16. H. H. Hodson and R. R. Davies, J. Chem. Soc., 806 (1939).
17. H. H. Hodson and R. R. Davies, J. Chem. Soc., 101 (1939).
18. S. A. Safarov and M. A. Proskurin, Dokl. Akad. Nauk Azerb. SSR, 17, No. 10, 837 (1961).
19. V. N. Belov, L. A. Kheifits, and S. I. Virezub, Reactions and Methods of Investigation of Organic Compounds [in Russian], Book 10, Goskhimizdat, Moscow (1961), p. 7.
20. L. A. Badovskaya, V. G. Kul'nevich, G. F. Muzychenko, and T. Ya. Kaklyugina, in: Theory and Practice of Liquid-Phase Oxidations [in Russian], Nauka, Moscow (1974), p. 283.
21. L. V. Tsygankova, L. A. Badovskaya, and V. G. Kul'nevich, USSR Inventor's Certificate No. 348555; Byull. Izobr., No. 25, 90 (1972).
22. L. A. Badovskaya, G. F. Muzychenko, S. V. Abramyants, V. G. Kul'nevich, and V. M. Latashko, USSR Inventor's Certificate No. 470516; Byull. Izobr., No. 18, 53 (1975).
23. L. A. Badovskaya, V. G. Kul'nevich, and V. M. Latashko, Prospects in the Utilization of the Products and Waste Products of the Furfural Industry for the Synthesis of Monomers and Physiologically Active Substances. Review. Series IV [in Russian], ONTI Glavmikrobioprom., Moscow (1976).
24. K. Nakanishi, Infrared Spectroscopy, Practical, Holden-Day, San Francisco (1962).

SYNTHESIS OF γ-PYRONES, FLAVONES, AND ISOCOUMARINS BY DESTRUCTIVE OXIDATION OF PYRANYLIDENES AND THEIR BENZO ANALOGS

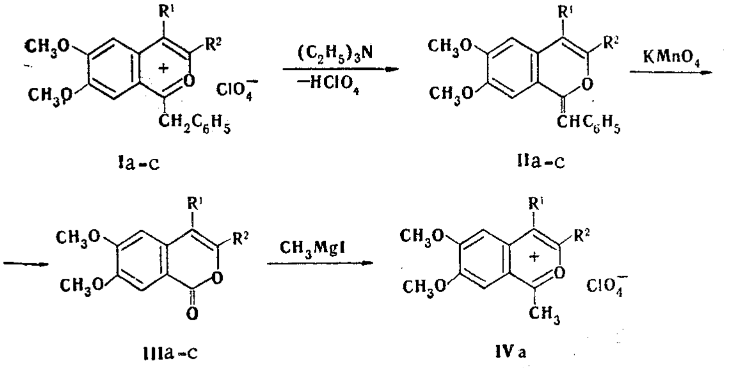
E. V. Kuznetsov, D. V. Pruchkin,
A. I. Pyshchev, and G. N. Dorofeenko

UDC 547.812.816.07:542.943

Preparative methods for the synthesis of isocoumarins, γ-pyrones, and flavones by destructive oxidation of methylenepyrans with potassium permanganate in acetone were developed.

A method for the conversion of carbonyl-containing pyran derivatives to pyrylium salts has been worked out [1] and is widely used in synthetic practice. There is virtually no method for the reverse transition from pyrylium salts or their derivatives. Thus various attempts to accomplish this conversion by nucleophilic reaction of pyrylium salts with hydroxide ion have been unsuccessful because of the instability of the resulting pyranols [2].

In the present communication we describe the synthesis of some pyrones and their benzo analogs by oxidative destruction of pyranylidenes, which are readily obtained from pyrylium salts.



I–IV a $R^1=R^2=C_6H_5$; b $R^1=H$, $R^2=3{,}4\text{-}(OCH_3)_2C_6H_3$; c $R^1=H$, $R^2=4\text{-}OC_2H_5C_6H_4$

Thus $HClO_4$ is split out when 1-benzyl-2-benzopyrylium salts (I) are treated with triethylamine in an anhydrous medium to give stable bases — benzylideneisochromenes II. The

