6-Nitro-8-chloro-4-hydroxyquinoline (VI). Repeated crystallization of the precipitates obtained by evaporation of the alcohol mother liquors after separation of cyclization product V gave light-brown crystals of VI. PMR spectrum: 6.67 (H_α, d, J = 7.5 Hz, 1H), 7.05 (H_β, d, J = 7.5 Hz, 1H), 8.23 (H_{arom}, d, J = 2.5 Hz, 1H), and 8.52 ppm (H_{arom}, d, J = 2.5 Hz, 1H). UV spectrum, λ_{max} (log ε): 332 (4.78), 317 (4.83), and 250 (4.04). The 2,4-dinitrophenylhydrazone of VI was obtained as bright-red crystals with mp 325-327°C (from ethanol). Found: N 20.8%. $C_{15}H_9ClN_6O_6$. Calculated: N 20.8%. Compound V was obtained in 8% yield, and VI was obtained in 14.5% yield in the case of more prolonged cyclization of IV (20 h).

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CONDENSATION REACTIONS BASED ON 3-FORMYLINDAZOLE

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The chemical properties of 3-formylindazole were studied in the case of nucleophilic addition reactions (Knoevenagel, Rodionov, and crotonic condensations). The possibility of the preparation of Schiff bases in the unsubstituted 3-formylindazole series was investigated. 3-Indazolylacrylic and β-(3-indazolyl)-β-aminopropionic acids, the products of crotonic condensation, and azomethines were synthesized.

Despite the interest currently being displayed in the chemistry of indazole, up until now very little data on the chemical behavior of 3-formylindazole have been available.

The chemical properties of 1-methyl-3-formylindazole have been studied [1], and the increased reactivity of the formyl group with respect to nucleophilic reagents and the impossibility of carrying out similar reactions with 3-formylindazole [2] have been noted. In this connection, it seemed of interest to study the chemical properties of unsubstituted 3-formylindazole under the conditions of nucleophilic addition reactions (the Knoevenagel and Rodionov reactions and crotonic condensation). In addition, the possibility of the preparation of Schiff bases in the unsubstituted 3-formylindazole series was studied.

We have established that unsubstituted 3-formylindazole also quite readily undergoes condensation with malonic acid in the presence of pyridine and catalytic amounts of piperidine (a modified Knoevenagel reaction).

In the PMR spectrum of 3-indazolylacrylic acid (I) the protons of the ethylene group form an AB system (7.39 and 6.79 ppm) with a spin–spin coupling constant (SSCC) of 16 Hz; this confirms the trans configuration of the compound.*

When we carried out the condensation of 3-formylindazole with malonic acid in the presence of an alcohol solution of ammonia (the Rodionov reaction), we isolated β-(3-indazolyl)-β-aminopropionic acid (II) in 25% yield. The β-amino acid was obtained in somewhat higher yield (33%) by means of the Johnson modification.

The IR spectral data show that the β-amino acid obtained exists in the form of a dipolar ion, as evidenced by the presence of an amino acid I band at 1640 cm^{-1} and an amino acid II band at 1550 cm^{-1} due to the sym-

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* See display at top of next page after Table 1.

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TABLE 1. Characteristics of the Products of Condensation of 3-Formylindazole

Compound	mp, °C	Found, %			Empirical formula	Calc., %			IR spectra, cm^{-1}				UV spectra, λ_{max}, nm (log ε)	Yield, %
		C	H	N		C	H	N	NH	C=C	C=O	CN		
I	225—226^a	63,7	4,4	14,7	$C_{10}H_8N_2O_2$	63,8	4,3	14,9	3200—3300	965 1645	1720 1690		216 (4,32), 252 (3,9), 310 (4,17)	78
II	217—218^b	58,3	5,5	20,1	$C_{10}H_{11}N_3O_2$	58,2	5,4	20,5	3160—3185		1640 1550		209 (4,65), 244 (3,76), 293 (3,82)	33
III	156—157^c	70,9	5,5	15,0	$C_{11}H_{10}N_2O$	70,9	5,4	15,0	3195	1625	1670		207 (4,24), 253 (3,89), 330 (4,23)	93
IV	175—176^c	77,1	5,2	11,2	$C_{16}H_{13}N_2O$	77,1	5,3	11,2	3245	1612	1660		207 (4,39) 266 (4,02), 351 (4,17)	92
V	144—145^d	75,8	5,2	19,2	$C_{14}H_{11}N_3$	76,0	5,0	19,0	3200—3400			1670	210 (4,02), 244 (3,49), 294 (3,40)	60
VI	152—153^d	63,2	4,0	20,8	$C_{14}H_{10}N_4O_2$	63,2	3,8	21,0	3350—3400			1675	206, 346, 244	52
VII	168—169^d	71,5	5,2	17,0	$C_{15}H_{13}N_3O$	71,7	5,2	16,7	3350—3400			1680	209 (4,29), 259 (3,88), 339 (4,24)	67

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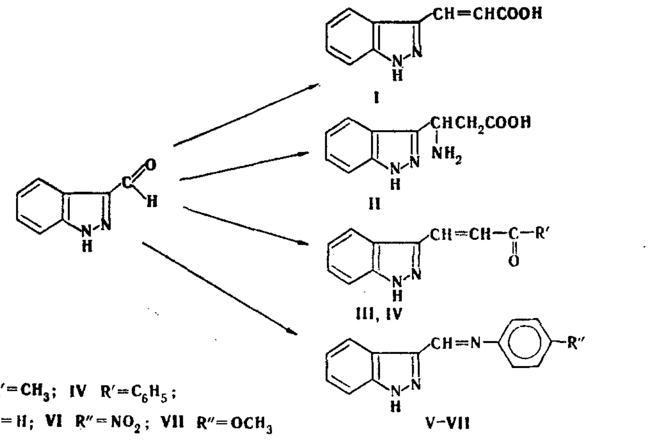
^{a}From acetic acid. ^{b}From dilute alcohol. ^{c}From methanol. ^{d}From dimethylformamide.



