SYNTHESIS OF HETEROCYCLES FROM 1,5-DIKETONES.

3.* ALICYCLIC 1,5-DIKETONES IN REACTION WITH PHENYLHYDRAZINE

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8-R-7aH-5,6,7,8,9,10,11,12-Octahydroindolo[3.2.1-d,e]acridines, 1,2,3,4-tetrahydrocarbazole, 9-R-sym-octahydroacridines, and 9-R,10-phenyl-sym-octahydroacridinium salts are formed by the action of phenyl-hydrazine on alkylidene-2,2'-dicyclohexanone or the corresponding 8-R-tricyclo(7.3.1.$0^{2,7}$)tridecan-2-ol-13-ones in an acid medium. Postulations were made for the paths of formation of these compounds.

2,2-Dimethyl-3-oxa-4a-(2',2'-dimethyltetrahydropyran-4'-on-5'yl-methyl)-4aH-1,2,3,4-tetrahydrocarbazole, 3,3,14,14-tetramethyl-2-oxa-5a,10b-(methanoxyisobutane)-1,2,3,4,5a,10b,11,11a-octahydroquinindoline,2,2-dimethyl-3-oxa-1,2,3,4-tetrahydrocarbazole and 3,3,6,6-tetramethyl-2,7-dioxa-sym-octahydroacridine were obtained by the reaction of methylene-3,3'-di(6,6-dimethyltetrahydropyran-4-one) with phenylhydrazine in acetic acid. The quinindoline structure was confirmed by the synthesis of this compound from 2,2-dimethyl-3-oxa-4a-(2',2'-dimethyltetrahydropyran-4'-on-5'-ylmethyl)-4aH-1,2,3,4-tetrahydrocarbazole by the action of ammonia.

In a continuation [1, 2] of the study of the reaction of 1,5-diketones with phenylhydrazone, we studied the transformations taking place during the reaction of methylene-2-2'dicyclohexanone (I) with phenylhydrazine in the presence of acids. As the result, the previously unknown heterocyclic compound, indoloacridine (Va), whose A, B, C, D rings are analogous to the corresponding structural fragment of strychnine, and also the already known tetrahydrocarbazole (VI), acridine (VIIIa) [3] and acridinium salt (IXa) [4] were isolated from the reaction mixture. The paths of the reaction of diketone I with phenylhydrazine are represented by the scheme given below (following page).

The data obtained show that diketone I reacts with an equimolar amount of phenylhydrazine in acid medium with no clear-cut results - together with the indolization processes (paths A, B) leading to indoloacridine Va and tetrahydrocarbazole VI, pyridination process (path C) also takes place, as the result of which compounds VIIIa and IXa are formed.

Indoloacridine Va is formed as the result of the indolization of monohydrazone II with the participation of the α-CH_2 group of the hydrazone fragment, followed by dehydration of compound III. The appearance of tetrahydrocarbazole VI in the reaction mixture can be explained as occurring by splitting of a substituent from the position 4a of the intermediate carbazolenine IV. A similar splitting was observed [5, 6] during the indolization of 2-R-substituted derivatives of cyclohexanone.

The formation of acridine VIII is explainable by the possible splitting of aniline from the intermediate decahydroacridine VII. These data conform with previous reports on the reaction of I with phenylhydrazine in the presence of CH_3COOH and KBH_4 [7]. The acridinium salt IXa can be considered to be a product of the reaction of I with aniline, similarly to that described in [4].

*For article 2, see [1].

