ELECTRONIC AND STERIC FACTORS IN REACTIONS INVOLVING THE FORMATION OF SPIROPYRANS

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A study of the properties of six-membered heterocyclic cations with a methyl group in the α position makes it possible to reveal the relative roles played by electronic and steric factors for the conversion of the corresponding o-oxidostyryl derivatives to spiropyrans. The positive charge on the carbon atom in the investigated bicyclic heterocations increases in the order 1,2-dimethylisoquinolinium < 1,2-dimethylquinolinium < 1,2,3-trimethylquinolinium < 1,2-dimethyl-3,4-dihydroisoquinolinium, whereas the rates of reaction with p-dimethylaminobenzaldehyde follow a different sequence – 1,2-dimethylisoquinolinium < 1,2,3-trimethylquinolinium < 1,2-dimethyl-3,4-dihydroisoquinolinium < 1,2-dimethylquinolinium. The ability of o-oxidostyryl isoquinolinium and 1,3-dimethylquinolinium derivatives to form spiropyrans, in contrast to 1-methylquinolinium derivatives, is due to the steric effect of the hydrogen atom in the peri position or of the methyl group near the reaction center, which leads to disruption of the coplanarity and a decrease in the stabilities of the corresponding merocyanine molecules.

Previously on the basis of calculations by the Hückel MO method for quaternary salts of six-membered nitrogen heterocycles we concluded that the possibility of the formation of spiropyrans from oxidostyryl derivatives of heterocycles is determined by the magnitude of the positive charge (q) on the carbon atom that participates in cyclization and by the localization energy (L) of this reaction center [1]. Minkin and Simkin recently calculated these values by the Pariser – Parr – Pople (PPP) method with the Dewar σ,π parametrization within the π approximation for a large number of heterocyclic cations [2]. A comparison of these results with the experimental data on the stabilities of the corresponding spiropyrans confirmed the expediency of the utilization of the q and L values as the criteria of the possibility of intramolecular cyclization. The results of calculations of the quinolinium, isoquinolinium, and 3,4-dihydroisoquinolinium systems (the results of calculation of the isoindolinium system, which has the same π system, were used for the latter) are presented in Table 1 [2].

In conformity with the calculated q and L values for isoquinolinium derivatives, the tendency to form spiropyrans should only slightly exceed the tendency observed for quinolinium derivatives. However, these calculations do not take into account the differences in the geometries of the molecules near the reaction center. A study of 2-methyl-1-(o-oxido)styryl derivatives of the isoquinolinium system showed that, in contrast to the quinolinium analogs [3], they are capable of undergoing cyclization to spiropyrans [4]. Inasmuch as the electron density in the 2 and 1 positions of the quinolinium and isoquinolinium cations, respectively, differ only slightly, the behavior of 1-(o-oxido)styryl derivatives of the isoquinolinium system was explained by a decrease in their stabilities because of disruption of the coplanarity under the influence of the hydrogen atom in the 8 position. It was recently observed that 1-methyl-2-(o-oxidostyryl)quinolinium salts are also capable of intramolecular cyclization when a methyl group is present in the 3 position [5]. Thus in the evaluation of the possibility of the formation of spiropyrans one must take into account not only the electronic factors but also the steric factors. To uncover the roles played by these factors we made an experimental comparison of several properties of the quaternary salts of the quinoline and isoquinoline derivatives (I-IV), which can be considered to be models of the cationic fragments of the corresponding o-oxidostyryl compounds.

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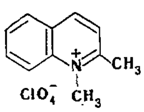
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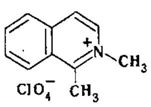
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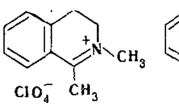
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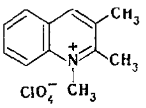
IV

$$X^-[\overset{+}{Het}-CH_3] \underset{+HX}{\overset{-HX}{\rightleftarrows}} Het{=}CH_2$$

I–IV Ia–IVa

It is known that the ease of acidic ionization of the methyl groups bonded to the carbon atom of the heteroring depends on the magnitude of the positive charge on this atom. The pK_a values for the 1,2-dimethylquinolinium (I) and 1,2-dimethylpyridinium systems in acetonitrile are, respectively, 19.7 and 24.8 [6]. However, the acid properties of II-IV under comparable conditions have not been studied. The acidities of the cations of I-IV in aqueous solutions are very low. The conjugate base (Ia) of the cation of I is not detected spectrophotometrically even in a 1 M aqueous sodium hydroxide solution, and this is in agreement with the observations of Metzger and co-workers [7]. However, in 10^{-5}-10^{-4} M alcohol solutions of salts I-IV in the presence of a fivefold to tenfold excess of alkali the cations of I-IV are converted practically completely to the conjugate methylene bases (Iz-IVa). The absorption spectra of these solutions do not depend on the substrate concentration, do not undergo any changes 2-3 h after the addition of alkali, and, after acidification, were completely identical to the spectra of the starting salts; this makes it possible to disregard possible dimerization of the methylene bases. To compare the acidities of I-IV we used a spectrophotometric method to measure the degree of their conversion to methylene bases Ia-IVa in dilute alkali solutions and in triethylamine solutions (Table 2).