III R′=CH$_3$; IV R′=C$_6$H$_5$;
V R″=H; VI R″=NO$_2$; VII R″=OCH$_3$

metrical and asymmetrical deformation vibrations of the $\overset{+}{N}H_3$ group. The absorption band of an ionized carboxyl group is found at 1618 cm^{-1}, and the $\overset{+}{N}H_3$ band is found at 3080 cm^{-1}.

We have established that 3-formylindazole readily undergoes crotonic condensation under alkaline conditions. The products of the reactions with acetone and acetophenone were isolated in quantitative yields.

The α,β-unsaturated ketones obtained are characterized by a trans orientation of the substituents attached to the double bond; this is confirmed by the PMR spectral data: The SSCC is 16 Hz.

Information regarding the preparation of azomethines of 1-methyl-3-formylindazole is available [3]. The reaction was carried out in methanol solution in the presence of catalytic amounts of piperidine or by fusing the starting compounds.

Azomethines of unsubstituted 3-formylindazole were obtained in good yields in the reaction of equimolar amounts of the aldehyde and the corresponding amine in benzene solution by heating (Table 1). m-Nitrobenzenesulfonic acid was used as the catalyst in the reaction with aniline and p-nitroaniline. The reaction with p-anisidine proceeds smoothly and without a catalyst.

The electronic spectra of I-VII are characterized by three absorption bands of approximately equal intensity (log ε 4.01-4.39) at 206-216, 250-260, and 294-350 nm due to π-electron transitions in a conjugated system of bonds.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in dimethyl sulfoxide (DMSO) – acetone (1:3) were recorded with a CFT-20-16K spectrometer with tetramethylsilane as the internal standard. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The electronic spectra of ethanol solutions of the compounds at a layer thickness of 1 cm were recorded with a Specord spectrophotometer.

β-(3-Indazolyl)acrylic Acid (I). A mixture of 1.46 g (0.01 mole) of 3-formylindazole, 2.08 g (0.02 mole) of malonic acid, and 6 ml of pyridine containing three to four drops of piperidine was refluxed for 3 h, after which it was cooled and acidified with dilute hydrochloric acid. The resulting precipitate was removed by filtration, washed with water, dried, and recrystallized from dilute acetic acid to give colorless crystals.

β-(3-Indazolyl)-β-aminopropionic Acid (II). A mixture of 2 g (0.01 mole) of 3-formylindazole, 3.1 g (0.03 mole) of malonic acid, and 2 g of anhydrous ammonium acetate was heated on a water bath for 5 h, after which the residue was dissolved in 50 ml of 2 N hydrochloric acid, and the solution was filtered. The impurities were extracted to the minimal volume, and the residue was treated with dilute ammonium hydroxide to pH 6. The mixture was then cooled to precipitate acid II.

4-(3-Indazolyl)-3-buten-2-one (III). A 0.27-g (0.004 mole) sample of acetone and 2 ml of a 20% solution of potassium hydroxide were added successively with stirring to a hot solution of 0.29 g (0.002 mole) of 3-formylindazole in 5 ml of ethanol, and the mixture was refluxed for 15 min, cooled, and diluted with water. The resulting precipitate was removed by filtration, washed with water, and dried to give yellow crystals of III.

1-Benzoyl-2-(3-indazolyl)ethylene (IV). This compound was prepared by the preceding method by the addition of 0.74 g (0.004 mole) of acetophenone.

3-Formylindazole Anil (V). A 1.39-g (0.015 mole) sample of aniline and a catalytic amount of m-nitrobenzenesulfonic acid were added to a solution of 1.46 g (0.01 mole) of 3-formylindazole in 50 ml of benzene, and the mixture was refluxed for 3 h. It was then vacuum evaporated to two-thirds of its original volume, and hexane was added. The resulting precipitate was separated, washed with benzene and ether, and dried to give light-yellow crystals that were only slightly soluble in organic solvents.

3-Formylindazole p-Nitroanil (VI). A 2.07-g (0.015 mole) sample of p-nitroaniline and a catalytic amount of m-nitrobenzenesulfonic acid were added to a solution of 1.46 g (0.01 mole) sample of 3-formylindazole in 50 ml of benzene, and the mixture was refluxed for 1.5 h and allowed to stand overnight. The resulting precipitate was removed by filtration, washed with benzene and alcohol, and dried to give light-yellow crystals that were only slightly soluble in organic solvents.

3-Formylindazole p-Methoxyanil (VII). A 1.84-g (0.015 mole) sample of p-anisidine was added to a solution of 1.46 g (0.01 mole) of 3-formylindazole in 50 ml of benzene, and the mixture was refluxed for 1 h. It was then cooled, and the precipitate was removed by filtration, washed with alcohol, and dried.

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