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DIQUINOLYLS

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A convenient method was developed for the synthesis of diquinolyls by recombination of quinoline anion radicals formed by reaction of quinolines with active metals. A series of diquinolyls, their homologs, and partially hydrogenated derivatives were obtained.

Heteroaromatic anion radicals obtained by one-electron reduction of aromatic heterocycles *in situ* readily hetarylate organic compounds [1] or recombine to give bisheteroaromatic systems [2]. This is the basis of the well-known syntheses of dipyridyls, but diquinolyls have not been obtained by this method because of low yields and the formation of difficult-to-separate mixtures of isomers [2]. 2,2'-Diquinolyl (cuproin), which is widely used in industry as an extracting agent for monovalent copper ions, is currently obtained in ∿60% yields by decarboxylation of 2,2'-dicinchoninic acid, which in turn is usually synthesized in 50% yield from isatin and 3-chloro-2-butanone [3]. Thus the overall yield of 2,2'-diquinolyl in this two-step synthesis, which has been adopted industrially, does not exceed 30%. It seemed of interest to attempt to develop a direct method for the preparation of cuproin and other diquinolyls and their homologs in high yields directly from quinoline, quinaldine, and lepidine, which are the components of quinoline bases of coal tar and have not yet found qualified application despite the considerable resources available [4].

It was found that the reaction of quinoline with metal in an inert gas atmosphere gives isomers of partially hydrogenated diquinolyls, the oxidation of which with nitrobenzene leads to a mixture of diquinolyls, the composition of which depends on the nature of the metal used. In particular, we were able to obtain, in one step almost pure 2,2'-diquinolyl in 50% yield when we heated quinoline with aluminum dust, activated by mercuric chloride, in nitrobenzene solution [5]. Quinoline homologs react similarly with aluminum dust. A mixture of 4,4'- and 2,2'-diquinolyls in a ratio of 4:1 is formed when zinc dust is used; mixtures of approximately equal amounts of 2,3'-, 2,2'-, and 4,4'-diquinolyls are obtained, as a rule, in the presence of other metals, and the remaining isomers are formed in vanishingly small amounts, which we detected only by chromatography. Carrying out the reaction in inert solvents in a nitrogen atmosphere makes it possible to also obtain various partially hydrogenated diquinolyls.

To ascertain the possibilities of the proposed method for the synthesis of diquinolyls and to establish the nature of the reactions occurring during it, we preparatively obtained and characterized all the types of compounds formed in this process. However, we did not attempt to isolate the intermediates in all cases, since the partially hydrogenated diquinolyls are oxidized to give diquinolyls III, VI, VIII, and XI when the reaction is carried out