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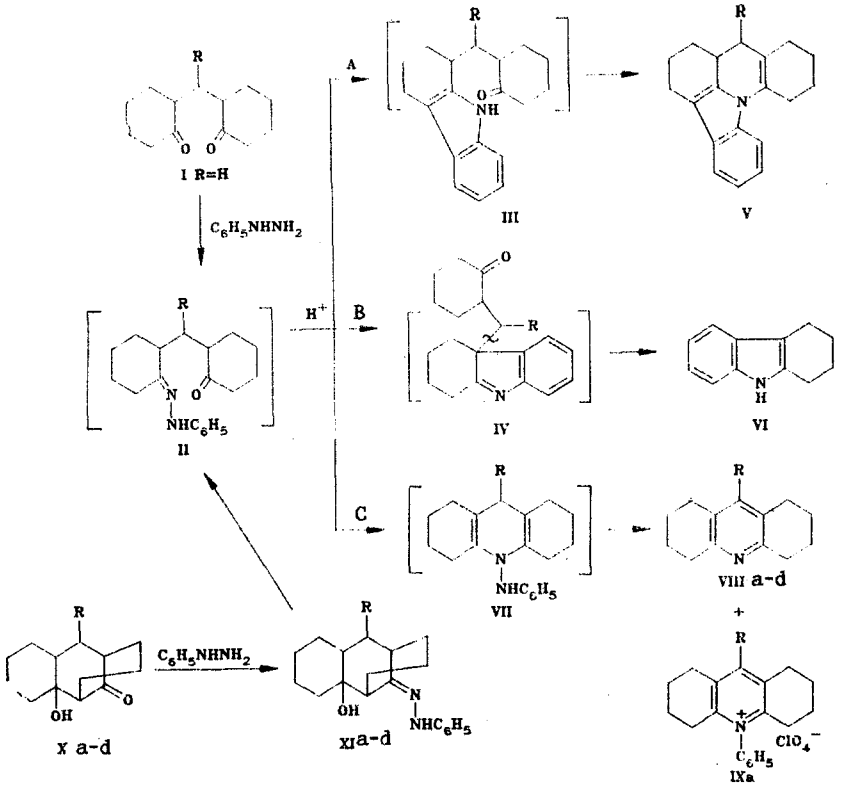


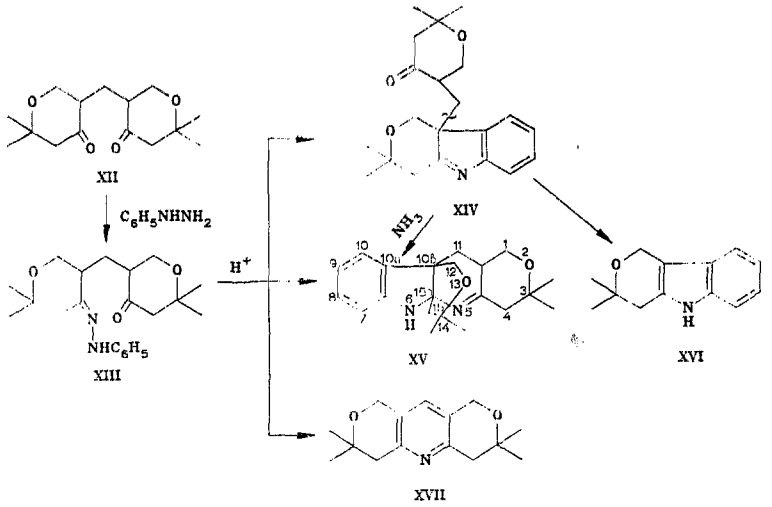
V, X a R=H; b R=CH_3; c R=C_6H_5; d R=*p*-CH_3O—C_6H_4

The structure of indoloacridine Va particularly follows from the analysis of its spectral characteristics. Thus, in the mass spectrum, a peak of the molecular ion is observed at m/z 263. In the IR spectrum, there is no absorption of the C=O and NH groups and absorption bands are observed at 1660 cm^{-1} (C=C), while in the UV spectrum there is a long-wave maximum at 312 nm, indicating a conjugation of the tetrahydrocarbazole ring with the C=C bond (in the UV spectrum of tetrahydrocarbazole, a long-wave maximum is observed at 282 nm [5]).

The structure of other reaction products (VI, VIIIa, IXa) was confirmed by comparison with the corresponding standard samples (comparison of constants, spectra, mixed melting point) [3-5].

It should be noted that the preparation of indoloacridine (Va) and its 8-R-substituted derivatives (obtained from other alicyclic 1,5-diketones) proceeds in low yield and is impeded by the necessity for the chromatographic separation of the mixture of compounds obtained. Another variant of the synthesis of indoloacridines that we have developed is to some extent free of these drawbacks. It involves the use of tricyclohexanolones Xa-d as the starting materials, which are the products of an intramolecular adolization of the corresponding 1,5-diketones [8-10]. During the reaction of compounds Xa-d with phenylhydrazine, we obtained phenylhydrazones XIa-d in good yields. Heating of these compounds in concentrated acetic acid led to the formation of indoloacridines Va-d, after which compounds Vb-d were isolated by crystallization (Table 1).

