HOMOLYTIC ALKYLATION OF OXINE (8-HYDROXYQUINOLINE) WITH 1,4-DIOXANE

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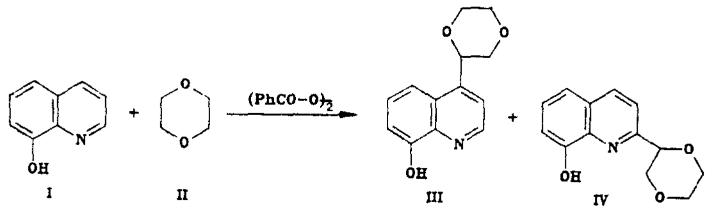
UDC 547.841'831.07

Products of substitution of the α- and γ-hydrogen atoms of the nitrogen-containing heteroring are formed in the homolytic alkylation of protonated quinoline bases by cyclic ethers in the presence of initiating systems that contain metals with variable valence [1, 2].

In the present research we investigated the possibility of the homolytic alkylation of oxine (8-hydroxyqinoline) (I) by 1,4-dioxane. On the one hand, one might have expected that, owing to the ability of oxine (I) to undergo complexing with metal ions with variable valence, the yield of alkylation products would increase substantially due to effective intramolecular oxidation of the intermediately formed cation-radical complex [1]. On the other hand, phenols are effective traps for alkyl radicals, which should have had an unfavorable effect on the course of the alkylation.

It was established that the reaction of protonated oxine (I) with 1,4-dioxane (II) in the presence of the Fe^{2+} + tert-BuOOH or Ti^{3+} + NH$_2$OH initiating system at 20°C does not give alkylation products. Two isomeric alkylation products III and IV in 30% yield based on the oxine introduced into the reaction are formed in the initiation of the reaction with benzoyl peroxide, which generates phenyl radicals, in the absence of the ion of a metal with variable valence at 100°C.



The reaction was carried out by refluxing a mixture of oxine and benzoyl peroxide in 1,4-dioxane in an argon atmosphere for 2 h. The unchanged I and II were removed from the reaction solution by distillation with steam at pH 7.5-8.5. The nonvolatile material was extracted with chloroform and separated by crystallization from hexane and ether. The structures of the individual isomers were confirmed by PMR spectroscopy and the results of elementary analysis.

Thus we have unexpectedly ascertained that chelate formation does not lead to the desired result as a consequence of tying up of the metal ion in an inactive form, whereas oxine (I) does not prevent the incorporation of 1,4-dioxa-2-cyclohexyl radicals in the protonated heteroring.

Dialkylation products were not detected when the reaction was carried out under conditions of high degrees of transformation.

4-Dioxanyl-8-hydroxyquinoline. This compound had mp 134-135°C. PMR spectrum (d$_6$-acetone, hexamethyldisiloxane (HMDS)): 3.1-4.1 (6H, m, CH$_2$O), 5.2 (1H, dd, CHO, J_1 = 10 Hz, J_2 = 3 Hz), 6.9-7.5 (3H, m, 5-, 6-, 7-H), 7.6 (1H, d, 3-H, J_{32} = 4.5 Hz), 8.7 ppm (1H, d, 2-H, J_{23} = 4.5 Hz).

2-Dioxanyl-8-hydroxyquinoline. This compound had mp 111-113°C. PMR spectrum (d$_6$-acetone, HMDS): 3.2-4.3 (6H, m, CH$_2$O), 4.7 (1H, dd, CHO, J_1 = 10 Hz, J_2 = 3.2 Hz), 6.9-7.5 (3H, m, 5-, 6-, 7-H), 7.6 (1H, d, 3-H, J_{34} = 8.5 Hz), 8.2 ppm (1H, d, 4-H, J_{43} = 8.5 Hz).

Ufa Petroleum Institute, Ufa 450062. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, p. 1143, August, 1988. Original article submitted September 28, 1987; revision submitted January 26, 1988.

0009-3122/88/2408-0943$12.50

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SYNTHESIS OF 2-AROYLMETHYL-5-PHENYL-1,3,4-THIADIAZOLES

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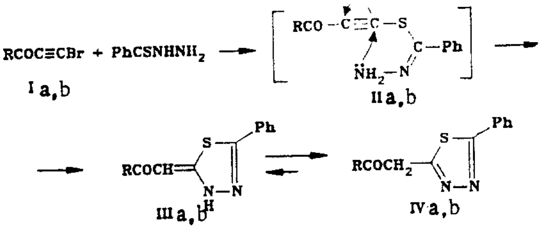
UDC 547.794.3.07

It is known that the reaction of arylthiohydrazides with dimethyl acetylenedicarboxylate and methyl propiolate in refluxing methanol leads to the formation of 5-methoxycarbonylmethyl-5-methoxycarbonyl- and 5-methoxycarbonylmethyl-4,5-dihydro-1,3,4-thiadiazoles [1].

We have established that 2-acylmethyl-5-phenyl-1,3,4-thiadiazoles IVa, b are formed in the reaction of 1-bromo-2-acylacetylenes Ia, b with thiobenzhydrazide in an equimolar ratio in methanol at −30°C in the presence of an equimolar amount of triethylamine. The reaction probably proceeds via a mechanism involving nucleophilic substitution of the bromine atom attached to the ethynyl carbon atom [2, 3] with the formation of intermediate ethynyl sulfides II.



I—IV a R=Ph; b R=2-thienyl

Compound IVa. This compound was obtained in 90% yield and had mp 175-177°C (from MeOH) and M$^+$ 280. IR spectrum (KBr): 670 (C—S), 1400 (ring C=N), 1550, 1580, 16-5 (aromatic C=C), 1680 cm^{-1} (C=O). ^{1}H NMR spectrum (CDCl$_3$): 4.88 (2H, s, CH$_2$), 7.50-8.03 ppm (10H, m, aromatic). ^{13}C NMR spectrum (CDCl$_3$): 193.68 (s, C=O), 170.06, 161.88 [s, C$_{(2)}$ and C$_{(5)}$], 40.00 (s, CH$_2$), 127.86-134.14 ppm (m, two C$_6$H$_5$, eight signals).

Compound IVb. This compound was obtained in 73% yield and had mp 149-151°C (from EtOH) and M$^+$ 286. IR spectrum (KBr): 695 (C—S), 1410 (ring C=N), 1520, 1580 (aromatic C=C), 1660 cm^{-1} (C=O). ^{1}H NMR spectrum (CDCl$_3$): 4.80 (2H, s, CH$_2$), 7.46-7.94 ppm (8H, m, C$_6$H$_5$ and C$_4$H$_3$S).

The results of elementary analysis of the synthesized compounds corresponded to the calculated values.

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Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterosiklicheskikh Soedinenii, No. 8, p. 1144, August, 1988. Original article submitted August 10, 1987; revision submitted February 15, 1988.

0009-3122/88/2408-0944$12.50