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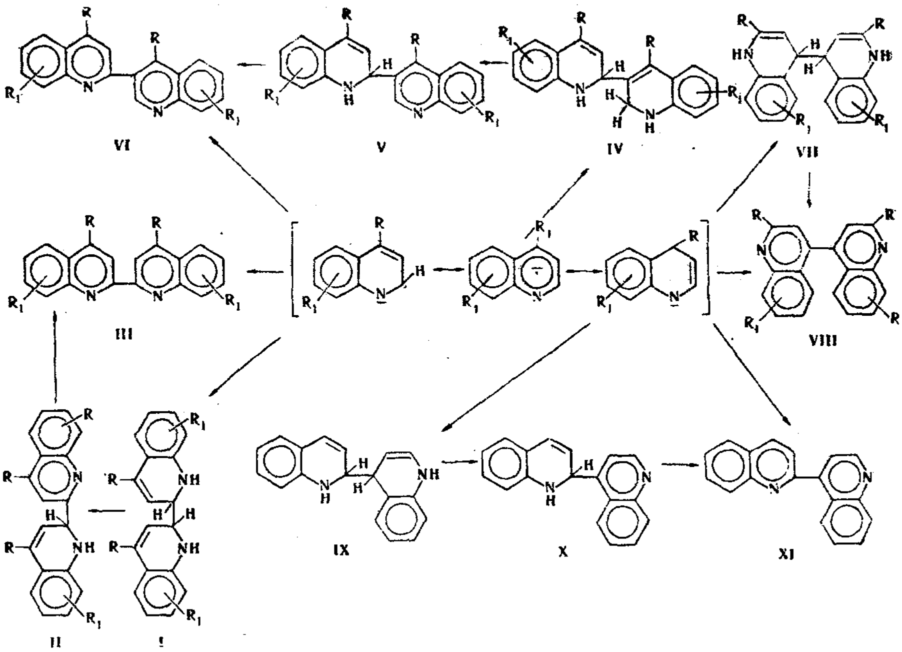
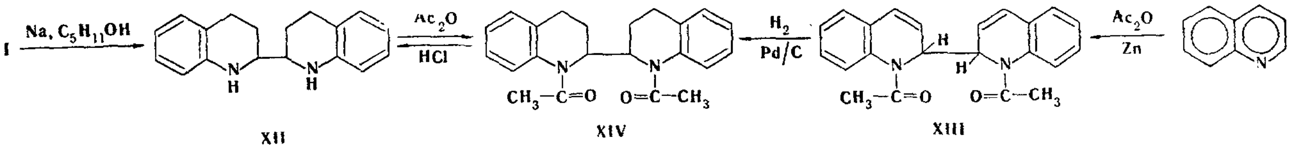
in nitrobenzene. We proved the structures of all the types of intermediately formed partially hydrogenated compounds by chemical means and by their IR and mass spectra. Thus the band of an NH group at 3200-3400 cm^{-1} and a $\nu_{C=C}$ band at 1620 cm^{-1} (except for VII) are observed in the IR spectra of the diquinolyl derivatives (I, II, IV, V, VII, IX, and X). We obtained the diquinolyls described in the literature by oxidation of all of these compounds; reduction gave derivatives with a completely hydrogenated pyridine ring, the structure of one of which



I $R=R_1=H$; III a $R=R_1=H$; b $R=CH_3$, $R_1=H$; c $R=H$, $R_1=7\text{-}CH_3$; d $R=H$, $R_1=8\text{-}CH_3$; IV $R=R_1=H$; VI a $R=R_1=H$; b $R=4CH_3$, $R_1=H$; VII $R=2CH_3$, $R_1=H$; VIII a $R=R_1=H$, b $R=2CH_3$, $R_1=H$

was proved by alternative synthesis via the scheme:



Quinoline reacts with acetic anhydride and zinc dust under the conditions of the Dimroth reaction [6] to give 1,1'-diacetyl-1,2,1',2'-tetrahydro-2,2'-diquinolyl (XIII), the hydrogenation of which led to the corresponding octahydro derivative XIV. As a result of the acid hydrolysis of XIV we obtained 1,2,3,4,1',2',3',4'-octahydro-2,2'-diquinolyl (XII), which proved to be identical to the compound obtained by reduction of I with sodium in amyl alcohol. We also obtained 1,2,3,4,1',2',3',4'-octahydro-2,3'-diquinolyl (XV), the IR spectrum of which was similar to the spectrum of XII, by similar reduction of the intermediately formed 2-(1',2'-dihydro-3'-quinolyl)-1,2-dihydroquinoline IV.

