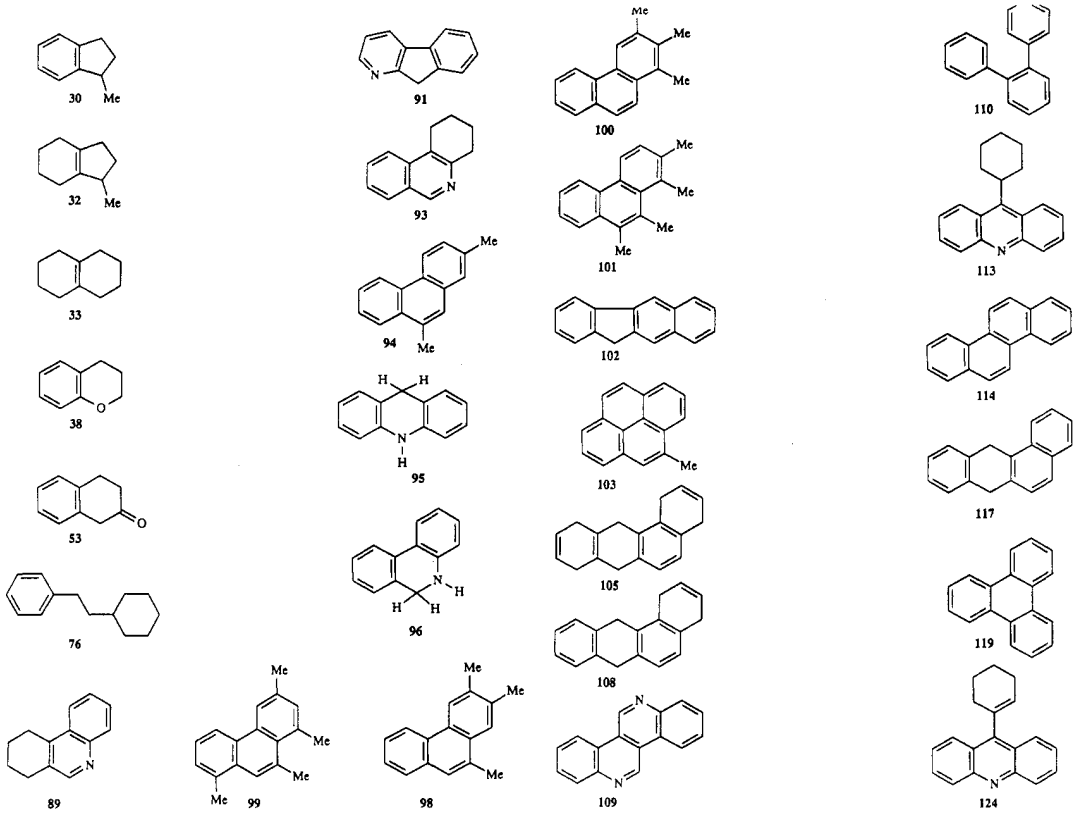
The purpose of coal liquefaction and oil shale retorting processes is to depolymerize the coal and oil shale structures and obtain liquid products with increased hydrogen content and a reduced heteroatom content. Coal and shale kerogens can be considered to be large networks of aromatic species connected by heteroatom and alkyl bridged structures.[2,3] Predominant heteroatoms found in coals and oil shales are sulfur, oxygen, and nitrogen. Predominant hydrocarbon bridges are methylene and ethylene structures. Some of these heteroatoms and bridging atoms are cleaved when a coal or oil shale is converted to liquids. Various catalysts have been shown to be effective in liquefying coal;[4,6] however, the efficiency of a particular catalyst for removal of specific heteroatoms can be obscured by the complex combination of structures involved. Thus, the use of model species and model reactions improves our understanding of heteroatom removal processes.

The development of catalysts for nitrogen removal from oil shales is needed, since liquids derived from them are of high nitrogen content due to the nature of the raw resources.[7] These nitrogen-containing compounds are detrimental for at least three major reasons: (i) they poison and deactivate catalysts used in further refining;[8] (ii) they form toxic nitrogen oxides upon combustion; and (iii) they confer instability on the product fuel, causing discoloration and other detrimental reactions.[9-11] As heavier feedstocks containing substantial amounts of nitrogen-containing compounds are brought into use (oil shale, tar sands, etc.), improved methods are needed to produce clean fuels.

To date, most of the model-reaction studies have been restricted to hydrodenitrogenation (HDN) of six-membered heterocycles. Among the model compounds studied, quinoline has received the most attention.[12-15] HDN involves hydrogenolysis of strong C–N bonds, which requires significant prehydrogenation of the heteroaromatic and/or aromatic rings. For complex feeds, hydrogenation and hydrogenolysis are both important insofar as overall HDN is concerned. The HDN reaction network, even for a simple compound, involves a large number of intermediate species with vastly different reactivities. Progressive decarboxylations, dehydrations, and C–C or C–N bond cleavages occur, leading to the generation of alkane chains and fragmentation of polycyclic and heterocyclic nuclei. Many workers have suggested that a catalyst is required to reduce the activation energies of these decomposition reactions sufficiently for the reactions to occur at low temperature.[16]

(1) Part 17: Katritzky, A. R.; Balasubramanian, M.; Siskin, M. *Energy Fuels*, preceding paper in this issue.
(2) Shinn, J. H. *Fuel* **1984**, *63*, 1187.
(3) Scouten, C. G.; Siskin, M.; Aczel, T.; Rose, K. D.; Colgrove, S. G.; Pabst, R. E., Jr. *Prep.—Pap Am. Chem. Soc., ACS Div. Pet. Chem.* **1989**, *34*, 43.
(4) Curtis, C. W.; Pellegrino, L. J. *Energy Fuels* **1989**, *3*, 160.
(5) Kottenstelte, R. J. Sandia Report No. SAND-82-2495; *Energy Abstr.* **1983**, 22936.
(6) Chianelli, R. R.; Dines, M. B. *Inorg. Chem.* **1978**, *17*, 2758.
(7) Newman, S. A. *Shale Oil Upgrading and Refining*; Butterworth Publishers: Boston, 1984.
(8) Stohl, F. V.; Stephens, H. P. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1986**, *31*, 251.
(9) Frankenfeld, J. W.; Taylor, W. F.; Brinkman, D. W. *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, *22*, 608, 615, 622.
(10) Kartzmark, R.; Gilbert, J. B. *Hydrocarbon Process.* **1967**, *46*, 143.
(11) Satterfield, C. N.; Gultekin, S. *Ind. Eng. Chem. Process. Des. Dev.* **1981**, *20*, 62.
(12) Satterfield, C. N.; Cocchetto, J. F. *Ind. Eng. Chem. Process. Des. Dev.* **1981**, *20*, 53.
(13) Satterfield, C. N.; Yang, S. H. *Ind. Eng. Chem. Process. Des. Dev.* **1984**, *23*, 11.
(14) Houser, J. M.; Tiffany, D. M.; Li, Z.; McCarville, M. E.; Houghton, M. E. *Fuel* **1986**, *65*, 827.
(15) Patterson, J. M.; Issidorides, C. H.; Papadopoulos, E. P.; Smith, Jr., W. T. *Tetrahedron Lett.* **1970**, 1247.

