ALKYLATION OF HETEROAROMATIC BASES BY α-HYDROXYALKYL RADICALS (REVIEW)

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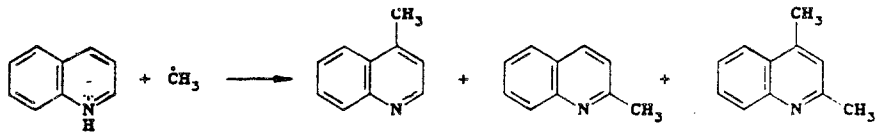
UDC 547.831.04:541.513(047)

The synthetic possibilities of reactions involving the homolytic α-hydroxylation of protonated heteroaromatic bases are examined. Factors that affect the yields and structures of the products formed are discussed.

Processes involving free-radical substitution in the aromatic ring have been responsible for the increased interest of researchers in recent years [1–5]. A great deal of attention is being directed to the homolytic alkylation of protonated aromatic bases, which is distinguished by regioselectivity and, in many cases, by a high degree of conversion of the aromatic base.

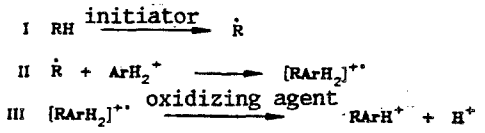
In this connection, we have correlated and thoroughly analyzed the published data on the α-hydroxylation of protonated heteroaromatic bases.

It is known that protonated aromatic bases (pyridine, quinoline, quinoxaline, etc.) have clearly expressed electrophilic properties; this facilitates the additional of nucleophilic radicals in the α and γ positions of the aromatic ring [2]. Even weakly polar methyl radicals react with protonated quinoline with the formation of only 2- and 4-substituted derivatives [6].



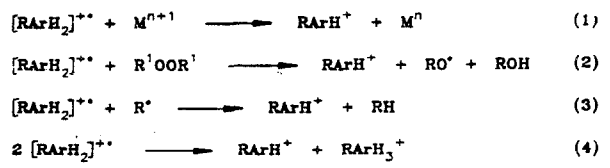
Mono- and dialkoxyalkyl radicals are characterized by increased nucleophilicity [7, 8]; this determines the effectiveness of their use in the homolytic alkylation of protonated bases.

The generation of α-hydroxyalkyl radicals generally occurs via the detachment by initiator radicals of hydrogen from alcohols, linear and cyclic ethers, acetals, etc. [7, 8].



The intermediate $[RArH_2]^{+\cdot}$ cation radical has a quinoid structure, which decreases its energy substantially, and attack by the nucleophilic radical in the β position therefore does not occur.

The oxidation of the $[RArH_2]^{+\cdot}$ cation radical may occur in different ways [2]:



Ufa Petroleum Institute, Academy of Sciences of the Bashkir SSR, Ufa 450062. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 579–587, May, 1990. Original article submitted July 16, 1987; revision submitted September 15, 1988.

0009-3122/90/2605-0487$12.50

TABLE 1. Conditions and Results of α-Hydroxyalkylation of Protonated Aromatic Bases

