1660, 1630, 1590, 1500, 1260, and 1085 cm^{-1}. Found: C 55.9; H 4.9; N 2.8; Cl 7.2%. $C_{23}H_{24}NClO_9$. Calculated: C 55.9; H 4.9; N 2.8; Cl 7.2%.

8-Methyl-2,3,10,11-tetramethoxy-6-acetoxydibenzo[*a*,g]quinolizinium Perchlorate (VIa). A 0.5-g (0.001 mole) sample of salt Va was refluxed for 10 min in 3 ml of acetic anhydride, during which a precipitate formed. The mixture was cooled, and the precipitate was removed by filtration, washed with ether, and dried to give 0.43 g (88%) of orange-red crystals with mp 248 deg C (from acetic acid). IR spectrum: 1785, 1600, 1545, 1500, and 1080 cm^{-1}. Found: C 55.4; H 4.5; N 2.7; Cl 6.8%. $C_{24}H_{24}NClO_{10}$. Calculated: C 55.2; H 4.6; N 2.7; Cl 6.6%.

8-Ethyl-2,3,10,11-tetramethoxy-6-acetoxydibenzo[*a*,g]quinolizinium Perchlorate (VIb). This compound, with mp 260-262 deg C (from acetic acid), was similarly obtained in 85% yield from salt Vb. IR spectrum: 1785, 1595, 1540, 1490, and 1090 cm^{-1}. Found: C 56.9; H 4.6; N 2.7; Cl 6.9%. $C_{25}H_{26}NClO_{10}$. Calculated: C 56.7; H 4.8; N 2.6; Cl 6.7%.

LITERATURE CITED

1. E. V. Kuznetsov, D. V. Pruchkin, and G. N Dorofeenko, Khim. Geterotsikl. Soedin., No. 11, 1479 (1977).
2. K. Y. Zee-Cheng and C. C. Cheng, J. Heterocycl. Chem., 10, 85 (1973).
3. C. K. Bradsher and N. L. Dutta, J. Org. Chem., 26, 2231 (1961).
4. I. Ninomiya and T. Naito, Chem. Commun., 137 (1973).
5. T. Kametani, Tetrahedron, 29, 73 (1973).
6. S. F. Dyke and E. P. Tiley, Tetrahedron, 31, 561 (1975).
7. M. Shamma, Tetrahedron Lett., 1415 (1976).
8. G. N. Dorofeenko and V. G. Korobkova, Khim. Geterotsikl. Soedin., No. 12, 1601 (1971).
9. J. M. Elliot and S. L. Evans, J. Org. Chem., 38, 3425 (1973).

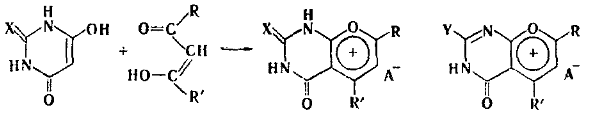
PYRYLIA[2,3-d]PYRIMIDINE SALTS

V. A. Chuiguk and N. N. Vlasova

UDC 547.859'816'83:542.953

The condensation of 2-amino- and 2-methylthio-4,6-dihydroxypyrimidines and barbituric and thiobarbituric acids with β-diketones in strong acids leads to pyrylia[2,3-d]pyrimidine salts, which on treatment with ammonia or aniline are converted to pyrido[2,3-d]pyrimidines or to 8-phenylpyrido[2,3-d]pyrimidinium salts, respectively.

The reaction of 4-hydroxypyrimidines that have electron-donor substituents in the 2 and 6 positions with β-keto acids and malonic acids and their derivatives leads to pyrano[2,3-d]pyrimidinones [1, 2]. In the present research we studied the condensation of 2-amino- and 2-methylthio-4,6-dihydroxypyrimidines and barbituric and thiobarbituric acids with β-diketones in strong acids. As a result we obtained the previously unknown pyrylia[2,3-d]pyrimidine salts (I and II). The latter, which have a methyl substituent in the pyrylium ring, form blue polymethine dyes when they are heated in acetic anhydride with p-dimethylaminobenzaldehyde or ethyl orthoformate.