3,3'-Methylenedi(6,6-dimethyltetrahydropyran-4-one) (XII) [11] considerably differed in its behavior in the reaction with phenylhydrazine in acetic acid from other alicyclic 1,5-diketones. When the corresponding monophenylhydrazone XIII was treated with glacial acetic acid at room temperature, we also obtained new heterocyclic compounds: 2,2-dimethyl-3-oxa-4-*a*-(2',2'-dimethylpyran-4'-on-5'-ylmethyl)-4*a*H-1,2,3,4-tetrahydrocarbazole (XIV), 3,3,14,14-tetramethyl-2-oxa-5*a*,10b-(methanoxyisobutane)-1,2,3,4,5*a*,10,11,11*a*-octahydroquinindoline (XV), and 2,2,-dimethyl-3-oxa-1,2,3,4-tetrahydrocarbazole (XVI), as well as the known 3,3,6,6-tetramethyl-2,7-dioxa-sym-octahydroacridine (XVII) [11].



The formation of compound XIV is explainable by the occurrence of indolization of monophenylhydrazone XIII with the participation of a -CH group α with respect to the hydrazone fragment. The absence in the reaction mixture of indolization products with the participation of the α-CH_2 group clearly results from its being screened.

Compounds XV and XVI can be regarded as products of further transformations of carbazolenine XIV under the reaction conditions. 3-Oxatetrahydrocarbazole (XVI) was probably formed by splitting a substituent from the 4*a*-position of compound XIV, while quinindoline XV by the addition of NH_3 to the C=N bond, followed by the closing of the six-membered ring during the reaction of the carbonyl group and the NH_2 group. It is known that indolenines are capable of adding ammonia, amines, and phenylhydrazine at the C=N bond [12]. According to the Fischer reaction mechanism, ammonia is liberated during the indolization of hydrazone XIII.

We obtained confirmation for the formation of compound XV by this path by carrying out the reaction XIV with ammonia in ethanol at room temperature. As the result, quinindoline XI was obtained in a yield of 50%.

The structure of compound XIV is confirmed by the IR spectrum, with an absorption band of the C=O group at 1713 cm^{-1}. In the mass spectrum of this compound, a peak of a molecular ion (m/z 341) and characteristic peaks of fragmentary ions with m/z 201 and 143 are present. The latter indicate a splitting of a γ-pyranonylmethyl fragment from the molecular ion, and a molecule of acetone from the ion with m/z 201. In the PMR spectrum, signals of three isolated methylene groups (AB system) and the CH_2—CH—CH_2 fragment were revealed by the spin-decoupling and differential spectroscopy methods, as well as the signals of four aromatic protons and four methyl groups. The $C_{(4)}$ methylene group protons appear as doublets at 4.0 and 3.11 ppm (J = 11.5 Hz). Irradiation of the signal at 4.0 ppm leads to degeneration of the signal at 3.11 into a singlet. Similar experiments were carried out for signals of the methylene group protons at $C_{(1)}$ (doublets at 3.01 and 2.69 ppm, J = 13.0 Hz) and at $C_{(3)}$ (doublets at 2.28 and 2.10 ppm, J = 13.5 Hz). The CH_2—CH—CH_2 fragment is revealed as a four-proton multiplet at 3.25 ppm and one-proton multiplet at 1.55 ppm.

In the IR spectrum of quinindoline XV, there are absorption bands of NH and C=N groups at 3370 and 1660 cm^{-1}. In the mass spectrum, a peak of the molecular ion is observed with m/z 340.