Scheme I



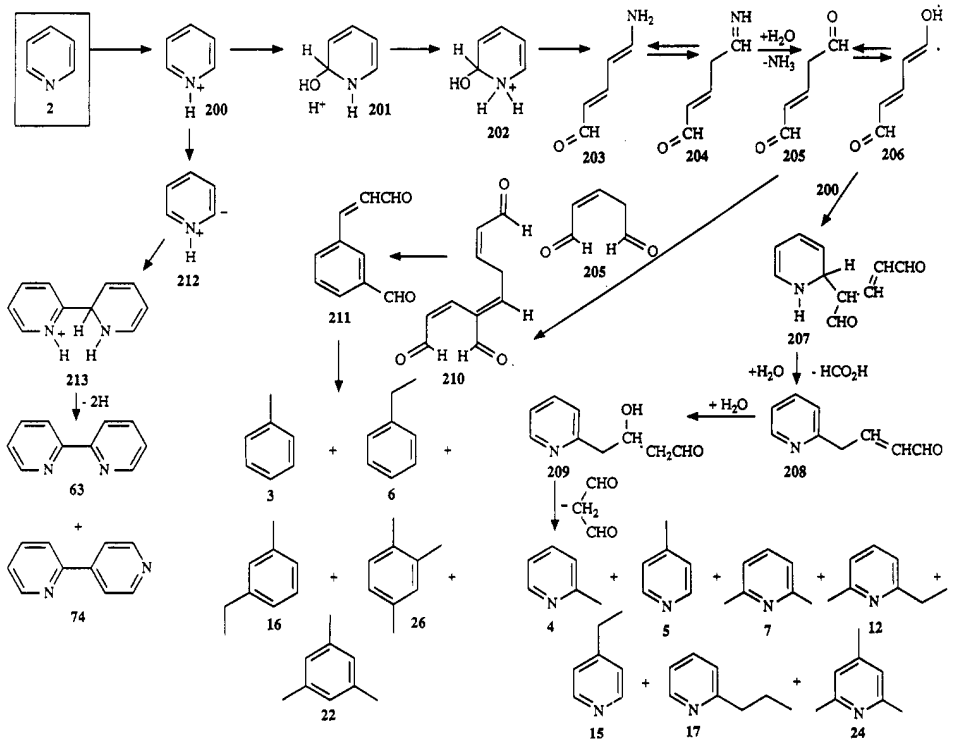
We can advantageously consider the natural maturation of shales to yield oil liquids. The most obvious natural catalysts are the clay minerals of the matrix in which the kerogen is dispersed. Grim[17] suggested that clay minerals in shales and natural sediments concentrate organic constituents by absorption and later act as catalysts in petroleum conversion. Most of the published research on the formation, stability, and reactions of clay-organic complexes, comprehensively summarized by Theng[18] and by Louis[19] has shown that a variety of clay minerals can catalyze the types of reactions thought to occur in petroleum formation. Cracking reactions were explained by acid catalysis via carbocation mechanisms. Reactions of model compounds, as well as kerogens, with clays to convert them to petroleum-like hydrocarbon mixtures have been carried out by several groups.[20-23]

Our major goal was to learn how to use aqueous chemistry to provide new options for upgrading feedstocks without added hydrogen. Currently, denitrogenation (and desulfurization) are achieved commercially by hydrogenolysis of the feedstock using transition-metal catalysts. Approaches which involve pyrolysis are not promising because the aromatic C–N and C–S bonds are not preferentially broken and pyrolysis of heavier feedstocks leads to excessive coking. On the other hand, the hydrolytic cleavage of nitrogen in pyrrole and pyridine ring systems has reasonable potential for success, especially at moderate temperatures (<350 °C) and high pressures (~3000 psi) in the presence of dilute acids. Such reactions represent the reversal of well-known syntheses for these ring systems and should be favored thermodynamically.

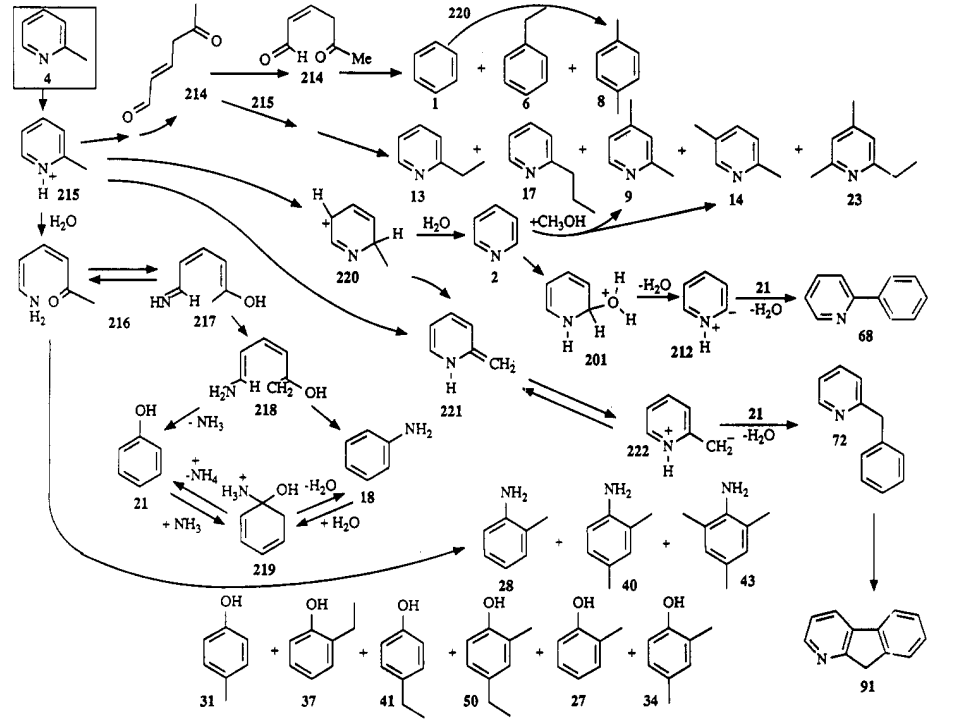
The last report in this series dealt with sulfur-containing heterocycles, i.e., thiophene and its derivatives.[1] While it has long been recognized that hydrodenitrogenation (HDN) is more difficult than hydrodesulfurization (HDS),[24] with present technology the removal of both N and S proceeds extremely slowly unless hydrogen and/or catalysts are employed. The nitrogen compounds found in petroleum or synthetic oils include both heterocycles and nonheterocycles. The latter comprise anilines and aliphatic amines. While aromatic amines are rather stable under neutral aquathermolysis conditions,[25] their aliphatic analogs undergo denitrogenation rapidly.[26] Five-membered nitrogen heterocycles such as pyrrole undergo nitrogen removal under aquathermolysis conditions relatively readily.[27] By contrast, no nitrogen removal was observed for pyridine and various substituted pyridines under either aquathermolysis or thermolysis conditions at 250 °C.[28-30] However, we now report that, under aqueous conditions at higher temperatures (350 °C), in the presence of different additives, six-membered nitrogen heterocycles can

(16) Hunt, J. M. *Petroleum Geochemistry and Geology*; W. H. Freeman and Co.: San Francisco, 1979.
(17) Grim, R. E. *Am. Assoc. Pet. Geol. Bull.* **1947**, *31*, 1491.
(18) Theng, B. K. G. *The Chemistry of Clay-Organic Reactions*; Wiley: New York, 1974.
(19) Louis, M. *World Pet. Congr. Proc. 7th* **1967**, *2*, 47; CA 71: 63086u.
(20) Huizinga, B. J.; Tannenbaum, E.; Kaplan, I. R. *Geochim. Cosmochim. Acta* **1987**, *51*, 1083.
(21) Tannenbaum, E.; Kaplan, I. R. *Geochim. Cosmochim. Acta* **1985**, *49*, 1041.
(22) Eglington, T. I.; Rowland, S. J.; Curtis, C. D.; Douglas, A. G. *Adv. Org. Geochem.* **1985**, *10*, 2589.
(23) Tannenbaum, E.; Ruth, E.; Kaplan, I. R. *Geochim. Cosmochim. Acta* **1986**, *50*, 805.
(24) Ho, C. T. *Catal. Rev.—Sci. Eng.* **1988**, *30*, 117.
(25) Katritzky, A. R.; Murugan, R.; Balasubramanian, M.; Siskin, M. *Energy Fuels* **1990**, *4*, 547.
(26) Katritzky, A. R.; Lapucha, A. R.; Siskin, M. *Energy Fuels* **1990**, *4*, 555.
(27) Katritzky, A. R.; Luxem, F. J.; Murugan, R.; Greenhill, J. V.; Siskin, M. *Energy Fuels*, following paper in this issue.
(28) Katritzky, A. R.; Lapucha, A. R.; Murugan, R.; Luxem, F. L.; Siskin, M.; Brons, G. *Energy Fuels* **1990**, *4*, 493.
(29) Katritzky, A. R.; Lapucha, A. R.; Siskin, M. *Energy Fuels* **1990**, *4*, 506.
(30) Katritzky, A. R.; Lapucha, A. R.; Siskin, M. *Energy Fuels* **1990**, *4*, 510.

Scheme II



Scheme III



undergo significant nitrogen removal, as well as other reactions.

