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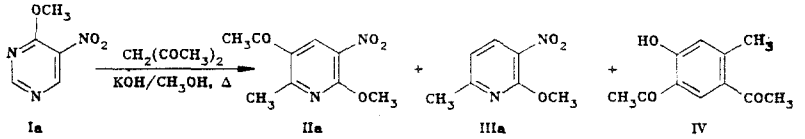
A study was carried out on the reaction of 5-nitro and 5-nitromethoxypyrimidines with the acetylacetone carbanion. Benzene and pyridine derivatives are formed as a result of recyclization. The direction of the reaction depends on the position of the substituents in the pyrimidine ring and the nature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

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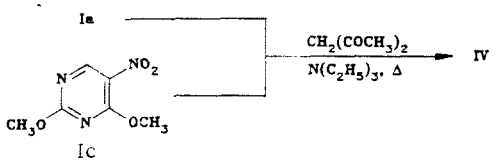
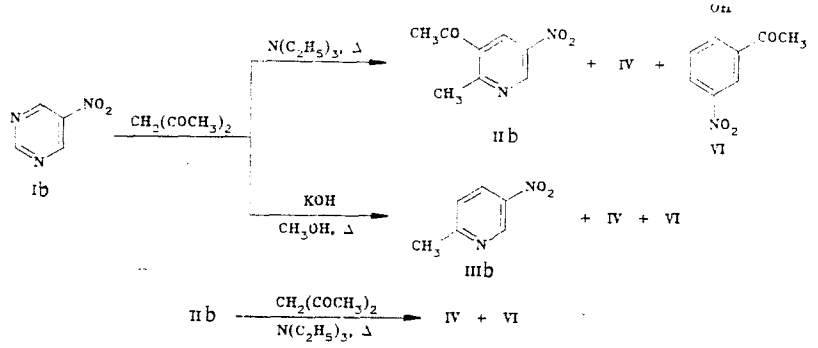
dimethoxypyrimidine (Ic) recyclizes only under the conditions of method B. In this case, m-cresol IV is also formed. The recyclization of the pyrimidine ring in this case apparently does not stop upon the formation of picoline IIa.

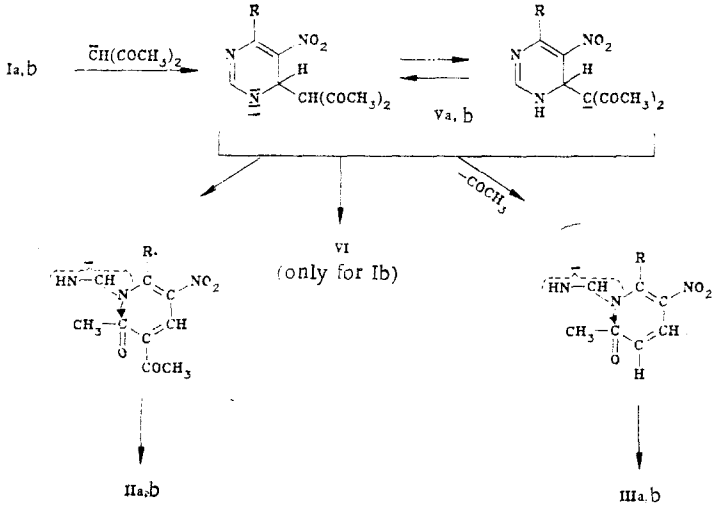


The conversion of 5-nitropyrimidine by the action of acetylacetone carbanion to give 5-nitro-3-acetyl-2-methylpyridine was described by Barczynski [2]. 5-Nitropyrimidine (Ib) recyclizes under the conditions of method B to give picoline IIb, m-cresol IV and 5-nitro-2-hydroxyacetophenone (VI). Picoline IIb under the conditions of method B also gives m-cresol IV and acetophenone VI. Thus, the formation of VI is possible by the recyclization of the pyrimidine ring in Ib or the pyridine ring in picoline IIb.

The recyclization of 5-nitropyrimidine Ib under the conditions of method A leads to 5-nitro-2-methylpyridine (IIIb) in addition to benzene compounds.