In the ^{13}C NMR spectrum, in the absorption region of the aromatic carbon atoms (110-128 ppm), there are four signals giving doublets under the off-resonance conditions. This indicates the presence of a disubstituted phenyl ring in compound XV. Two other signals of this ring are displayed as signlets at 130.0 and 164.4 ppm. The shift of one of these signals into a weak field shows that the carbon atom is bound to the hetero atom. The signal at 148.7 ppm (s) confirms the presence of the C=N fragment in the quinindoline structure. The three singlet signals (72.7, 74.8, 80.5 ppm) indicate the presence of a further three quaternary carbon atoms ($C_{(3)}$, $C_{(14)}$, $C_{(15a)}$), having a hetero atom as one of the substituents. The signal at 42.2 ppm is characteristic of a quaternary alkyl-substituted carbon atom ($C_{(10b)}$). In the spectrum, signals of carbon atoms belonging to four methyl groups

TABLE 1. Characteristics of Phenylhydrazones of 8-R-Tricyclo(7.3.1.$0^{2,7}$)tridecan-2-ol-13-ones (XIa-d) and 8-R-7*a*H-5,6,7,8,9,10,11,12-Octahydroindolo[3.2.1-d, d,e]acridines (Va d)

Compound*	Mp, °C	IR spectrum, cm^{-1}	UV spectrum λ_{max} (log ε)	Found				Empirical formula	Calculated				Yield, %
				C, %	H, %	N, %	*M*		C, %	H, %	N, %	*M*	
Hydrochloride XIa	132—133	1650 (C=N), 3000, 3342 (NH, OH) ‡ several peaks	—	67,85	7,98	8,17	—	$C_{19}H_{26}N_2O \cdot HCl$	68,10	7,77	8,37		63
Hydrochloride XIb	153—154	1655 (C=N), 3000—3400 (NH, OH) ‡ several peaks	—	68,60	8,30	7,83	—	$C_{20}H_{28}N_2O \cdot HCl$	68,86	8,33	8,03		70
XI c	158—159	1602 (C=N), 3330 (NH), 3600 (OH)	—	80,0	8,40	7,90	374	$C_{25}H_{30}N_2O$	80,20	8,0	7,40	374	78
XI d	159—160	1602 (C=N), 3440 (NH), 3580 (OH)	—	77,11	7,92	6,73	404	$C_{27}H_{32}N_2O_2$	77,20	7,70	6,90	404	41
V a	—	1660 (C=C)	312 (4,24)	87,30	7,79	5,40	263	$C_{19}H_{21}N$	87,60	7,98	5,32	263	7 (15)
V b	99—100	1660 (C=C)	314 (3,90)	86,92	8,90	5,15	277	$C_{20}H_{23}N$	86,60	8,30	5,10	277	15
V c	160—161	1650 (C=C)	318 (4,40)	88,06	7,62	4,10	339	$C_{25}H_{25}N$	88,5	7,38	4,12	333	40
V d	195—196	1655 (C=C)	318 (4,40)	84,78	7,75	3,75	369	$C_{26}H_{27}NO$	84,55	7,30	3,80	369	25

*V, XIa, R = H; b R = CH_3; c R = C_6H_5; d R = p-CH_3O-C_6H_4.

†The compounds were crystallized: XIa from a 1:3 ethanol—ethyl acetate mixture, XIb from a 1:4 ethanol—ethyl acetate mixture, XIc, d from methanol, Vb, c from ethanol, Vd from ethyl acetate.

‡The spectra were run in mineral oil.

(22.4, 23.5, 30.5, 32.6 ppm) and five methylene groups (23.5, 42.5, 48.1, 66.4, 69.3 ppm) are also observed.

In the PMR spectrum of compound XV, signals are observed of protons of four methyl groups (1.16, 1.25, 1.29, 1.49 ppm), four protons of a disubstituted benzene ring, 6.7-7.1 ppm), and a signal of an NH group proton (which disappears during a deutero exchange) at 4.37 ppm. The presence of three isolated methylene groups (at the 4, 12, 15-positions) was revealed by double resonance. For the corresponding AB systems, the following chemical shifts and SSCC were found: C_4 (2H) A part 2.15, B 2.03 ppm (J = 13.5 Hz); C_{12} (2H) A 2.57, B 3.37 ppm (J = 12.5 Hz); C_{15} (2H) A 1.4, B 2.13 ppm (J = 14.5 Hz). There is also a CH_2—CH—CH_2 fragment. The only nonaromatic methine proton is displayed as a multiplet at 2.38 ppm. It interacts with two methylene groups. One of them at C_{11} (2H) is represented by a doublet of doublets at 1.83 ppm (J = 14; 11 Hz) and a broadened doublet at 2.03 ppm (J = 14 Hz), while the other at C_2 (2H) is in the form of a doublet of doublets at 3.95 ppm (J = 11.3; 7.5 Hz) and a broadened doublet at 3.46 ppm (J = 11.3 Hz).

