jugated with the tosylamino group to 9%. One cannot exclude the possibility that the intramolecular hydrogen bond peculiar to this compound also affects the direction of attack.

EXPERIMENTAL

The mass spectra were obtained with an MS-702 spectrometer. The accelerating voltage was 10 kV, the ionizing-electron energy was 70 eV, and the temperature of the sample vaporization block was 120°. The spectra were recorded with the aid of a source with direct introduction of the sample into the ionization region. The percentage enrichments of the fragments presented in Table 1 have a confidence interval of ± 1%.

2-Phenyl-4H-3,1-benzoxazin-4-one and its substituted derivatives were obtained by reaction of the aroyl chloride with the appropriate anthranilic acid in pyridine [3,4]. 2-(2-Tosylaminophenyl)-4H-3,1-benzoxazin-4-one was obtained by reaction of anthranilic acid with p-toluenesulfonyl chloride in refluxing pyridine [5].

Hydrolysis of 2-Aryl-4H-3,1-benzoxazin-4-ones in O^{18}-Enriched Water. A 1 sodium hydroxide solution enriched with O^{18} was obtained by dissolving sodium metal in 30% heavy-oxygen water. A 50-mg sample of 2-aryl-4H-3,1-benzoxazin-4-one was added to 2.5 cm^3 of the sodium hydroxide solution, and the mixture was allowed to stand at 50° until the solid has dissolved almost completely. The mixture was filtered, and the N-aroylanthranilic acid was isolated from the filtrate by acidification with hydrochloric acid. Hydrolysis with a nonenriched sodium hydroxide solution was carried out under similar conditions.

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REACTIONS OF 1,5-DIKETONES. XX*. SEMICYCLIC 1,5-DIKETONES IN THE FISCHER REACTION

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UDC 547.759.3

Monophenylhydrazones involving both the phenacyl carbonyl group and the ring carbonyl group are formed as intermediates in the reaction of semicyclic 1,5-diketones of the 2-(phenacylobenzyl)cyclohexanone type with phenylhydrazine in acid media. The former undergo subsequent conversion to the corresponding substituted indoles, whereas the latter are converted to substituted 1H-2,3,3a,4-tetrahydropyrido[3,2,1-j,k]carbazoles; in addition, the corresponding 5,6,7,8-tetrahydroquinoline derivatives are also partially formed.

The Fischer reaction in the 1,5-diketone series is unknown, although the reactions of 1,5-diketone derivatives with phenylhydrazine in acidic media have been described [2,3]. We made a detailed study of the behavior of semicyclic 1,5-diketones Ia-d with respect to phenylhydrazine. Judging from the structure of the isolated compounds, the process can be represented by the scheme

*See [1] for communication XIX.

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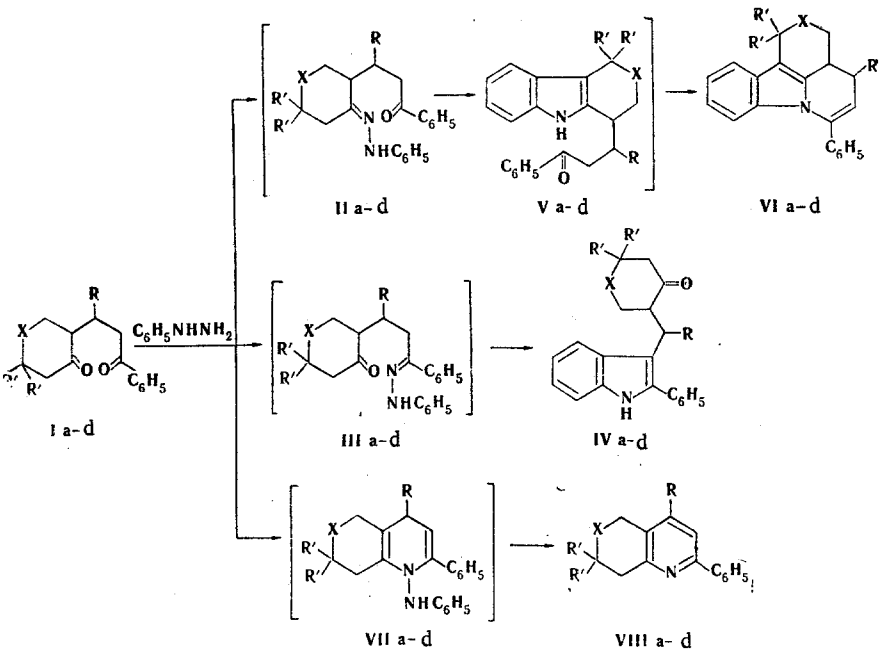


