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INTRAMOLECULAR CATALYTIC CYCLIZATION OF SUBSTITUTED 2-ALKENYLANILINES

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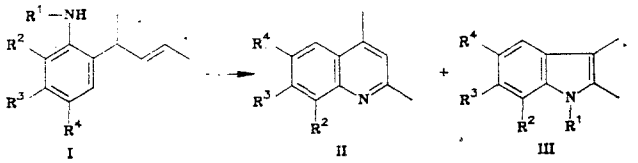
A study was carried out on the effect of the nature and structure of the substituent in the aromatic ring of 2-(1-methyl-2-butenyl)anilines on the direction and structural selectivity of the their intramolecular cyclization to derivatives of quinoline and indole by the action of catalytic amounts of $PdCl_2$ or $PdCl_2$—$(DMSO)_n$ complexes.

Transition metal complexes are rather commonly used in the synthesis of heterocyclic compounds [1, 2]. In particular, derivatives of indole and quinoline are obtained from N- and 2-alkenylarylamines by the action of palladium and nickel catalysts [3, 4]. In most cases, these reactions require stoichiometric amounts of the catalysts. We have recently developed an efficient method for the preparation of indole and quinoline derivatives by the intramolecular cyclization of N- and 2-(1-methyl-2-butenyl)anilines by the action of catalytic amounts of $PdCl_2$—$(DMSO)_n$.

In a continuation of an investigation of the intramolecular cyclization of alkenylarylamines and to expand the use of this method, we studied the effect of the substituent in the aromatic ring and at the nitrogen atom of 2-alkenylamilines on the direction of the intramolecular cyclization by the action of $PdCl_2$ complexes and $PdCl_2$—$(DMSO)_n$ in nitrobenzene. In the 2-alkenylaniline series studied (see Table 1), the nature of the substituents in the aromatic ring affects the direction and structural selectivity of the intramolecular cyclization and a mixture of the corresponding quinolines II and indoles III is formed in each experiment. The yield and composition of the reaction mixture depends significantly on the structure of the starting anilines. Thus, for example, the presence of a methyl or methoxy group at C-4 of the 2-alkenylanilines facilitates the predominant formation of quinolines II. The quinoline content in the reaction mixture is about 70% in this case. The yield of indole derivatives increases upon the introduction of substituents at C-5 and C-6 in the aromatic ring. However, we should note that the fraction of the quinolines is significantly greater in both cases. Unsubstituted and 4,6-dimethyl-substituted 2-(1-methyl-2-butenyl)anilines cyclize upon the action of catalytic amounts of $PdCl_2$ or $PdCl_2$—$(DMSO)_n$ with the formation of a mixture of equal amounts of quinolines II and indoles III.



The conversion of 2,6-di(1-methyl-2-butenyl)aniline (IV) in the presence of these catalysts at 180°C over 2 h to 2,4-dimethyl-8-(1-methyl-2-butenyl)quinoline (V) proceeds with high selectivity in 65% yield.

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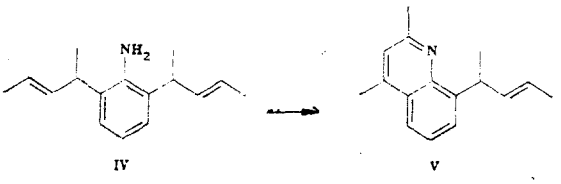

IV V

These results indicate that by changing the nature of the substituent in the aromatic ring of these anilines, we may control the direction of the intramolecular cyclization of 2-alkenylanilines, thereby obtaining predominantly quinoline or indole derivatives.

A study of the conversion of 2-(1-methyl-2-butenyl)anilines by the action of Pd^{2+} complexes showed that a significant amount of hydrogen is formed in addition to the intramolecular cyclization products. We propose that dihydro- and tetrahydroquinolines or dihydro- and tetrahydroindoles are initially formed under these reaction conditions and are then dehydrogenated by the action of palladium ions to the corresponding quinolines and indoles with the liberation of free hydrogen. A stoichiometric amount of 1-heptene was purposely added to the reaction mixture in order to bind this hydrogen. Heptane was obtained in addition to the heterocyclic products, indicating the possibility of using the hydrogen liberated in the intramolecular cyclization of 2-alkenylarylamines for the reduction of alkenes.