The structure of 2,2-dimethyl-3-oxa-1,2,3,4-tetrahydrocarbazole (XVI) was confirmed by elemental analysis, mass spectrum [a molecular ion is observed at m/z 201 and a fragmentary ion at m/z 143, due to splitting of $(CH_3)_2CO$] and by IR spectrum (3473 cm^{-1}, the NH group).

EXPERIMENTAL

The course of the reaction and the identification of individual compounds were controlled by the TLC method [Silufol UV-254; petroleum ether—ethyl acetate 5:2 (system 1, the spots on the chromatograms were developed by iodine vapors]. The preparative TLC was carried on plates (20 × 35 cm) with nonstationary Al_2O_3 layer (grade II of activity) in a 10:1 petroleum ether—ethyl acetate mixture (system 2) and in a 5-1 heptane—ethyl acetate mixture (system 3).

The IR spectra were obtained on a Specord IR-75 spectrophotometer (in $CHCl_3$), the NMR spectra (in $CDCl_3$) on spectrometers Bruker WH-250 for ^1H, Bruker HX-90-E for ^{13}C, at 250 and 22.63 MHz, respectively. The chemical shifts are given with reference to TMS. The mass spectra were determined on LKV 9000 mass spectrometer at 70 eV, and the UV spectra on Specord UV-vis in methanol.

The initial 1,5-diketones I, XII and ketones Xa-d were obtained by methods described in [8-11, 13], respectively.

The characteristics of compounds Va-d and XIa-d are listed in Table 1.

Reaction of Methylene-2,2'-Dicyclohexanone (I) with Phenylhydrazine. A. A 5.18 g (48 mmole) portion of phenylhydrazine is added to a solution of 10 g (48 mmoles) of diketone I in 100 ml of glacial acetic acid. The mixture heats up to 60°C, and is left to stand for 24 h at room temperature. It is then diluted by 150 ml of water, and the oil that separates is extracted by ether (3 × 30 ml). The extract is washed with water (2 × 30 ml) and a NA_2CO_3 solution to a neutral reaction. The aqueous layer and the wash waters are combined. The ether extract is dried over $MgSO_4$, and evaporated to yield 3.2 g of reaction products. The mixture is separated by preparative TLC in system 3. From the zone with Rf 0.74, 0.88 g (7%) of 7*a*H-5,6,7,8,9,10,11,12-octahydroindolo[3,2,1-d,3]acridine (Va), bp 167-170°C (1 mm), n_D^{20} 1.6319, is obtained.

From the zone with R_f 0.40, 0.58 g (7%) of tetrahydrocarbazole (VI), mp 114-116°C is isolated; according to the data in [5], mp 115-116°C.

The aqueous solution is made alkaline with potassium carbonate to pH 9. The oil that separated is extracted by ether (3 × 25 ml). The extract is dried over $MgSO_4$, the solvent is distilled off to yield 6.5 g of a mixture of products, which are separated by distillation in vacuo. Two fractions are collected: the first, aniline, 1.1 g, bp 48-50°C (10 mm), n_D^{20} 1.5863; the second, sym-octahydroacridine, 4.1 g, 46%, bp 151-153°C (5 mm), mp 72-73°C (petroleum ether), according to the data in [3], mp 74°C.

B. A mixture of 6.2 g (30 mmoles) of diketone I and 4.3 g (30 mmoles) of phenylhydrazine hydrochloride in 25 ml of dry dioxane is boiled for 6 h. When cool, the NH_4Cl precipitate is filtered. Dioxane is evaporated, and the residue is dissolved in ether. The ether solution is washed with a dilute hydrochloric acid, 1:3 (2 × 20 ml), and water to neutral reaction. The aqueous layer is combined with wash waters (aqueous solution 1). The ether extract is dried over $MgSO_4$ and ether is distilled to yield 2.3 g of a mixture of compounds in the form of a partially crystallized mass. A 20 ml portion of petroleum is added, and

crystals of compound VI are filtered, mp 115-116°C. From the filtrate, 0.3 g (3%) of indoloacridine Va and in addition, 0.2 g (3%) of tetrahydrocarbazole VI are obtained by preparative TLC.

