EXPERIMENTAL

The IR spectra of thin layers or mineral-oil suspensions of the compounds were recorded with a UR-10 spectrometer. The PMR spectra were recorded with a Varian spectrometer (100 MHz) with tetramethylsilane as the external standard.

Acetylenic δ-keto alcohols IIe-g, k and formyl alcohol acetals Ia-c were obtained by the method in [1]; γ-keto alcohols IIh-j were obtained by the method in [6].

γ-Dihydropyrones (V) and β-Dihydrofuranones (VII). A solution of 0.05 mole of the appropriate acetal Ia-d or keto alcohol IIe-k was added to a solution of 12 ml of concentrated H_2SO_4 in 50 ml of ethanol and 50 ml of water, and the mixture was refluxed for 8 h. The ethanol was removed by distillation, the residue was extracted with ether, and the ether layer was washed with sodium carbonate solution and dried with $MgSO_4$. The solvent was removed by distillation, and the residue was vacuum fractionated. The physical constants of V and VII are presented in Table 1.

1,5-Diphenyl-4-pentene-1,3-dione (VIk). This compound, with mp 106-107°, was obtained in 89% yield by a similar method from 0.01 mole of 1,5-diphenyl-5-hydroxy-2-pentyn-1-one (IIk). Found: C 81.6; H 5.7%. $C_{17}H_{14}O_2$. Calculated: C 81.6; H 5.6%. IR spectrum, cm^{-1}: 1640 (C=O), 953, 970 (C=C).

LITERATURE CITED

1. L. I. Vereshchagin, L. D. Gavrilov, E. I. Tikhonova, and L. P. Vologdina, Zh. Organ. Khim., 9, 247 (1973).
2. C. Massyn, R. Pastor, and A. Cambon, Bull. Soc. Chim. France, 975 (1974).
3. T. K. Mamedov, N. E. Kolobova, K. N. Anisimov, and A. N. Nesmeyanov, Zh. Organ. Khim., 3, 1349 (1967).
4. R. Hansbrouck and A. Anderson, J. Org. Chem., 38, 2103 (1973).
5. I. N. Nazarov, Izv. Akad. Nauk SSSR, Ser. Khim., 107 (1948).
6. L. I. Vereshchagin, C. R. Gainulina, and L. P. Kirillova, in: Zh. Organ. Khim., "Biologically Active Compounds," 154 (1968).
7. E. Kosower and T. Sorensen, J. Org. Chem., 28, 687 (1963).
8. L. I. Vereshchagin, L. D. Gavrilov, E. I. Titova, and L. P. Vologdina, Zh. Organ. Khim., 9, 276 (1973).

CHEMISTRY OF HETEROANALOGS OF ISOFLAVONES

V.* REACTION OF FURAN AND BENZOFURAN ANALOGS OF ISOFLAVONES WITH ALKALIS AND HYDRAZINE

V. T. Khilya, L. G. Grishko, and F. S. Babichev

UDC 547.814.5'7?8.1.778.2.3

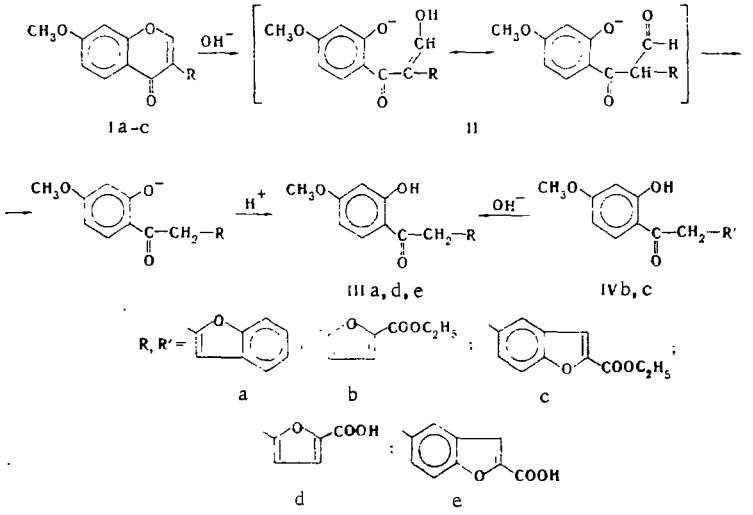
It is shown that treatment of 3-hetarylchromones with alkalis and hydrazine hydrate leads to opening of the pyrone ring and subsequent conversion of the intermediate to α-hetaryl-2-hydroxyacetophenones and 2-hydroxyphenylpyrazole derivatives.