I-VIII a $R = C_6H_5$ $R' = H$, $X = CH_2$; b $R = C_6H_4OCH_3$-*p*, $R' = H$, $X = CH_2$; c $R = R' = H$, $X = CH_2$; d $R = C_6H_5$ $R' = CH_3$, $X = O$

Monophenylhydrazones IIa-c and IIId— the primary intermediates — can be isolated in small amounts (Table 1) only at room temperature; on heating they undergo subsequent transformation and are not detected in the reaction mixtures. The structure of the monophenylhydrazones was confirmed by their IR spectra: the absorption of a phenacyl carbonyl group (1695 cm^{-1}) is retained in the spectra of IIa-c, and the spectrum of IIId contains the absorption of a ring carbonyl group (1710 cm^{-1}); in addition, there are intense bands of NH and C = N absorption (3300 and 1605 cm^{-1}) in all cases. The primary formation from Id of a hydrazone involving the phenacyl carbonyl group is evidently explained by the shielding effect of the gem-methyl groups, which hinder approach of the reagent to the ring carbonyl group (this effect was noted for other reactions with diketones of this type [4] and also with α,α-dimethyltetrahydro-γ-pyrone [5]).

The indolization of the hydrazones proceeds readily when they are heated in acetic acid, as established in the case of hydrazones IIa,c, and IIId. Pyridocarbazoles VIa,c (carbazoles Va,c are evidently intermediates) were isolated from the indolization products in the case of IIa,c, whereas indole IVd was isolated in the case of IIId.

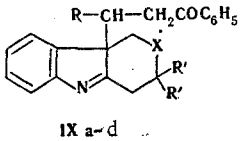
TABLE 1. Yields of the Products of the Reaction of Diketones Ia-d with Phenylhydrazine

Diketone I	Reaction conditions			Reaction products (yield, %)			
	method*	temp., °C	time, h	monophenylhydrazone	indole IV	pyridocarbazole VI	tetrahydroquinoline VIII
a	A	20	24	II (3)	13	53	8
a	A	100	5	—	10	55	10
a	B	80	5	—	18	50	5
b	A	20	24	II (4)	10	60	8
b	A	100	5	—	6	58	10
c	A	20	24	II (12)	28	11	14
c	A	100	5	—	25	16	19
c	B	80	5	—	30	15	17
d	A	20	24	III (17)	20	5	15
d	A	100	5	—	35	10	19

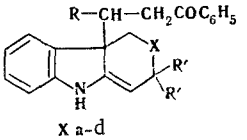
*In method A the reaction was carried out in 98% acetic acid, whereas in method B the reaction was carried out in 2% alcoholic HCl.

However, pyridocarbazoles VI and indoles IV (Table 1) are formed in the reaction of diketones Ia-d with phenylhydrazine. This provides evidence that diketones Ia-c form, along with intermediate hydrazones II, intermediate hydrazones III (through the phenacyl carbonyl group), whereas diketone Id gives, in addition to hydrazone IIId, a small amount of hydrazone IId (through the ring carbonyl group).

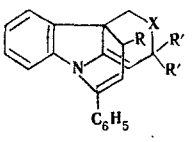
The IR spectra of pyridocarbazoles VIa-d do not contain the absorption bands characteristic for the C = O and NH groups, and this distinguishes them from the



IX a-d



X a-d



XI a-d

other possible products of indolization of monophenylhydrazones of the II type (for example, from Va-d, IXa-d, and Xa-d).

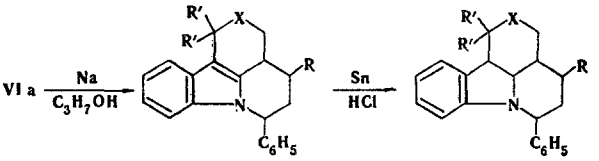
The transition from IIa-d to VIa-d is evidently realized as a result of cyclodehydration of intermediates Va-d (similar cyclization was previously observed in the indolization of 1,5-keto esters [6]). The spectral data confirm this assumption. Thus molecular ion peaks are observed in the mass spectra of VIa-d and have m/e values that are 18 units lower than the values calculated for Va-d, IXa-d, and Xa-d and are in complete agreement with the molecular weights calculated for structures VIa-d.

