9-Methyl-9-phenyl-10-methylene-9,10-dihydro-9-sila-3-azaanthracene (XIV). A 0.8-g (2.5 mmole) sample of silaazaanthrol X was refluxed for 11 h in 20 ml of xylene with 2.5 g (0.02 mole) of phosphoric anhydride, after which 10 ml of water was added, and the mixture was made alkaline to pH 12 with ammonium hydroxide. The xylene solution was dried with magnesium sulfate, the xylene was removed by distillation, and the residue (0.5 g) was chromatographed [elution with heptane—ethyl acetate (5:1)] to give 0.14 g (18%) of XIV as colorless crystals with mp 130-132°C (from heptane) and R_f 0.72 [ethyl acetate—hexane (1:4)]. PMR spectrum (in $CDCl_3$), δ: 0.83 ppm (3H, s, CH_3). Found: C 79.9; H 5.6; N 4.6%; M^+ 299. $C_{20}H_{17}NSi$. Calculated: C 80.3; H 5.7; N 4.7%; M 299.

1,2-Dimethyl-1,2-diphenyl-1,2-bis(2-nicotinoylphenyl)disiloxane (XV). A 0.08-g (0.002 g-atom) sample of potassium was dissolved in 1.5 ml of absolute tert-butyl alcohol, after which a solution of 0.3 g (1.3 mmole) of azaanthrone VI in 40 ml of absolute alcohol was added, and the mixture was refluxed for 1 h. Water (1 ml) was added, the alcohol was removed by distillation, and the residue (0.25 g) was chromatographed [h = 30 cm, d = 2 cm, elution with heptane—ethyl acetate (4:1)] to give 0.1 g (32%) of disiloxane XV as colorless crystals with mp 154-155°C and R_f 0.76 [ethyl acetate—hexane (1:4)]. PMR spectrum (in $CDCl_3$), δ: 8.6 (4H, m, α-H of the pyridine ring), 7.7 (2H, dd, γ-H of the pyridine ring), and 0.57 ppm (6H, s, CH_3). Found: N 4.4%; M^+ 620. $C_{38}H_{32}N_2O_3Si_2$. Calculated: N 4.5%; M 620.

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PREPARATION AND IONIC HYDROGENATION OF SUBSTITUTED 4-(3-OXOPROPYL)-5-PYRAZOLONES

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UDC 547.775'778:542.941

4-(3-Oxopropyl)-5-pyrazolone derivatives were obtained under mild conditions of alkaline catalysis by condensation of 1-phenyl-3-methyl-5-pyrazolone and substituted chalcones. During ionic hydrogenation of the products they undergo heterocyclization with the formation of 5,6-dihydropyrano[3,2-d]pyrazoles.

Individual data on the ability of 1-phenyl-3-R-5-pyrazolones to undergo the Michael reaction with α,β-unsaturated compounds has recently begun to appear in the literature more and more frequently [1-4], whereas data on the heterocyclization of the resulting 4-(3-oxopropyl)-5-pyrazolones are virtually absent. We set out to study the ability of 1-phenyl-3-R-5-pyrazolones (I, II) to react with chalcones III-VI and the behavior of the resulting 1,5-dicarbonyl compounds under ionic hydrogenation conditions.

Fusion of the starting 3-R-5-pyrazolones with chalcones at 160°C for 3 h is used in most cases as the principal method of carrying out the Michael reaction [2, 4]. Heating of an alcohol solution of the components in the presence of NaOH can also be used in the case of 1,3-diphenyl-5-pyrazolone [2], while refluxing of equimolar amounts of the substances in the presence of sodium ethoxide for 3 h is proposed for the condensation of 1-phenyl-3-methyl-5-pyrazolone [4].

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TABLE 1. Yields and Constants of Propanonylpyrazolones

Compound	mp,* °C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
VII	142—144	78,6	5,9	7,3	$C_{25}H_{22}N_2O_2$	78,5	5,8	7,3	82
VIII	162—164	69,8	5,3	10,6	$C_{25}H_{21}N_3O_4$	70,2	5,0	9,8	85
IX	145—147	75,0	6,0	7,1	$C_{26}H_{24}N_2O_2$	75,7	5,9	6,8	83
X	150—152	74,0	5,4	7,2	$C_{23}H_{20}N_2O_3$	73,6	5,5	7,7	70

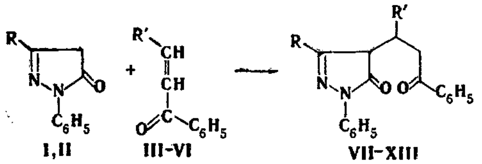
*Compounds VII, IX, and X were recrystallized from alcohol; VIII was purified by column chromatography on KSK silica gel by elution with hexane—ethyl acetate (5:3).