As seen from the results, the acidities of the methyl groups of I-IV decrease in the order III > IV > I > II. When the pK_a and q values have similar trends in the same sequence, the positive charges on the carbon atoms should decrease. The maximum aciditiy displayed by the 1,2-dimethyl-3,4-dihydroisoquinolinium salt (III) is undoubtedly due to the considerably lower charge delocalization than that observed for the aromatic cations of I, III, and IV (see Table 1). However, the lower acidity of the quinaldinium ion (I) as compared with the 3-methyl-substituted ion (IV) and the extremely low acidity of the 1,2-dimethylisoquinolinium system are somewhat unexpected if one takes into account the equality of the calculated charges for the quinolinium and isoquinolinium systems (Table 1). The reason for this is evidently the fact that evaluation of the charges on the ring carbon atoms with respect to the acidities of the attached methyl groups is an indirect method. For example, it does not take into account the possible differences in the character of the stabilization of the methylene bases that participate in the equilibria. Thus an examination of Stuart models shows that, in contrast to the cations, the methylene group of methylene bases IIa and IIIa cannot be found in the plane of the molecule, and this should decrease their stabilities. In the case of the dihydro derivatives (III-IIIa) this destabilization is insignificant, inasmuch as it is overlapped by the considerably stronger effect of the large positive charge.

TABLE 1. Localization Energies (L) and π Charges (q) of the Carbon Atoms of Heterocyclic Cations [2]

Cation	Quinolinium		Isoquinolinium		3,4-Dihydroisoquinolinium
atom	2	4	1	3	1
L,eV	6.36	6,09	6.22	7,30	5.90
q	0.138	0,173	0,138	0,026	0,298

TABLE 2. Degree of Conversion of Quaternary Salts I-IV to Methylene Bases Ia-IVa in Alcohol Solutions (c_{in} $1.16 \cdot 10^{-4}$ M) and Chemical Shifts (δ-^{13}C) of the Ring Carbon Atoms

Compound	Degree of conversion of the base in alcohol solution, %				δ-^{13}C, ppm from CS_2
	$1,2 \cdot 10^{-3}$ M NaOH	$(C_2H_5)_3N$ concn., M			
		0,14	0,014	0,5	
I	75	25	13	54.3	31,2*
II	43	5.2	1.4	—	32,0
III	91,5	90	63	—	15.5
IV	—	38	—	67.2	30,8

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*The δ-^{13}C value for $C_{(2)}$ of 1-ethyl-2-methylquinolinium iodide in dimethyl sulfoxide is 31.2 ppm [9].

TABLE 3. Primary Half-Wave Potentials of Cathode Reduction of I-III and V-VII

Compound	I	II	III	V	VI	VII
$-E_{1/2}$,eV*	0,94 (0,96)	(1,26)	0,92	0,68	0,93	0,62

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*The $E_{1/2}$ values were measured for 10^{-4} M solutions of the depolarizers with a 0.1 M sodium acetate base electrolyte in 20% acetic acid. The values obtained with a 0.1 M $(C_2H_5)_4NClO_4$ base electrolyte are presented in parentheses.

TABLE 4. Kinetic Characteristics of the Reaction of Quaternary Salts with p-Dimethylaminobenzaldehyde*

Compound	Neutral condensation, $k_0^{71.8} \cdot 10^4$ liters/mole · min	Condensation in a 0.01 M alcohol solution of piperidine				
		$k_{eff} \cdot 10^4$ liters/mole · min			E, kcal/mole	lg A
		39.0°	56,1°	71.8°		
I	8.0±0.3	130±7	191±8	256±15	4,4±0.2	1,21
II	0.0	1,2±0,1	2.25±0.06	3.9±0,1	7.73±0,17	1,49
III	0,8±0.03	21±1	33.4±0,9	49±0.7	5.55±0,04	1,21
IV†	—	—	—	4.53±0.2	—	—
X†	0.9 (70°)	—	48 (50°)	96 (70°)	—	—
XI†	3.8 (70°)	—	126 (50°)	260 (70°)	—	—

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*The starting concentrations of the reagents in the neutral condensation were 0.02 M for I and 0.04 M for III. In the remaining cases c_{st} was 0.01 M.

