investigated compounds were reckoned relative to a saturated calomel electrode with respect to a "standard" (potassium) scale [8]. The polarograms were recorded with a Radiometer PO-4 polarograph.

The DMF was dried with fused KOH and vacuum distilled.

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SYNTHESIS OF HYDROGENATED HETEROCYCLIC COMPOUNDS BY THE ADDITION OF NUCLEOPHILIC REAGENTS TO SEMICYCLIC α-METHENYL 1,5-DIKETONES*

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UDC 547.814'832.5

The addition of primary and secondary amines and hydrogen cyanide to semicyclic α-methenyl 1,5-diketones of the 1,3-diphenyl-1-(2-oxocyclohexyl)-2-methenyl-3-propanone type leads, respectively, to compounds with hydrogenated quinoline, γ-flavenone, and chroman structures.

The study of reactions with nucleophilic reagents [3] was begun for semicyclic α-methenyl 1,5-diketones in [1, 2]. We present here the results of our studies of the addition of primary amines to semicyclic α-methenyl 1,5-diketones Ia-c and IV and of secondary amines and HCN to diketone Ia.

The reaction with primary amines leads to the hydrochlorides of IIa-d and V, and the reaction with ethanolamine leads to perhydrooxazolinoquinolines IIIa, b. The latter could be formed from both N,O-hemiacetals of the A form (R' = CH_2CH_2OH) by splitting out of a molecule of water through the hemiacetal and alcohol hydroxyl groups and from enamines II (R' = CH_2CH_2OH) by intramolecular addition of alcohol to the double bond of the enamine.

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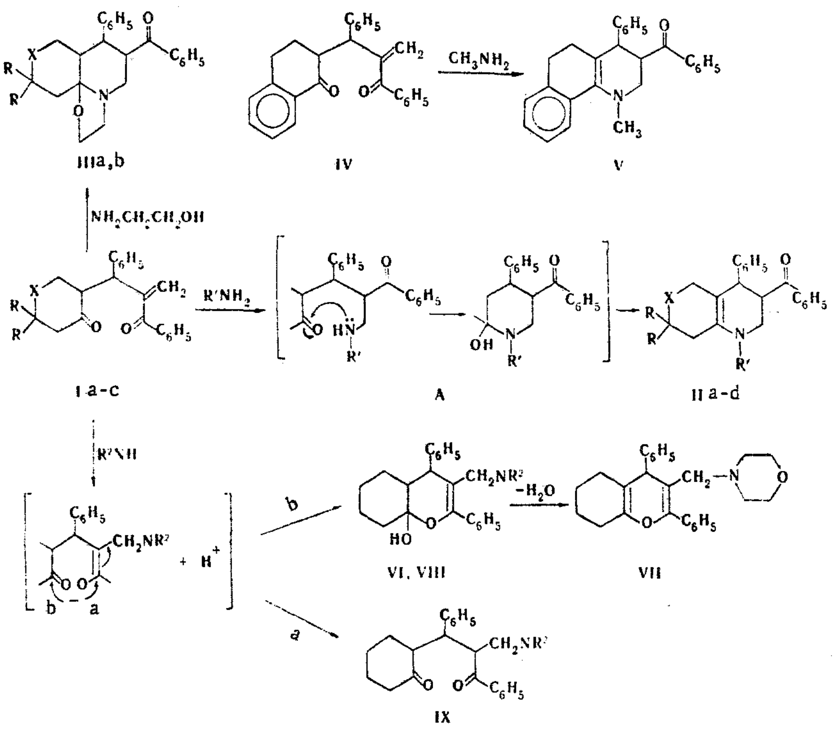
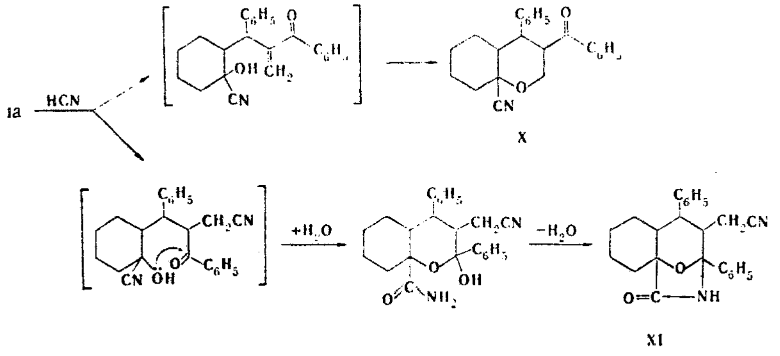