TABLE 2. Yields and Constants of Dihydropyrano[3,2-d]pyrazoles

Compound	R_f	mp,* °C	Found, %			Empirical formula	Calculated, %			Yield, %
			C	H	N		C	H	N	
XIV	0,76	169—171	82,2	5,8	7,1	$C_{25}H_{22}N_2O$	82,0	6,1	7,6	64
XV	0,52	177—179	72,9	5,1	10,1	$C_{25}H_{21}N_3O_3$	73,0	5,2	10,2	68
XVI	0,64	123—125	78,8	6,2	7,6	$C_{26}H_{24}N_2O_2$	78,8	6,1	7,1	59
XVII	0,82	174,5—175	83,7	5,6	6,5	$C_{30}H_{24}N_2O$	84,1	5,7	6,5	71
XVIII	0,68	213—214	76,3	4,8	8,6	$C_{30}H_{23}N_3O$	76,1	4,9	8,9	69
XIX	0,74	209—210	81,5	5,6	6,1	$C_{31}H_{26}N_2O$	81,2	5,7	6,1	60

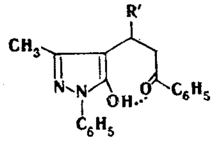
*Compounds XIV, XV, and XVII-XIX were recrystallized from ethanol, while XVI was recrystallized from ether.

We have established that the condensation of 1-phenyl-3-methyl-5-pyrazolone (I) with chalcones III-VI takes place readily in an alcohol solution of sodium ethoxide at 40°C and gives the products in 70-85% yields. The reaction of m-nitrobenzylideneacetophenone (IV) with pyrazolone I proceeds less smoothly and under more severe conditions; this should be explained by the negative inductive effect of the nitro group, which reduces the electron density of the π bond of chalcone IV.



I R=CH_3; II R=C_6H_5; III R′=C_6H_5; IV R′=$C_6H_4NO_2$-*m*; V R′=$C_6H_4OCH_3$-*p*; VI R′= 2-furyl; VII R=CH_3, R′=C_6H_5; VIII R=CH_3, R′=$C_6H_4NO_2$-*m*; IX R=CH_3, R′=$C_6H_4OCH_3$-p; X R=CH_3, R′= 2-furyl; XI* R=R′=C_6H_5; XII* R=C_6H_5, R′=$C_6H_4NO_2$-*m*; XIII* R=C_6H_5, R′=$C_6H_4OCH_3$-*p*

Judging from their IR spectra in the solid state, 1,5-dicarbonylcompounds VII-X exist, in all likelihood, in the chelate form:



The appearance in the IR spectra of a broad diffuse band of an associated hydroxy group at 2700-3200 cm^{-1} and an intense absorption band of a carbonyl group at 1685 cm^{-1} constitutes evidence in favor of this.

We have previously established the ability of 1,5-diketones and 1,5-dialdehydes to undergo conversion to tetrahydropyrans under the influence of triethylsilane and trifluoro-

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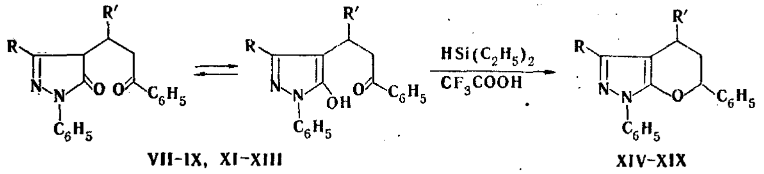
*Compounds XI-XIII were obtained by the method with NaOH [2].

acetic acid [5]. It seemed of interest to study the behavior of 1,5-dicarbonyl compounds that contain an amide carbonyl group under ionic hydrogenation conditions. We found that 4-(3-oxopropyl)pyrazolones VII-IX and XI-XIII undergo hydrogenation by triethylsilane and CF_3COOH in a 3% solution of boron trifluoride etherate in CF_3COOH with the formation of the corresponding 1,6-diphenyl-3-R-4-R'-5,6-dihydropyrano[3,2-d]pyrazoles (XIV-XIX) [6]:

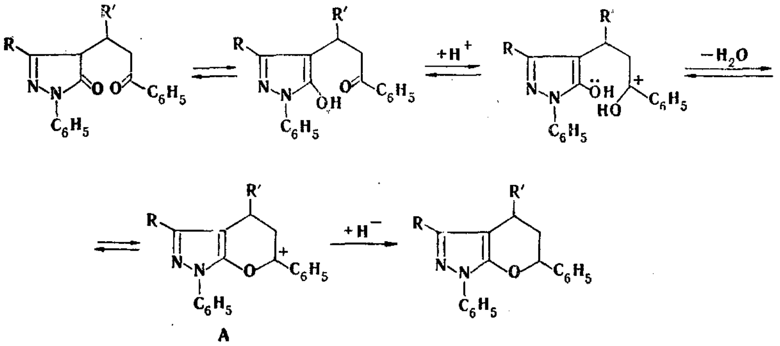


VII, XIV R=CH_3, R'=C_6H_5; VIII, XV R=CH_3, R'=$C_6H_4NO_2$-*m*; IX, XVI R=CH_3, R'=$C_6H_4OCH_3$-*p*; XI, XVII R=R'=C_6H_5; XII, XVIII R=C_6H_5, R'=$C_6H_4NO_2$-*m*; XIII, XIX R=C_6H_5, R'=$C_6H_4OCH_3$-*p*