†The iodide was used in the case of IV. The condensation was carried out in butanol [13] in the case of 1,2- and 1,4-dimethylpyridinium iodides (X and XI).

TABLE 5. Spectral Characteristics of I-IV and Conjugate Methylene Bases Ia-IVa

Compound	In alcohol		Compound	In 10^{-3} M alcoholic NaOH		λ_{an},* nm
	λ_{max} (λ_{min}),nm	$\varepsilon \cdot 10^{-3}$		λ_{max} (λ_{min}),nm	$\varepsilon \cdot 10^{-3}$	
I	315 (257)	9,00 (0,1)	Ia	390 (340)	3,60 (1,27)	390
II	330, 325 (295)	4,50; 4,83 (0,67)	IIa	370 (295)	6,97 (0,5)	370
III	315†, 278 (236)	2,45; 12,8 (1,10)	IIIa	300, 236 (270)	2,83; 10,6; (2,0) 2,36	278
IV	315 (260)	9,7 (0,5)	IVa	380 (332)	6,00 (1,47)	380

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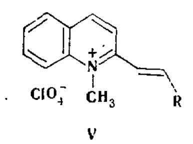
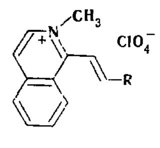
*This is the wavelength at which the optical density was measured for the determination of the concentration of the methylene base.

†Shoulder.

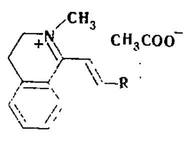
A more direct method for the evaluation of the charges is a comparison of the chemical shifts of comparable carbon atoms by means of ^{13}C NMR spectroscopy [8]. A one-electron change in the charge gives rise to a shift of 160 ppm of the resonance signal. This method was previously successfully applied to quaternary salts of benzazoles [9]. To record the ^{13}C NMR spectra we used 20-25% aqueous solutions of the nitrates of the cations of I-IV, inasmuch as the solubilities of the perchlorates were inadequate. In order to assign the signals of the carbon nuclei we used the method of partial recording of proton decoupling, which makes it possible to unambiguously determine the signals of quaternary atoms [10]. The chemical shifts of the ring carbon atoms adjacent to the heteroatom are presented in Table 2. In conformity with the δ-^{13}C values, the same order of change in the positive charges on the carbon atoms bonded to the methyl group as was observed on the basis of the acidities of the methyl groups was obtained. The higher charge on the cation of IV relative to I was also confirmed. Thus one observes a qualitative correspondence in the evaluation of the charges by both methods. However, one's attention is directed to the extremely small difference for the aromatic cations of I, II, and IV (~1 ppm), which attests to the closeness of the q values for the carbon atoms in these ions. At the same time, the charge on $C_{(1)}$ of the 3,4-dihydroisoquinolinium system (III) should be ~0.1 e higher than the values observed for the cations of I, II, and IV, and this is in good agreement with the calculated values (Table 1).



V



VI



VII

R = 2-HOC_6H_4

The formation of spiropyrans from o-oxidostyryls can be considered to be an intramolecular reaction of the cationic fragment of the molecule with the nucleophile. It is interesting to compare the electrophilicities of the model cations from this point of view. We measured the half-wave potentials of polarographic reduction of the cations of I-III and of the corresponding o-oxidostyryl compounds (V-VII) (Table 3).

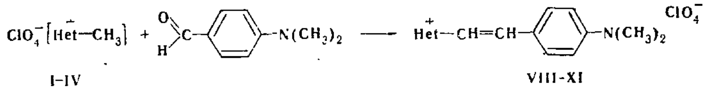
The half-wave potentials of the cations of I-III are practically independent of the nature of the background and the pH. In an aqueous acetate buffer solution (pH 2.84) the first wave of one-electron reduction of the dihydroisoquinolinium ion (III) is only 0.02 V more positive than the value observed for the quinaldinium ion (I). At the same time, the cation of II is reduced with considerably greater difficulty, and in this medium its wave is masked by the wave of reduction of hydrogen. The $E_{1/2}$ value of the cation of II in a 0.1 M tetraethylammonium perchlorate base electrolyte is 0.3 V lower than the value observed for I.