Example	Aromatic base	Alkylating agent	Resulting R	Method of initiation	T_{re}, °C	Position of R in the reaction product	Conversion of the base	Yield based on the converted base, %	Literature
1	2	3	4	5	6	7	8	9	10
1	Pyridine	1,3-Dioxolane	1,3-Dioxolan-2-yl	$C_6H_5(CH_3)_2OOH$, Fe^{2+}	10	4	30	65	[19]
			1,3-Dioxolan-4-yl			2		15	
2			1,3-Dioxolan-2-yl	H_2O_2, Fe^{2+}	10	4	43	6	[19]
			1,3-Dioxolan-4-yl			2		4	
						4		38	
						2		11	
3		2,2-Dimethyl-1,3-dioxolane	2,2-Dimethyl-1,3-dioxolan-4-yl	H_2O_2, Fe^{2+}	10	4		22	
						2		20	
						2	30	29	[19]
4		2-Methyl-2-ethyl-1,3-dioxolane	2-Methyl-2-ethyl-1,3-dioxolan-4-yl	H_2O, Fe^{2+}	10	4		61	
						2		32	[19]
5	4-Cyanopyridine	Methanol	Hydroxymethyl	NH_3OSO_3, F^{2+}	20	4	30	58	
6		1,4-Dioxane	1,4-Dioxan-2-yl	$S_2O_8^{2-}$	80	2	35,9	78	[17]
7	Quinoline	Ethane-1,2-diol	Hydroxymethyl*	$S_2O_8^{2-}$, Ag^+	20	2		65	
						2,6		8	[7]
8			1,2-Dihydroxyethyl	$S_2O_8^{2-}$	80	2	11	36,2	[7]
9		Trioxane	Trioxanyl	*t*-BuOOH	80	2		32,9	
						4	—	6	
10	Quinaldine	Methanol	Hydroxymethyl	*t*-BuOOH	20	4		42	[22]
11		Methanol	Hydroxymethyl	NH_3OSO_3	20	4	—	58	
12		1,3-Dioxolane	1,3-Dioxolan-2-yl		10	2	55	86	[7]
			1,3-Dioxolan-4-yl			4		90,0	[8]
13		1,3-Dioxane	1,3-Dioxan-2-yl	H_2O_2, Fe^{2+}	10	2		14	[21]
			1,3-Dioxan-4-yl			4	62	76	
14			1,3-Dioxan-2-yl	H_2O_2, Fe^{2+}	10	4	—	8	[21]
15		1,3-Dioxepane	Dioxepan-2-yl	$C_6H_5(CH_3)_2OOH$	10	4	—	22	[21]
			Dioxepan-4-yl	H_2O_2, Fe^{2+}	10	4	—	7	[21]
16			Dioxepan-2-yl	H_2O_2, Fe^{2+}	10	4	—	2	[21]
			Dioxepan-4-yl	$C_6H_5(CH_3)_2OOH$	10	4	—	31	[21]
								2	[21]
				$C_6H_5(CH_3)_2OOH$	10	4	—	31	[21]

TABLE 1 (continued)

Example	Aromatic base	Alkylating agent	Resulting R	Method of initiation	T_{re}, °C	Position of R in the reaction product	Conversion of the base	Yield based on the converted base, %	Literature
1	2	3	4	5	6	7	8	9	10
17		Trioxane	Trioxanyl	H_2O_2, Fe^{2+}	10	4	—	24	[22]
18			Trioxanyl	*t*-BuOOH	80	4	65	94	[22]
19		18-Crown-6	18-Crown-6-2-yl	*t*-BuOOH	20	4	80	78	[24]
20		1,3-Oxathiolane	1,3-Oxathiolan-2-yl	$C_6H_5(CH_3)_2OOH$	10	4	70	90	[25]
21		Benzo-1,3-dioxolane	Benzo-1,3-dioxolan-2-yl	*t*-BuOOH	20	4	72	88	[26]
22		Benzo-1,4-dioxane	Benzo-1,4-dioxan-1,4-yl	*t*-BuOOH	20	4	65	80	[27]
23	Lepidine	Methanol	Hydroxymethyl	NH_3OSO_3, Fe^{2+}	20	2	51	81	[8]
24				NH_2OH, Ti^{3+}	20	2	91	70	[8]
25				$(PhCOO)_2$	65	2	98	95	[8]
26		Ethanol	1-Hydroxyethyl	NH_2OH, Ti^{3+}	20	2	91	70	[8]
27				$(PhCOO)_2$	60	2	24	90	[8]
28				$(PhCOO)_2$	79	2	38	87	[8]
29				$(PhCOO)_2$	20	2	68	95	[8]
30		Propanol	1-Hydroxypropyl	$(PhCOO)_2$	98	2	53	39	[8]
31				$(PhCOO)_2$	20	2	62	91	[8]
32		Butanol	1-Hydroxybutyl	NH_2OH, Ti^{3+}	20	2	—	43,3	[8]
33				NH_3OSO_3, Ti^{3+}	20	2	—	44,6	[8]
34				NH_3OSO_3, Fe^{2+}	20	2	—	13,1	[8]
35				H_2O_2, Ti^{3+}	20	2	—	41,7	[8]
36				H_2O_2, Fe^{2+}	20	2	—	2,2	[8]
37				*t*-BuOOH, Ti^{3+}	20	2	—	44,3	[8]
38				*t*-BuOOH	20	2	—	5,7	[8]
39				$S_2O_8^{2-}$, Ti^{3+}	20	2	—	27,7	[8]
40				$S_2O_8^{2-}$, Fe^{2+}	20	2	—	2,7	[8]
41				$S_2O_8^{2-}$	80	2	—	6,5	[8]
42				$(PhCOO)_2$	80	2	—	59,4	[8]
43		Tetrahydrofuran		NH_3OSO_3, Fe^{2+}	80	2	25	84	[20]
44			2-Tetrahydrofuryl	NH_2OH, Ti^{3+}	20	2	69	65	[8]
45		1,3-Dioxolane	1,3-Dioxolan-2-yl	NH_3OSO_3, Fe^{2+}	10	2	67	35	[21]
			1,3-Dioxolan-4-yl			2		35	
46			1,3-Dioxolan-2-yl	*t*-BuOOH	80	2	—	30	[22]
			1,3-Dioxolan-4-yl			2	—	61	
47		1,4-Dioxane	1,4-Dioxan-2-yl	NH_3OSO_3, Fe^{2+}	20	2	93	96	[20]
48		1,4-Dioxane	1,4-Dioxan-2-yl	NH_3OSO_3, Fe^{2+}	20	2	93	96	[20]
				t-BuOOH	20	2	—	54	[7]
49				$S_2O_8^{2-}$	80 ... 90	2	—	68	[7]
50		Trioxane	Trioxanyl	H_2O_2, Fe^{2+}	10	2	—	32	[22]
51				*t*-BuOOH	80	2	65	95	[22]
52	4-Methoxyquinoline	1,4-Dioxane	1,4-Dioxan-2-yl	*t*-BuOOH	20	2	—	35	[7]
53	4-Chloroquinoline		1,4-Dioxan-2-yl	*t*-BuOOH	20	2	—	45	[7]
54	4-Cyanoquinoline		1,4-Dioxan-2-yl	*t*-BuOOH	20	2	—	55	[7]