The thermolyses and aquathermolyses were carried out as previously described.[28] All reactions reported here were done at 350 °C in stainless steel bombs. As in earlier parts of the series, the GC behavior of all the compounds included in the present paper (starting materials and products) are collected in Table I. Table II records the source and mass spectral fragmentation patterns of the authentic compounds used, either as starting materials or for the identification of products. Tables III and IV record the mass spectral fragmentation patterns of products for which authentic samples were not available, and which are identified by comparison with a published MS (Table III), or by deduction of their structure from the MS fragmentation pattern (Table IV). All the results obtained are collected in Tables V–XI; less common structures are presented in Scheme I, and the transformations are shown in Schemes II–VIII. Tables II, III, and IV and the mass spectral assignments have been deposited as supplementary material (see Supplementary Material Available paragraph at the end of this article).

Results and Discussion

In the schemes, numbers ≥200 are used for intermediates which were not detected by the GC-MS system.

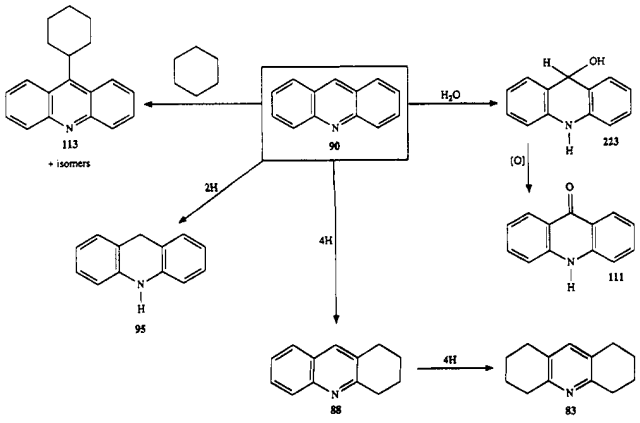
Table I. Structure and Identification of Starting Materials and Products

no.	t_R, min	structure	mol wt	equiv wt	identificn basis	response factor
1	0.50	benzene	78	78	Table II	1.09
2	0.62	pyridine	79	79	Table II	0.80
3	0.68	toluene	92	92	Table II	1.12
4	0.80	2-picoline	93	93	Table II	0.86
5	1.00	4-picoline	93	93	Table II	0.82
6	1.02	ethylbenzene	106	106	Table II	0.96
7	1.06	2,6-lutidine	107	107	Table II	0.88
8	1.07	*p*-xylene	106	106	Table II	1.05
9	1.10	2,4-lutidine	107	107	Table II	0.83
10	1.12	styrene	104	104	Table II	0.96
11	1.18	*o*-xylene	106	106	Table II	0.96
12	1.20	2-ethyl-6-methylpyridine	121	121	Table III	0.82
13	1.23	2-ethylpyridine	107	107	Table II	0.91
14	1.38	2,5-lutidine	107	107	Table II	0.83
15	1.51	4-ethylpyridine	107	107	Table II	0.83
16	1.53	3-ethyltoluene	120	120	Table III	0.95
17	1.65	2-propylpyridine	121	121	Table II	0.82
18	1.67	aniline	93	93	Table II	0.81
19	1.80	2-ethyltoluene	120	120	Table II	0.95
20	1.81	propylbenzene	120	120	Table II	0.95
21	1.85	phenol	94	94	Table II	0.76
22	1.87	1,3,5-trimethylbenzene	120	120	Table II	0.95
23	2.02	2,4-dimethyl-6-ethylpyridine	135	135	Table III	0.82
24	2.15	2,4,6-trimethylpyridine	121	121	Table II	0.86
25	2.24	indane	118	118	Table II	0.95
26	2.29	1,2,4-trimethylbenzene	120	120	Table III	0.95
27	2.45	*o*-cresol	108	108	Table II	0.79
28	2.50	*o*-toluidine	107	107	Table II	0.71
29	2.52	benzyl alcohol	108	108	Table II	0.89
30	2.80	1-methylindane	132	132	Table III	0.95
31	2.85	*p*-cresol	108	108	Table II	0.77
32	2.99	1-methyl-4,5,6,7-tetrahydroindane	136	136	Table IV	0.95
33	3.35	1,2,3,4,5,6,7,8-octahydronaphthalene	136	136	Table IV	0.95
34	3.47	2,4-dimethylphenol	122	122	Table II	0.77
35	3.48	4-methylacetophenone	134	134	Table II	0.78
36	3.60	1,2,3,4-tetrahydronaphthalene	132	132	Table III	0.95
37	3.64	2-ethylphenol	122	122	Table II	0.78
38	3.79	3,4-dihydrobenzopyran	134	134	Table III	0.76
39	3.81	naphthalene	128	128	Table II	0.98
40	3.83	2,4-dimethylaniline	121	121	Table II	0.71
41	4.38	4-ethylphenol	122	122	Table II	0.78
42	4.53	quinoline	129	129	Table II	0.79
43	4.60	2,4,6-trimethylaniline	135	135	Table II	0.70
44	4.67	isoquinoline	129	129	Table II	0.80
45	5.09	1-methyl-1,2,3,4-tetrahydronaphthalene	146	146	Table III	0.94
46	5.11	2-methyl-1,2,3,4-tetrahydroquinoline	147	147	Table III	0.70
47	5.14	indole	117	117	Table II	0.88
48	5.22	1-methylnaphthalene	142	142	Table II	0.94
49	5.30	2-methylnaphthalene	142	142	Table II	0.94
50	5.32	2-methyl-4-ethylphenol	136	136	Table III	0.77
51	5.44	3-methylisoquinoline	143	143	Table IV	0.81
52	5.51	2-methylquinoline	143	143	Table II	0.81
53	5.57	2-decalone	152	152	Table III	0.77
54	5.64	1,2,3,4-tetrahydroquinoline	133	133	Table II	0.70
55	5.69	1-methylisoquinoline	143	143	Table II	0.81
56	5.85	3-methylquinoline	143	143	Table IV	0.81
57	5.91	4-methyl-1,2,3,4-tetrahydroquinoline	147	147	Table IV	0.70
58	6.13	4-methylquinoline	143	143	Table II	0.81
59	6.37	4-methylisoquinoline	143	143	Table IV	0.81
60	6.43	2-ethylquinoline	157	157	Table III	0.81
61	6.74	2,4-dimethylquinoline	157	157	Table II	0.81
62	6.81	2,4-dimethyl-1,2,3,4-tetrahydroquinoline	161	161	Table IV	0.71
63	6.88	2,2′-bipyridine	156	78	Table II	0.68
64	6.98	2,6-dimethylquinoline	157	157	Table III	0.81
65	6.99	1,2-dimethylnaphthalene	156	156	Table II	0.94
66	7.09	3-ethylquinoline	157	157	Table III	0.81
67	7.11	2,8-dimethylquinoline	157	157	Table III	0.81
68	7.13	2-phenylpyridine	155	77.5	Table IV	0.81
69	7.16	4-ethylquinoline	157	157	Table III	0.81
70	7.43	1-ethylindole	145	145	Table III	0.70
71	7.57	2,3,4-trimethylquinoline	171	171	Table III	0.80
72	7.61	2-benzylpyridine	169	84.5	Table IV	0.80
73	7.92	2,3-dimethyl-1,2,3,4-tetrahydroquinoline	161	161	Table III	0.71
74	7.96	2,4′-bipyridine	156	78	Table II	0.68
75	8.00	2-propylquinoline	171	171	Table III	0.80
76	8.10	1-cyclohexyl-2-phenylethane	188	188	Table III	0.93
77	8.26	3-propylquinoline	171	171	Table III	0.80