Thus the reduction potentials of the cations of I-III increase in the same order as the positive charges on the carbon atoms adjacent to nitrogen. However, the difference between the isoquinolinium (II) and quinolinium (I) systems in this series is considerably greater than the difference observed between I and III and does not correspond to the δ-^{13}C values presented above. The low reduction potential of II can hardly be due to steric factors, since replacement of the methyl group attached to nitrogen by a bulkier substituent (C_2H_5, iso-C_3H_7, $CH_2C_6H_5$) leads to a small change in the $E_{1/2}$ values (−1.30, −1.36, and −1.16 V in a 0.1 M aqueous tetraethylammonium perchlorate base electrolyte) in conformity with the polar effect of these groups. The large difference in the reduction potentials of salts I and II is in agreement with the data of Kato and co-workers [11] who studied the reduction of quaternary salts of a number of heterocycles, including 1-methylquinolinium and 2-methylisoquinolinium iodides, in aprotic and aqueous media. The potentials of the first waves in the two types of solvents did not differ significantly, although reduction in aprotic solvents gave more distinct and in no way complicated one-electron waves. For I in acetonitrile we found $E_{1/2} = -0.95$ V. In [11] it was shown that the $E_{1/2}$ values of the first waves correlate well with the energies of the lower vacant orbitals rather than with the π charges. The certain nonconformity of the $E_{1/2}$ and δ-^{13}C values is also evidently explained by precisely this observation.

It is interesting to note that the differences in the reduction half-wave potentials found for quaternary salts I-III are also retained for the corresponding o-oxidostyryl derivatives (V-VII), although the reduction potentials of the latter are ~0.3 V higher than the values observed for salts I-III.

In comparing the results obtained by the various methods in the evaluation of the charges on the carbon atoms one may conclude that there is a high positive charge on $C_{(1)}$ only in the case of the dihydroisoquinolinium system (III). The charges differ only slightly in the remaining investigated cations (I, II, and IV), and the charge on the $C_{(2)}$ atom of the quinolium ion is somewhat higher than that on the $C_{(1)}$ atom of the isoquinolinium ion.

As a test of the reactivities (which are sensitive to steric factors) of the cations of I-IV, we used their rates of reaction with p-dimethylaminobenzaldehyde, which gives deeply colored styryls (VIII-XI). The kinetics of the formation of the styryls were monitored by spectrophotometry.



I-IV

VIII-XI

Condensation proceeded sufficiently effectively for all of the cations in the presence of a catalyst (piperidine). Only the cations of I and III underwent reaction without a catalyst. A first-order reaction with respect to both the reagents and the catalyst (for catalytic condensation) was established by control experiments, and it hence follows that the rate-determining step is reaction of the corresponding methylene bases (Ia-IVa) with the aldehyde. This sort of reaction mechanism was recently convincingly proved for the alkali-catalyzed reaction of 1,4-dimethylpyridinium iodide with dimethylaminobenzaldehyde in aqueous alcohol [12]. In the case of the catalyzed condensation we calculated the effective rate constants as second-order constants (first-order in each reagent) at a constant piperidine concentration (c_{cat} 0.01 M).

The 1,2-dimethylquinolinium ion (I), which has a considerably lower acidity than the cation of III, was found to be the most reactive in the condensation (Table 4). Inasmuch as the concentrations of methylene bases Ia-IVa during the condensation are determined precisely by the acidities of quaternary salts I-IV, it hence follows that the 2-methylene-1-methyl-1,2-dihydroquinoline molecules (Ia) are considerably more active than IIIa. In our opinion, the low activity of the latter is due primarily to steric hindrance at the reaction center. Because of this, III reacts with the aldehyde even more slowly than the 1,2-dimethylpyridinium ion (Table 4). At the same time, the exceptionally low activity of the 1,2-dimethylisoquinolinium ion is explained by the simultaneous effect of steric factors and the low acidity. The role played by steric hindrance is particularly clearly discernible when one compares the rate constants of the quinaldinium ion (I) and its 3-methyl derivative (IV). The methyl group in the 3 position, without substantially affecting the acidity of the 2-methyl group (Table 2), lowers the rate of reaction with aldehyde by a factor of more than 50. It is extremely likely that the difference in the rates of condensation of 1,2- and 1,4-dimethylpyridinium iodides (X, XI), which have almost identical acidities [6], with the same aldehyde is also due to steric factors.