We also used a mass-spectrometric method to confirm the structures of XII and XV, Proceeding from the analogy with piperidines [7] and 1,2,3,4-tetrahydroquinoline [8], we assumed that products would have molecular ions (M^+) with low stabilities with respect to electron impact and that their fragmentation pathways in the first stages of fragmentation would be associated with processes involving the successive dehydrogenation of $M^+$and cleavage of the bond connecting both rings in the molecule. These assumptions were completely confirmed. In fact, the fragmentation of XII and XV under the influence of electron impact is described by the following scheme:*

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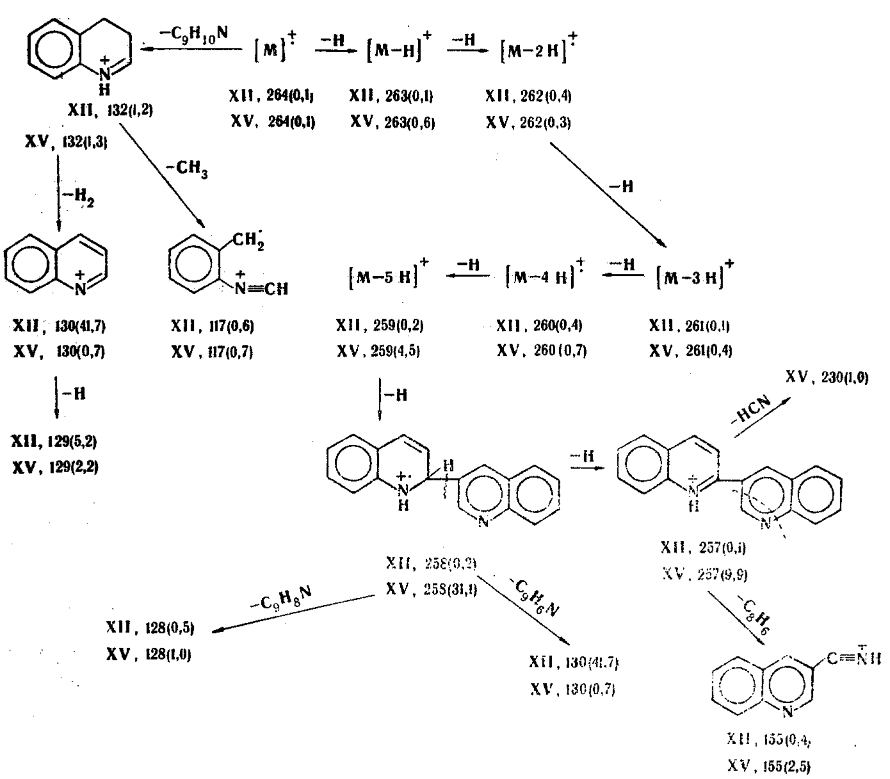
*The numbers under the formulas correspond to the mass number (m/e) of the ion, and the numbers in parentheses correspond to the intensity of the ion peak in percent of the total ion current.



When the ionizing-electron energy is reduced to 15 eV, an increase in the contribution to the total ion current from processes due to aromatization of the system as a whole during fragmentation (by factor of four to six) is observed for both isomers. This sort of effect is characteristic for cyclic amines and was previously noted in [7, 8]. The successive elimination of hydrogen atom from M^{+} promotes the formation of fragment ions with a 2- or 3-(1',2'-dihydroquinolyl)quinoline structure, the fragmentation of which has been studied in detail (ion peaks with m/e 258, 257, 155, 130, and 128) [9]. Ejection of a neutral HCN particle is realized from the $(M - 7H)^{+}$ fragment ion (XV, ion peak with m/e 230). This is possible because of the absence of blocking in the case of 2,3'-fusion of 1,2,3,4-tetrahydroquinoline rings; this process is not observed in the case of 2,2'-fusion.

It should be noted (this is evident from the fragmentation scheme) that a change in the site of the σ bond (2,2' or 2,3') between the rings of the system has a pronounced effect on the trend of the dissociative ionization of XII and XV. Thus for XII the initial step in the fragmentation of M^{+} is associated to a greater degree with cleavage of the bond between the heterocyclic rings. The ion peak with m/e 130 with a quinolinium ion structure is the maximum peak in the mass spectrum. Dehydrogenation processes predominate in the case of XV. The ion peak with mass 258 will be the maximum peak in the spectrum in this case. The observed appreciable difference in the intensities of the ion peaks in the spectra of XII and XV is extremely surprising. The reason for this possibly involves steric factors. Thus in [10] it was shown that tetrahydroquinoline derivatives may exist in two stereoisomeric forms: the α isomer with an axial α-C-H bond and an equatorial γ-C—H bond, and the β isomer with axial α- and γ-C—H bonds. In both cases there is exocyclic conjugation of the σ electron of the C—H bond and the π electrons of the nitrogen atom (the "ortho effect"), which is different for each of the isomers. It is possible that this fact is manifested to a greater degree in the initial process of elimination of hydrogen atoms from M^{+}.

