HOMOLYTIC REPLACEMENT OF A HYDROGEN ATOM IN 2-METHYLQUINOLINE BY A 1,3-DIOXOLANYL RESIDUE

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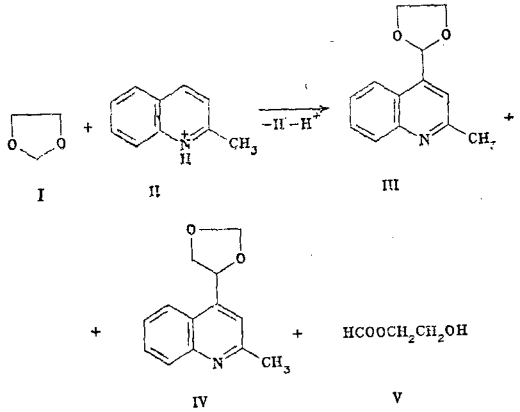
The reaction of 1,3-dioxolane with sulfuric-acid-protonated 2-methylquinoline initiated by the ROOH + Fe^{2+} system [where R = H, $(CH_3)_3C$, or $C_6H_5C(CH_3)_2$] at 5-10°C in water forms 4-(1,3-dioxacyclopent-2-yl)-2-methylquinoline and 4-(1,3-dioxacyclopent-4-yl)-2-methylquinoline. The selectivity of the formation of the first reaction product increases on passing from hydrogen peroxide to cumyl and tert-butyl hydroperoxide and with an increase in the pH of the medium.

It is known that nucleophilic radicals readily replace the hydrogen atoms in positions 2 and 4 of protonated heteroaromatic bases [1]. Under the action of radical initiators, 1,3-dioxacyclanes form mono- and dialkoxyalkyl radicals [2] which are capable of replacing hydrogen atoms in aromatic bases, giving isomeric products.

It has been established previously that in the reaction of 1,3-dioxolane (I) with protonated quinoxaline in the presence of the $(CH_3)_3COOH + Fe^{2+}$ initiating system 4-(quinoxalin-2-yl)-1,3-dioxolane is formed selectively [3].



In the present work we have studied the interaction of the dioxolane (I) with protonated 2-methylquinoline (II) and have investigated the influence of the nature of the initiator and the pH of the medium on the composition of the reaction products. The use of 2-methylquinoline as the heteroaromatic base is connected with the presence in its molecule of only one readily substituted hydrogen atom, in position 4 of the heterocycle [1], which excludes the formation of a mixture of position isomers and simplifies the isolation and identification of the products of the replacement of a hydrogen atom by the radicals generated from the dioxolane (I). We have established for the first time that, in contrast to previous results [3] the interaction of the dioxolane (I) with protonated methylquinoline (II) initiated by the $C_6H_5C(CH_3)_2OOH + Fe^{2+}$ or $(CH_3)_3COOH + Fe^{2+}$ system at 5-10°C in aqueous solution forms as the main product 4-(1,3-dioxacyclopentan-2-yl)-2-methylquinoline (III) and, in considerably smaller amount 4-(1,3-dioxacyclopent-4-yl)-2-methylquinoline (IV) (yields 76 and 14% and 72 and 18%, respectively, on the base (II) converted). On the initiation of the reaction by the $H_2O_2 + Fe^{2+}$ system under similar conditions, again two isomers were formed — (III) and (IV) — but in roughly equal yields (40 and 35%, respectively). The conversion of the protonated base (II) was 75% in all the experiments.

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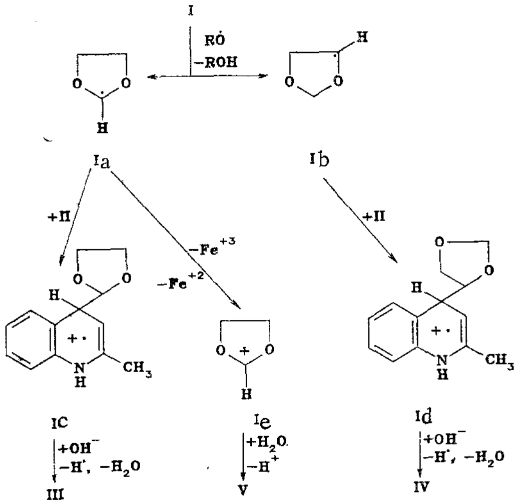
In all cases, ethylene glycol monoformate was formed, in addition to substances (III) and (IV).