On the basis of the study of quaternary salts I-IV and the properties of the corresponding spiropyrans it can be concluded that the formation of spiropyrans from o-oxidostyryl derivatives of 1-methylisoquinolinium and 1,3-dimethylquinolinium ions is entirely due to steric factors. Dihydroisoquinoline spiropyrans are more stable because of the increased charge on the $C_{(1)}$ atom. To evaluate the steric factors, one can use the activities of the quaternary salts in condensation reactions similar to those involved in the formation of styryls. The steric hindrance from the substituent, which leads to a decrease in the reaction rate by 1.5-2 orders of magnitude, turns out be completely sufficient to render the stabilities of the merocyanine and spiropyran structures comparable. At the same time, the higher charge and the lower localization energy in the 4 position of the quinolinium system as compared with the 2 position (Table 1) are inadequate for the formation of spiropyrans from 4-(o-oxidostyryl)quinolines [3]. It should be noted that the q and L values calculated for the 4 position of the quinolinium ion do not differ from the values calculated for the phenanthridinium ion [2]; however, phenanthridine spiropyrans are readily formed and are stable even when they have acceptor substituents in the chromene ring [3]. In this connection, there is no doubt that the 3-methyl-substituted 4-(o-oxidostyryl)-quinolinium ion, because of the steric effect of the methyl group in the 3 position, should give spiropyrans with stabilities similar to the stabilities of derivatives of the phenanthridine series.

EXPERIMENTAL

The UV spectra of octane, benzene, and alcohol solutions of the compounds were recorded with an SF-8 spectrophotometer. The ^{13}C NMR spectra of solutions of the nitrates of the heterocation (see below) were recorded with a Bruker HFX-90 spectrometer at 22.63 MHz by the pulse method with Fourier transformation and proton decoupling; dioxane was the internal standard.* The chemical shifts relative to CS_2 (Table 2) were calculated from the formula $\delta\,(CS_2) = 125 + \delta_{\text{dioxane}}$, where δ_{dioxane} is the chemical shift relative to dioxane.

Polarographic reduction on a dropping mercury cathode was accomplished with LP-7 and PPT-1 electron polarographs.

1,2-Dimethylisoquinolinium Perchlorate (II). A 2.85-g (0.01 mole) sample of 1,2-dimethylisoquinolinium iodide [14] was dissolved in 7-8 ml of boiling alcohol, after which perchloric acid was added to pH 1-2, and the mixture was cooled. The precipitated II was separated and crystallized from methanol (1 : 20) to give a product with mp 164-166° in 80% yield. Found: Cl 13.6%. $C_{11}H_{12}ClNO_4$. Calculated: Cl 13.8%.

1,2-Dimethylquinolinium (I), 1,2-Dimethyl-3,4-dihydroisoquinolinium (III), and 1,2,3-Trimethylquinolinium (IV) Perchlorates. These compounds were obtained in 80-75% yields by the method used to prepare II. Salt I had mp 154° [15], and III had mp 119-120°. Found: Cl 13.6%. $C_{11}H_{14}ClNO_4$. Calculated: Cl 13.7%. Salt IV had mp 227°. Found: Cl 13.6%. $C_{12}H_{14}ClNO_4$. Calculated: Cl 13.4%.

The equilibrium concentrations of the cations of I-IV and the conjugate bases in alcoholic sodium hydroxide solutions ($1.2 \cdot 10^{-4}$ M) and triethylamine solutions (0.5, 0.14, and 0.014 M) were determined spectrophotometrically at initial I-IV concentrations of $1.16 \cdot 10^{-4}$ M and a layer thickness of 1 cm with an SF-8 spectrophotometer. The absorption spectra of methylene bases Ia-IVa were measured in the presence of a large excess of sodium hydroxide. For all of the compounds ($c \sim 10^{-4}$ M) the spectra of the solutions remained constant as the alkali concentration was varied from 10^{-3} to 10^{-2} M. The starting salt was regenerated quantitatively when these solutions were acidified. The concentrations of bases Ia, IIa, and IVa were determined from the

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*The authors sincerely thank Yu. A. Ignat'ev for recording the ^{13}C NMR spectra.

optical densities at the long-wave absorption maxima (the corresponding salts do not absorb in this region). The concentration of base IIIa (c_{IIIa}) was calculated from the total optical density of the solution at 278 nm (D_{278}).

$$c_{IIIa} = \frac{\varepsilon_{278}^{III} \cdot c_{tot} - D_{278}}{\varepsilon_{278}^{III} - \varepsilon_{278}^{IIIa}}.$$

The degrees of conversion (C) of salts I-IV were calculated from the formula $C = (c_{base}/c_{tot}) \cdot 100\%$ (Table 2).