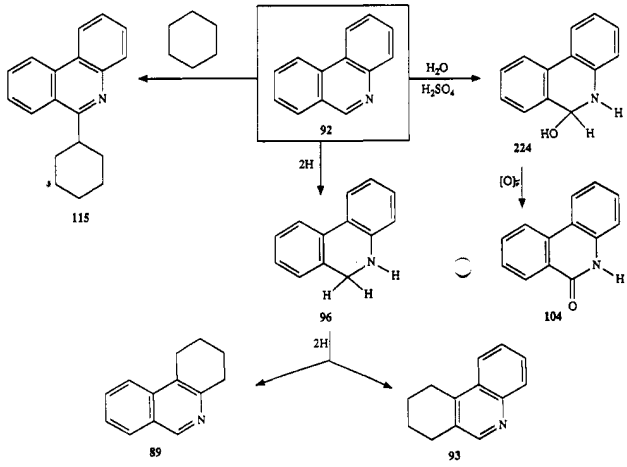
Table I (Continued)

no.	t_R, min	structure	mol wt	equiv wt	identifcn basis	response factor
78	8.34	4-propylquinoline	171	171	Table III	0.80
79	8.78	2-isobutylquinoline	185	185	Table III	0.80
80	8.80	2-butylquinoline	185	185	Table III	0.80
81	9.10	2-*n*-butylquinoline	185	185	Table III	0.80
82	10.06	2-isopentylquinoline	199	199	Table III	0.79
83	10.23	1,2,3,4,5,6,7,8-octahydroacridine	187	187	Table IV	0.80
84	10.25	2-phenyl-4-methylquinoline	219	109.5	Table III	0.78
85	10.29	2(1*H*)-quinolone	145	145	Table II	0.53
86	10.37	2-pentylquinoline	199	199	Table III	0.79
87	10.53	1(2*H*)-isoquinolone	145	145	Table III	0.53
88	10.68	1,2,3,4-tetrahydroacridine	183	183	Table IV	0.80
89	10.88	7,8,9,10-tetrahydrophenanthridine	183	183	Table IV	0.80
90	10.95	acridine	179	179	Table II	0.80
91	11.27	1-azafluorene	167	83.5	Table IV	0.80
92	11.32	phenanthridine	179	179	Table II	0.80
93	11.37	1,2,3,4-tetrahydrophenanthridine	183	183	Table IV	0.80
94	11.64	3,6-dimethylphenanthrene	206	103	Table II	0.92
95	11.70	9,10-dihydroacridine	181	181	Table IV	0.68
96	11.93	5,6-dihydrophenanthridine	181	181	Table IV	0.68
97	11.99	2-neopentylquinoline	199	199	Table III	0.79
98	12.15	2,3,5-trimethylphenanthrene	220	110	Table III	0.91
99	12.31	2,4,5,7-tetramethylphenanthrene	234	117	Table III	0.90
100	13.82	2,3,4-trimethylphenanthrene	220	110	Table III	0.91
101	14.86	3,4,5,6-tetramethylphenanthrene	234	117	Table III	0.90
102	14.89	2,3-benzofluorene	216	108	Table II	0.91
103	15.04	2-methylpyrene	216	108	Table III	0.91
104	15.10	6(5*H*)-phenanthridinone	195	195	Table III	0.51
105	15.30	1,4,7,8,11,12-hexahydrobenz[*a*]anthracene	234	117	Table III	0.90
106	15.45	1-phenyl-4-methylisoquinoline	219	109.5	Table III	0.78
107	15.53	2-phenylnaphthalene	204	102	Table III	0.92
108	16.13	1,4,7,12-tetrahydrobenz[*a*]anthracene	232	116	Table III	0.91
109	16.16	dibenzo[*c*,*h*]-2,6-naphthyridine	230	115	Table III	0.65
110	16.31	*o*-terphenyl	230	115	Table II	0.91
111	16.45	9(10*H*)-acridone	195	195	Table II	0.51
112	16.52	9-ethylacridine	207	207	Table IV	0.79
113	16.87	9-cyclohexylacridine	261	261	Table IV	0.77
114	16.89	chrysene	228	114	Table II	0.91
115	17.00	6-cyclohexylphenanthridine	261	261	Table IV	0.77
116	17.30	9,10-dihydro-9-cyclohexylacridine	263	263	Table IV	0.66
117	17.54	7,12-dihydro-benz[*a*]anthracene	230	115	Table III	0.91
118	17.75	4-cyclohexylacridine	261	261	Table IV	0.77
119	18.00	triphenylene	228	114	Table II	0.91
120	18.17	2-cyclohexylacridine	261	261	Table IV	0.77
121	18.21	2,2′-biquinoline	256	128	Table II	0.64
122	18.50	9-phenylacridine	255	255	Table IV	0.77
123	18.89	2,4′-biquinoline	256	128	Table IV	0.64
124	18.91	9-cyclohexenylacridine	259	259	Table IV	0.77
125	19.05	2-cyclohexenylacridine	259	259	Table IV	0.77
126	20.22	4,4′-biquinoline	256	128	Table IV	0.64

Scheme IV



Scheme V



Pyridine and 2-Picoline. (Tables V and VI; Schemes II and III). Heterocyclic aromatics such as pyridines are minor but important components of coals. In conventional hydrogenation, nitrogen is notoriously difficult to remove from pyridine rings. Very recently, iodomethane was found to promote liquefaction of bituminous coals and generally to give lower concentrations of nitrogen in the liquid products.[31] Hydrogenation of pyridine in the presence of iodomethane formed a wide range of products, including

(31) Vassallo, A. M.; Wilson, M. A.; Attalla, M. I. *Energy Fuels* **1988**, *2*, 539.

Table V. Products of Aquathermolysis of Pyridine (2) (at 350 °C for 3 days)

no.	solvent / additive / structure	C_6H_{12}	H_2O	H_2O 10% HCO_2H	H_2O 10% H_3PO_4	H_2O 10% H_2SO_4	H_2O Ca-Mont[a]
2	pyridine	99.6	99.6	97.1	90.4	99.4	95.1
3	toluene				0.6		
4	2-picoline		0.2		1.6	0.2	0.8
5	4-picoline			0.8			
6	ethylbenzene				0.5		
7	2,6-lutidine				0.3		
10	styrene	0.2					
12	2-ethyl-6-methylpyridine				0.9		
13	2-ethylpyridine		0.2			0.2	0.2
15	4-ethylpyridine			2.0			
16	3-ethyltoluene				0.5		
17	2-propylpyridine				0.5		
22	1,3,5-trimethylbenzene				0.1		
24	2,4,6-trimethylpyridine				0.1		
26	1,2,4-trimethylbenzene				0.1		
63	2,2′-bipyridine				3.5	0.2	3.0
74	2,4′-bipyridine				0.9		1.0
76	1-cyclohexyl-2-phenylethane	0.2					

[a] Ca-Mont = calcium montmorillonite.

Table VI. Products of Aquathermolysis of 2-Picoline (4) (at 350 °C for 3 days)

no.	solvent / additive[a] / structure	C_6H_{12}	H_2O	H_2O HCO_2H	H_2O H_3PO_4	H_2O H_2SO_4	H_2O Nont	H_2O Al-Pill	H_2O Ca-Mont
1	benzene				0.5				
2	pyridine	0.4	0.4	0.4	0.8	5.0	0.9	0.4	0.8
4	2-picoline	99.0	94.0	95.9	75.3	92.2	98.3	99.1	97.0
6	ethylbenzene	0.2	0.2	0.2	0.5	0.2	0.2	0.2	0.2
8	*p*-xylene	0.5	0.4		0.9	0.5	0.4	0.3	0.4
9	2,4-lutidine		0.2	3.5	1.8	0.2			0.2
13	2-ethylpyridine				0.7	0.1			
14	2,5-lutidine				1.2	0.1			
17	2-propylpyridine		0.6		3.8	0.3			0.7
21	phenol		3.6		5.2	1.1	0.1	0.1	0.9
23	2,4-dimethyl-6-ethylpyridine				0.3				
27	*o*-cresol				0.3				
28	*o*-toluidine				1.7				
29	benzyl alcohol		0.2						
31	*p*-cresol		0.2		0.7				
34	2,4-dimethylphenol		0.2						
35	4-methylacetophenone				1.1				
37	2-ethylphenol		0.2		0.7				
40	2,4-dimethylaniline				0.6				
41	4-ethylphenol				0.5				
43	2,4,6-trimethylaniline				0.3				
50	2-methyl-4-ethylphenol				0.2				
68	2-phenylpyridine				0.8				
72	2-benzylpyridine				1.2				
76	1-cyclohexyl-2-phenylethane	0.1							
91	1-azafluorene				1.0	0.2			

[a] Clay minerals: Nont = Nontronite; Al-Pill = alumina-pillared clay; Ca-Mont = calcium montmorillonite.