We have previously [9] proved the structures of the diquinolyls of the V, IX, X, etc. types formed intermediately in these reactions by mass spectrometry.

EXPERIMENTAL

The mass spectra were obtained with a Varian Mat-311 spectrometer at an ionizing-electron energy of 70 eV, a cathode emission current of 1.5 mA, and an accelerating voltage of 3 kV. The samples were introduced directly into the ion source of the apparatus at 150°. The IR spectra of $CHCl_3$ or CCl_4 solutions of the compounds were recorded with a UR-20 spectrometer.

TABLE 1. Diquinolyls

Compound	mp, °C (crystallization solvent)	R_f	Found, %			Empirical formula	Calc., %			Yield, %	Picrate			
			C	H	N		C	H	N		mp, °C	N found, %	Empirical formula	N calc., %
I	95—96	0,43	83,2	6,4	10,9	$C_{18}H_{16}N_2$	83,0	6,2	10,8	30	—	—	—	—
IIIa	194—196[11] (ethanol)	0,80	84,3	4,6	11,9	$C_{18}H_{12}N_2$	84,3	4,7	10,9	52	210	12,9	$C_{18}H_{12}N_2 \cdot C_6H_3N_3O_7$	12,6
IIIb	273—274[12] (butanol)	0,84	83,3	5,9	9,8	$C_{20}H_{16}N_2$	84,5	5,7	9,9	52	350	10,8	$C_{20}H_{16}N_2 \cdot C_6H_3N_3O_7$	10,9
IIIc	208—209[13] (ethanol)	0,39	84,3	5,6	9,8	$C_{20}H_{16}N_2$	84,5	5,7	9,9	42	285—286	10,8	$C_{20}H_{16}N_2 \cdot C_6H_3N_3O_7$	10,9
IIId	145—147[13] (ethanol)	0,53	84,4	5,9	9,7	$C_{20}H_{16}N_2$	84,5	5,7	9,9	89	256	10,9	$C_{20}H_{16}N_2 \cdot C_6H_3N_3O_7$	10,9
V	167—168 (isopropyl alcohol)	0,32	83,3	4,7	10,9	$C_{18}H_{14}N_2$	83,7	5,4	10,8	60	—	—	—	—
VIa	173—175[14] (ethanol)	0,30	84,7	4,6	11,0	$C_{18}H_{12}N_2$	84,3	4,7	10,9	58	194	12,6	$C_{18}H_{12}N_2 \cdot C_6H_3N_3O_7$	12,6
VIb	265—267 (CCl_4)	0,67	84,6	5,5	10,0	$C_{20}H_{16}N_2$	84,5	5,6	9,9	28	342	10,8	$C_{20}H_{16}N_2 \cdot C_6H_3N_3O_7$	10,9
VII	279—281 (butanol)	0,28	84,3	5,7	10,0	$C_{20}H_{20}N_2$	84,4	5,7	9,9	18	—	—	—	—
VIIIa	165—166 (ethanol)	0,70	84,2	5,1	10,7	$C_{18}H_{12}N_2$	84,3	4,7	10,9	35	192	12,4	$C_{18}H_{12}N_2 \cdot C_6H_3N_3O_7$	12,6
VIIIb	263—265 (ethanol—butanol, 3 : 1)	0,55	84,6	5,8	9,6	$C_{20}H_{16}N_2$	84,5	5,7	9,9	15	—	10,9	$C_{20}H_{16}N_2 \cdot C_6H_3N_3O_7$	10,9
X	162—164 (methanol)	0,32	84,2	5,3	10,7	$C_{18}H_{14}N_2$	83,7	5,4	10,8	47	322	—	—	—
XI	177—179 (butanol—ethanol, 1 : 3)	0,35	84,7	4,9	10,9	$C_{18}H_{12}N_2$	84,3	4,7	10,9	14	—	—	—	—
XV	214—215 (alcohol)	0,30	81,6	8,0	10,6	$C_{18}H_{20}N_2$	81,8	7,6	10,6	20				

