ACID-CATALYZED REACTION OF 6-HYDROXY-2,4-DIMETHYL-1,3-BENZODIOXANE WITH 1-AMINOANTHRAQUINONE

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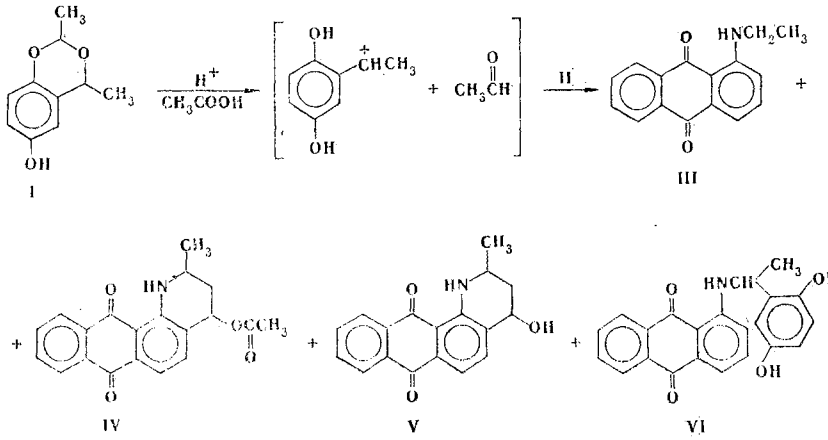
The reactions of 6-hydroxy-2,4-dimethyl-1,3-benzodioxane (I), which is obtained by condensation of hydroquinone and acetaldehyde [1], have not been investigated. Bearing in mind the common property of 1,3-benzodioxanes to undergo cleavage with opening of the heteroring [2] and the ability of 6,8-dinitro-1,3-benzodioxane to aralkylate alcohols and thiols in the presence of Lewis acids [3] we expected that the acid-catalyzed reaction of benzodioxane I with 1-aminoanthraquinone (II) would be suitable for the introduction of a hydroquinone residue into the amine II molecule. If successful, this reaction could become the basis of a simple one-step synthesis of anthraquinone derivatives with hydroquinone groups, which find application as developing dyes in color photography [4-6].

The formation of compounds, the deep color of which indicated substitution in the amino group of amine II, was observed by means of thin-layer chromatography (TLC) when concentrated hydrochloric acid (5.5 mmole) was added to a mixture of benzodioxane I (2.75 mmole), amine II (2.75 mmole), and acetic acid (0.83 mole) with subsequent stirring at 25°C for 4 h. Column chromatography on silica gel (elution with chloroform) of the precipitate obtained by dilution of the reaction mixture with water and alkalization to neutrality yielded (in the order of emergence from the column) 1-ethylaminoanthraquinone (III) (3%), starting amine II (51%), 4-acetoxy-2-methyl-1,2,3,4-tetrahydro-1-azabenz[a]anthraquinone (IV) (4%), 4-hydroxy-2-methyl-1,2,3,4-tetrahydro-1-azabenz[a]anthraquinone (V) (22%), and 1-[1-(2,5-dihydroxyphenyl)ethylamino]anthraquinone (VI) (12%). The very same reaction products were obtained under similar conditions but with 95% sulfuric acid (1.7 mmole) in place of hydrochloric acid: III (4%), IV (16%), V (3%), and VI (8%).



Ethylamino derivative III [7] and IV and V [8] were identified by comparison with genuine samples. Their formation constitutes evidence that under the reaction conditions benzodioxane I undergoes cleavage with the ejection of acetaldehyde. Compound VI was obtained in the form of violet crystals with mp 180-181°C [from benzene–acetone (4:1)]. PMR spectrum (d_6-acetone): 1.31 (3H, d, J ≈ 6 Hz, CH_3), 4.20-4.75 (1H, m, CH), 6.45-8.40 (10H, m, aromatic protons), 7.28 (2H, s, OH), and 9.98 ppm (1H, m, NH). The C, H, and N content was in agreement with the empirical formula $C_{22}H_{17}NO_4$.

