5. O. M. Glozman, N. S. Tolmacheva, L. A. Zhmurenko, and V. A. Zagorevskii, Khim.-farm. Zh., No. 2, 9 (1973).
6. N. Uccella, I. Howe, and D. H. Williams, Org. Mass Spectrom., 6, 229 (1972).
7. C. S. Barnes and J. L. Occolowitz, Austr. J. Chem., 17, 975 (1964).
8. M. M. Badawi, M. B. E. Fayez, T. A. Bryce, and R. I. Read, Chem. Ind., 498 (1966).
9. G. Barker and G. P. Ellis, Org. Mass Spectrom., 5, 857 (1971).
10. Q. N. Porter and J. Baldas, Mass Spectrometry of Heterocyclic Compounds, General Heterocyclic Chemistry Series, edited by A. Weissberger and E. C. Taylor, New York—London—Sidney—Toronto (1971), p. 189.
11. H. G. Viehe and V. Jaeger, Angew. Chem., Inter. Ed., 8, 979 (1969).
12. C. P. Lewis, Anal. Chem., 36, 176 (1964).
13. C. P. Lewis, Anal. Chem., 36, 1582 (1964).
14. Y. B. Thomson, P. B. Brown, and C. Djerassi, J. Amer. Chem. Soc., 88, 4049 (1966).
15. W. E. Pereira, B. Halpern, M. D. Solomon, and A. M. Duffield, Org. Mass Spectrom., 5, 157 (1971).
16. R. T. Aplin and Y. H. Yones, Chem. Commun., 794 (1966).

REACTION OF METHYL-SUBSTITUTED PYRYLIUM SALTS WITH TERTIARY AMINES

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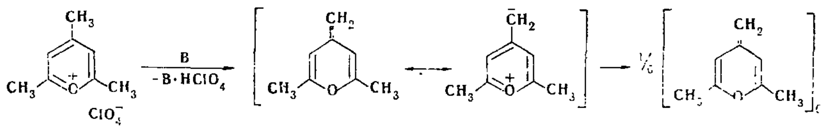
2,4,6-Trimethylpyrylium perchlorate reacts with heterocyclic compounds containing a pyridine nitrogen atom and having basicities higher than 9 pK_a units (in acetonitrile) through a step involving the formation of a methylenepyran. 4-Methyl-2,6-diphenyl- and 2-methyl-4,6-diphenylpyrylium perchlorates react with benzimidazole to give 1,2-ethanediylidenebispyrans. Methyl-substituted pyrylium salts react with 2,6-diphenylpyrylium and flavylium perchlorates in the presence of benzimidazole to give methylidynecyanines and with acetic anhydride to give trimethylidynecyanines.

We have observed that triethylamine and many heterocyclic compounds (Table 1) containing a tertiary (pyridine) nitrogen atom split out of a molecule of perchloric acid from 2,4,6-trimethylpyrylium perchlorate (I) to give 2,6-dimethyl-4-methylenepyran (II), which, as previously shown in [1], is subsequently converted to hexamer III:



I II III

It follows from Table 1 that a decrease in the basicity of the amine leads to a decrease in the yield of hexamer III, and bases with pK_a values below 9 do not split out perchloric acid from salt I. The basicity constant of methylenepyran II evidently should range from 8 to 9 pK_a units, and weaker bases therefore cannot remove a proton from the conjugate acid I.

It is known [4, 5] that 4-methylflavylium perchlorate (IV), under the influence of pyridine, is converted to methylene base V, which reacts with the starting salt to give 1,2-ethanediylidenebis(4-H-flavene) (VI), prob-

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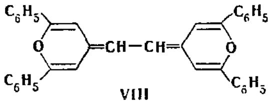
TABLE 1. Yields of Hexamer III as a Function of the Basicity of the Amine