The aqueous solution of I is made alkaline with sodium carbonate to pH 9. The oil that is obtained is extracted by ether and separated from the equeous layer (aqueous solution 2). The extract is evaporated to yield 3.5 g of a mixture of products, from which 2.2 g (40%) of acridine VIIIa and 0.5 g of aniline are obtained, as described under A. Ammonium perchlorate is added to aqueous solution 2, and the precipitate of N-phenyloctahydroacridinium perchlorate IXa is filtered. Yield 1.1 g (10%), mp 198-199°C (from ethanol); according to the data in [4], mp 199-200°C.

C. A 2 g portion of polyphosphoric acid is added to 2.08 g (10 mmoles) of 2.08 g (10 mmoles) of diketone I in 10 ml of absolute dioxane. A solution of 1.08 g (10 mmoles) of phenylhydrazine in 6 ml of dioxane is added, with stirring, to this mixture, which is then stirred at room temperature for 6 h. Dioxane is evaporated, 50 ml of water are added to the residue, and the oil is extracted by ether. From the extract, indoloacridine Va (0.13 g, 5%) and tetrahydrocarbazole VI (0.2 g, 14%) are isolated, as described under A. From the aqueous solution, compounds VIIIa (0.7 g, 35%) and IXa (0.2g, 5%) were isolated.

Phenylhydrazones of 8-R-Tricyclo(7.3.1.$0^{2,7}$)tridecan-2-ol-13-ones (IXa-d). A 4.3 g (40 mmole) portion of phenylhydrazine is added to 40 mmoles of the corresponding ketone Xa-d in 150 ml of absolute benzene. The reaction mixture is boiled in a flask fitted with a Dean-Stark trap up to the end of separation of water (5 h). Benzene is evaporated, and the residue obtained in the form of a glass-like mass, crystallized under ethanol only in the case of XIc,d. Hydrazones XIa,b could not be crystallized and they were obtained as hydrochlorides.

Transformation of Phenylhydrazones of 8-R-Tricyclo(7.3.1.$0^{2,7}$)tridecan-2-ol-13-ones (XIa-d) by the Action of CH_3COOH and Polyphosphoric Acid. A. A 20 g portion of polyphosphoric acid is added to 6.6 g (20 mmoles) of hydrochloride of phenylhydrazone XIa. The reaction mixture is heated on a boiling water bath for 2 h, then cooled, and poured into 50 ml of H_2O. The oil is extracted by ether (3 × 30 ml), the extract is washed with water to neutral reaction, dried, and evaporated to yield 2.5 g of an oily product. From this product, 0.82 g (15%) of indoloacridine Va and 1.1 g (30%) of tetrahydrocarbazole VI are isolated by preparative TLC. From the aqueous solution, 1 g (27%) of acridine VIIIa and 0.4 g (10%) of acridinium salt IXa are isolated in a similar way as described above.

B. A corresponding phenylhydrazone XIb-d (30 mmoles) is heated in CH_3COOH for 2 h. The hydrazone thus dissolves and a new crystalline precipitate separates. The mixture is cooled, the precipitate is filtered, washed on the filter with CH_3COOH (2 × 5 ml) and alcohol, and dried to yield indoloacridines Vb-d.

The mother liquor from the isolation of compounds Vb-d is neutralized with sodium carbonate to pH 7. The oily products are extracted by ether. After evaporation of ether, the residue is separated by preparative TLC. Additional amounts of indoloacridine Vb-d and tetrahydrocarbazole VI (10-15%) are thus isolated. The aqueous layer is made alkaline with sodium carbonate to pH 9 to give the corresponding acridines: 9-methyl-sym-octahydroacridine (VIIIb 20%, 9-phenyl-sum-octahydroacridine (VIIIc) 22%, and 9-p-methoxyphenyl-sum-octahydroacridine (VIIId) 20%. Acridines VIIIb,c were identified by direct comparison with the corresponding samples [3]. Acridine VIIId has been prepared by us for the first time, mp 230-231°C (from ethanol). IR spectrum: 1580, 1608 cm^{-1} (vibrations of the aromatic ring). Found: C 81.83; H 7.68; N 4.90%. M 293. $C_{20}H_{23}NO$. Calculated: C 81.90; H 7.80; N 4.70%; M 293.