In the ESR spectrum of 1,3-dioxolane treated with hydroxy ($\dot{O}H$), cumyloxyl [$C_6H_5C(CH_3)_2\dot{O}$], or tert-butoxy [$(CH_3)_3C\dot{O}$] radicals, using the jet method [2], signals were present which related to the 1,3-dioxacyclopent-2-yl radical (Ia): a doublet (1:1) with a HFC constant $a(\alpha\text{-H}) = 21.5$ Oe split into a multiplet with a constant $a(\gamma\text{-H}) = 1.4$ Oe and a g-factor = 2.0032 — from the 1,3-dioxacyclopentan-2-yl radical (Ib): a doublet (1:1), with an HFC constant $a(\alpha\text{-H}) = 11.4$ Oe, of triplets (1:2:1) with $a(\beta\text{-H}) = 27.2$ Oe, split into triplets (1:2:1) with $a(\gamma\text{-H}) = 1.5$ Oe and a g-factor = 2.0032. While, under the action of hydroxyl radicals, the ratio of the intensities of the signals of (Ia) to those of (Ib) amounted to 2:1, on passing to cumyloxy and tert-butoxyl radicals it amounted to ∿10.

In agreement with those of previous work [1-4], the results obtained permit the assumption of the following scheme for the formation of the reaction products:



R=H, $C_6H_5C(CH_3)_2$, $(CH_3)_3C$

The reaction of oxygen-centered radicals ($\dot{O}H$ or $C_6H_5C(CH_3)_2\dot{O}$ or $(CH_3)_3C\dot{O}$) with 1,3-dioxolane leads to the formation of 1,3-dioxacyclopent-2-yl (Ia), and 1,3-dioxacyclopent-4-yl (Ib) radicals in parallel, and they possess an increased nucleophilicity [5], which, in agreement with [1, 4], permits them readily to be introduced into the protonated heterocycle (II), giving the cation radicals (Ic) and (Id). After the splitting out of a hydrogen atom and deprotonation, compounds (III) and (IV) are formed.

The formation of the monoformate (V) takes place as the result of the one-electron oxidation of the radicals (Ia) by Fe^{3+} ions to the carbocations (Ie), which on reacting with water form 2-hydroxy-1,3-dioxolane [6]. The latter is unstable under the conditions studied and rapidly isomerizes into ethylene glycol monoformate [6].

The results obtained show that on passing from the $H_2O_2 + Fe^{2+}$ initiating system, which is a donor of highly active hydroxyl radicals ($\dot{O}H$) to the $(CH_3)_3COOH + Fe^{2+}$ or $C_6H_5C(CH_3)_2OOH + Fe^{2+}$ system, giving the less active tert-butoxyl $(CH_3)_3C\dot{O}$ or cumyloxyl $C_6H_5C(CH_3)_2\dot{O}$ radicals, respectively, the yield of compound (III) rises in comparison with that of compound (IV), which is due to an increase in the selectivity of the formation of the radicals (Ia) as compared with the radicals (Ib).

As was found, the selectivity of the formation of products (III) and (IV) in the reaction of 1,3-dioxolane with protonated 2-methylquinoline depends on the pH of the medium. With a rise in the pH of the medium the selectivity of the formation of the quinoline (III) rose and that of the quinoline (IV) fell (Table 1).

Thus, with a change in the pH of the medium from 1 to 8 the ratio of the yields of the isomers (III)/(IV) changes from 1.8 to 7.4, respectively (Table 1). Such a dependence of the ratio of the yields of compounds (III) and (IV) on the pH of the medium may be connected with a decrease in the selectivity of the formation of the 1,3-dioxocyclopent-2-yl radicals with a lowering of the pH as a consequence of the protonation of the 1,3-dioxolane. The decrease in

TABLE 1. Influence of the pH of the Medium on the Yield of the Products of the Reaction of Dioxolane with 2-Methylquinoline on Initiation by the $C_6H_5 \cdot C(CH_3)_2OOH + Fe^{2+}$ System

pH	Yield in % on the 2-methylquinoline that reacted		$Z=\frac{III}{IV}$
	III	IV	
1	58	31,5	1,8
3	70	22,0	3,2
5	76	14,0	5,4
6	78	12,5	6,2
8	78	10,5	7,4

the yield of compound (III) with a fall in the pH of the medium may also be connected with an increase in the rate of exhaustion of the 1,3-dioxacyclopent-2-yl radicals in one-electron oxidation by Fe^{3+} ions [6] as a result of the increase in the concentration of unhydrated iron ions Fe^{3+}.