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LITERATURE CITED

1. E. P. Fokin and V. Ya. Denisov, USSR Inventor's Certificate No. 480702; Ref. Zh. Khim., 14N210 (1977).
2. R. Elderfield, in: Heterocyclic Compounds, Vol. 6, Wiley.
3. A. C. Hazy and J. V. Karabinos, J. Org. Chem., 33, 2557 (1968).
4. Polaroid Corp., US Patent No. 3131061; Ref. Zh. Khim., 16N393 (1965).
5. Polaroid Corp., US Patent No. 3135606; Ref. Zh. Khim., 7N635 (1967).
6. Polaroid Corp., US Patent No. 3288778; Ref. Zh. Khim., 17N396 (1975).
7. J. D. Wool and A. F. Peters, J. Chem. Soc., No. 10, 3373 (1962).
8. E. P. Fokin and I. V. Fomicheva, Zh. Org. Khim., 6, 1282 (1970).

NEW SYNTHESIS OF 5,6,7,8-TETRAHYDROQUINOLINES WITH THE PARTICIPATION OF THE 4-(3-INDOLYL)PYRIMIDINE ANHYDRO BASE

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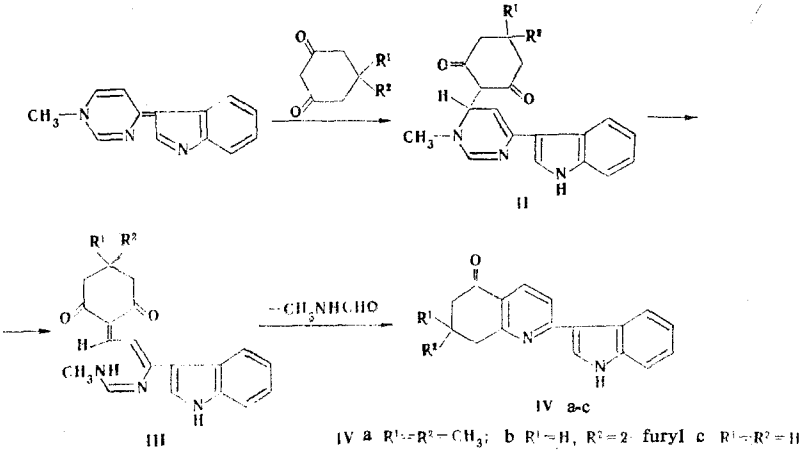
Whereas 1,2,3,4-tetrahydroquinolines are extremely accessible and are obtained in one step by the reduction of quinoline and its derivatives, the corresponding 5,6,7,8-tetrahydroquinolines are much less well known, and their synthesis is fraught with a number of difficulties [1]. We have found a new method for the synthesis of such structures in the recyclization of the 4-(3-indolyl)pyrimidine anhydro base (I) under the influence of 1,3-cyclohexanedione and its analogs in dry acetonitrile.



II

III

IV a-c

IV a $R^1=R^2=CH_3$; b $R^1=H$, $R^2=2$-furyl c $R^1=R^2=H$

Inasmuch as they have an extremely acidic methylene proton, 1,3-cyclohexanediones attack the electron-deficient $C_{(6)}$ atom of the pyrimidine ring to give adduct II, which then undergoes ring opening to give intermediate III. Open form III undergoes recyclization with the participation of the electron-surplus nitrogen atom of the starting substance and the carbonyl group of the reagent to give 5,6,7,8-tetrahydroquinoline derivatives IVa-c in 10-14% yields. Compound IVa had mp 195-196°C (from methanol). PMR spectrum: 0.86 (s, 6H, CH_3), 2.4 (s, 2H, 8-H), 2.94 (s, 2H, 6-H), 7.84 (d, 1H, 3-H), 8.39 (d, 1H, J_{34} = 9.0 Hz, 4-H), 7.99 (d, 1H, $J_{1'2'}$ = 3.0 Hz, 2'-H), and 6.86-7.66 ppm (m, 4'-, 5'-, 6'-, and 7'-H).

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