---

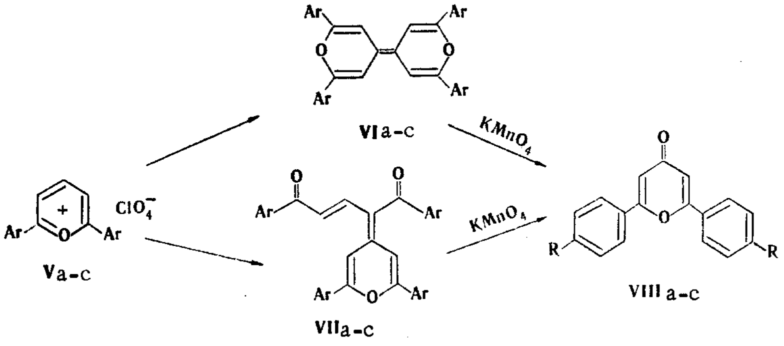
Rostov State University. Scientific-Research Institute of Physical and Organic Chemistry, Rostov-on-Don 344006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1320-1323, October, 1978. Original article submitted October 26, 1977.

0009-3122/78/1410-1067$07.50

TABLE 1. 1-Benzylidene-3-R^1-4-R^2-6,7-dimethoxyisochromenes

Compound	R^1	R^2	mp, °C	Found, %		Empirical formula	Calc., %		Yield, %
				C	H		C	H	
IIa	C_6H_5	C_6H_5	172	83,1	5,0	$C_{30}H_{24}O_3$	83,4	5,1	93
IIb	H	3,4-$(OCH_3)_2C_6H_3$	134	74,7	5,6	$C_{26}H_{24}O_5$	74,9	5,8	79
IIc	H	4-$OC_2H_5C_6H_4$	110	78,3	6,1	$C_{26}H_{24}O_4$	78,0	6,0	92

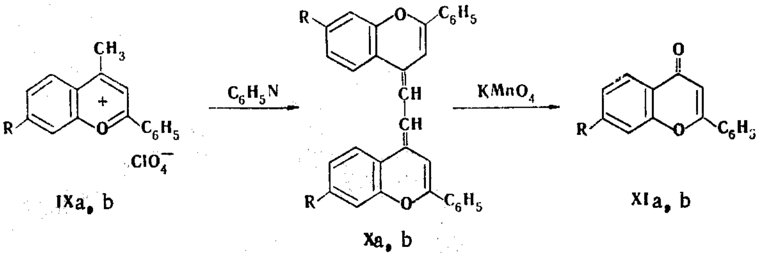
molecules of II contain a double bond, the oxidation of which to a carbonyl group with potassium permanganate in acetone gives isocoumarins III in almost quantitative yields.



V-VIII a R=H; b R=CH_3; c R=OCH_3

Bispyranylidenes VI or pyranylidenepentenediones VII, which are also readily formed from 2,6-diarylpyrylium salts, were used as the starting compounds for the preparation of γ-pyrones VIII.

Flavones XI were obtained by oxidation of ethanediylidenebisflavenes — products of conversion of 4-methylflavylium salts under the influence of pyridine.



IX-XI a R=OCH_3; b R=CH_3

The yields of the γ-pyrone obtained by oxidation of intermediates VI were 18-45%, the yields of γ-pyrones obtained through VII were 26-40%, and the yields of the flavones were 26-40%.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer.

1-Benzylidene-3,4-diphenyl-6,7-dimethoxyisochromene (IIa). A 2-ml sample of dry triethylamine was added to a suspension of 0.53 g (1 mmole) of 1-benzyl-3,4-diphenyl-6,7-dimethoxy-2-benzopyrylium perchlorate (Ia) [3] in 25 ml of absolute toluene, and the mixture was refluxed for 30 min until the suspension dissolved completely. The toluene layer was then decanted from the oily precipitate of triethylamine perchlorate and subjected to evaporation to give 0.4 g (93%) of yellow crystals with mp 172°C (from alcohol). IR spectrum: 1640, 1600, and 1520 cm^{-1}.

Benzylideneisochromenes IIb, c were similarly obtained (Table 1).

3,4-Diphenyl-6,7-dimethoxyisocoumarin (IIIa). A saturated solution of potassium permanganate in acetone was added to 0.43 g (1 mmole) of 1-benzylidene-3,4-diphenyl-6,7-dimethoxyisochromene (IIa). The odor of benzaldehyde was detected during the reaction, and MnO_2 precipitated. A solution of potassium permanganate was added in the course of 20-30 min until the mixture took on a persistent crimson coloration and the odor of benzaldehyde