Tertiary amine	pK_a in acetonitrile (25 ± 0.1°C)	Yield of crude hexamer III, %
Triethylamine	18.46^2	Quantitative
4,5,6,7-Tetrahydrobenzimidazole	16.21^3	The same
2-Methylimidazole	16.09	" "
Imidazole	14.99^3	" "
Benzimidazole	13.25^3	91
3-Methylnaphth[1,2-d]imidazole	12.83	87
Pyridine	12.33^2	81
Phenanthr[9,10-d]imidazole	12.31^3	80
Quinoline	11.93	63
3-Methylpyrazole	10.29	37
Pyrazole	9.21^3	8
Benzothiazole	7.84^3	-

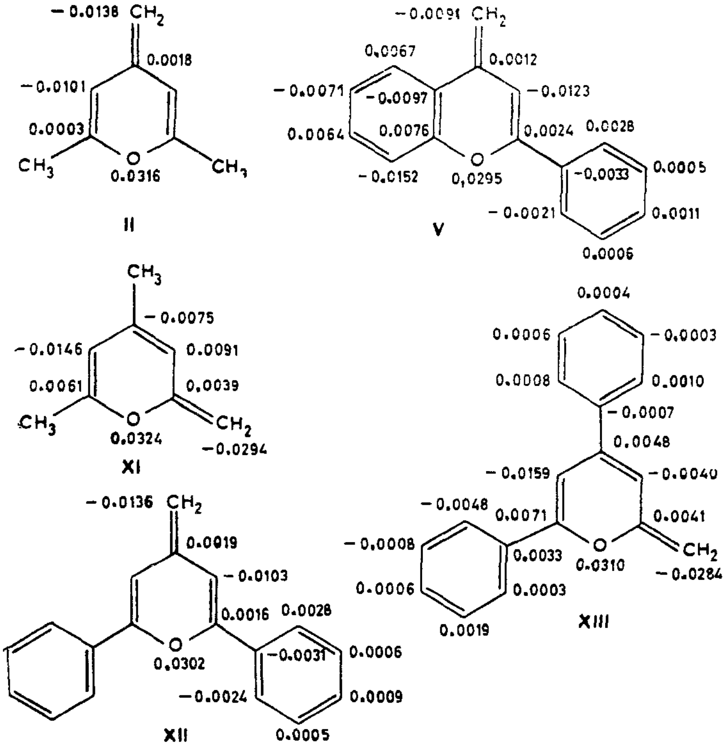
ably via a radical mechanism. Since several structures can be proposed for hexamer III, it seemed of interest to study the reaction of benzimidazole with monomethyl-substituted pyrylium salts.

It was found that 2,6-diphenyl-4-methylpyrylium perchlorate (VII) on refluxing with benzimidazole in nitromethane forms a rather unstable red compound, to which one can assign structure VIII:



The PMR spectrum of VIII contains a multiplet at 6.60-7.20 ppm (24 H) and a singlet at 2.34 (2 H). The molecular weight of this compound corresponds to the value calculated for dimer VIII. A similar but less-stable violet-colored dimer IX is formed from 2-methyl-4,6-diphenylpyrylium perchlorate (X).

The explanation of the differences in the stabilities can be made on the basis of calculations of the electron density distribution in the methylene-pyran molecules. For some of the methylenepyrans examined by us these calculations were made by the Hückel method [6]. The results of quantum-mechanical calculations by the Pariser—Parr—Pople (PPP) method within the Dewar σ-π parametrization are presented below.*



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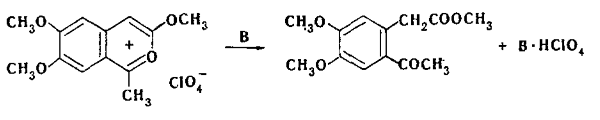
*The authors thank B. Ya. Simkin and L. N. Talanova for performing the calculations.