TABLE 1 (continued)

Example	Aromatic base	Alkylating agent	Resulting R	Method of initiation	T_{re}, °C	Position of R in the reaction product	Conversion of the base	Yield based on the converted base, %	Literature
1	2	3	4	5	6	7	8	9	10
55	Quinoxaline	Diethyl ether	1-Ethoxyethyl	*t*-BuOOH	20	2	—	6	[7]
56		1,3-Dioxolane	1,3-Dioxolan-4-yl	*t*-BuOOH	10	2	—	35	[7]
57			1,3-Dioxolan-2-yl	$S_2O_8^{2-}$	90, 20	2		45	[7]
			1,3-Dioxolan-4-yl			2,3		25	[7]
58		1,4-Dioxane	1,4-Dioxan-2-yl	*t*-BuOOH	20	2		50	[7]
						2,3		6	[7]
59		Trioxane	Trioxanyl	*t*-BuOOH	80	2	38	94	[22]
60			Trioxanyl	H_2O_2, Fe^{2+}	10	2	—	18	[22]
61	Pyrazine	1,4-Dioxoane	1,4-Dioxan-2-yl	*t*-BuOOH	20	2		38	[7]
						2,5		20	[7]
62	1-Methylbenzimidazole	Methanol	Hydroxymethyl	$S_2O_8^{2-}$	100	2	—	43	[13]
63	1-phenylbenzimidazole		Hydroxymethyl	$S_2O_8^{2-}$	28	2	—	8	[13]
64	1-Phenylbenzimidazole		Hydroxymethyl	$S_2O_8^{2-}$	100	2	—	13	[13]
65	1,6-Diphenylbenzimidazole		Hydroxymethyl	$S_2O_8^{2-}$	100	2	—	13	[13]
66	1-Phenyl-6-nitrobenzimidazole		Hydroxymethyl	$S_2O_8^{2-}$	100	2	—	9	[13]
67	γ,γ'-Bipyridyl	2,2-Dimethyl-1,3-dioxolane	2,2-Dimethyl-1,3-dioxolan-4-yl	H_2O_2, Fe^{2+}	10	2	88	65	[23]
						2,2	88	15	[23]
68	Benzothiazole	1,4-Dioxane	1,4-Dioxan-2-yl	*t*-BuOOH	20	2	—	40	[7]
69		Trioxane	Trioxanyl	*t*-BuOOH	80	2	37	90	[22]
70			Trioxanyl	H_2O_2, Fe^{2+}	10	2	—	18	[22]
71	Isoquinoline		Trioxanyl	*t*-BuOOH	80	1	37	90	[22]

*The radical was formed from the 1,2-dihydroxyethyl radical.