EXPERIMENTAL

The PMR spectra of compounds (III) and (IV) were recorded on a Tesla BS-467 (60 MHz) instrument at 20°C in CCl_4 solution (concentration in CCl_4 ~10-20%; internal standard HMDS). The ^{13}C NMR spectra were recorded on a Bruker WH-90 (22.63 MHz) instrument at 20°C in CCl_4 with HMDS as internal standard. The ESR spectra of radicals (Ia) and (Ib) were recorded on a modified EPR-2 radiospectrometer [7] using the jet method [2, 7]. Quantitative analysis of the reaction mixtures was carried out by chromatography, using an LKhM-8MD chromatograph with a thermal conductivity detector. Analytical regime: stationary phase Carbowax-15,000 (15%) on Chromaton NAW HMDS, carrier gas helium at a rate of flow of 30 ml/min, 1-m column with an internal diameter of 3 mm, temperature of the column thermostat 230°C, temperature of the evaporator 280°C.

Synthesis of Substances (III) and (IV). A glass reactor with a stirrer was charged with 0.1 mole of dioxolane (I) and 0.02 mole of 2-methylquinoline. The necessary pH value was established with 20% sulfuric acid. The reaction mixture was cooled to 5-10°C and, in an atmosphere of argon, 0.03 mole of a saturated aqueous solution of $FeSO_4$ and 0.03 mole of the hydroperoxide $(CH_3)_3COOH$ or $C_6H_5C(CH_3)_3OOH$, or a 33% solution of hydrogen peroxide were added simultaneously with vigorous stirring over 30 min. The pH of the mixture was maintained with a saturated aqueous solution of Na_2CO_3. After the addition of the solutions, the reaction mixture was stirred for another 30 min. Then its pH was brought to 12-13. Compounds (III) and (IV) were extracted with ether and were isolated by liquid column chromatography. Column with Al_2O_3; eluent petroleum ether–diethyl ether (4:1). Products (III) and (IV) were identified by PMR and ^{13}C NMR methods.

4-(1,3-Dioxacyclopent-2-yl)-2-methylquinoline (III). Yellow oil; n_D^{20} 1.6058; PMR spectrum (ppm): 2.58 (s, 3H, CH_3); 3.86 (s, 4H, OCH_2CH_2O); 6.15 (s, 1H, OCHO); 7.23 (s, 1H 3-H in Ar); 7.28-8.00 (m, 4H, 5- to 8-H in Ar). ^{13}C NMR spectrum (ppm): 25.9 (q, CH_3); 65.6 (t, 2C, OCH_2CH_2O); 101.1 (d, OCHO); 118.3 (d, 3-C); 124.5 (d, 6-C); 125.7 (s, 10-C); 129.0 (d, 3C, 5-, 7-, and 8-C); 142.6 (s, 4-C); 148.6 (s, 9-C); 158.7 (s, 2-C).

4-(1,3-Dioxacyclopent-4-yl)-2-methylquinoline (IV). Yellow oil; n_D^{20} 1.5835; PMR spectrum (ppm): 2.58 (s, 3H, CH_3); 4.1-4.7 (m, 2H, OCH_2CHO); 4.94 (s, 1H, OCHO); 5.10 (s, 1H, OCHO); 5.33 (t, 1H, $OCHCH_2O$); 7.21 (s, 1H, 3-H); 7.20-8.03 (m, 4H, 5- to 8-H in Ar); ^{13}C NMR spectrum (ppm): 25.9 (q, CH_3); 71.3 (t, $OCHCH_2O$); 74.3 (d, $OCHCH_2O$); 96.0 (t, OCH_2O); 117.7 (d, 3-C); 122.5 (d, 6-C); 125.7 (s, 10-C); 129.7 (d, 2C, 5- and 7-C); 130.3 (d, 8-C); 145.2 (s, 4-C); 148.3 (s, 9-C); 158.3 (s, 2-C).

LITERATURE CITED

1. F. Minisci, Top. Curr. Chem., 62, 1 (1976).
2. V. V. Zorin, S. S. Zlotskii, V. F. Shuvalov, A. P. Moravskii, D. L. Rakhmankulov, and Ya. M. Paushkin, Dokl. Akad. Nauk SSSR, 236, 106 (1977).
3. W. Buratti, G. P. Gardini, F. Minisci, F. Bertini, R. Galli, and M. Perchinuno, Tetrahedron, 27, 3655 (1971).
4. A. Porta and G. Sesena, Tetrahedron Lett., No. 38, 3571 (1978).
5. D. L. Rakhmankulov and S. S. Zlotskii, Khim. Geterotsikl. Soedin., No. 8, 1011 (1977).
6. V. N. Trifonova, V. V. Zorin, S. S. Zlotskii, and D. L. Rakhmankulov, Zh. Org. Khim., 18, 1050 (1982).
7. V. F. Shuvalov and A. P. Moravskii, Kinet. Katal., 17, 870 (1976).