Aqueous Solution (25%) of 1,2-Dimethylisoquinolinium Nitrate. A 2.85-g (0.01 mole) sample of 1,2-dimethylisoquinolinium iodide [14] was dissolved in boiling water, after which an aqueous solution of 1.7 g (0.01 mole) of silver nitrate was added. The precipitated silver iodide was removed by filtration, and the aqueous solution was evaporated to 4 ml.

Aqueous Solutions (25%) of 1,2-Dimethylquinolinium, 1,2-Dimethyl-3,4-dihydroisoquinolinium, and 1,2,3-Trimethylquinolinium Nitrates. These solutions were similarly obtained.

1-Methyl-2-(2-hydroxystyryl)quinolinium Perchlorate (V). A 0.25-ml (2.5 mmole) sample of salicylaldehyde and 0.03 g (0.35 mmole) of piperidine were added to a suspension of 0.72 g (2.5 mmole) of 1,2-dimethylquinolinium iodide in 3 ml of alcohol, and the mixture was refluxed for 30 min. It was then cooled and acidified to pH 1-2 with $HClO_4$, and the resulting orange precipitate [0.6 g (62%)] was removed by filtration and crystallized from glacial acetic acid to give a product with mp 239-240°. Found: N 3.8%. $C_{18}H_{16}ClNO_5$. Calculated: N 3.9%.

2-Methyl-1-(2-hydroxystyryl)isoquinolinium Perchlorate (VI). This salt was obtained by the method used to prepare V and had mp 172-175°. Found: N 3.8%. $C_{18}H_{16}ClNO_5$. Calculated: N 3.9%.

Solution of 2-Methyl-3,4-dihydro-1-(2-hydroxystyryl)isoquinolinium Acetate (VII). This solution was prepared for polarographic study by dissolving a weighed sample of 2-methylspiro(1,2,3,4-tetrahydroisoquinoline-1,2'-[2H]chromene) [4] in 20% acetic acid, after which sodium acetate was added.

The quaternization of 1-methylisoquinoline with ethyl bromide, isopropyl iodide, and benzyl chloride was carried out by refluxing a mixture of the base with a twofold excess of the alkyl halide for 6-7 h. The quaternary salts (which were obtained, respectively, in 60, 40, and 50% yields) were removed by filtration, washed with benzene, and, without additional purification, converted to the perchlorates.

1-Methyl-2-ethylisoquinolinium Perchlorate. A 0.25-g (1 mmole) sample of 1-methyl-2-ethylisoquinolinium bromide was dissolved in 5 ml of boiling water, the solution was acidified to pH 1-2 with perchloric acid, and the precipitated 1-methyl-2-ethylisoquinolinium perchlorate [0.12 g (45%)] was removed by filtration and crystallized from isobutyl alcohol (1 : 25) to give a product with mp 135-138°. Found: Cl 13.0%. $C_{12}H_{14}ClNO_4$. Calculated: Cl 13.1%.

1-Methyl-2-isopropylisoquinolinium Perchlorate. This compound, with mp 166-168°, was obtained in 30% yield by the method used in the preceding experiment. Found: Cl 12.3%. $C_{13}H_{16}ClNO_4$. Calculated: Cl 12.4%.

1-Methyl-2-benzylisoquinolinium Perchlorate. A 0.27-g (1 mmole) sample of 1-methyl-2-benzylisoquinolinium chloride was dissolved in 3 ml of refluxing alcohol, the solution was acidified to pH 1-2 with perchloric acid, and the precipitated 1-methyl-2-benzylisoquinolinium perchlorate [0.15 g (53%)] was crystallized from acetic acid (1 : 20) to give a product with mp 179-181°. Found: Cl 10.1%. $C_{17}H_{16}ClNO_4$. Calculated: Cl 10.6%.

p-Dimethylaminobenzaldehyde. Prior to the kinetic measurements, the pure-grade aldehyde was crystallized from alcohol to give a product with mp 74°. Pure-grade piperidine with n_D 1.453 was also used for the measurements.

2-Methyl-1-(4-dimethylaminostyryl)isoquinolinium Iodide. A 0.37-g (2.5 mmole) sample of p-dimethylaminobenzaldehyde and 0.25 ml (2.5 mmole) of piperidine were added to a suspension of 0.78 g (2.5 mmole) of 1,2-dimethylisoquinolinium iodide in 3 ml of alcohol, after which the mixture was refluxed for 20 min. It was then cooled, and 0.75 g of dark-red crystals were removed by filtration. Two crystallizations from ethanol (1 : 15) gave 0.5 g (48%) of a product with mp 257° (mp 257° [14]).