TABLE 2. 3-R^1-4-R^2-6,7-Dimethoxyisocoumarins

Compound	R^1	R^2	mp, °C	Found, %		Emprical formula	Calc., %		Yield, %
				C	H		C	H	
IIIa	C_6H_5	C_6H_5	197	77,2	5,1	$C_{23}H_{18}O_4$	77,1	5,0	90
IIIb	H	3,4-$(OCH_3)_2C_6H_3$	189	67,1	5,0	$C_{19}H_{18}O_6$	66,7	5,3	87
IIIc	H	4-$OC_2H_5C_6H_4$	142	69,8	5,6	$C_{19}H_{18}O_5$	70,0	5,5	94

vanished. The acetone was removed by vacuum evaporation, and the organic substances were extracted from the dry residue with chloroform. The chloroform was removed from the extract by evaporation, and the residue was recrystallized from alcohol to give 0.32 g (90%) of colorless crystals with mp 197°C (from alcohol) (mp 197°C [4]). IR spectrum: 1719, 1603, and 1512 cm^{-1}.

Colorless crystals of isocoumarins IIIb, c were similarly obtained (Table 2).

1-Methyl-3,4-diphenyl-6,7-dimethoxy-2-benzopyrylium Perchlorate (IV). A suspension of 0.35 g (0.001 mole) of 3,4-diphenyl-6,7-dimethoxyisocoumarin (IIIa) in 100 ml of absolute ether containing 0.18 g (0.0011 mole) of methylmagnesium iodide was refluxed with shaking for 1 h in a flask equipped with an efficient reflux condenser sealed with a calcium chloride tube. The suspension was then poured into 100 ml of a 10% solution of NH_4Cl, the mixture was stirred, and the colorless organic precipitate was removed by filtration. The ether layer of the mother liquor was separated, dried over anhydrous $CaCl_2$, and evaporated to give another small amount of product, which was combined with the previously isolated substance. The product was dried and dissolved in 5 ml of acetic anhydride, and 10 drops of 70% $HClO_4$ were added gradually. After 15-20 min, the yellow salt was removed by filtration to give 0.37 g (81%) of a product with mp 239°C (mp 239°C [3]). IR spectrum: 1600, 1590, and 1520 cm^{-1}.

2,6-Diphenyl-γ-pyrone (VIIIa). 1) A 2.5-g sample of $KMnO_4$ was added to a suspension of 0.5 g of 2,2,6,6-tetraphenyl-4,4-bispyranylidene (VIa) [5] in 20 ml of acetone, and the mixture was shaken. After a few minutes, the mixture was warmed to 50-60°C and shaken for another 40 min. The acetone was removed by evaporation in vacuo at room temperature, and the 2,6-diphenyl-γ-pyrone was extracted from the dry residue with warm ether (five 30-ml portions). The ether was removed by evaporation to give light-yellow needles of 2,6-diphenyl-γ-pyrone with mp 140°C (from aqueous alcohol) (mp 139-140°C [6]) in 45% yield.

γ-Pyrones VIIIb (22%), with mp 178°C (from alcohol) (mp 180°C [7]), and VIIIc (20%) with mp 192°C (from methanol) (mp 190°C [8]), were similarly obtained.

2) The oxidation of 1,5,2,6-tetraphenylpyranylidenepentene-1,5-dione (VIIa) [9] and the isolation of 2,6-diphenyl-γ-pyrone (VIIIa) were carried out similarly, except that the ether extract was washed with aqueous $NaHCO_3$ solution to remove the benzoic acids that were formed as side products. The yields of pyrones were as follows: 40% VIIIa, 26% VIIIb, and 29% VIIIc. The IR spectra of the γ-pyrones contain characteristic absorption bands [7] at 1650-1660, 1610-1615, and 1500-1520 cm^{-1}.

7-Methoxyflavone (IXa). A 3-g sample of $KMnO_4$ was added to a suspension of 1 g of 4,4-(1,2-ethanediylidene)bis(4H-7-methoxyflavone) (Xa) [10] in 30 ml of acetone, and the mixture was shaken for a few minutes, during which warming of the mixture to 50-60°C was observed. Shaking was then continued for another 40 min, after which the acetone was removed by vacuum evaporation. The flavone was extracted from the dry residue with ether (four 60-ml portions). Removal of the ether by evaporation gave 0.3 g (30%) of colorless crystals with mp 110°C (from aqueous alcohol) (mp 111°C) [11]). IR spectrum: 1660, 1635, and 1380 cm^{-1}.

7-Methylflavone. This compound, with mp 126°C (from alcohol) (mp 123°C [12]), was similarly obtained as colorless crystals in 28% yield. IR spectrum: 1660, 1615, and 1380 cm^{-1}.