The reaction of chromones with alkalis can be used to establish the structure of compounds of this series [2]. We have studied the effect of alkalis on furan and benzofuran analogs [3] of isoflavones (Ia-c). It was es-

*See [1] for communication IV.

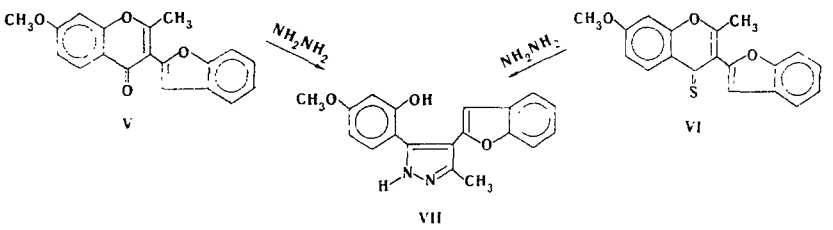
T. G. Shevchenko Kiev State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1474-1476, November, 1976. Original article submitted November 20, 1975.

tablished that when chromone Ia is heated with a fourfold excess of a 5% solution of sodium hydroxide in aqueous alcohol, the pyrone ring is opened to give benzofurylacetophenone IIIa, identical to the product of methylation of α-(2-benzofuryl)-2,4-dihydroxyacetophenone [4]. In addition to cleavage of the pyrone ring, in the case of 7-methoxychromones Ib, c we observed saponification of the ester groups to give IIId, e. The same substances were obtained by alternative synthesis from the corresponding 4-methoxyacetophenones IVb, c. 4-Methoxy-2-hydroxyacetophenones III and IV give a positive reaction with a solution of ferric chloride. The 2-OH group appears as a singlet at 12.22-12.45 ppm [dimethyl sulfoxide (DMSO)] in the PMR spectra of the products of alkaline destruction of chromones Ia-c.

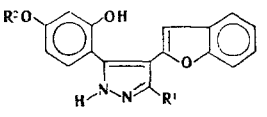


Compound IIIa is reconverted to chromone Ia on reaction with methyl formate or ethyl orthoformate by the method in [3]; this is an additional confirmation of the structure of the chromones mentioned above.

It is known that chromones [5, 6] and 4-thioxochromones [7, 8] containing methyl, phenyl, or hydroxyl groups in the 3-position of the chromone ring undergo opening of the pyrone ring with subsequent closing of the intermediate to give a pyrazole derivative. Only those chromones that do not contain substituents in the 3 position form hydrazones.



We have shown that both chromone V and thioxochromone VI react with hydrazine hydrate to give the same compound, which is evidently an o-hydroxyphenylpyrazole derivative (VII): It gives a blue-green coloration with a solution of ferric chloride and is readily soluble in warm 2 N sodium hydroxide solution; this constitutes evidence for the development of a phenolic hydroxyl group in the molecule. Products with similar structures (VIII and IX) are also formed by the action of hydrazine hydrate on other 3-(2-benzofuryl)chromones [3, 9]. The IR spectra of VII-IX contain absorption bands of stretching vibrations of the pyrazole ring at 1520-1535 cm^{-1}, of stretching vibrations of the C=N bond at 1620-1630 cm^{-1}, and of OH and NH stretching vibrations at 3245-3400 cm^{-1}.



VIII, IX

VIII $R^1=CH_3$, $R^2=H$; IX $R^1=H$, $R^2=CH_3$

EXPERIMENTAL

The UV spectra of $5 \cdot 10^{-5}$ M solutions of the compounds in ethanol were recorded with an SF-4A spectrophotometer. The IR spectra of KBr pellets of the compounds were recorded with a UR-10 spectrometer.

TABLE 1. Physical Characteristics of VII-IX

Compound	mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %
			C	H	N	C	H	N	
VII	166	$C_{19}H_{16}N_2O_3$	70,9	4.9	8,5	71,2	5,0	8,7	90
VIII	208,5	$C_{18}H_{14}N_2O_3$	70,2	4.7	8,9	70,6	4,6	9,1	83
IX	190	$C_{18}H_{14}N_2O_3$	70,0	4.6	8,9	70,6	4,6	9,1	95

The PMR spectra of DMSO solutions of the compounds (0.25 mole) were recorded with a ZKR-60 spectrometer (60 MHz) at 25° with tetramethylsilane as the internal standard.

