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Chemistry

P. B. Terent'ev, A. N. Kost, A. A. Shchegolev

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Abstract

Full Text

Chemistry

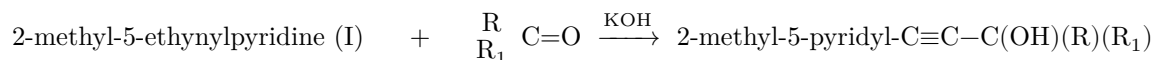
P. B. Terent'ev, A. N. Kost, A. A. Shchegolev

and Corresponding Member of the Academy of Sciences of the USSR **A. P. Terent'ev**

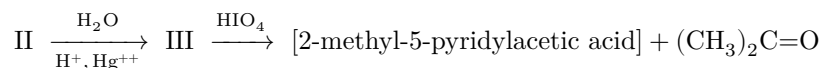
Synthesis and Some Reactions of Pyridylethynylcarbinols

Heterocyclic bases having a triple bond in the side chain have been studied very little. Yet such compounds may serve as starting materials for the synthesis of a whole series of new systems.

In studying the properties of the acetylene group attached to the pyridine nucleus, we carried out the condensation of 2-methyl-5-ethynylpyridine (I) ⁽¹⁾ with aldehydes and ketones under the conditions of the Favorskii reaction. As in the case of other substituted acetylenes ⁽²⁾, the best yields of carbinols were achieved with the use of a 4-5-fold excess of alkali. Condensation of (I) with ketones proceeds readily and in good yields in anhydrous ether at 0°. At the same time, the reaction of I with aldehydes could be carried out only at -20, -40° and at high dilution, using tetrahydrofuran as the solvent.



The Kucherov reaction with the tertiary carbinols obtained does not take place in 15-20% sulfuric acid. Only by using 25% sulfuric acid were we able to obtain from carbinol II ($R = R_1 = CH_3$) the corresponding α -keto alcohol (III), the structure of which was proved by the infrared spectrum (the presence of a frequency at 1714 cm^{-1} , characteristic of a C=O group not conjugated with an aromatic nucleus) and by isolation from the products of its periodate oxidation of acetone (as the 2,4-dinitrophenylhydrazone).

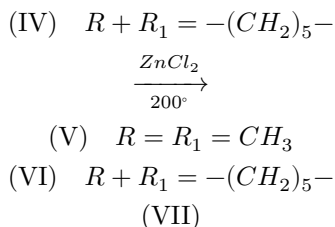


Oxyketone III was subjected to the Fischer reaction by heating its phenylhydrazone with catalytic amounts of anhydrous zinc chloride at 190-210°. As a result, the sole product isolated was 2-(1-methyl-1-hydroxyethyl)-3-(6-methylpyridyl-3)-indole (V). It was identified by its IR spectrum (there is a frequency of N-H and OH vibrations in the region of 3200 cm^{-1} , and the vibration frequencies of an unsaturated bond in the region of $1640\text{-}1660 \text{ cm}^{-1}$ are absent) and

by its UV spectrum (a maximum in the region of 267 m μ , characteristic of β -phenylindoles).

When an analogous reaction was carried out with oxyketone IV, in addition to 2-(1-hydroxycyclohexyl-1)-3-(6-methylpyridyl-3)-indole (VI), there was also isolated the pro-

product of its dehydration, 2-(cyclohexenyl-1)-3-(6-methylpyridyl-3)-indole (VII), in the IR spectrum of which there are vibration frequencies in the region of 1644 cm⁻¹.



Experimental Part

Condensation of I with ketones. To a mixture of 0.1 mole of I and 0.4 mole of powdered KOH in 25 ml of abs. ether at 0° and with stirring, 0.1 mole of ketone was added, the mixture was left overnight, saturated with carbon dioxide gas, and the carbinol was isolated (see Table 1).

Condensation of I with aldehydes. To a mixture of 0.05 mole of I and 0.25 mole of powdered KOH in 25 ml of abs. tetrahydrofuran, with stirring and cooling (-25, -40°), a solution of 0.1 mole of aldehyde in 20 ml of abs. tetrahydrofuran was slowly (1.5-2 hours) added, and the mixture was stirred for another 2 hours. On the following day it was acidified, extracted with ether, the aqueous solution was neutralized, extracted with ether, and the residue after removal of the solvent was chromatographed on alumina, eluting I with petroleum ether, and the carbinol with a mixture of benzene and acetone (1 : 1).