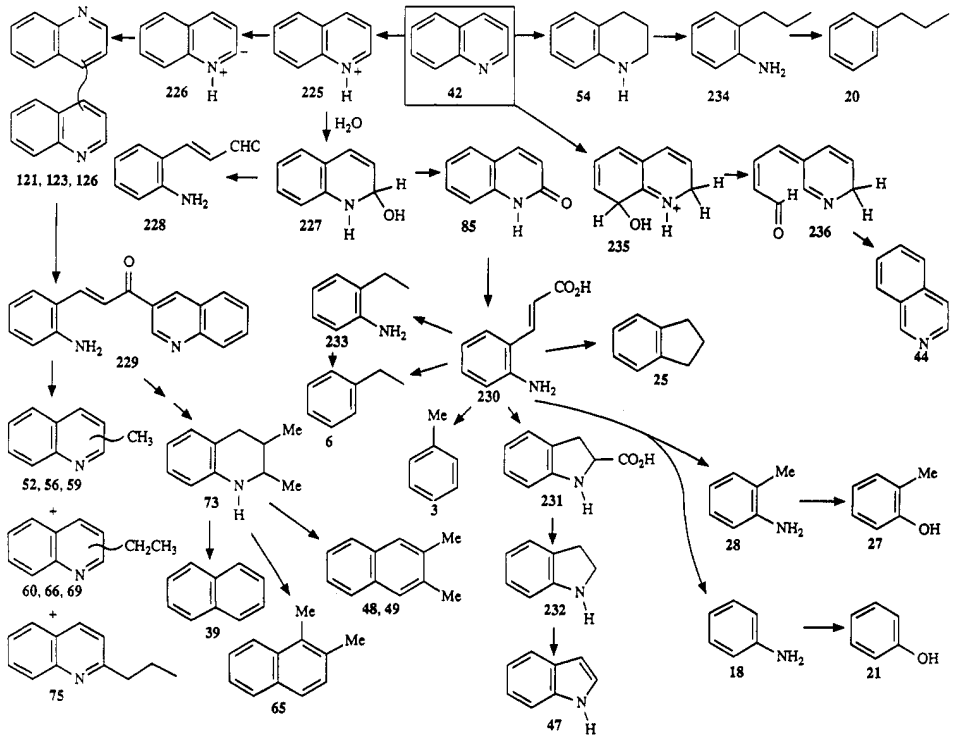
Table VII. Products of Aquathermolysis of Acridine (90) (at 350 °C for 3 days)

no.	solvent / additive / structure	C_6H_{12}	H_2O	H_2O 10% HCO_2H	H_2O 10% H_3PO_4	H_2O Nont	H_2O Al-Pill	H_2O Ca-Mont
83	octa[*H*]acridine			1.4	2.7			
88	tetra[*H*]acridine	1.4	4.7	43.5	47.3	12.8	31.2	6.5
90	acridine	51.1	49.7	8.7	15.4	11.3	12.5	25.8
95	9,10-di[*H*]acridine	31.2	41.1	46.5	28.6	43.2	56.4	32.7
111	9(10*H*)-acridone		4.2		6.2	32.7		35.1
112	9-ethylacridine	3.8						
113	9-cyclohexylacridine	4.4						
116	9,10-di[*H*]-9-cyclohexylacridine	0.8						
118	4-cyclohexylacridine	2.1						
120	2-cyclohexylacridine	2.7						
122	9-phenylacridine	0.4						
124	9-cyclohexenylacridine	0.9						
125	2-cyclohexenylacridine	0.9						

Table VIII. Products of Aquathermolysis of Phenanthridine (92) (at 350 °C for 3 days)

no.	solvent additive structure	C_6H_{12}	H_2O	H_2O 10% HCO_2H	H_2O 10% H_3PO_4	H_2O 10% H_2SO_4	H_2O Nont	H_2O Al-Pill	H_2O Ca-Mont
76	1-cyclohexyl-2-phenylethane	0.4							
89	7,8,9,10-tetra[*H*]phenanthridine			2.2	0.5				
92	phenanthridine	99.1	99.3	60.4	91.2	48.9	98.4	76.0	87.5
93	1,2,3,4-tetra[*H*]phenanthridine			10.9	7.2			12.1	
96	5,6-di[*H*]phenanthridine			26.5	0.4				
104	6(5*H*)-phenanthridinone		0.7		0.7	51.1	1.6	11.9	12.5
115	6-cyclohexylphenanthridine	0.5							

Scheme VI



Scheme VII

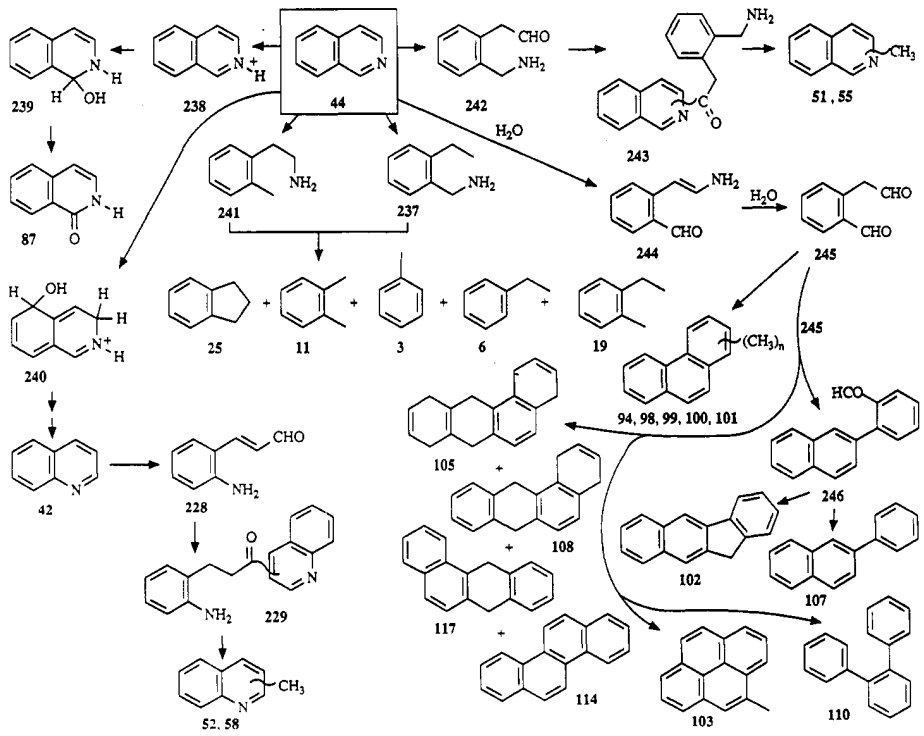


Table IX. Products of Aquathermolysis of Quinoline (42) (at 350 °C for 3 days)

no.	solvent / additive / structure	C_6H_{12}	H_2O	H_2O 10% HCO_2H	H_2O 10% H_3PO_4	H_2O 10% H_2SO_4	H_2O Nont	H_2O Al-Pill	H_2O Ca-Mont
3	toluene					0.3			
4	2-picoline					0.3			
6	ethylbenzene			0.2					
10	styrene	0.3							
11	*o*-xylene			0.2	0.4			0.5	0.4
18	aniline			0.7	4.4	0.4		2.8	1.2
20	propylbenzene			0.5	0.5				
21	phenol				4.0				
25	indane			0.2	1.6			0.4	0.5
27	*o*-cresol				1.6				
28	*o*-toluidine			1.3	1.7			0.7	0.5
38	3,4-dihydrobenzopyran			0.6					
39	naphthalene					0.3			
42	quinoline	93.4	95.1	58.9	57.7	91.2	94.9	66.0	83.3
44	isoquinoline	5.4	4.7	2.8		3.3	4.5	4.8	2.6
47	indole				1.3				0.6
48	1-methylnaphthalene	0.5	0.3	0.4	0.8		0.4	1.4	0.5
49	2-methylnaphthalene	0.2							
52	2-methylquinoline	0.2		0.3	7.7			5.3	2.6
54	1,2,3,4-tetra[*H*]quinoline			30.2	5.1			15.9	
56	3-methylquinoline			0.2	1.6			1.4	0.7
58	4-methylquinoline				2.3			0.8	0.9
59	4-methylisoquinoline				0.8				
60	2-ethylquinoline				0.5				
65	1,2-dimethylnaphthalene				0.4				
66	3-ethylquinoline			0.8	0.8				
69	4-ethylquinoline				1.2				
73	2,3-di-Me-1,2,3,4-tetra[*H*]quinoline			0.2					
75	2-propylquinoline				2.2				0.4
76	1-cyclohexyl-2-phenylethane	0.2							
84	2-Ph-4-Me-quinoline				1.2				
85	2(1*H*)-quinolone					2.6			2.1
119	triphenylene				1.0				
121	2,2′-biquinoline			1.3		1.6			3.5
123	2,4′-biquinoline			0.8	1.2				
126	4,4′-biquinoline			0.5					