α-(5-Carboxy-2-furyl)-2-hydroxy-4-methoxyacetophenone (IIId). A solution of 0.3 g (1 mmole) of chromone Ib in 15 ml of alcohol and 10 ml of water was refluxed for 30 min with 3.2 ml (4 mmole) of a 5% sodium hydroxide solution, after which the mixture was diluted with 50 ml of water and acidified to pH 5 with dilute hydrochloric acid. The resulting precipitate was removed by filtration and purified to give 0.2 g (80%) of needles with mp 186° (from aqueous alcohol). Found: C 60.9; H 4.5%. $C_{14}H_{12}O_6$. Calculated: C 60.9; H 4.4%.

Compound IIId was obtained under similar conditions from 0.29 g (1 mmole) of acetophenone IVb and 1.6 ml (2 mmole) of 5% sodium hydroxide. Purification gave 0.25 g (90%) of a product with mp 186°.

α-(2-Carboxy-5-benzofuryl)-2-hydroxy-4-methoxyacetophenone (IIIe). This compound was similarly obtained in 72% yield from chromone Ic and in 90% yield from acetophenone IVc [3]. The reaction time was 30 min, and the product had mp 223.5° (from aqueous alcohol). Found: C 65.9; H 4.5%. $C_{18}H_{14}O_6$. Calculated: C 66.3; H 4.3%.

2-Methyl-3-(2-benzofuryl)-4-thioxo-7-methoxychromone (VI). A finely triturated mixture of 1 mmole of chromone [9] and 0.6 mmole of phosphorus pentasulfide in 6 ml of absolute pyridine was heated at 100° for 1 h, after which it was added to 50 ml of water. The solid material was removed by filtration and washed thoroughly on the filter with water. Purification gave 0.25 g (78%) of a product with mp 233° (from n-butanol). IR spectrum, cm^{-1}: 1630 ($\nu_{C=S}$) and 1587 (chromone $\nu_{C=C}$). UV spectrum, λ_{max}, nm (log ε): 285 (4.40), 375 (4.46). Found: S 10.0%. $C_{19}H_{14}O_3S$. Calculated: S 9.9%.

4-Hetaryl-5(3)-(2-hydroxyphenyl)pyrazoles (VII-IX). A total of 6 ml (12 mmole) of a 2 N alcohol solution of hydrazine hydrate was added to a hot solution of 1 mmole of 3-hetarylchromone [3, 9] or thioxochromone VI in the minimum volume of alcohol. After 5-10 min, the reaction mixture was poured into 100-120 ml of water, and the resulting precipitate was removed by filtration and crystallized from alcohol to give colorless needles, the characteristics of which are presented in Table 1.

LITERATURE CITED

1. V. P. Khilya, L. G. Grishko, and T. I. Zhul', Khim. Geterotsikl. Soedin., No. 8, 1108 (1976).
2. K. Venkataraman, in: The Chemistry of Flavonoid Compounds, edited by T. A. Geissman, Oxford–London–New York–Paris (1962), p. 94.
3. B. Szabo, L. G. Grishko, S. Borbei, and V. P. Khilya, Khim. Geterotsikl. Soedin., No. 2, 174 (1975).
4. M. Yu. Kornilov, V. P. Khilya, and L. G. Grishko, Zh. Organ. Khim., 9, 2568 (1973).
5. W. Baker, and V. S. Butt, J. Chem. Soc., 2142 (1949).
6. J. S. P. Schwarz, A. J. Cohen, W. D. Ollis, E. A. Kaczka, and L. M. Yackman, Tetrahedron, 20, 1317 (1964).
7. W. Baker, J. B. Harborne, and W. D. Ollis, J. Chem. Soc., 1303 (1952).
8. W. Baker, G. G. Harke, and J. B. Harborne, J. Chem. Soc., 998 (1954).
9. V. I. Khilya, L. G. Grishko, and N. V. Sukharenko, Zh. Organ. Khim., 8, 1085 (1972).