By analogy with the scheme for the recyclization of 5-nitropyrimidine given by Barczynski [2], the formation of acetylpicolines IIa and IIb apparently proceeds through an S_N(ANRORC) mechanism through intermediate Meisenheimer σ-complexes Va and Vb. In addition, the formation of picolines IIa and IIIb is a consequence of the deacylation of σ-complexes Va and Vb up to the step involving the opening of the pyrimidine ring by the action of electron-withdrawing substituents. Acetophenone VI is the product of the recyclization only of pyrimidine Ib by an S_N(ANRORC) mechanism or by a meta-bonding mechanism.

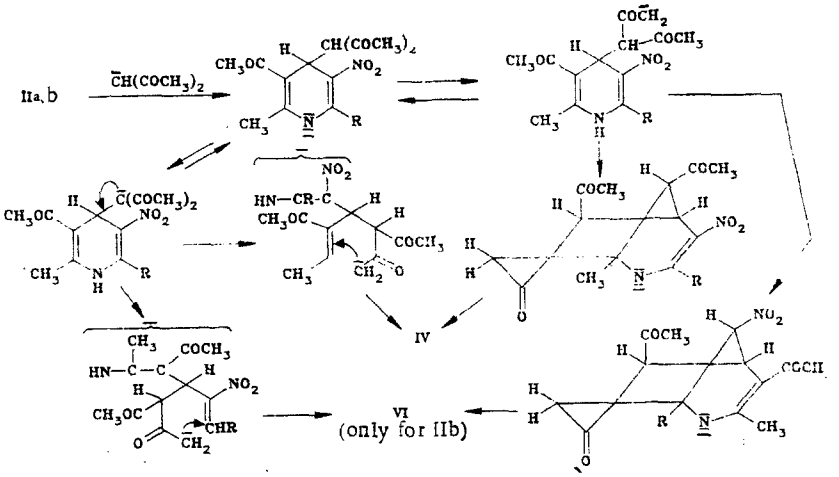


Va R=OCH_3; b R=H

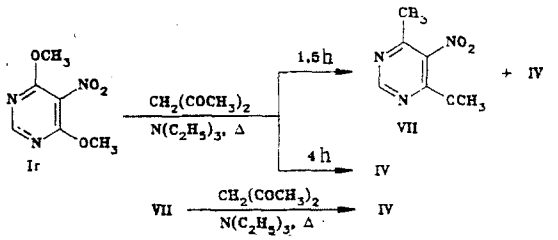
The finding of m-cresol IV in the conversion products of Ia-Ic may be attributed to recyclization of the pyridine ring of IIa and IIb proceeding by the two possible pathways in accord with the scheme:

TABLE 1. Conditions and Products of the Recyclization of Ia-d, IIb, and VII

Starting compounds	Method	Reaction time, h	Reaction product	Yield, %	Starting compounds	Method	Reaction time, h	Reaction product	Yield, %
Ia	A	3	IIa	5,5	Ic	B	5	IV	7,2
			IIIa	4,2	IIb	B	10	IV	8,0
			IV	4,0				VI	9,3
Ia	B	4	IV	8,3	Id	B	4	IV	11,3
Ib	A	5	IIIb	4,0	Id	B	1,5	VII	5,0
			IV	3,5				IV	5,3
			VI	3,0	VII	B	4	IV	7,5
Ib	B	4	IIb	23,0					
			IV	4,3					
			VI	4,5					



In our previous work [1], we established that 5-nitro-4,6-dimethoxypyrimidine (Id) does not react with the acetylacetone carbanion at 20°C while C-2 in the ring is attacked with formation of a stable anionic σ-complex [3]. Dimethoxypyrimidine Id under the conditions of method B recyclizes to m-cresol IV.



The nucleophilic attack of diacetylmethanide initially occurs at C-4 in the pyrimidine ring with substitution of the methoxy group (scheme 3). Salt VIII which is formed in the presence of triethylamine is deacylated to form methylpyrimidine VII by analogy with our previous work [4]. Methylpyrimidine VII is attacked by the acetylacetone carbanion at C-2 in the ring to give an anionic σ-complex, which is them converted to m-cresol IV by analogy with the work of Matsumura et al. [5]. This support is indicated by the finding that heating of the reaction mixture for 1.5 h at reflux gives methylpyrimidine VII in addition to m-cresol IV. Furthermore, pyrimidine VII recyclizes under the conditions of method B to give m-cresol IV.