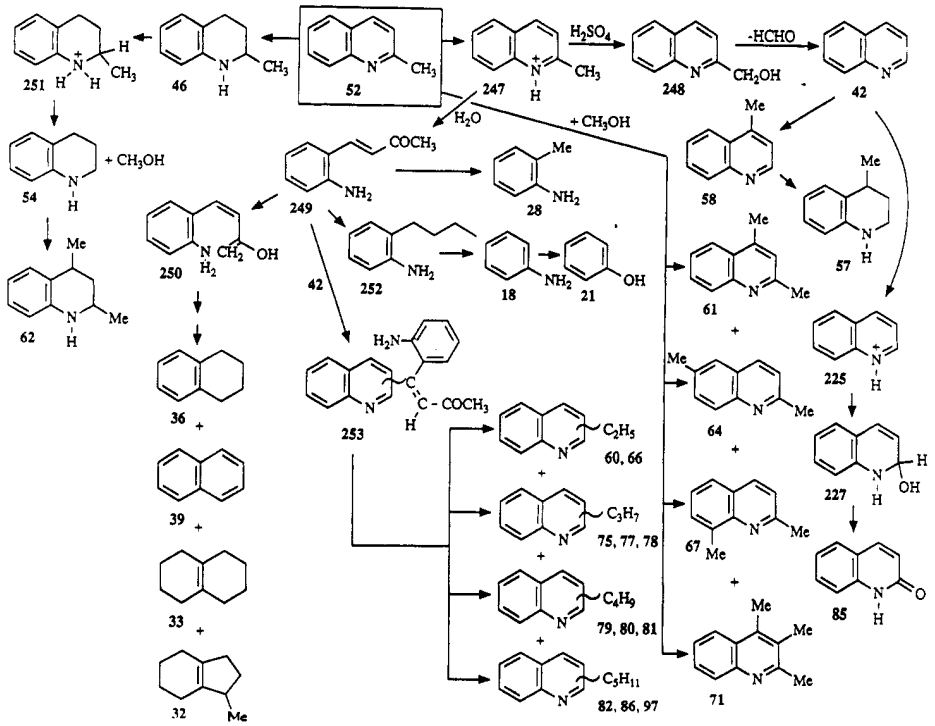
Table X. Products of Aquathermolysis of Isoquinoline (44) (at 350 °C for 3 days)

no.	solvent / additive / structure	C_6H_{12}	H_2O	H_2O 10% HCO_2H	H_2O 10% H_3PO_4	H_2O 10% H_2SO_4	H_2O Nont	H_2O Al-Pill	H_2O Ca-Mont
3	toluene				0.5	1.7			0.9
6	ethylbenzene				0.2				0.5
10	styrene	0.3							
11	*o*-xylene			3.9	2.2	1.4	0.2	0.2	2.9
19	2-ethyltoluene			5.5	0.3				0.2
25	indane			2.6	3.4				1.3
30	1-methylindane			1.2	0.4				
39	naphthalene			0.3					
42	quinoline	0.3	0.3	0.5		0.9	0.4	0.6	
44	isoquinoline	98.4	98.9	68.9	61.0	90.8	98.5	98.0	89.4
51	3-methylisoquinoline	0.8	0.8	0.8			0.9	0.7	1.2
52	2-methylquinoline			0.6					
55	1-methylisoquinoline			1.1					
58	4-methylquinoline			0.6	3.6				
76	1-cyclohexyl-2-phenylethane	0.2							
87	1(2*H*)-isoquinolone				2.5	2.1			0.9
94	3,6-dimethylphenanthrene			0.8					
98	2,3,5-tri-Me-phenanthrene			1.0					
99	2,4,5,7-tetramethylphenanthrene			0.3					
100	2,3,4-tri-Me-phenanthrene			1.6	0.7				
101	3,4,5,7-tetramethylphenanthrene			2.5					
102	2,3-benzo[*a*]fluorene				5.3				
103	2-methylpyrene				1.9	0.6			0.8
105	1,4,7,8,11,12-hexahydrobenz[*a*]anthracene			0.5					
106	1-Ph-4-Me-isoquinoline			0.5					
107	2-phenylnaphthalene			1.1					
108	1,4,7,12-tetrahydrobenz[*a*]anthracene			1.7					
109	dibenzonaphthyridine				6.1				
110	*o*-terphenyl			0.8	1.2	2.5			1.9
114	chrysene			2.1	10.8			0.5	
117	7,12-dihydrobenz[*a*]anthracene			1.1					

Table XI. Products of Aquathermolysis of 2-Methylquinoline (52) (at 350 °C for 3 days)

no.	solvent / additive / structure	C_6H_{12}	H_2O	H_2O 10% HCO_2H	H_2O 10% H_3PO_4	H_2O 10% H_2SO_4	H_2O Nont	H_2O Al-Pill	H_2O Ca-Mont
18	aniline		0.3	3.6	1.3	1.6	0.5	0.5	0.9
21	phenol			1.0	3.1				
28	o-toluidine			1.5		0.9			
32	1-Me-4,5,6,7-tetra[*H*]indane			0.9					
33	octahydronaphthalene			1.4					
36	1,2,3,4-tetra[*H*]naphthalene			2.2	2.7	0.5			
39	naphthalene				0.3				
42	quinoline			1.5	1.6	31.9	0.9	0.7	1.5
45	isoquinoline				0.4				
46	2-Me-1,2,3,4-tetra[*H*]quinoline			1.8	0.6	0.3			0.6
52	2-methylquinoline	99.0	98.1	72.6	38.4	54.1	98.3	95.5	89.5
53	2-decalone			0.4					
54	1,2,3,4-tetra[*H*]quinoline					1.4			
57	4-Me-tetra[*H*]quinoline	0.8	0.2	4.8		1.0		0.3	
58	4-methylquinoline				1.4				
60	2-ethylquinoline				0.4	0.5			0.4
61	2,4-dimethylquinoline		1.7	0.7	0.4	2.6			0.2
62	2,3-di-Me-1,2,3,4-tetra[*H*]quinoline				1.1				
64	2,6-dimethylquinoline			1.3	28.7			2.1	3.9
66	3-ethylquinoline			0.4	1.5	0.5			0.4
67	2,8-dimethylquinoline			0.7					
70	1-ethylindole			1.1					
71	2,3,4-trimethylquinoline			0.4					
75	2-propylquinoline			1.5					
76	1-cyclohexyl-2-phenylethane	0.1							
77	3-propylquinoline			0.8	1.1				
78	4-propylquinoline				6.0	2.9			0.8
79	2-isobutylquinoline				0.2				
80	2-butylquinoline			0.9	0.5				
81	2-*n*-butylquinoline				0.3				
82	2-isopentylquinoline							0.2	
85	2(1*H*)-quinolone					1.7		0.7	2.0
86	2-pentylquinoline			0.4	6.6				
97	2-neopentylquinoline				3.7				

Scheme VIII



methyl-substituted naphthalenes, benzene, pyridine, and tetralin.[32] Alkylpyridines, except for 2,6-dimethyl- and 2-methylpyridine, are more resistant to hydrodenitrogenation (HDN) than pyridine.[33] Pyridine and alkylpyridines are stable under thermal pyrolytic conditions at 450 °C.[34] However, it is well-known that 2,6-

(32) Attalla, M. I.; Wilson, M. A.; Quezada, R. A.; Vassallo, A. M. *Energy Fuels* **1989**, *3*, 59.

(33) Cox, K. E.; Berg, L. *Chem. Eng. Prog.* **1962**, *56*, 54.

(34) Stalick, W. M.; Mushrush, G. W., Cooney, J. V.; Hohman, J. *J. Chem. Res. (S)* **1987**, 6.

lutidine reacts with methyl iodide followed by NaOH at 150 °C to give *m*-cresol and methylamine,[35] and that pyridine treated first with sulfur trioxide and subsequently with NaOH gives glutaconic aldehyde and sulfamic acid.[36]

Thermolysis of pyridine in cyclohexane gave small amounts of styrene (**10**), and 1-cyclohexyl-2-phenylethane (**76**); contact with the metal surface of the tubing bombs may have catalyzed these unexpected reactions.