2-Methyl-1-(4-dimethylaminostyryl)isoquinolinium Perchlorate (VIII). A 0.5-g sample of the iodide of the same styryl was dissolved in boiling methanol, and the solution was acidified to pH 1-2 with perchloric acid.

It was then cooled, and the resulting precipitate was crystallized from methanol (1:10) to give 0.3 g (63%) of red crystals with mp 268-269°. UV spectrum (in alcohol), λ_{max}, nm ($\varepsilon \cdot 10^{-4}$): 235, 315, and 480 (2.79, 0.99 and 1.12). Found: Cl 8.9%. $C_{20}H_{21}ClN_2O_4$. Calculated: Cl 9.1%.

1-Methyl-2-(4-dimethylaminostyryl)quinolinium Perchlorate (IX). The procedure in the preceding experiment was used to obtain this compound, with mp 232°, in 60% yield. UV spectrum, λ_{max}, nm ($\varepsilon \cdot 10^{-4}$): 230, 280, 330, and 530 (1.10, 0.5, 0.6, and 2.9). Found: Cl 9.0%. $C_{20}H_{21}ClN_2O_4$. Calculated: Cl 9.1%.

1,3-Dimethyl-2-(4-dimethylaminostyryl)quinolinium Iodide (X). A 0.38-g (2.5 mmole) sample of p-dimethylaminobenzaldehyde and 0.03 g (0.35 mmole) of piperidine were added to a suspension of 0.75 g (2.5 mmole) of 1,2,3-trimethylquinolinium iodide [16, 17] in 3 ml of alcohol, and the mixture was refluxed for 20 min. The precipitated dark-lilac-colored dye [0.5 g (50%)] was crystallized twice from ethanol (1:50) to give 0.3 g (30%) of a product with mp 247-249°. UV spectrum (in alcohol), λ_{max}, nm ($\varepsilon \cdot 10^{-4}$): 307 and 505 (2.43 and 1.11). Found: I 29.8%. $C_{21}H_{23}IN_2$. Calculated: I 29.5%.

2-Methyl-1-(4-dimethylaminostyryl)-3,4-dihydroisoquinolinium Perchlorate (XI). A 0.38-g (2.5 mmole) sample of p-dimethylaminobenzaldehyde and 0.25 ml (2.5 mmole) of piperidine were added to a suspension of 0.65 g (2.5 mmole) of salt III in 3 ml of alcohol, and the mixture was allowed to stand for 12 h. The precipitated dye [0.6 g (62%)] was crystallized twice from ethanol (1:20) to give 0.35 g (36%) of orange crystals with mp 154-158°. UV spectrum (in alcohol), λ_{max}, nm ($\varepsilon \cdot 10^{-4}$): 300 and 494 (0.45 and 1.13). Found: Cl 8.9%. $C_{20}H_{23}ClN_2O_4$. Calculated: Cl 9.1%.

The rates of reaction of I-IV with p-dimethylaminobenzaldehyde were monitored spectrophotometrically with respect to the buildup of the corresponding dye. The styryl concentrations were determined from the optical densities of the solutions near the absorption maxima of the dyes. The linear character of the dependence of the optical density on the concentration was verified by preliminary experiments. The measurements were made with a KF-5 photoelectrocolorimeter through light filters with transmission maxima of ~480 nm (BG 7 for VIII), 510-520 nm (BG 18, for IX), and 510 nm (VG9, for X and XI). The reactions were carried out in a flask equipped with a refluxing condenser in a thermostat at 39.2, 56.1, and 71.8° (± 0.1°). The initial concentrations of the starting materials in 96% alcohol were $1 \cdot 10^{-2}$M with a molar ratio of the reagents and catalyst of 1:1:1. In the case of II and IV ratios with piperidine of 1:4 and 1:5 were used to accelerate the reaction, and this was taken into account in the calculation of the rate constants. It was established by preliminary experiments that the reaction is first-order with respect to each reagent and the catalyst. Prior to each experiment, the appropriate weighed samples of the salts (I-IV) and p-dimethylaminobenzaldehyde containing piperidine (or without it) were dissolved in alcohol in 25-ml volumetric flasks, and the flasks were thermostatted and filled to the mark at the reaction temperature, after which they were stirred in the reactor-flask. Monomethylidynecyanine dyes [7] were formed at an appreciable rate from I and IV in the presence of piperidine. The absorption due to these dyes was measured during a blank experiment (without p-dimethylaminobenzaldehyde), which was carried out simultaneously with the principal experiment, and the result was subtracted in the determination of the styryl concentration. Samples of the reaction mixture (1-5 ml) were selected at definite time intervals with thermostated pipettes; these samples were immediately diluted with alcohol in a volumetric flask (25-50 ml), and the optical density of the resulting solution was measured. The concentration of the styryl was determined, with allowance for the coefficient of dilution, on calibration graphs for VIII-XI from the optical densities. The maximum degree of conversion in experiments with I was 3.5%, as compared with 0.5% for II, 1.2% for III, and 0.5% for IV. Rate constants k_t were calculated as second-order constants