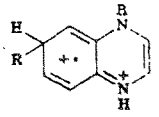
The relative rates of α-hydroxyalkylation of 4-substituted quinolines by dioxanyl radicals (initiating system tert-BuOOH + Fe^{2+}, 10°C) k_X/k_H: 0.12 (X = $-OCH_3$), 0.75 (X = $-CH_3$), 1.0 (X = –H) , 2.7 (X = –Cl), 7.1 (X = $-COOC_2H_5$), 22.0 (X = –CN).

Correlation of the relative rates of the reaction with the Hammett constants is not observed [2, 7].

The deactivating effect of the CH_3O group is probably associated with the donor effect of the substituent; the donor effect decreases the electron-acceptor properties of the heteroaromatic ring.

This assumption is confirmed by similar investigations of the alkylation of 4-substituted pyridines [9, 12] and benzimidazoles. The presence of substituents in benzimidazole has a substantial effect on the yields of hydroxymethylation products (examples 62–66, Table 1). Thus, the presence of a nitro group even in the 5 position, which is remote from the reaction center, decreases the yield of the product [13].

In a strongly acidic medium doubly protonated quinoxaline forms products of substitution in the 6 position [9]. This course of the reaction can be explained by the lower (than in the monoprotonated molecule) electron density in the quinoxaline molecule in the case of secondary protonation. The most favorable conditions for substitution develop at the $C_{(6)}$ atom, and the structure of the transition σ complex can be represented in the form



In this case, one of the charges is most effectively "pushed out" into the phenyl ring.

Mono- and disubstituted derivatives are formed as a result of the alkylation of pyridine, quinoline, bipyridyl, and quinoxaline (examples 1–4, 9, 57, 58, 61, 67; Table 1); this is associated with the presence of active α and γ positions in these bases. Thus, 2,2'-(2,2-dimethyl-1,3-dioxan-4-yl)-4,4'-bipyridyl is formed in addition to the monosubstitution product in the reaction of monoprotonated 4,4'-bipyridyl with 2,2-dimethyl-1,3 dioxalane (example 67; Table 1). However, a 2,6-disubstituted product could not be detected.

3. Effect of the Nature of the Initiator on the Homolytic α-Hydrocyalkylation of Protonated Aromatic Bases

The conversion, yield, and regioselectivity of alkylation depend to a great extent on the method and conditions of initiation [1-5].

An analysis of the data obtained shows that initiation of the reaction with systems that include Ti^{3+}–hydroxylamine (20°C) (examples 23, 24, 44; Table 1), Fe^{2+}–benzoyl hydroperoxide (65°C or UV irradiation at 20°C) (examples 6, 16, 18; Table 1), and $K_2S_2O_8$ (80–90°C) (example 49; Table 1) ensures high conversion of the protonated base and good yields of the hydroxyalkylation products.

In the case of initiation with the Ag^+–$K_2S_2O_8$ system (examples 7, 8, 63; Table 1) the conversion of the base is low (~11%). The intermediate α-hydroxyalkyl radicals are evidently oxidized by Ag^{2+} ions, which have a high oxidation potential (E^0 = +2.00 V [14]), to carbonium ions, and this decreases the yields of alkylation products.

The presence in the system of Ti^{4+} and Fe^{3+} ions, which have lower oxidation potentials (E^0 = 0.092 V and 0.77 V, respectively [14]) than Ag^{2+} or initiation of the reaction with systems that do not contain transition metal ions gives rise to high conversion of the base.