Pyridine (**2**) (Scheme II) is unchanged over 3 days at 350 °C in water in the presence of nontronite clay or aluminum-pillared clay and is little changed in water, 10% formic acid, or 10% sulfuric acid. In the presence of calcium montmorillonite, it is 5% degraded to give 2,2′-bipyridyl, 2,4′-bipyridyl, and some minor products. Treatment with phosphoric acid gives almost 10% conversion, but the yield of denitrogenated (DN) products is very low (1.7%). Products obtained can be divided into three classes: alkylpyridines, alkylbenzenes, and bipyridyls. Pyridine, after protonation and nucleophilic attack by a molecule of water, can undergo ring opening and after loss of ammonia form glutaconic aldehyde (**205**). This aldehyde reacts with pyridinium cation **200** to form intermediate **207** which is converted on to **208** and **209**. This loses malondialdehyde to give 2-picoline (**4**). Other alkylated pyridines: **5**, **7**, **12**, **15**, **17**, and **24** are formed similarly. Aldehyde **205** can also react with another molecule of itself to form intermediate **210**, and after ring closure, dehydration and aromatization and reduction processes via **211**, form alkylbenzenes. Protonated pyridine can lose protons from the 2- or 4-positions to give carbanion(s) **212**, which react with other molecules of protonated pyridine followed by oxidation to give bipyridyls **63** and **74**.

2-Picoline (**4**) (Scheme III) is much more reactive than pyridine especially in the presence of H_3PO_4, where almost 25% conversion was observed with a DN yield of 13.2%. Besides products similar to those mentioned above for pyridine, two additional classes were detected, phenols and anilines, in relatively high yields (up to 5%). A possible practical approach to the denitrogenation of pyridines using dilute phosphoric acid under pressure is thus in sight, and phenol and ammonium phosphate are the byproducts of this reaction. Alkylbenzenes and alkylpyridines can be formed via intermediate **214** in a similar way to that discussed above. The alternative pathway is demethylation, which leads via **220** to pyridine (**2**) and methanol. The alcohol is the source of methyl cations which give methylpyridines. When intermediate **218** loses ammonia, phenol (**21**) is formed, and loss of H_2O gives aniline (**18**), which under acidic conditions is hydrolyzed to phenol.[25] Tautomeric form **216** can recyclize to give *o*-toluidine (**28**) which is methylated to **40** and **43**. Alkylations of phenol give the minor products **27**, **31**, **34**, **37**, **41**, and **50**. Carbanions **212** and **222** after reaction with phenol can form 2-phenyl- and 2-benzylpyridine (**68** and **72**). Compound **72** is the source of azafluorene (**91**) via an oxidative cyclization.

Acridine (90) and Phenanthridine (92) (Tables VII and VIII and Schemes IV and V). Acridine is readily hydrogenated to 9,10-dihydroacridine over metal catalysts.[37] Anthracene similarly gives 9,10-dihydroanthracene and is reduced further to hexahydro- and 1,2,3,4,5,6,7,8-octahydroanthracene.[4] On the other hand, N-substituted acridines can easily be oxidized by molecular oxygen to 9-acridones in high yield.[38]

Acridine (**90**) is reactive at 350 °C for 3 days under all sets of conditions tested, but no DN products were detected. The main products are 9,10-dihydroacridine (**95**), 1,2,3,4-tetrahydroacridine (**88**), and 9(10*H*)-acridone (**111**). Aquathermolysis in the presence of 10% H_2SO_4 gives 100% of acridone **111**, whereas in 10% H_3PO_4 it gives only 6.2% of **111** with the partially reduced acridines as the main products. 10% Formic acid gives no acridone, but the proportions of di- and tetrahydroacridines are closely similar to those for 10% phosphoric acid. Even in water, significant partial reduction to 9,10-dihydroacridine (41%) occurs. Water must be able to provide the hydrogen for this process, possibly after reaction with the metal of the reaction bomb. With formic or phosphoric acid present, more tetrahydroacridine is produced. Nontronite and calcium montmorillonite clays give higher yields of 9-(10*H*)-acridone along with some reduced products while aluminium-pillared clay gives a mixture of the di- and tetrahydroacridines. Clearly, sulfuric acid is in this case an oxidizing agent as well as an acid. Acridone can be formed via nucleophilic attack of a molecule of water at C-9 of the protonated acridine molecule followed by oxidation of intermediate **223**. Runs carried out in cyclohexane gave a wide range of cyclohexyl derivatives of acridine, via radical coupling with the solvent.

Phenanthridine (**92**) behaves similarly to acridine but is less reactive. Reaction with 10% H_2SO_4 gives only 51% of 6(5*H*)-phenanthridinone (**104**). Along with recovered starting material, major products in runs carried out in the presence of HCO_2H and H_3PO_4, are 5,6-dihydrophenanthridine (**96**) and 1,2,3,4-tetrahydrophenanthridine (**93**), although the former gives 40% conversion, but the latter only 9%, attesting to the reducing abilities of formic acid. Phenanthridine after nucleophilic attack of water gives intermediate **224**, which is oxidized to 6(5*H*)-phenanthridone (**104**). Reduction of phenanthridine leads to 5,6-dihydrophenanthridine (**96**) and to tetrahydrophenanthridines **89** and **93**. Runs carried out in cyclohexane gave a cyclohexyl derivative (**115**) of the starting material.

Quinoline (42) (Table IX, Scheme VI). The hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline is much faster than the hydrogenation of quinoline to 5,6,7,8-tetrahydroquinoline.[24] This is to be expected since pyridine is reduced much faster than benzene. Oxidation of N-substituted quinolinium salts with oxygen leads to 2-quinolones,[38] which can subsequently be converted into indoles.[39] Thermal interconversion between quinoline and isoquinoline at 850 °C has been reported, but isoquinoline to quinoline gives the higher yield.[15] Hydrogenation with a large excess of hydrogen, and in the presence of $NiMo/Al_2O_3$ and some other catalysts, leads via *o*-propylaniline to propylbenzene as a final product.[24,40,41] Treatment of quinoline with "supercritical" water in the presence of $ZnCl_2$ is reported to give a wide range of products including methylanilines, methylphenols, methylquinolines, and methylindanes.[14]

Quinoline (42, Table IX) and Isoquinoline (44, Table X). Under the conditions of the present reactions (350 °C, stainless steel bombs), quinoline is converted to isoquinoline more efficiently than the reverse reaction occurs.

(35) Katritzky, A. R. *Handbook of Heterocyclic Chemistry*; Pergamon Press: Oxford, U.K., 1985; p 170.
(36) Katritzky, A. R. *Handbook of Heterocyclic Chemistry*; Pergamon Press: Oxford, U.K., 1985; p 171.
(37) Katritzky, A. R. *Handbook of Heterocyclic Chemistry*; Pergamon Press: Oxford, U.K., 1985; p 189.
(38) Ruchirawat, S.; Sunkul, S.; Thebtaranouth, Y.; Thirasasna, N. *Tetrahedron Lett.* **1977**, 2335.
(39) Jones, G. *Quinolines*; John Wiley & Sons: London, 1977; Part I, p 40.
(40) Curtis, C. W.; Chung, W. J. *Energy Fuels* **1989**, *3*, 148.
(41) Curtis, C. W.; Cahela, D. R. *Energy Fuels* **1989**, *3*, 168.

Table XII. Summary of Aqueous Reactivity of Basic Nitrogen Heterocycles (350 °C/3 days)

	H_2O		H_2O/HCO_2H (10%)		H_2O/H_3PO_4 (10%)		H_2O/H_2SO_4 (10%)		H_2O/Nont		H_2O/Al-Pill		H_2O/Ca-Mont	
structures	% con[a]	% DN[a]	% con	% DN	% con	% DN	% con	% DN	% con	% DN	% con	% DN	% con	% DN
pyridine	0.4	0	2.9	0	9.6	1.8	0.6	0					4.9	0
2-picoline	6.0	5.0	4.1	0.2	24.7	10.6	7.8	1.8	1.7	0.7	0.9	0.6	3.0	1.5
acridine	50.3	0	91.3	0	84.6	0			88.7	0	87.5	0	74.2	0
phenanthridine	0.7	0	39.6	0	8.8	0	51.1	0	1.6	0	24.0	0	12.5	0
quinoline	4.9	0.3	41.1	0.4	42.3	10.3	8.8	0.6	5.1	0.4	34.0	2.3	16.7	1.4
isoquinoline	1.1	0	31.1	27.5	39.0	26.9	9.2	6.2	1.5	0.2	2.0	1.2	10.6	8.5
2-methylquinoline	1.9	0	27.4	5.5	61.6	6.1	45.9	0.5	1.7	0	4.5	0	10.5	0

[a] % con = % conversion; % DN = % denitrogenation.