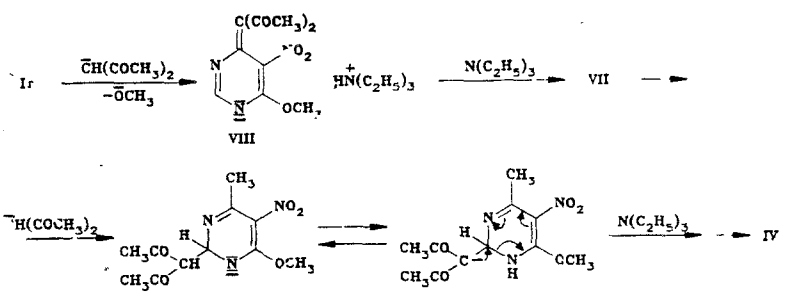


TABLE 2. Physical Indices of IIa, IIb, IIIa, IIIb, IV, VI, and VII

Compound	mp, °C (from hexane)	PMR spectrum, δ, ppm	Found, %			Chemical formula	Calculated, %		
			C	H	N		C	H	N
IIa	73—75	8,45 (s, CH); 3,80 (s, OCH_3); 2,38 (s, $COCH_3$); 2,30 (s, CH_3)	51,2	4,9	13,4	$C_9H_{10}N_2O_4$	51,4	4,8	13,3
IIIa	57—58	8,67 (d, CH); 7,30 (d, CH); 4,50 (s, OCH_3); 2,90 (s, CH_3)	49,9	4,9	16,7	$C_7H_8N_2O_3$	50,0	4,8	16,7
IV	108—109	12,26 (s, OH); 8,10 (s, CH); 6,76 (s, CH); 2,81 (s, $COCH_3$); 2,84 (s, $COCH_3$)	68,8	6,4	—	$C_{11}H_{12}O_3$	68,7	6,3	—
IIIb	104—105	9,30 (s, CH); 8,35 (d.d, CH); 7,41 (d, CH); 2,93 (s, CH_3)	52,2	4,6	20,4	$C_6H_6N_2O_2$	52,2	4,4	20,3
VI	101—102	12,80 (s, CH); 8,63 (d, CH); 8,28 (d.d, CH); 7,00 (d, CH); 2,65 (s, CH_3)	52,8	3,9	7,7	$C_8H_7NO_4$	53,0	4,2	7,6
IIb	56	9,50 (d, CH); 8,90 (d, CH); 3,00 (s, $COCH_3$); 2,92 (s, CH_3)	53,3	4,5	15,6	$C_8H_8N_2O_3$	53,3	4,5	15,5
VII	81—83	8,97 (s, CH); 4,36 (s, OCH_3); 2,80 (s, CH_3)	42,7	4,0	25,1	$C_6H_7N_3O_3$	42,6	4,2	24,8

EXPERIMENTAL

The PMR spectra were taken on a Tesla BS-467 spectrometer at 60 MHz in $CDCl_3$ with HMDS as the external standard. The purity of the compounds obtained was checked by thin-layer chromatography on Silufol UV-254 plates. The reaction mixture was purified by chromatography on a column packed with 20 g LSL-254 silica gel with chloroform as the eluent. The starting nitropyrimidines were synthesized by the following procedures. Pyrimidine Ia was prepared according to our previous method [6], Ib was prepared according to van der Plas [7], Ic was prepared according to Besly and Goldberg [8], while Id was prepared according to Rose and Brown [9].

The reaction conditions and products obtained are given in Table 1, while their physical indices are given in Table 2.

Recyclization of Nitropyrimidines Ia and Ib. A mixture of 7.0 mmoles pyrimidine Ia or Ib, 0.7 ml (7.0 mmoles) acetylacetone and 0.4 g (7.1 mmoles) potassium hydroxide was heated in 20 ml methanol at reflux with stirring. The solution was evaporated to dryness. The syrupy residue was dissolved in 10 ml water and treated with 0.6 N H_2SO_4 to pH 7. The suspension formed was extracted thrice with 100 ml chloroform and dried over $MgSO_4$. The solvent was distilled off and the residue was separated by chromatography on a silica gel column.

Recyclization of Nitropyrimidines Ia-d, VII and Nitropicoline IIb. A mixture of 7.0 mmoles pyrimidine Ia (Ib-d, VII or picoline IIb) was heated in 20 ml acetylacetone at reflux in the presence of 0.98 ml (7.1 mmoles) triethylamine. The reaction mixture was evaporated to dryness and the residue was separated by chromatography on a silica gel column.

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