LITERATURE CITED

1. G. N. Dorofeenko, E. I. Sadekova, and E. V. Kuznetsov, The Preparative Chemistry of Pyrylium Salts [in Russian], Izd. RGU, Rostov-on-Don (1972).
2. W. D. Cotteril, C. J. France, R. Livingstone, and J. R. Atkinson, J. Chem. Soc., Perkin Trans. I, No. 6, 817 (1972).

3. E. V. Kuznetsov and G. N. Dorofeenko, Zh. Org. Khim., 6, 578 (1970).
4. E. V. Kuznetsov, D. V. Pruchkin, A. V. Bicherov, and G. N. Dorofeenko, Khim. Geterotsikl. Soedin., No. 12, 1575 (1974).
5. L. A. Polyakova, Author's Abstract of Master's Degree, Institute of Heteroorganic Compounds, Moscow (1973).
6. C. R. Hauser and T. M. Harris, J. Am. Chem. Soc., 80, 6360 (1958).
7. H. C. Smitherman and L. N. Ferguson, Tetrahedron, 24, 923 (1967).
8. A. Schönberg and M. Elkaschev, J. Am. Chem. Soc., 80, 6312 (1958).
9. A. I. Pyshchev, Author's Abstract of Master's Degree, Rostov State University, Rostov-on-Don (1977).
10. J. A. Van Allan and G. A. Reynolds, Tetrahedron Lett., 25, 2047 (1969).
11. G. N. Dorofeenko, V. V. Tkachenko, and V. V. Mezheritskii, Zh. Org. Khim., 12, 432 (1976).
12. F. D. Cramer and G. H. Elsching, Ber., 89, 12 (1956).

SYNTHESIS OF STYRYL-SUBSTITUTED 2-PHENYL- AND 1,2-DIPHENYLCYCLOPENTA[b]-CHROMENES

Yu. N. Porshnev, V. A. Churkina,
and V. V. Titov

UDC 547.816.07

A number of styryl derivatives that are capable of undergoing formylation and acylation at the side CH=CH group were obtained from 1,2-diphenyl-3-formyl- and 2-phenyl-1,3-diformylcyclopenta[b]chromene by means of the Wittig reaction. It was observed that the Wittig reaction is structurally selective for 2-phenyl-1,3-diformylcyclopenta[b]chromene; the reaction proceeds only at the aldehyde group in the 3 position. Sulfuration of 2-phenyl-1,3-distyrylcyclopenta[b]chromene with sulfur leads to the formation of a new system — benzo[2',3']thiepino[4',5':4,5]cyclopenta[b]chromene. A significant bathochromic effect of the styryl groups on the electronic spectra of the cyclopentachromenes was noted.

We have obtained a number of styryl-substituted pseudoazulenes (III-IX) from 1,2-diphenyl-3-formyl- and 2-phenyl-1,3-diformylcyclopenta[b]chromenes (I and II) by means of the Wittig reaction.

It was shown that aldehyde I reacts with cinnamylidenephosphorane to give the virtually individual trans isomer (V), whereas cis (III) and trans (IV) isomers are formed in 24 and 52% yields, respectively, with benzylidenephosphorane. The structures of cis and trans isomers III and IV are confirmed by the presence in the IR spectra of bands of out-of-plane deformation vibrations of the hydrogen atoms in disubstituted cis- and trans-ethylenes [1] at 730 and 965 cm^{-1}; the alternative bands were absent in each case. Bands with λ_{max} 542 and 570 nm, respectively, are present in the electronic spectra of cis and trans isomers III and IV; this can be explained by partial deviation of the cisoid styryl group from the plane of the cyclopentachromene ring. In addition, cis isomer III was converted quantitatively to the trans isomer by the action of catalytic amounts of iodine in analogy with the isomerization of cis-1-styrylazulene [2]. Compound IV is capable of undergoing electrophilic substitution at the side CH=CH group, i.e., in the α position of the styryl residue farthest from the cyclopentachromene ring and simultaneously conjugated with it. A hypsochromic shift of 30 nm (40 nm in the case of XI) as compared with the spectrum of IV is observed in the spectrum of aldehyde X (as in the case of trifluoroacetyl derivative XI) (see Table 1).

The fact that stilbene does not undergo Vilsmeier formylation and the fact that approximately the same hypsochromic effect is also characteristic for β-(1-azulenyl)acrolein [3,

---

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1324-1328, October, 1978. Original article submitted November 24, 1976; revision submitted February 28, 1978.

0009-3122/78/1410-1070$07.50