I-III a R = H, X = CH$_2$, R' = CH$_3$; b R = CH$_3$, X = O, R' = CH$_3$; I, II c R = CH$_3$, X = S, R' = CH$_3$; d R = H, X = CH$_2$, R' = CH$_2$C$_6$H$_5$; VI NR^2 = N O; VIII, IX R = CH$_3$

In the reaction with secondary amines the initial product is apparently an enolate ion, which is subsequently stabilized via pathway a or b or simultaneously in both directions. We note that the same products VI-IX could have been formed as a result of competition between 1,2- and 1,4-addition to diketone Ia. The addition of morpholine proceeds only via pathway b (to give flavene VI in quantitative yield). With dimethylamine we obtained flavene VIII and the known [2] amino diketone IX in equal yields (~ 30%).

The addition of hydrogen cyanide to Ia gives, in equal yields, compounds to which we assigned structures X and XI.

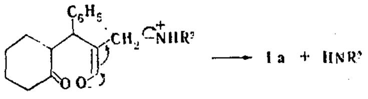


The structures of IIa-d, IIIa, b, and V follow from a comparison of their IR spectra with the IR spectra of methenyl diketones Ia-c and IV. As a result of the addition of RNH$_2$, the ring C = O and > C = CH$_2$ bands vanish, as do the corresponding absorption bands at 1715 and 1635 cm^{-1}, and the carbonyl chain freed from the effect of > C = CH$_2$ appears as absorption at 1690 cm^{-1}; enamine absorption also appears at 1660 cm^{-1}. In addition to the above evidence, the IIIa, b structures are confirmed by the absence in the IR spectra of absorption bands corresponding to the hydroxyl group and the enamine double bond.

The IR spectra of VI and VIII do not contain carbonyl absorption and absorption of a > C = CH$_2$ group.

The spectrum of VI contains bands at 1660 (medium intensity), 2820 and 3420 (broad), and 3610 cm^{-1}, which correspond, respectively, to the absorption of a double bond, conjugated with a ring oxygen atom, a CH$_2$–N bond, and free and associated hydroxyl groups. Its PMR spectrum contains, in addition to the other signals, a doublet at 3.35 ppm corresponding to a benzylidene proton in the 4 position; signals of vinyl protons are absent. In the PMR spectrum of VII, obtained as a result of dehydration of VI, the signal of the same proton appears in the form of a singlet at 3.9 ppm; two bands of medium intensity at ~ 1670 and 1710 cm^{-1}, which are characteristic for thepyran ring [4], appear in the IR spectrum, and absorption at 2820 cm^{-1} (CH_2-N) is retained. The IR spectrum of the hydrochloride of VIII (see the experimental section) also corresponds to the proposed structure.

The hemiacetal character of VI and VIII is manifested in terms of their facile ketonization. Thus when VI • HCl is dissolved in hot water, starting methenyl diketone Ia begins to precipitate immediately. When an aqueous solution of VIII • HCl is made alkaline, methenyl diketone precipitates instead of free base VIII; other attempts to obtain free base VIII from its hydrochloride gave similar results. The VI (VIII) → Ia conversion can be conceived of as the reverse process: the hemiacetal is cleaved to the enolate ion and a proton, the latter quaternizes the amine group, and the resulting dipolar ion rapidly decomposes via the scheme



The hemiacetal → IX → Ia conversion is excluded, since amino diketone IX and its hydrochloride are completely stable in aqueous media.