It has been noted that the presence of catalytic amounts of boron trifluoride etherate, which accelerates ionic hydrogenation [7], is necessary only in the case of 3-methyl-substituted oxopropylpyrazolones VII-IX; the ionic hydrogenation of XI-XIII, where R = C_6H_5, may also take place without the addition of a catalyst. Chromatography of XIV-XIX makes it possible to propose the formation in each case of two isomers with close R_f values, the separation of which will be the subject of future research. It should be noted that 6-ethoxydihydropyrano[3,2-d]pyrazoles, which are unstable cyclic acetals, were obtained in the reaction of 1,3-diphenyl-4-arylidene-5-pyrazolones with ethoxyethylene [8]. The dihydropyrano[3,2-d]pyrazoles that we obtained constitute a new series of stable compounds that are similar to uncondensed dihydropyrans.

The IR spectra of XIV-XIX do not contain the absorption of carbonyl and hydroxy groups, but absorption bands appear at 1000-1150 cm^{-1}. The characteristic bands at 2960, 2930, and 2860 cm^{-1} in the IR spectra of XVII and XVIII indicate the presence of a CH_2 group, and this excludes the presence of a double bond in the 4,5 and 5,6 positions of dihydropyrano-[3,2-d]pyrazoles XIV-XIX. Signals of vinyl protons are absent in the PMR spectra of XIV and XVII (in CF_3COOH), but two doubled doublets due to coupling of the protons in the 4 and 6 positions with the methylene group of the dihydropyran ring are observed. Thus the PMR spectrum of XIV contains a multiplet of a methylene group (2.12 ppm), doubled doublets of 4-H and 6-H protons at 4.02 and 5.40 ppm, respectively, a singlet of three protons of a methyl group (1.64 ppm), and a multiplet of aromatic protons at 7.24-7.42 ppm.

The formation of dihydropyranopyrazoles XIV-XIX can be represented, in our opinion, by the scheme



It is apparent from the probable scheme of the ionic hydrogenation of propanonylpyrazolones that the product of protonation is stable conjugated (with the phenyl group) tertiary carbonium ion A, the reactivity and stability of which are sufficient for it to irreversibly split out a labile hydride hydrogen from triethylsilane with the formation of the final dihydropyrano[3,2-d]pyrazole product.

Thus we have shown that 3-substituted 5-pyrazolones are capable of reacting with chalcones under mild conditions. For the first time we carried out the heterocyclization of the resulting 1,5-dicarbonyl compounds with one amide carbonyl group to give dihydropyrano[3,2-d]pyrazoles by the action of triethylsilane and trifluoroacetic acid, and we obtained a new series of stable dihydropyrano[3,2-d]pyrazoles.

EXPERIMENTAL

The IR spectra of Vaseline oil and hexachlorobutadiene suspensions of the compounds were recorded with a UR-20 spectrometer. The PMR spectra were recorded with a Varian T-60 spectrometer with tetramethylsilane as the external standard. The purity of the products and the course of the reaction were monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates in an ethyl acetate—hexane system (12:27) with development in iodine vapors.

3-Methyl-1-phenyl-4-(1-R-3-phenyl-3-oxopropyl)-2-pyrazolin-5-ones (VII-X) (Table 1). A mixture of 46 mmole of pyrazolone I and 47 mmole of the corresponding chalcone (III-VI) was sprinkled with stirring into a solution of sodium ethoxide (0.5 g of Na in 20 ml of absolute ethanol), and the mixture was heated at 35-40°C for 1 h (for 5 h in the case of chalcone IV). It was then allowed to stand at room temperature for 16 h, after which it was poured into water. The aqueous mixture was neutralized with dilute hydrochloric acid, and the precipitated crystals were washed with water, dried, and crystallized.

1,6-Diphenyl-3-R-4-R'-5,6-dihydropyrano[3,2-d]pyrazoles (XIV-XIX) (Table 2). A 2.4-mmole sample of triethylsilane and 3 ml of a 3% solution of boron trifluoride etherate in absolute CF_3COOH were added to 2 mmole of the propanonylpyrazolone (VII-IX, XI-XIII), and the mixture was maintained at room temperature (VII was heated at 60°C for 1 h) until the starting propanonylpyrazolone vanished (according to monitoring by TLC). The volatile substances were evaporated, the residue was treated with ethanol, and the precipitated substance was crystallized. PMR spectrum of XVII (CF_3COOH): 2.09 (2H, m, CH_2), 4.20 (1H, dd, 4-H), 5.33 (1H, dd, 6-H), and 6.73-7.24 ppm (20H, m, aromatic protons).

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