The PMR spectra of VIa-d have signals of vinyl protons — a doublet at 5.12-5.24 ppm (J = 3 Hz) for VIa,b,d and a doublet of doublets at 5.30 ppm (J_1 = 2.5 Hz, J_2 = 7.5 Hz) for VIc, which is in agreement with the structure of the latter. This makes it possible to reject alternative structure XI, in the spectrum of which one would observe signals of two vinyl and benzyl protons.

The UV spectra of VI have a longwave absorption maxima at 314-318 nm, which is 30 nm higher than the maximum in the spectrum of 1,2,3,4-tetrahydrocarbazole [7]. This bathochromic shift apparently should be explained by the presence in the VIa-d structures of additional conjugation of the tetrahydrocarbazole ring with the double bond of the phenylpyrido fragment.

In contrast to tetrahydrocarbazolenine derivatives and similarly substituted tetrahydrocarbazoles of analogous form [6], VIa-d do not form hydrochlorides when solutions of them are treated with hydrogen chloride.

We carried out the two-step reduction of hydropyridocarbazole VIa:



XII XIII

The absorption band at 1640 cm^{-1} ($\nu_{C=C}$) vanishes in the IR spectrum of XII, and a longwave maximum is observed at 288 nm (in place of λ_{max} 314 nm for the starting compound) in its UV spectrum.

In contrast to VIa and XII, XIII, like other indoline derivatives [8], forms a hydrochloride.

The IR spectra of indoles IVa-d contain bands at 3470 cm^{-1} (indole ring NH) and 1710 cm^{-1} (alicyclic C = O group), and this constitutes evidence for their formation from hydrazones III; a direct experimental confirmation was obtained in the case of the IIId → IVd transition (see above). Absorption maxima are observed in the UV spectra of IV at 223 and 306 nm; these are close to the maxima in the UV spectra of analogous compounds, for example 2-phenyl-3-methylindole [9].

EXPERIMENTAL

The IR spectra of $CHCl_3$ solutions were recorded with a UR-20 spectrometer. The UV spectra of methanol solutions were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of carbon tetrachloride solutions were recorded with a Bruker-90 spectrometer with hexamethyldisiloxane as the standard. The mass spectra were recorded with an MKh-1303 spectrometer equipped with a system for direct introduction of the samples into the ion source at vaporization temperatures of 150-200° and an ionizing-electron energy of 70 eV. The individuality of the products was verified by thin-layer chromatography (TLC) on silica gel [Silufol UV-254 in petroleum ether—ethyl acetate (5:2) and petroleum ether—chloroform (2:1) systems]. Diketones Ia-d were obtained by the methods in [11-14].

Reaction of Diketones I with Phenylhydrazine. A) A solution of 0.04 mole of diketone Ia-d in 100 ml of 98% acetic acid was mixed with 4.32 g (0.04 mole) of phenylhydrazine. In one series of experiments the mixtures were allowed to stand at room temperature for 24 h, and in another series of experiments they were heated on a boiling-water bath for 5 h. Precipitates were formed at room temperature in the case of diketones Ia,b,d. When the temperature was raised, precipitates were formed only in experiments with Ia,b. The precipitates were removed by filtration (filtrate 1), washed with two 15-ml portions of acetic acid and three 30-ml portions of water to give chromatographically pure VIa, VIb, and IIId.