Depending on the method of initiation and the temperature, one observes different ratios of the 2- and 4-substituted dioxolanes in the alkylation of aromatic bases with 1,3-dioxolane (examples 1, 2, 12, 45, 46, 56, 57; Table 1). Initiation of the reaction at 10°C with a system based on cumyl hydroperoxide, which gives highly selective cumyloxy radicals with divalent iron ions, leads to the formation of primarily 2-substituted dioxolanes. At the same time, 2- and 4-substituted reaction products are obtained in equal amounts from dioxolane when less selective hydroxyl radicals formed from hydrogen peroxide are used.

The reaction with ions of variable-valence metals that enter into the composition of the initiating system [pathway (1)] seems most likely [2].

The voluminous data (Table 1) show that the structures of the reagents, the method of initiation, and the reaction conditions have a substantial effect on the results of α-hydroxyalkylation of protonated aromatic bases.

1. Effect of the Alkylating Agent on the Products of α-Hydroxyalkylation of Aromatic Bases

In the alkylation of aromatic bases with methanol, 1,4-dioxane, 1,3,5-trioxane, and 18-crown-6 (examples 5, 10, 11, 23–25, 62–66; 6, 40, 47–52, 61, 68; 17–19, 53, 54, 59, 60, 59, 70; Table 1) the products of α-hydroxyalkylation are formed with high selectivity, since nucleophilic radicals of only one type are generated from these alkylating agents.

Only α-hydroxyalkyl radicals are formed from ethanol (examples 26–29, Table 1) and 2,2-dimethyl-1,3-dioxolane (examples 3 and 67, Table 1), and the reaction is characterized by high selectivity. In the case of propanol (examples 30 and 31, Table 1) the yields of α-hydroxyalkylation products decrease appreciably; this is associated with the formation of both α- and β-hydroxyalkyl radicals under the investigated conditions. Even lower selectivity is observed in the reaction with the participation of butanol (examples 32–42, Table 1). The presence of a large number of C–H bonds with close strengths leads to the formation of radicals with different structures and, as a result, the yield of α-hydroxyalkylation products do not exceed 60%.

In the alkylation of quinoline with ethylene glycol (example 7, Table 1) the formation of primarily hydroxymethylation products was observed vis-a-vis low conversion of the base (~10%); this is evidently associated with decomposition of the ethylene glycol radical:

$$HO\text{-}\dot{C}H\text{-}CH_2OH \longrightarrow \dot{C}H_2OH + CH_2O$$

Only a heteroaromatic diol is formed with an increase in the temperature (example 8, Table 1). At 80°C the rate of addition to the aromatic base of the radical that develops from ethylene glycol is evidently much higher than the rate of its monomolecular decomposition.

The alkylation of aromatic bases with 1,3-dioxolane, 1,3-dioxane, and 1,3-dioxepane leads to the formation of 2- and 4-substituted derivatives of 1,3-dioxacycloalkanes (examples 13–16, Table 1).

The more thermodynamically stable trans isomer is primarily formed in the α-hydroxyalkylation of pyridine with 2-methyl-2-ethyl-1,3-dioxolane (example 4, Table 1).

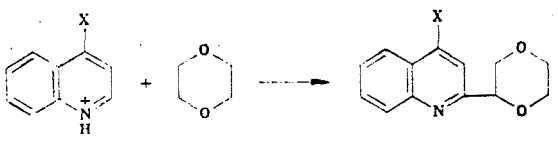
2. Effect of the Nature of the Aromatic Base and the Acidity of the Medium on the Composition of the α-Hydroxylation Products

Unprotonated aromatic bases react with alkyl radicals at a rate that is two orders of magnitude lower than the rate with protonated aromatic bases [9]. An appreciable increase in the reaction rate is observed even in acetic acid, in which only a small part of the aromatic base exists in the protonated form [10].

In media in which the bases are protonated completely by mineral acids, the rate of this reaction may reach the diffusion limit [9].

In the reaction of protonated pyridines with the 1,4-dioxanyl radical, in addition to the principal products of α- and γ-alkylation, one observes the formation in trace amounts of β-substitution products [11]. Such products cannot be detected in reactions of condensed aromatic bases [1–5]. Protonated isoquinoline forms only products of substitution at the $C_{(1)}$ atom (example 71, Table 1).

The effect of substituents on the rates of reaction of bases with dioxanyl radicals was evaluated in [7].