2-Methyl-5-(3-methyl-3-oxobutyl)-pyridine (III). A solution of 8.7 g of 2-methyl-5-(3-methyl-3-hydroxybutyn-1-yl)-pyridine (II, $R = R_1 = CH_3$) in 50 ml of 25% sulfuric acid was boiled in the presence of 0.1 g of mercuric oxide for 10 hours, neutralized with soda, extracted with chloroform, and after removal of the solvent the residue was distilled in vacuum. Yield 50.5%, b.p. 158-162°/7 mm, m.p. 52-54°.

Found, %: N 6.95; 7.05
 $C_{11}H_{15}O_2N$. Calculated, %: N 7.25

2-(1-Methyl-1-hydroxyethyl)-3-(6-methylpyridyl-3)-indole (V). 1.9 g of

III and 1 g of phenylhydrazine were heated (150°) for 0.5 hour, 0.2 g of anhydrous zinc chloride was added, and heating was continued for another 1.5 hours at 200-220°. The mixture was cooled, and the reaction mass was reprecipitated twice from an acidic solution. Yield 0.5 g (19%), m.p. 150-152° (from benzene + petroleum ether 1 : 1). λ_{\max} 267 m μ ($\lg \epsilon$ 4.08) (from methanol).

Found, %: N 10.92; 10.81

$C_{17}H_{19}ON_2$. Calculated, %: N 10.53

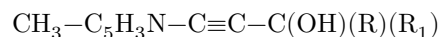
2-Methyl-5-(2-(1-hydroxycyclohexyl-1)-2'-oxoethyl)-pyridine (IV). A solution of 4.3 g of II ($R + R_1 = -(CH_2)_5$) in 25 ml of 25% sulfuric acid with addition of 0.05 g of mercuric oxide was boiled for 7 hours, neutralized with soda, extracted with benzene, the extract was evaporated and chromatographed on alumina. 2.7 g (49%) of a substance with m.p. 64-65° was isolated.

Found, %: N 6.51; 6.15

$C_{14}H_{19}O_2N$. Calculated, %: N 6.00

2-(1-Hydroxycyclohexyl-1)-3-(6-methylpyridyl-3)-indole (V). 5.8 g of IV and 2.7 g of phenylhydrazine were heated (150°) for 0.5 hour, add-

Table 1



R	R ₁	Yield, %	M.p., °C	B.p., °C mm	C, % found	C, cal- cu- lated	H, % found	H, cal- cu- lated	N, % found	N, cal- cu- lated
CH ₃	CH ₃	90	101	—	75,4375	75,43	7,527,55	7,43	—	—
			—							
			102							
C ₂ H ₅	CH ₃	80	98—	—	75,9875	75,99	7,948,15	7,94	—	—
			99							
C ₃ H ₇	CH ₃	48	30—	146	76,5376	76,53	8,468,48	8,37	—	—
			32							
				150°/2						
(CH ₃) ₃	CH ₃	70	100	—	77,5277	77,53	9,229,39	9,20	—	—
			—							
			101							
—	—	98	116	—	78,3878	78,41	8,027,93	8,91	—	—
(CH ₂) ₅	(CH ₂) ₅		—							
—	—		118							

R	R ₁	Yield, %	M.p., °C	B.p., °C mm	C, % found	C, % cal- cu- lated	H, % found	H, % cal- cu- lated	N, % found	N, % cal- cu- lated
C ₆ H ₅	CH ₃	60	104	—	—	—	—	—	5,695,71	5,91
			—							
			105							
C ₂ H ₅	H	38,7*	120	165	50,32505	52,50**	4,314,03	3,99	—	—
			—	—						
			123**	167°/8						
C ₃ H ₇	H	20,0*	103	182	—	—	—	—	9,469,43	9,09***
			—	—						
			104***	184°/8						
—	H	35,0*	112	178	52,37**	52,72	4,804,91	4,66	—	—
C ₄ H ₉			—	—						
			114**	180°/6						

* Based on pyridylacetylene charged.

** Picrate.

*** Phenylurethane.

0.2 g of anhydrous zinc chloride was added and the mixture was heated for another 2.5 hours at 175-190°. It was cooled, reprecipitated twice from an acidic solution, and the resulting oil was extracted with benzene. From the extract, 0.9 g (12%) of V was obtained, m.p. 152-154°, λ_{\max} 275 m μ ($\lg \epsilon$ 4.01) (from methanol).

Found, %: N 9.03; 8.98

C₂₀H₂₂ON₂. Calculated, %: N 9.11

The residue insoluble in benzene was chromatographed on alumina. 0.3 g of VI was obtained, m.p. 70-71°.

Found, %: N 9.46; 9.33

C₂₀H₂₀N₂. Calculated, %: N 9.72

Moscow State University
named after M. V. Lomonosov

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2. A. I. Zakharova, ZhOKh, **11**, 939 (1941).

Note: Figure translations are in progress. See original paper for figures.

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