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*Obtained by reaction with Na.

†Obtained by reaction with Zn; the remaining compounds were obtained in the presence of Al.

Chromatography in a thin layer of Al_2O_3 was carried out in all cases by elution with benzene—hexane—chloroform (6:1:30) with development with iodine vapors.

2,2'-Diquinolyl (Cuproin). A mixture of 32.3 g (0.25 mole) of anhydrous quinoline, 6.75 g (0.25 mole) of aluminum dust, and 1 g of mercuric chloride was heated at 195-200° in a nitrogen atmosphere for 8 h, after which the resulting viscous resinous mass was dissolved in hot nitrobenzene, and the solution was refluxed for 3 h. The nitrobenzene and unchanged quinoline were then removed by vacuum distillation, and the residue was reprecipitated several times from acetic acid by the addition of water dried, and recrystallized from aqueous ethanol to give 16.6 g (52%) of 2,2'-diquinolyl with mp 194-196° [11] and R_f 0.8. Mass spectrum, m/e:* 29 (3.8); 39 (3.9); 41 (8.4); 42 (2.9); 43 (7.8); 51 (3.0); 54 (2.1); 55 (8.2); 56 (3.0) 57 (5.0); 60 (3.1); 63 (2.0); 67 (3.3); 68 (2.1); 69 (4.3); 70 (2.5); 71 (2.7); 73 (2.9); 75 (4.6); 76 (3.9); 77 (5.4); 81 (2.8); 82 (2.0); 83 (2.3); 84 (2.0); 85 (2.0); 91 (2.2); 95 (2.9); 97 (2.7); 98 (2.9); 100 (2.4); 101 (9.3); 102 (6.0); 113.5 (1.2); 114 (2.9); 114.5 (1.0); 127 (4.3); 127.5 (2.8); 128 (20.5); 128.5 (2.3); 129 (4.3); 154 (2.3); 155 (2.9); 227 (3.5); 228 (3.7); 229 (2.4); 253 (4.0); 255 (64.7); 256 (100.0); 257 (19.3); 258 (2.3); W_m 31.3%.

The other diquinolyls (Table 1) were similarly obtained. When it was necessary to obtain partially hydrogenated derivatives, the reaction was carried out without subsequent refluxing in nitrobenzene. The isomers were isolated and purified by chromatography and subsequent crystallization from suitable solvents (Table 1).

1,1'-Diacetyl-1,2,1',2'-tetrahydro-2,2'-diquinolyl (XIII). A 10-g sample of activated zinc was added with stirring (in the course of 1-1.5 h) to a solution of 25.6 g (0.2 mole) of quinoline in 38 ml of acetic anhydride, during which the temperature rose to 40°, the mixture turned green and a precipitate formed. Stirring was continued for another 3 h at 75°, after which the mixture was cooled, and the precipitate was removed by filtration and washed with acetic anhydride. The mother liquor was steam distilled, and the residue in the distillation flask was collected to give 24 g of an orange amorphous mixture, which was purified by column chromatography with aluminum oxide in a chloroform—benzene—hexane system (30:6:1). Mixtures of stereoisomers with R_f 0.20 and 0.40 were isolated. The overall yield of product with mp 147-148° (from cyclohexane) was 15 g (28%). Found: C 77.94; H 6.48; N 8.28%. $C_{22}H_{20}N_2O_2$. Calculated: C 78.0; H 6.50; N 8.0%.