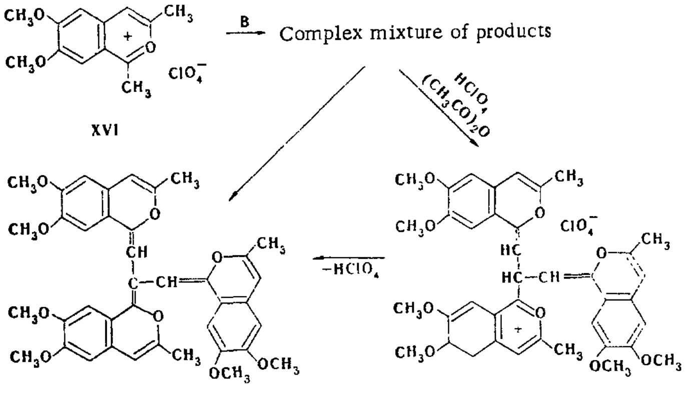
It is evident from the molecular diagrams that the surplus electron density in the methylenepyran molecules is concentrated on the carbon atom of the methylene group, thereby ensuring its considerable activity. The higher this electron density, the lower the stability of the resulting dimer (IX). It is interesting to note that the calculated electron density on the methylene groups of II and XII are practically identical, and this indicates the absence of conjugation between the pyran and phenyl rings. The same can also be stated regarding methylenepyrans XI and XIII.

The behavior of methyl-substituted 2-benzopyrylium salts with nitrogen heterocycles differs from the behavior of salts I, IV, VII, and X. Thus 1-methyl-3,6,7-trimethoxy-2-benzopyrylium perchlorate (XIV) on refluxing with benzimidazole is converted to keto ester XV rather than to a methylenepyran:



XIV XV

A complex mixture of the products of opening of the pyrylium ring and products of conversion of the methylenepyran is formed in the reaction of 1,3-dimethyl-6,7-dimethoxy-2-benzopyrylium perchlorate (XVI)* with benzimidazole, as attested to by the elementary analysis (it is closer to a methylenepyran) and the IR spectrum (it contains carbonyl absorption at 1710 cm^{-1}). A compound to which one can assign trimer structure XVII on the basis of the results of elementary analysis and the IR spectrum (carbonyl absorption is absent) can be isolated in low yield from the reaction mixture:



XVI

XVII

XVIII

Trimer XVII is also formed from perchlorate XVIII, obtained by treatment of a complex mixture of products of reaction of concentrated $HClO_4$ in acetic anhydride. It must be noted, as one should have expected, that in the reaction of perchlorate XVI with sodium carbonate the product is not a methylenepyran but rather 1-(3,4-dimethoxy-6-phenylacetyl)-2-propanone, which is recyclized to salt XVI on treatment with $HClO_4$ in acetic anhydride.

The presence in the reaction mixture of the starting pyrylium salt with an active methyl group made it impossible to carry out the reaction of the methylenepyrans with 2,6-di-tert-butylphenol, phenyl azide, and

TABLE 2. Pyrylocyanines

Compound	mp, °C (from nitromethane	Empirical formula	Found, %			Calculated, %			Yield, %
			C	H	Cl	C	H	Cl	
XXI	267—269[a]	$C_{33}H_{23}ClO_6$	72,4	4,5	6,4	71,9	4,2	6,4	25
XXIII	306—308[b]	$C_{47}H_{33}ClO_7$	75,5	4,8	5,2	75,8	4,5	4,8	9
XXV	275—276[c]	$C_{33}H_{23}ClO_6$	72,3	4,5	6,2	71,9	4,2	6,4	37
XXVI	284[d]	$C_{35}H_{25}ClO_6$	72,7	4,6	6,0	72,9	4,4	6,1	23
XXVII	249—251[b]	$C_{35}H_{25}ClO_6$	72,5	4,6	6,4	72,9	4,4	6,1	28
XXIV	306—307	$C_{38}H_{29}ClO_6$	73,6	5,1	5,7	74,0	4,7	5,7	20
XXVIII	234—236	$C_{38}H_{29}ClO_6$	73,5	4,9	5,6	74,0	4,7	5,7	14

[a] According to [8], this compound has mp 280-281°.
[b] Recrystallized from glacial acetic acid.
[c] According to [8], this compound has mp 294-295°.
[d] According to [9], this compound has mp 310-311°.

