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HOMOLYTIC ALKYLATION OF 2-METHYLQUINOLINE BY BENZODIOXOLANE AND BENZODIOXANE

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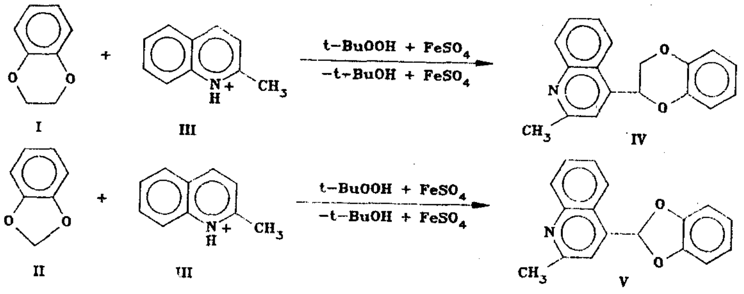
UDC 547.729.7'831.2'841.07

Known methods for obtaining substituted benzodioxanes and benzodioxolanes from pyrocatechol differ little in efficiency [1, 2]. At the same time, compounds of this type possess a wide spectrum of biological activity [3, 4].

In this connection we have investigated the possibility of obtaining substituents in the hetero-fragments of benzodioxanes and benzodioxolanes by homolytic alkylation of a heteroaryl base using the readily available benzodioxane (I) and benzodioxolane (II).

Reaction of protonated 2-methylquinoline (III) with I or II is initiated by the redox system $(CH_3)_3COOH+FeSO_4$ and yields, selectively, 4-(5,6-benzo-1,4-dioxan-2-yl)quinaldine (IV) or 4-(4,5-benzo-1,3-dioxolan-2-yl)quinaldine (V). The yields are 85 and 90%, respectively, and are based on the amounts of reacted base (conversion of III = 70%).



The high yields and selectivity illustrate the synthetic importance of the reaction discussed.

EXPERIMENTAL

Tert-butylhydroperoxide was added dropwise over 30 min to an aqueous-DMSO solution of 2-methylquinoline sulfate (0.02 mole), benzodioxacyclane I or II (0.04 mole), and $FeSO_4$ (0.01 mole) in a stream of argon. Compounds IV and V were separated using column chromatography (Al_2O_3, hexane—ether, 5:1).

4-(5,6-Benzo-1,4-dioxan-2-yl)quinaldine (IV). n_D^{20} 1.6155. PMR spectrum (CCl_4, HMDS) 2.53 (3H, s, CH_3), 3.58-3.86 (1H, m, CH_2—O), 4.18-4.42 (1H, m, CH_2—O), 5.40-5.60 (1H, m, CH—O), 6.60-6.90 (4H, m, C_6H_4), 7.08-7.98 ppm (5H, m, Ar).

4-(4,5-Benzo-1,3-dioxalan-2-yl)quinaldine (V). Isolated in the form of a monohydrate losing water at 85°C, mp 87-89°C. PMR spectrum (DMSO-d_6, HMDS): 2.67 (3H, s, CH_3), 2.81 (2H,

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Ufa Petroleum Institute, Ufa 450062. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 565-566, April, 1986. Original article submitted April 10, 1985; revision submitted August 25, 1985.

0009-3122/86/2204-0467$12.50

s, H_2O), 6.85 (4H, s, C_6H_4), 7.38-8.18 ppm (6H, m, Ar + OCHO). Elemental analytical data was in agreement with that calculated.

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REACTION OF 4-METHOXY(METHYLTHIO)-5-AMINO-6-MERCAPTOPYRIMIDINES WITH ω,ω-DIBROMOACETOPHENONE

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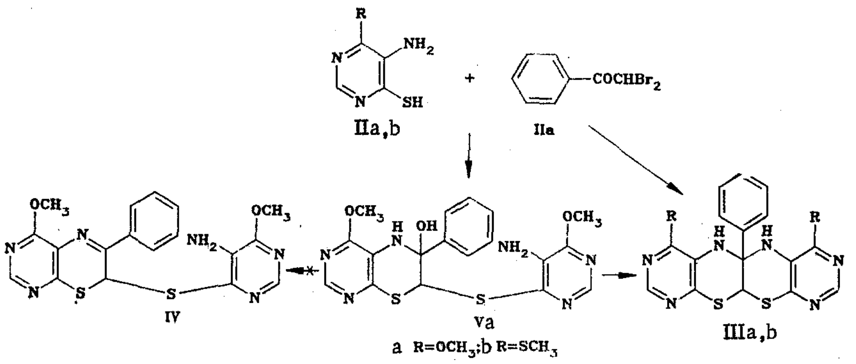
UDC 547.854.83'869.2.07

It is known that reaction of 5-amino-6-mercaptopyrimidines with ω-haloacetophenones gives 6-aryl-6-hydroxy-5H-6,7-dihydropyrimido[4,5-b][1,4]thiazines which are readily dehydrated to 6-aryl-7H-pyrimido[4,5-b][1,4]thiazines [1].

We have found that the reaction of 4-methoxy- and 4-methylthio-5-amino-6-mercaptopyrimidines (Ia,b) with ω,ω-dibromoacetophenone (under conditions for the synthesis of 6-aryl-7H-pyrimido[4,5-b][1,4]thiazines) unexpectedly produces 4,7-dimethoxy(dimethylthio)-5a-phenylpyrimido[4,5-b][1,4]thiazino[7,8-g]pyrimido[4,5-b][1,4]thiazines (IIIa,b) which represent a new heterocyclic system.

The product expected was 6-aryl-7H-pyrimido[4,5-b][1,4]thiazine (IV) (substituted at the 7-position) but this was not formed in the reaction.

In the case of Ia and IIa it was possible to separate the cyclic carbinol, Va, which is postulated intermediate in this process. It may be converted to IIIa but not to IV.



Compounds IIIa,b and Va were crystalline materials, stable on standing.

IIIa: mp 243-245°C (DMFA–water), yield 66%
IIIb: mp 253-254°C (DMFA–water), yield 64%
Va: mp 165-167°C (methanol), yield 80%

Elemental organic analytical data agreed with that calculated and IR, UV and PMR spectra confirmed the structures proposed for IIIa,b and Va.

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