1,2,3,4,1',2',3',4'-Octahydro-2,2'-diquinolyl (XII). The mixture of stereoisomers XIII was dissolved in glacial acetic acid and hydrogenated with hydrogen in the presence of 5% (based on the weight of XIII) of a Pd-on-carbon catalyst. The resulting 1,1'-diacetyl-1,2,3,4,1',2',3',4'-octahydro-2,2'-diquinolyl (XIV), with mp 216-218°, was refluxed in a 20% hydrochloric acid solution, after which the mixture was neutralized with alkali solution, and the precipitated XII, with mp 134-136° and R_f 0.35, was separated. Found: C 81.8; H 8.0; N 10.6%. $C_{18}H_{20}N_2$. Calculated: C 81.8; H 7.9; N 10.4%. No melting-point depression was observed for a mixture of a sample of this product with a sample of XII obtained by refluxing I in amyl alcohol with sodium for 12 h.

1,2,3,4,1',2',3',4'-Octahydro-2,3'-diquinolyl (XV) was similarly obtained (Table 1).

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POLYMETHINE DYES — FURO[3,2-f]QUINOL-7-YL AND FURO[3,2-f]QUINOL-9-YL DERIVATIVES

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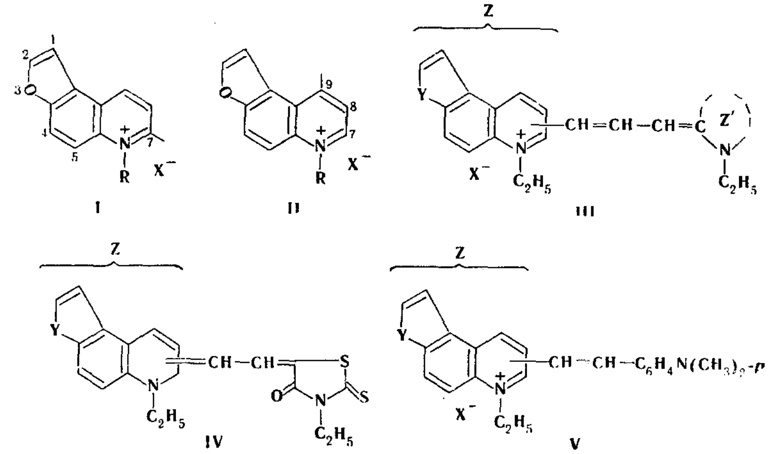
New heterocyclic bases — 7- and 9-methylfuro[3,2-f]quinolines — were synthesized by condensation of 5-aminobenzofuran double tin hydrochloride salt with paraldehyde in dilute hydrochloric acid and with methyl vinyl ketone in ethanol in the presence of ferric chloride and zinc chloride. Polymethine dyes of various types were obtained from the quaternary salts of the synthesized bases. The introduction of a furan ring in the 5,6 position of quino-2- and quino-4-carbocyanines gives rise to a smaller bathochromic effect than the analogous introduction of a thieno and, particularly, a benzo group.

It has been previously shown that the introduction of a thieno group in the 5,6 position of quino-4-carbocyanines gives rise to a smaller bathochromic effect than the analogous introduction of a benzo group. However, there is practically no difference in the color of dyes with 5,6-benzoquinol-2-yl and thieno[3,2-f]quinol-7-yl residues. In order to ascertain the effect of the analogous replacement of a vinylene group by an oxygen atom on the spectra of the dyes, we synthesized carbocyanines, merocyanines, and p-dimethylaminostyryl dyes with residues with furo[3,2-f]quinol-7-yl and furo[3,2-f]quinol-9-yl structures (I, II), respectively: III, IV, and V:



Y=O, Z'=Z= benzothiazolyl, 2-quinolyl, or 4-quinolyl,X — acid residue

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