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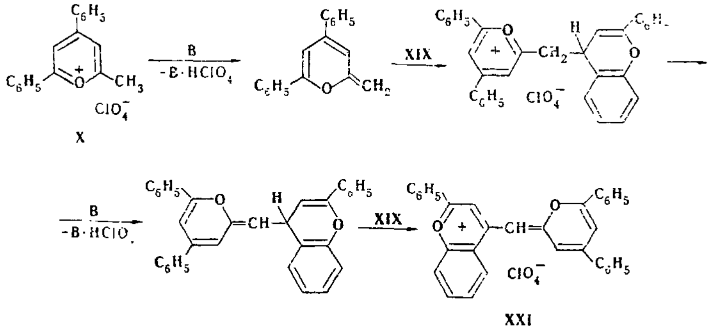
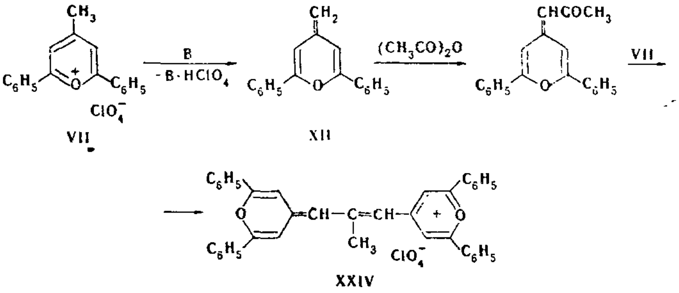
*Only the methyl group in the 1 position is active in this salt [7].

maleic anhydride. The reactions, as usual, proceeded with the formation of dimers. The primary reaction of methylenepyrans was observed with γ-unsubstituted pyrylium salts. One such reaction for flavylium (XIX) and X perchlorate in pyridine was previously described in [8]. We studied the reaction of methylenepyrans XII and XIII with equimolar amounts of 2,6-diphenylpyrylium (XX) and XIX perchlorate. This transformation evidently proceeds via the following mechanism:



Some of the deeply colored monomethylidynecyanines isolated in this way have been previously obtained by condensation of pyrylium salts containing methyl groups with α- and γ-pyrones. A dark-violet product of reaction at two methyl groups (XXIII) was obtained with 2,4-dimethyl-6-phenylpyrylium perchlorate (XXII). We were unable to isolate products of reaction at three methyl groups in the case of perchlorate I. Moreover, we found that methylenepyrans XII and XIII are acylated by acetic anhydride, and the resulting acyl derivatives react with the starting salts to give trimethylidynecyanines, for example:



This reaction does not occur in the absence of base.

EXPERIMENTAL

The pK_a values were measured potentiometrically in acetonitrile at 25 ± 0.1°. The IR spectra of mineral-oil suspensions of the compounds were recorded with a UR-20 spectrometer. The PMR spectrum in CCl_4 was recorded with a BS 487 C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The molecular weight was determined cryoscopically in benzene.

The reaction of perchlorate I with bases was carried in ethanol by the method described in [1].

Reaction of Perchlorate VII with Benzimidazole. This reaction was carried out with equimolar amounts of reagents for 15 min in refluxing nitromethane. The solvent was then removed by vacuum distillation, and red VIII was extracted from the residue with ether (the yield of crude product was 57%). The ether was evaporated, and the product was purified by chromatography with a column filled with Al_2O_3 (elution with benzene) to give VIII with mp 81-83° in 20% yield. Found: C 87.8; H 5.6%; M 460 ± 10. $C_{36}H_{26}O_2$. Calculated: C 88.1; H 5.3%; M 490.