The difference in the course of the reactions in the addition of RNH_2 and R_2NH to a methenyl diketone of the Ia type is explained by the fact that in the first case, as a result of the addition, one observes the formation of a secondary amino group, which in the case of attack on the ring C = O group may lead to a valence-saturated (stabilized) N,O-hemiacetal of the A form. In the second case, as a result of the addition, one observed the formation of a tertiary amino group, which in the case of similar attack cannot lead to a stabliized N,O-hemiacetal, and control of the reaction remains with the enol hydroxyl group; this leads to a valence-compensated hemiacetal of the VI and VIII form.

The carbonyl absorption in the IR spectrum of X is expressed only by the band at 1690 cm^{-1} (C_6H_5CO); this is in complete agreement with the proposed scheme for its formation. Absorption of a $C \equiv N$ group is absent, but its presence is confirmed by a Feigl test [5]; the absence of its absorption is apparently due to the close influence of the oxygen atom attached to the same carbon atom [6]. The absorption at 1715 cm^{-1} in the IR spectrum of XI should be ascribed to the carbonyl group of the lactam, the weak absorption at 2260 cm^{-1} should be ascribed to the $C \equiv N$ group, and the narrow and weak bands at 3300, 3410, and 3530 cm^{-1} should be ascribed to free and associated lactam NH groups. The formation of a similar lactam has been previously observed [7] in the hydrocyanation under the same conditions of a methylenedicyclohexanone by the action of acetone cyanohydrin.

EXPERIMENTAL

The IR spectra of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of $CHCl_3$ solutions of the compounds were recorded with a ZKR-60 spectrometer. Methenyl diketones Ia-c and IV [1-3] were prepared by method B in [2]. The perchlorates were obtained by mixing a solution of the base in dilute acetic acid with a saturated solution of ammonium perchlorate. The identity of the compounds was confirmed by mixed-melting-point determinations and comparison of the IR spectra. The R_f values were determined in a thin layer of activity II Al_2O_3.

Addition of Primary Amines to Methenyl Diketones Ia-c and IV. Methylamine (in the form of the hydrochloride and a 30% aqueous solution of the free base), benzylamine (the hydrochloride and the free base), and ethanolamine were added. A solution of 0.02 mole of the methenyl diketone and 0.04 mole of the amine in DMF was allowed to stand overnight (in the case of the salt another 1.8 g of KOH in 3 ml of water was added to the solution to liberate the amine from the salt), after which the solution was diluted with water. The hydroquinoline precipitated in crystalline form (IIb, c and V) or in the form of an oil (IIa, d and IIIa, b); the oil was extracted with ether, and the extract was washed with water and dried. The ether was removed by distillation, and the residual viscous oil was treated with cold alcohol to give the hydroquinoline in crystalline form.

Addition of Dimethylamine and Morpholine to Methenyl Diketone Ia. The addition was carried out as in the preceding case (dimethylamine was used in the form of a 30% solution); in the case of morpholine, Ia was also dissolved in an excess amount of the base. After dilution of the solution with water, flavene VI precipitated in pure form and was separated by filtration (the yield was quantitative). Flavene VIII precipitated in the form of a mixture with starting methenyl diketone Ia. For its separation, the mixture was dissolved in dry