The PMR spectra of II have two three-proton signals at 2.24 and 2.42 ppm related to 2-CH_3 and 4-CH_3. The signal for 3-H in the quinoline ring appears as a singlet at 6.66 ppm. The IR spectra of II lack an NH band, while the indole derivatives have a strong band at 3400 cm^{-1}. The PMR spectra have signals for the ethyl group at 1.05 (t) and 2.48 ppm (q), for the methyl group at 2.13 ppm (s), and for the aromatic protons at 6.80-7.50 ppm.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer. The PMR spectra were taken on a Tesla 467 spectrometer at 60 MHz in CCl_4 with TMS as the internal standard. The mass spectra were taken on an MKh-13-06 mass spectrometer at 70 eV with 200°C ionization chamber temperature. The thin-layer and column chromatography was carried out on grade-II alumina with benzene as the eluent. The gas-liquid chromatography was carried out on an LKhM-8MD chromatograph using a 2700 × 3 mm column packed with 5% SE-30 on Chromaton N-AW-DMCS. The helium gas carrier flow rate was 40 ml/min. The starting compounds were prepared according to our previous procedure [6].

Intramolecular Cyclization of Alkenylanilines I. A sample of 1 g (6.2 mmoles) I and 0.62 mmole $PdCl_2$ or $PdCl_2$–$(DMSO)_n$ catalyst were placed in a 17-cm^3 autoclave and then 12 ml of nitrobenzene was added. The mixture was flushed with argon and then heated at 170°C for 2 h. The reaction mixture was filtered through a layer of alumina using benzene as the eluent. The eluent and nitrobenzene were distilled off. The products were isolated by chromatography on an alumina column.

TABLE 1. Intramolecular Catalytic Cyclization of Substituted 2-(1-Methyl-2-butenyl)anilines*

Substituents				Yield, % †		Composition of the reaction products	
R^1	R^2	R^3	R^4	*1*	*2*	II	III
H	H	H	H	69	81	57	43
C_2H_5	H	H	H	62	69	—	62
Ac	H	H	H	—	—	—	—
H	CH_3	H	H	63	65	61	39
H	H	CH_3	H	63	69	64	36
H	H	H	CH_3	67	67	79	21
H	OCH_3	H	H	61	66	63	37
H	H	H	OCH_3	65	70	71	29
H	CH_3	H	CH_3	58	61	52	48

*Reaction conditions: T = 170°C, 2 h reaction time, substrate–catalyst mole ratio equal to 10:1.
†1) $PdCl_2$–$(C_6H_5NO_2)_n$ as catalyst; 2) $PdCl_2$–$(DMSO)_n$ as catalyst.

The physicochemical indices of products II and III obtained were in accord with handbook values ([7], pp. 731, 870).

2,4-Dimethyl-8-(1-methyl-2-butenyl)quinoline. R_f 0.33. IR spectrum: 970 (C=C), 1380, 1470 (CH_3), 3030 cm^{-1} (Ar). PMR spectrum: 1.42 (3H, d, CH_3), 1.68 (3H, d, CH_3), 2.62 (3H, s, CH_3), 3.66 (3H, s, CH_3), 3.33-3.86 (1H, m, CH), 5.42-6.0 (2H, m, CH=CH), 7.08 (1H, s, 3-H), 7.42-8.16 ppm (3H, m, A-H). M^+ 225.

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PYRIMIDINE SIGMA-COMPLEXES.

7.* THE RECYCLIZATION OF 5-NITROPYRIMIDINE AND ITS METHOXY DERIVATIVES UPON REACTION WITH THE ACETYLACETONE CARBANION

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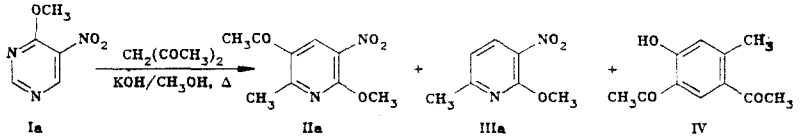
A study was carried out on the reaction of 5-nitro and 5-nitromethoxypyrimidines with the acetylacetone carbanion. Benzene and pyridine derivatives are formed as a result of recyclization. The direction of the reaction depends on the position of the substituents in the pyrimidine ring and the nature of the bases.

In our previous work [1], we showed that the reaction of 5-nitro-2-methoxypyrimidine with the acetylacetone carbanion gives recyclization of the pyrimidine ring and the formation of 5-nitro-2-hydroxyacetophenone as the only product.

In the present work, we studied the action of the acetylacetone carbanion on 5-nitropyrimidine and its methoxy derivatives, in which we provide for all the possible combinations of unsubstituted and substituted positions of the pyrimidine ring, which determines the direction of nucleophilic attack. Thus, the recyclization of these compounds is a complex process.

Heating 5-nitro-4-methoxypyrimidine (Ia) with equimolar amounts of acetylacetone and KOH in methanol at reflux (method A) gave 5-nitro-3-acetyl-6-methoxy-2-methylpyridine (IIa), 5-nitro-6-methoxy-2-methylpyridine (IIIa) and 4,6-diacetyl-m-cresol (IV).



Ia IIa IIIa IV

Under more vigorous conditions, heating pyrimidine Ia in acetylacetone in the presence of triethylamine at reflux (method B), m-cresol IV is formed as the only product. 5-Nitro-2,4-

*Communication 6, see [1].

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