4-Substituted dioxolanes are primarily formed when the reaction temperature is raised to 80°C (example 46; Table 1). The ratio of the 2- and 4-substituted dioxolanes (1:2) indicates the loss of selectivity of detachment of hydrogen by tert-butoxyl radicals at increased temperatures. The absence of 2-substituted dioxolanes in examples 56 and 57 (Table 1) is surprising.

4-Substituted 1,3-dioxacycloalkanes are primarily formed in the α-hydroxyalkylation of quinaldine with 1,3-dioxane and 1,3-dioxepane, regardless of the selectivity of the initiator (examples 13–16; Table 1); this is evidently associated with consumption of dioxacycloalkyl radicals in side one-electron oxidation by Fe^{3+} ions, the rate of which increases with an increase in the size of the ring. 2-Substituted 1,3-dioxanes and 1,3-dioxepanes can probably be obtained in good yields in the case of initiation of the reaction with systems that contain Ti^{3+}, the ion of which is inactive in oxidation of the radicals.

The rate of oxidation of α-hydroxyalkyl radicals also increases on passing from primary to secondary and tertiary radicals [17]. The reaction with primary radicals (CH_2OH) proceed with much better yields than with the secondary radicals from ethanol or diethyl ether (examples 5, 10, 11, 23–29, 62–66; Table 1). Products of alkylation of aromatic bases with tertiary radicals cannot be obtained [11]. The oxidation of the tertiary radical by metal ions probably proceeds considerably more rapidly than their addition to the aromatic ring.

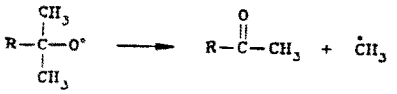
The type of initiator and the conditions under which the process is carried out determine the character of the side processes, which lower the yield of the desired product. In some cases the number of undesirable reactions can be reduced to a minimum. Thus, in the case of initiation with redox systems that contain variable-valence metal ions and hydroperoxides, the rate constant for reduction of the alkoxy radical (RO) by the metal ion is close to the diffusion value [15]:

$$ROOH + M^n \longrightarrow RO^{\cdot} + M^{n+1} + OH^-$$

$$RO^{\cdot} + M^n \longrightarrow RO^- + M^{n+1}$$

For this reason, initiator radicals, simultaneously with the detachment of hydrogen, are consumed in processes that do not lead to the desired products. Similarly, variable-valence metal ions reduce $NH_2^{\cdot}$ radicals and $S_2O_2^{-\cdot}$ anion radicals [15]. This side reaction is reduced to a minimum by increasing the alcohol or ether concentration [16, 17] or by carrying out the reaction in solutions of them (methanol, ethanol, THF, 1,4-dioxane, 1,3-dioxolane, trioxane [7, 18]) with a simultaneous decrease in the concentration of the metal ion [8] or the addition of a solution of the metal salt dropwise with vigorous stirring of the reaction mixture [7, 8]; the effectiveness of initiation can be brought up to 75% based on the converted hydroperoxide [7, 8].

Monomolecular decomposition of the alkoxy radical is another source of side products [10]:



The resulting methyl radical has nucleophilic properties and reacts with the protonated heteroaromatic base [2]. In reactions with active hydrogen donors such as cyclic acetals, the degree to which this process comes into play is generally low. Thus, the formation of methylation products was not observed in the initiation with hydroperoxides of the reaction of 1,3-dioxolane with bases [19], since at a 1,3-dioxacyclane concentration above 1 mole/liter the rate of detachment of a hydrogen atom from the 2 position of dioxolane is much greater than the rate of monomolecular decomposition of the alkoxyl radical. In the case of 2,2-dimethyl-1,3-dioxolane and 1,4-dioxane the percentage of methylation products amounts to 10% of the overall yield of reaction products [19].

The homolytic alkylation of protonated aromatic bases is a highly selective reaction that has great synthetic possibilities.

Small changes in the structures of the reagents and the reaction conditions have a substantial effect on the yields and structures of the resulting products. The great diversity of the hydroxyalkylation products obtained by this method and its universality make it possible to include homolytic alkylation among the important reactions of protonated aromatic bases.

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