$$k_{\tau} = \frac{x}{c(c-x)} \quad \frac{\text{liter}}{\text{mole} \cdot \text{min}},$$

where c is the initial concentration of the starting salt (I, II, III, or IV), and x is the styryl concentration (in moles per liter) at time t (in minutes) from the start of the reaction.

In the case of the catalytic reaction these constants were referred to a piperidine concentration of 0.01 M. The energies of activation (E) and the pre-exponential factor (log A) were calculated from the standard formulas

$$E = \frac{4{,}575 T_1 \cdot T_2}{T_2 - T_1} \lg \frac{k_2}{k_1} \text{ cal/mole;}$$

$$\lg A = \lg k + \frac{E}{4{,}575 \cdot T}.$$

The results are presented in Table 4.

1,3-Dimethyl-8'-methoxyspiro(1,2-dihydroquinoline-2,2'-[2H]chromene). A 0.38-g (2.5 mmole) sample of 3-methoxysalicylaldehyde and 0.03 g (0.35 mmole) of piperidine were added to a suspension of 0.75 g (2.5 mmole) of 1,2,3-trimethylquinolinium iodide in 3 ml of alcohol, and the mixture was refluxed for 30 min. It was then cooled, treated with 25 ml of water, and made alkaline to pH 9-10 with ammonia. The precipitated dark-orange merocyananine was removed by filtration and dissolved by heating in 10 ml of benzene. The benzene solution was filtered, and the filtrate was vacuum evaporated at 20-30° to give 3-4 ml of a light-green solution. Petroleum ether (10-15 ml) was added, and the mixture was evaporated under the same conditions to 5 ml and filtered to give 0.3 g (40%) of slightly yellowish crystals of the spiropyran with mp 145-148° [from hexane (1:40)]. UV spectrum (in octane), $\lambda_{\max}$, nm (log ε): 240 (4.47), 251 (4.39),* 267 (4.08),* and 320 (3.57); in alcohol: 244 (4.44), 305 (3.83), 325 (3.91),* 380 (4.05), and 580 (3.42). Found: C 78.6; H 6.8; N4.5%. $C_{20}H_{19}NO_2$. Calculated: C 78.7; H 6.2; N 4.6%.

1,3-Dimethyl-6'-bromospiro(1,2-dihydroquinoline-2,2'-[2H]chromene). The procedure of the preceding experiment was used to obtain this compound in 40% yield as slightly pinkish crystals with mp 135-136° [from petroleum ether (1:40)]. UV spectrum in octane, $\lambda_{\max}$, nm (log ε): 230 (4.66), 252 (4.50),* 270 (4.12),* and 320 (3.67); in alcohol: 243 (4.54), 288 (3.39),* 340 (4.05), 376 (4.05),* and 540 (3.68). Found: 22.8; N 4.0%. $C_{19}H_{16}BrNO$. Calculated: Br 22.6; N 3.9%.

1,3-Dimethyl-2-(2-oxido-3,5-dibromostyryl)quinolinium. The condensation of 1,2,3-trimethylquinolinium iodide with 3,5-dibromosalicylaldehyde (2.5 mmole each) was carried out as in the preceding experiment, after which the mixture was filtered to give 0.9 g (64%) of yellow crystals of the hydriodide. This material was dissolved in 150 ml of boiling 50% alcohol, after which the solution was cooled, made alkaline to pH 9-10 with ammonia, and filtered to give 0.7 g of a dark precipitate. Recrystallization from benzene (1:50) gave 0.54 g (50%) of lilac-colored crystals with mp 165-168°. UV spectra in benzene $\lambda_{\max}$, nm (log ε): 325 (3.72), 430 (2.47),* 530 (2.23), and 690 (2.65); in alcohol: 243 (4.51), 2.58 (4.37)* 305 (3.75),* 355 (4.08), and 530 (4.06). Found: 37.1%. $C_{19}H_{15}BrNO$. Calculated: Br 37.0%.

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*Here and subsequently the shoulders and inflection points are indicated by asterisks.