TABLE 1. Compounds Obtained

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
IIa	135—136[a]	83,3	7,9	4,8	$C_{23}H_{25}NO$	83,3	7,5	4,2	49
IIb	165—168[a]	79,5	7,5	4,1	$C_{24}H_{27}NO_2$	79,7	7,5	3,8	82
IIc	168—170[b]	76,7	7,4	3,5	$C_{24}H_{27}NOS$	76,4	7,1	3,7	77
IId	140—141[c]	85,3	7,5	3,5	$C_{29}H_{29}NO$	85,5	7,1	3,4	39
IIIa	131—132[c]	79,7	7,6	4,0	$C_{24}H_{27}NO_2$	79,7	7,5	3,8	43
IIIb	134—136[b]	76,4	7,3	3,9	$C_{25}H_{29}NO_3$	76,7	7,4	3,6	56
V	157—159[b]	85,4	6,6	4,2	$C_{27}H_{25}NO$	85,5	6,6	3,7	94
VI	133—134[a]	77,1	7,8	3,6	$C_{26}H_{31}NO_3$	77,0	7,7	3,5	100
VII	127—129[c]	80,5	7,3	3,9	$C_{26}H_{29}NO_2$	80,6	7,5	3,6	100
VIII	171—175 (dec.)[d]	72,2	7,7	3,7	$C_{24}H_{29}NO_2 \cdot HCl$[e]	72,1	7,5	3,5	30
X	163—164[c]	80,5	6,9	4,5	$C_{23}H_{23}NO_2$	80,0	6,7	4,1	29
XI	208—209[f]	77,4	6,5	7,8	$C_{24}H_{24}N_2O_2$	77,4	6,4	7,5	29
Perchlorate of IIa	156—158[c]	68,0	5,9	3,1	$C_{23}H_{25}NO \cdot HClO_4$	67,6	5,4	2,9	—
Perchlorate of IIb	195—196[g]	62,3	6,2	3,6	$C_{24}H_{27}NO_2 \cdot HClO_4$	62,4	6,1	3,2	—
Perchlorate of IIc	213—214[c]	60,6	6,0	3,1	$C_{24}H_{27}NO \cdot HClO_4$	60,3	5,7	2,9	—
Perchlorate of IId	173—174[c]	69,4	6,1	3,0	$C_{29}H_{29}NO \cdot HClO_4$	69,9	6,0	3,2	—
Picrate of IIb	160—162[c]	—	—	9,2	$C_{24}H_{27}NO_2 \cdot C_6H_3N_3O_7$	—	—	9,4	—
Picrate of IIIa	186—187[c]	—	—	9,5	$C_{24}H_{27}NO_2 \cdot C_6H_3N_3O_7$	—	—	9,4	—
Picrate of V	149—150[c]	—	—	7,5	$C_{27}H_{25}NO \cdot C_6H_3N_3O_7$	—	—	7.6	—
Hydrochloride of VI	144—146[d]	—	—	—	$C_{26}H_{31}NO_3 \cdot HCl$[h]	—	—	—	—
Hydrochloride of VII	145—146[c]	—	—	—	$C_{26}H_{29}NO_2 \cdot HCl$[i]	—	—	—	—

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[a] From hexane. [b] From methanol. [c] From alcohol. [d] From dioxane. [e] Found: Cl 9.0%. Calculated: Cl 8.9%. [f] From acetone. [g] From propanol. [h] Found: Cl 8.2%. Calculated: Cl 8.0%. [i] Found: Cl 8.5%. Calculated: Cl 8.4%.

ether, and the solution was treated with dry HCl. The precipitated mixture of hydrochlorides of aminoflavene VIII and amino diketone IX was separated by treatment with boiling dioxane (the hydrochloride of base IX was only slightly soluble in dioxane); removal of the ether by distillation gave starting Ia (30%). Methenyl diketone Ia was liberated instead of the free base when an aqueous solution of VIII • HCl was made alkaline.

1-Methyl-3-benzoyl-4-phenyl-1,2,3,4,5,6,7,8-octahydroquinoline (IIa). This compound was obtained in the form of colorless crystals. IR spectrum (in benzene): 1690 (C = O) and 1660 cm^{-1} (C = C). The hydrochloride was obtained in the form of a white precipitate when dry HCl was bubbled into a solution of IIa in absolute ether. We were unable to purify it by crystallization. It was very hygroscopic, quite soluble in water, and began to melt at 117°C. Found: Cl 9.5%. $C_{23}H_{25}NO \cdot HCl$. Calculated: Cl 9.5%.