3,3-Methylenedi(6,6-dimethyltetrahydropyran-4-one)monophenylhydrazone (XIII). A 16.1 g (60 mmole) portion of diketone XII is dissolved in 40 ml of ethanol with heating and 6.5 g (60 mmoles) of phenylhydrazine in 30 ml of ethanol are added to this solution in the course of 2 h. The reaction mixture is heated for another hour, and left to stand at room temperature for 18 h. The precipitate is filtered, washed with ethanol (2 × 20 ml), and dried. Yield, 4.3 g (20%) of hydrazone XIII, mp 142-143°C (from ethanol). IR spectrum: 1705 (C=O), 3315 cm^{-1} (NH). Found: C 69.97; H 8.41; N 7.73%; M 358. $C_{21}H_{30}N_2O_3$. Calculated: C 70.39; H 8.39; N 7.82%; M 358.

Transformation of 3,3'-Methylenedi(6,6-Dimethyltetrahydropyran-4-one)monophenylhydrazone (XIII) by the Action of CH_3COOH. A 7.16 g (20 mmole) portion of hydrazone XIII is dissolved

in 50 ml of CH_3COOH. The reaction mixture is left to stand for 24 h, and then is diluted by an equal volume of water, and neutralized by a Na_2CO_3 solution to pH 7. The reaction products that separate are extracted by diethyl ether (4 × 50 ml). The extract is dried over $MgSO_4$, the ether is evaporated, and 30 ml of ethanol are added to the residue weighing 7 g. The precipitate is filtered to yield 1.8 g (26%) of quinindoline XV, mp. 174-176°C. IR spectrum: 1660 (C=N), 3380 cm^{-1} (N–H). Found: C 74.27; H 8.47; N 8.21%; M 340. $C_{21}H_{28}N_2O_2$. Calculated: C 74.11; H 8.23; N 8.23%; M 340. The compounds remaining in the mother liquor after the isolation of quinindoline XV, are separated by column chromatography: 5 g of the mixture separated on a column (42 × 2.5 cm) with 300 g of silica gel 40/100 μ. A gradual elution is used (systems: petroleum ether–ethyl acetate, 6:1.3, 3:1, 1:1, 0:1, 500 ml in each case and fractions of 50 ml are collected. The following compounds are isolated: 3-oxatetrahydrocarbazole (XVI) [0.56 g (14%), mp 150-160°C (petroleum ether). IR spectrum: 3473 cm^{-1} (NH). Found: C 77.32; H 7.26; N 7.01%; M 201. $C_{13}H_{15}NO$. Calculated: C 77.61; H 7.16; N 6.96%; M 201], 2,2-dimethyl-4*a*-(2',2'-dimethyltetrahydropyran-4'-on-5'-ylmethyl)-3-oxa-4*a*H-1,2,3,4-tetrahydrocarbazole (XIV) [0.8 g (12%), mp 161-162°C (ethanol). IR spectrum: 1713 cm^{-1} (C=O). Found: C 73.70; H 8.10; N 4.25%; M 341. $C_{21}H_{27}NO_3$. Calculated: C 73.90; H 7.91; N 4.10%; M 341], and 3,3,6,6-tetramethyl-2,7-dioxa-sym-octahydroacridine (XVIII) [0.6 g (11%), mp 119-120°C (from petroleum ether), according to the data in [11], mp 118°C (from water)].

Preparation of Quinindoline XV from Compound XIV by the Action of Ammonia. A 2 ml portion of 25% NH_4OH is added to a solution of 0.7 g (2 mmoles) of compound XIV in 10 ml of ethanol. The mixture is left to stand at room temperature for 5 h, then evaporated to half its volume, and the precipitate that separates is filtered to yield 0.35 g (50%) of quinindoline XV, which was identified from TLC, IR spectrum and melting point of a previously isolated sample.

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