Reaction of Perchlorate XVI with Benzimidazole. This reaction was carried out in refluxing ethanol for 1 h. The hot mixture was filtered to give 10% of XVII with mp 231°. Found: C 72.3; H 6.3%. $C_{39}H_{38}O_9$. Calculated: C 72.0; H 5.9%. Ether was added to the filtrate to precipitate benzimidazolium perchlorate, the ether solution was evaporated and extracted with benzene, and the benzene extract was worked up to give a colorless oil, which was found to be a complex mixture. This mixture was dissolved in acetic anhydride, and the solution was cooled and treated dropwise with 70% $HClO_4$. The mixture was then allowed to stand, during which yellow perchlorate XVIII, with mp 205-206° (dec., from acetic acid), crystallized. Found: C 62.9; H 5.5; Cl 5.1%. $C_{39}H_{39}ClO_{13}$. Calculated: C 63.2; H 5.3; Cl 4.8%. IR spectrum, cm^{-1}: 1635, 1600, 1540, 1500, and 1085. Compound XVII was formed when perchlorate XVIII was refluxed in ethanol.

Reaction of Methylenepyran XII with Perchlorate XIX. An equimolar amount of perchlorate XIX was added to a hot mixture of equimolar amounts of perchlorate VII and benzimidazole in nitromethane, and the mixture was refluxed for 1 h. It was then cooled, and the dark-violet precipitate of 4-[(2,6-diphenyl-4H-pyran-4-ylidene)methyl]-2-phenylbenzopyrylium perchlorate (XXV), with mp 275-276° (from nitromethane), was removed by filtration. The yield was 37%.

Reaction of Perchlorate XX with the Methylenepyran Obtained from Perchlorate XXII. This reaction was carried out by the method presented above, except that the solvent was glacial acetic acid. The hot reaction mixture was filtered to give a shiny dark-violet precipitate of 2,4-di[(2,6-diphenyl-4H-pyran-4-ylidene)-methyl]-6-phenylpyrylium perchlorate (XXIII). A mixture of red products of reaction at one methyl group precipitated when the filtrate was cooled.

A similar procedure was used to obtain perchlorates XXI, 4-[(2,6-diphenyl-4H-pyran-4-ylidene)methyl]-2,6-diphenylpyrylium perchlorate (XXVI), and 4-[(4,6-diphenyl-2H-pyran-2-ylidene)methyl]-2,6-diphenylpyrylium perchlorate (XXVII). Data on all the monomethylidynecyanines are presented in Table 2.

Reaction of Methylenepyran XII with Acetic Anhydride. A mixture of 0.70 g (2.0 mmole) of perchlorate VII and 0.12 g (1.0 mmole) of benzimidazole was refluxed for 20 min in 10 ml of acetic anhydride, and the resulting greenish-blue precipitate of trimethylidynecyanine XXIV was removed by filtration.

The reaction of methylenepyran XIII with acetic anhydride proceeded similarly to give 2-{1-[2-methyl-3-(4,6-diphenyl-2H-pyran-2-ylidene)-1-propenyl]}-4,6-diphenylpyrylium perchlorate (XXVIII). Data on the trimethylidynecyanines obtained in this research are presented in Table 2.

LITERATURE CITED

1. É. A. Zvezdina, M. P. Zhdanova, V. A. Bren', and G. N. Dorofeenko, Khim. Geterotsikl. Soedin., No. 11, 1461 (1974).
2. J. F. Coetzee and G. R. Padmanabhan, J. Amer. Chem. Soc., 87, 5005 (1965).
3. V. I. Minkin, V. A. Bren', A. D. Garnovskii, and R. I. Nikitina, Khim. Geterotsilk. Soedin., No. 4, 552 (1972).
4. J. A. Van Allan and G. A. Reynolds, Tetrahedron Lett., 25, 2047 (1969).
5. G. A. Reynolds and J. A. Van Allan, J. Heterocycl. Chem., 6, No. 5, 623 (1969).
6. C. C. Rentia, A. T. Balaban, and Z. Simon, Rev. Roum. Chim., 11, 1193 (1966).
7. G. N. Dorofeenko, E. I. Sadekova, and V. M. Goncharova, Khim. Geterotsikl. Soedin., No. 10, 1308 (1970).
8. J. A. Van Allan and G. A. Reynolds, J. Heterocycl. Chem., 9, No. 3, 669 (1972).
9. J. A. Van Allan, G. A. Reynolds, and D. P. Maier, J. Org. Chem., 33, No. 12 (1968).