3-Morpholinomethyl-4-phenyl-5,6,7,8-tetrahydro-γ-flavene (VII). A solution of 2 g of hydroxyflavene VI in 50 ml of dry benzene was saturated with dry HCl, and the mixture was allowed to stand overnight. The benzene was removed by distillation to give 2.05 g (100%) of the chromatographically homogeneous hydrochloride of flavene VII. Free base VII was isolated by alkalization of an alcohol solution of the salt.

Decomposition of the Salts of Flavenes VI and VIII. VI • HCl: A 2-g sample of the salt was dissolved in 100 ml of hot water, and methenyl diketone Ia began to precipitate immediately. Workup gave 1.45 g (100%) of Ia with mp 122-123°C (from methanol) [2]. VIII • HCl: A 0.3-g sample of the salt was dissolved in 20 ml of water, and the mixture was filtered after 1 h to give 0.25 g (96%) of methenyl diketone Ia with mp 122-123°C. A 0.3-g sample of the salt was dissolved in 20 ml of water, and the solution was made alkaline with sodium hydroxide solution. The precipitate of methenyl diketone Ia that formed immediately was removed by filtration to give 0.26 g (100%) of a product with mp 122-123°C.

3-Benzoyl-4-phenyl-9-cyanoperhydrochroman (X). A 3-ml sample of acetone cyanohydrin, 5 ml of water, and 0.1 g of the salt were added to a solution of 5 g (0.015 mole) of methenyl diketone Ia in 200 ml of alcohol, and the mixture was refluxed in a flask for 10 h. It was then cooled and worked up to give 3.9 g of crystals. Two recrystallizations from alcohol gave 1.6 g (29.6%) of X with Rf 0.8 [benzene—chloroform (1 : 2)].

2-Amino-3-cyanomethyl-4-phenylperhydroflavan-9-carboxylic Acid Lactam (XI). All three of the mother liquors from the separation of X were mixed, the alcohol was removed by distillation, and the residue was dissolved in 20 ml of hot acetone. Cooling of the solution liberated 1.7 g (29%) of crystals of lactam XI with Rf 0.66 [benzene—chloroform (1 : 2)].

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HYDROBENZ[c]ACRIDINES AND THEIR ANALOGS BASED ON 1,5-DIKETONES*

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The reaction of 1,5-diketones containing an α-tetralone fragment with ammonia and primary amines gave hydrogenated benz[c]acridine and benzo[h]cyclopenta[b]quinoline derivatives, for which hydrocyanation, oxidation, and disproportionation reactions were studied.

Little study has been devoted to hydrogenated benz[c]acridines; biological activity has been noted for some of them [2]. Octa hydrobenz[c]acridines and derivatives with a higher degree of hydrogenation have not been described.

We have synthesized a number of derivatives of hydrobenz[c]acridines and their analogs by reaction of the accessible 1,5-diketones Ia-d and II [1] with ammonia and primary amines.

Pyridinization to give derivatives of 5,6,8,9,10,11-hexahydrobenz[c]acridine (IIIc, d) and 5,6,9,10-tetrahydro-8H-benzo[h]cyclopenta[b]quinoline (IIIa, b) occurs in the reaction of diketones Ia-d with ammonium acetate in acetic acid. Their IR spectra do not contain absorption bands in the multiple bond region.

The reaction of diketones Ia-d and II with primary aromatic amines (aniline, α-naphthylamine, and p-aminobenzoic acid) takes place more readily, since steric hindrance is absent. The IR spectra of the resulting 5,6,7,8,9,10,11,12-octahydrobenz[c]acridine derivatives (IVc-g), their oxa analog (IVh), and 5,6,7,9,10,11-hexahydro-8H-benzo[h]cyclopenta[b]quinoline derivatives (IVa, b) contain two characteristic bands at 1630-1650 ($C=C$ conjugated with a benzene ring) and 1680-1695 cm^{-1} (unconjugated $C=C$). The $C=O$ group in the spectra of IVe, g also absorbs at 1680 cm^{-1}.

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