Filtrates 1 and the wash liquids were combined, during which precipitates formed. Reaction mixtures from which precipitates were not formed after the experiments were carried out were poured into 100 ml of water, during which precipitates also formed. These precipitates were separated (filtrate 2) and dissolved in diethyl ether. The ether solutions were washed to neutrality with water, and the wash waters were added to filtrates 2. The ether solutions were dried over $MgSO_4$ and evaporated. The residues were subjected to chromatographic separation on 24 by 35 cm plates with a loose layer of activity II Al_2O_3. A 0.4-g sample of the substance was applied to each plate, and the chromatograms were developed in a petroleum ether—ethyl acetate (7:2) system. The zones (detected by iodine vapors) with R_f 0.8 (VI), 0.6 (VIII), 0.4 (II or III), and 0.2 (IV) were removed and diluted with ether. The eluates were evaporated, and the residues were recrystallized. Filtrates II were made alkaline to pH 8-9 with Na_2CO_3, and the liberated oils (in the case of Ia-c)* were extracted with ether. The solvent was removed, and aniline was identified in addition to the corresponding quinoline VIII in the residues (by TLC and a qualitative reaction with furfural). For isolation of VIIa,b, 5 ml of alcohol was added to the semicrystalline residues, and the resulting crystals were removed by filtration and recrystallized from alcohol. No melting-point depressions were observed for mixtures of these products with standard samples of VIIIa [10] and VIIIb [11]. Quinoline VIIIc was isolated from methanol solution in the form of the picrate, which, after recrystallization from methanol, did not depress the melting point of the picrate of a standard sample [12].

B) A 1.08-g (0.01 mole) sample of phenylhydrazine was added to a suspension of 0.01 mole of diketone Ia or Ic in 40 ml of 2% alcoholic HCl, and the mixtures were refluxed for 5 h. In the experiment with Ia, the precipitate was removed by filtration and washed successively with two 10-ml portions of alcohol and water (∿40 ml) to neutrality to give VIa. The wash alcohol was added to the filtrate, the solvent was removed by distillation to a volume of ∿30 ml, and the wash water was added to the residue. This procedure produced an oil. In the experiment with Ic, 20 ml of alcohol was removed from the mixture by distillation, and 30 ml of water was added to the residue. An oil also was liberated by this procedure. The liberated oils were extracted with ether, the ether solutions were washed with 5% HCl and water to neutrality, dried over $MgSO_4$, and evaporated. The residues were separated by means of preparative TLC as described in method A to give VIa (an additional amount), VIc, and IVa,c. As described in method A, VIIIa,c were isolated from the aqueous acid solutions by alkalization. The yields of the products are given in Table 1, and their characteristics are presented in Table 2.

*Quinoline VIIId was precipitated completely with water on dilution of the reaction mixture and was isolated subsequently by preparative TLC as described above.

TABLE 2. Physical Characteristics of the Isolated Compounds

Compound	mp, °C (crystallization solvent)	Empirical formula	Found, %			Calculated, %		
			C	H	N	C	H	N
2-(Phenacylobenzyl)cyclohexanone monophenylhydrazone (IIa)	175-177 (alcohol)	$C_{27}H_{28}N_2O$	81.4	7.4	7.2	81.7	7.1	7.1
2-Phenacylo-p-methoxybenzyl)cyclohexanone monophenylhydrazone (IIb)	178-179 (alcohol—dioxane) 1:1	$C_{28}H_{30}N_2O$	78.4	7.2	6.5	78.9	7.0	6.6
2-(Phenacylomethyl)cyclohexanone monophenylhydrazone (IIc)	148-149 (alcohol)	$C_{21}H_{24}N_2O$	78.9	7.6	8.5	78.7	7.5	8.7
1,3-Diphenyl-1-(2,2-dimethyltetrahydro-4-pyranon-5-yl)-3-propanone monophenylhydrazone (IIId)	177-178 (alcohol)	$C_{28}H_{30}N_2O_2$	79.0	7.4	7.0	78.9	7.0	6.6
α-Phenyl-β-(2-oxocyclohexylbenzyl)indole (IVa)	197-198 (alcohol)	$C_{27}H_{25}NO$	84.8	7.4	3.5	85.4	6.6	3.7
α-Phenyl-β-(2-oxocyclohexyl-p-methoxybenzyl)indole (IVb)	204-205 (alcohol—dioxane) 1:1	$C_{28}H_{27}NO$	81.9	6.9	3.5	82.2	6.6	3.4
α-Phenyl-β-(2-oxocyclohexylmethyl)indole (IVc)	117-118 (alcohol)	$C_{21}H_{21}NO$	83.2	7.2	4.9	83.1	6.7	4.9
α-Phenyl-β-(2,2-dimethyltetrahydro-4-pyranon-5-ylbenzyl)-indole (IVd)	203-204 (alcohol)	$C_{28}H_{27}NO$	82.2	6.9	3.3	82.2	6.6	3.4
4,6-Diphenyl-1H-2,3,3a,4-tetrahydropyrido[3,2,1-j,k]carbazole (VIa)	182-183 (alcohol—dioxane) 1:1	$C_{27}H_{23}N$	89.5	6.3	4.1	89.7	6.4	3.9
4-Phenyl-6-(p-methoxyphenyl)-1H-2,3,3a,4-tetrahydropyrido-[3,2,1-j,k]carbazole (VIb)	199-201 (benzene)	$C_{28}H_{25}NO$	86.2	6.8	3.8	85.9	6.4	3.5
4-Phenyl-1H-2,3,3a,4-tetrahydropyrido[3,2,1-j,k]carbazole (VIc)	107-108 (alcohol)	$C_{21}H_{19}N$	88.2	6.4	5.1	88.4	6.6	4.9
1,1-Dimethyl-2-oxa-4,6-diphenyl-1H-2,3,3a,4-tetrahydropyrido-[3,2,1-j,k]carbazole (VId)	203-204 (alcohol)	$C_{28}H_{25}NO$	86.2	6.7	—	85.9	6.4	—