In cyclohexane (6.6% conversion), 5.4% of isoquinoline is produced over 3 days and in water (4.9% conversion), 4.7% of isoquinoline is obtained. In the reverse reactions, there are 1.6 and 1.1% conversions in cyclohexane and water, respectively, but both reactions give only 0.3% of quinoline. The reactions in the presence of the various catalysts also favored the quinoline to isoquinoline conversion.

Quinoline (**42**), Scheme VI, treated with 10% HCO_2H (41% conversion) or Al-pillared clay (34% conversion) gives 1,2,3,4-tetrahydroquinoline (**54**) as the major product in 30.2 and 15.9% yields, respectively. The long list of products from the reaction with 10% H_3PO_4 (42% conversion) can be divided into several groups, i.e., alkylquinolines, biquinolines, tetrahydroquinolines, alkylbenzenes, anilines, phenols, and others, viz., indole (**47**), indane (**25**), 1-methylnaphthalene (**48**), and triphenylene (**119**). Phenol (**21**), which is obtained in 4% yield, is believed to be formed from aniline (**18**), which is also observed in relatively high yield (4.4%). The total amount of heterocyclic nitrogen removal is 16.4%, but 6.1% of the nitrogen is still present as anilines. Treatment of quinoline with 10% H_2SO_4 (8.8% conversion) leads to 2(1*H*)-quinolone (**85**, 1.2%) along with isoquinoline (**44**, 3.3%), 2,2′-biquinolyl (**121**, 1.6%), and some minor products.

In the presence of nontronite clay, there is a low conversion (4.1%) to a mixture of isoquinoline and 1-methylnaphthalene. With calcium montmorillonite, there is 17% conversion to give 13 products, all in low yields.

Quinoline is reduced to the tetrahydro derivative **54**, the protonated form of which probably undergoes Hoffmann elimination followed by further reduction to give propylbenzene (**20**). After protonation, nucleophilic attack by water and oxidation quinoline goes to 2-quinolone (**85**), which hydrolyses to key intermediates **230**. This compound appears to be a source of indole (**47**), indane (**25**), alkylbenzenes (**3**, **6**), and anilines 18 and 28. These anilines then react with water to give phenols **21** and **27**.[25] Biquinolines **121**, **123**, and **126** are formed in a similar manner to the bipyridyls, described above, via carbanions **226**. After ring-opening reactions, biquinolines would give intermediates such as **229**, which are responsible for the formation of the methyl-, ethyl-, and propylquinolines (**52**, **56**, **59**, **60**, **66**, **69** and **75**), as well as their tetrahydro derivatives such as **73**. The last are probably the source of naphthalene and its derivatives (**39**, **48**, **49**, and **65**): **73** could cleave at the 1,2-bond and then the four-carbon side chain undergo ipso substitution at the carbon carrying the nitrogen atom.

Isoquinoline (**44**), Scheme VII, reacts with "supercritical" water in the presence of $ZnCl_2$ to form *o*-xylene, ethylbenzene, toluene, and benzene.[14] On pyrolysis at 850 °C isoquinoline gave more phenanthrene and anthracene products than quinoline under the same conditions.[15] Oxidation with molecular oxygen of *N*-alkylisoquinolines leads to 1-isoquinolones.[38]

As can be seen from the results given in Table X, protonic acid catalysts increase the conversion of isoquinoline. Careful analysis of the data collected in Tables IX and X leads to the conclusion that the reaction routes for quinoline and isoquinoline are quite different. Whereas quinoline yields anilines, phenols, and alkylquinolines as dominant products, isoquinoline gives mainly alkylbenzenes, poly(alkylphenanthrenes), and other condensed aromatic systems including terphenyl, chrysene, and derivatives of pyrene and benzanthracene. Isoquinoline, under aquathermolysis conditions in the presence of formic acid, gives relatively large amounts of *o*-xylene (**11**) (3.9%), 2-ethyltoluene (**19**) (5.5%), and indane (**25**) (2.6%). The total yield of conversion products is 31% with 27% of DN. When HCO_2H is replaced by H_3PO_4, the proportion of polyaromatic systems increases, the most important of which are 2,3-benzo[*a*]fluorene (**102**, 5.3%), dibenzonaphthyridine (**109**, 6.1%), and chrysene (**114**, 10.8%). The total conversion is now 39%, with 26.9 of denitrogenation. In the case of isoquinoline two parallel reactions can occur through cleavage of the C1–N/or C3–N bonds. Both amines thus obtained are unstable, and lead to the same products, alkylbenzenes (**3**, **6**, **11**, **19**, and **25**). Dialdehyde **245** appears to be a key intermediate in the formation of polyaromatic compounds such as 2-phenylnaphthalene (**107**), *o*-terphenyl (**110**), methylphenanthrenes (**94**, **98**, **99**, **100**, **101**), chrysene (**114**), methylpyrene (**103**), and poly(hydrobenzanthracenes) (**105**, **108**, and **117**): aldol condensation of 2 molecules of **245** followed by loss of one carbonyl group gives **246** from which obvious routes lead to **102** and **107**. Intermediate **228** can be the source of methylquinolines (**52** and **58**), whereas intermediate **242** leads to methylisoquinolines **51** and **55**. Isoquinolone **87** is formed via nucleophilic attack of water on protonated isoquinoline to give **239** followed by oxidation.

2-Methylquinoline (52) (Table XI, Scheme VIII). 2-Methylquinoline (**52**) is more reactive than quinoline or isoquinoline, in phosphoric acid (62% conversion) or sulfuric acid (46% conversion). Sulfuric acid is mainly responsible for a demethylation reaction; 31.9% of quinoline is produced in this solvent. Runs carried out in the presence of phosphoric acid give a wide variety of products, of which the only one in high yield is 2,6-dimethylquinoline (**64**) (28.7%). Other prominent products are various propyl-, butyl-, and pentylquinolines formed via the hydrolysis product **249**. Reactions performed in the presence of 10% formic acid give more hydrogenated products such as the tetrahydroindane (**32**), tetrahydronaphthalene (**36**), and the tetrahydroquinolines **46** and **57**, reflecting the reducing properties of this acid. The presence of HCO_2H or H_3PO_4 leads to aniline (**18**) and phenol (**21**) as products. Contrary to the quinoline and isoquinoline reactions, no polycyclic high molecular weight products were detected. Although the total conversion in the presence of acids is high, the yields of DN are relatively low: H_3PO_4 –6.1%,

H_2SO_4 0.5%, and HCO_2H 5.9%. The demethylation to quinoline (**42**) in sulfuric acid is probably the result of an oxidation to the alcohol **248** which would lose formaldehyde. The formaldehyde would be reduced to methanol a source of methyl cations and lead to 2,4-dimethylquinoline. The formation of naphthalene and its polyhydro derivatives (**33**, **36**, and **39**) probably occurs from compounds **249** via its enol **250**. Formation of anilines **18** and **28** also takes place from intermediate **249**, but aniline (**18**), which is the source of phenol (**21**) can also be formed by acid-catalyzed dealkylation of 2-butylaniline (**252**). Quinolone (**85**) is formed after nucleophilic attack of water on protonated quinoline followed by oxidation.

Conclusions

Table XII summarizes the % conversions and denitrogenation for the seven six-membered heterocycles with one basic nitrogen atom studied at 350 °C for 3 days. In water only acridine showed a significant conversion (50%) and only picoline showed denitrogenation (5% against 6% total conversion). In 10% formic acid the monocyclic compounds showed very low conversions but all the polycyclics showed significant changes. However, only isoquinoline had a useful rate of denitrogenation. In 10% phosphoric acid all except pyridine and phenanthridine showed significant conversions and, in most cases, the denitrogenation was also increased. In 10% sulfuric acid three compounds, acridine, phenanthridine, and 2-methylquinoline showed high conversions, but the products all retained the nitrogen. Isoquinoline was unusual in that 2/3 or more of the converted material was also denitrogenated in all three of the acid solutions.

Of the three clay catalysts investigated, nontronite showed no advantage over water alone except that the conversion of acridine was higher. However, no significant denitrogenation was seen for any substrate. The aluminum-pillared clay and calcium montmorillonite increased the conversion rates for some of the heterocycles, but again failed to catalyze denitrogenation.

Clearly, none of the catalysts investigated is capable of giving useful rates of denitrogenation for the mixtures of six-membered, nitrogen-containing heterocyclic compounds likely to be present in natural oil resources.

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Supplementary Material Available: Mass spectral assignments and Tables II–IV listing properties of starting materials and mass spectral fragmentation data of products (12 pages). Ordering information is given on any current masthead page.