Cyclization of Hydrazones IIa,c and IIId. A solution of 5 mmole of the monophenylhydrazone in 30 ml of 98% acetic acid was heated on a water bath for 30 min (IIa) or 3 h (IIc, IIId). The precipitate formed in the case of IIa was removed by filtration and washed with acetic acid and water to give 1.1 g (61%) of VIa. As described in method A, 0.1 g (7%) of VIIIa was isolated from the filtrate by alkalization with sodium carbonate. In the case of IIc and IIId, the reaction solutions were diluted with water and made alkaline with sodium carbonate. The liberated oils were extracted with ether, and the ether solutions were washed with water, dried, and evaporated. Preparative TLC of the residues yielded 0.37 g (26%) of VIc, 0.2 g (20%) of VIIIc, 0.8 g (39%) of IVd, and 0.24 g (15%) of VIIId.

4,6-Diphenyl-1H-2,3,3a,4,5,6-hexahydro[3,2,1-j,k]carbazole (XII). A 4-g (11 mmole) sample of VIa was dissolved in 300 ml of refluxing propyl alcohol, and the mixture was refluxed for 3 h. Sodium (13 g) was added to the refluxing solution, after which the mixture was cooled, and the precipitated XII (2.4 g) was removed by filtration. The filtrate was evaporated to 100 ml and diluted with water, and an additional amount (0.9 g) of XII was removed

by filtration. The overall yield of product with mp 183-184° (from propyl alcohol) was 3.3 g (81%). IR spectrum, cm^{-1}: 1500, 1600 (aromatic ring C = C); 3020-3040 (aromatic = CH); 1465, 2860-2870, 2930, and 2950 (aliphatic CH). UV spectrum, λ_{max}, nm (log ε): 288 (4.25). Mass spectrum: m/e 363 (M^+). Found: C 88.9; H 7.8%. $C_{27}H_{25}N$. Calculated: C 89.2; H 6.9%.

4,6-Diphenyl-1H-1a,2,3,3a,4,5,6,7a-octahydropyrido[3,2,1-j,k]carbazole (XIII). Powdered tin (30 g) was added in 3-g portions with stirring to a refluxing solution of 3.6 g (0.01 mole) of XII in 100 ml of propyl alcohol, after which 150 ml of concentrated HCl was added dropwise in the course of 20 h. The mixture was cooled and made alkaline with concentrated NaOH, and the organic layer was diluted with ether. The ether solution was washed to neutrality with water and dried over $MgSO_4$. The solvent was removed, and the residue was recrystallized from propyl alcohol—dioxane (10:1) to give 2 g (55%) of XIII with mp 167-169°. IR spectrum (cm^{-1}): 1500, 1610, 3020-3070 (aromatic C = C and = CH); 1460, 2820, 2870, and 2945 (aliphatic C-H). Mass spectrum: m/e 365 (M^+). Found: C 88.5; H 7.6%. $C_{27}H_{27}N$. Calculated: C 88.7; H 7.4%. The hydrochoride of XIII had mp 203-205° (dec., from absolute dioxane saturated with HCl). Found: C 80.0; H 7.0; Cl 9.1%. $C_{27}H_{27}N \cdot HCl$. Calculated: C 80.7; H 6.9; Cl 8.8%.

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