I II

X = O, S; R, R' = CH_3, C_6H_5; A = ClO_4^-, $H_2PO_4^-$, CF_3COO^-; Y = NH_2, SCH_3

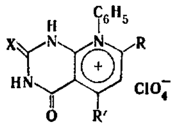
Compounds with methyl groups in the 5 and 7 positions initially react with p-dimethylaminobenzaldehyde to give a dye involving the methyl group in the 5 position; this was proved by the PMR spectra, in which the signal of the unchanged methyl group in the 7 position (2.53 ppm) is observed. The assignment of the signals of the

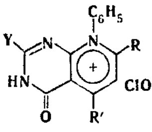
---

T. G. Shevchenko Kiev State University, Kiev 252017. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1484-1486, November, 1977. Original article submitted January 25, 1977.

methyl groups was made on the basis of analysis of the PMR spectra of a number of I and II with different substituents. Thus it is natural to assume that the phenyl group in the 5 position of I and II will give a singlet signal because of its deflection from the plane of the molecule by the carbonyl group in the 4 position. In fact, a singlet of one phenyl group at 7.24 ppm is observed in the spectrum of IIc, and the signal of the second phenyl group is split into two groups of bands with a distance of ~0.4 ppm between them. A signal of the methyl group in the 5 position at 2.77 ppm and a split signal of phenyl protons in the 7 position (two protons at 7.7 ppm and three protons at 7.3 ppm) are observed in the PMR spectrum of the product of condensation of 2-amino-4,6-dihydroxypyrimidine with benzoylacetone (IId). Thus the signals at 2.4-2.5 ppm in the spectra of 5,7-dimethyl derivatives belong to the methyl group in the 7 position, and the signals at 2.7-2.8 ppm belong to the methyl group in the 5 position. The pyrylium 6-H proton in the dimethyl derivatives falls in the region of absorption of phenyl protons at 7.3-7.5 ppm. The structures of the remaining products of condensation with benzoylacetone, obtained in the form of the perchlorates, for which we were unable to find a suitable solvent for recording the PMR spectra, were assumed to be similar to the IId structure. On the basis of the IR spectra it can be assumed that these compounds exist in the form of pyrimidinediones and pyrimidinonethiones (ν_{CO} 1700-1755, ν_{NH} 3100-3200 cm^{-1}; if $Y = NH_2$, ν_{NH_2} 3220-3350, ν_{NH} 3450, and ν_{CO} 1715 cm^{-1}).

Treatment of I and II with ammonia converts them to the corresponding pyrido[2,3-d]pyrimidines, previously obtained by condensation of 4-aminopyrimidines containing electron-donor substituents in the 2 and 6 positions with β-diketones in phosphoric acid [3]. The previously unknown 8-phenylpyrido[2,3-d]pyrimidinium salts III and IV were obtained by heating I and II with aniline in acetic acid. Salts III and IV form red-violet dyes with p-dimethylaminobenzaldehyde and ethyl orthoformate. Their structures were confirmed by the PMR spectra; in particular, the methyl group in the 7 position is shielded by the N-phenyl group (2.0 ppm as compared with 2.4 ppm in I and II). Compound IIIa was isolated in the form of a solvate with acetic acid; this was confirmed by the PMR spectrum, in which the signal of a methyl group of acetic acid (1.80 ppm), which is intensified by the addition of acetic acid, is observed.


III


IV

EXPERIMENTAL

The PMR spectra of trifluoroacetic acid solutions of the compounds were recorded with a ZKR-60 spectrometer with hexamethyldisiloxane as the internal standard. The IR spectra of KBr pellets or mineral oil suspensions of the compounds were obtained with a UR-10 spectrometer. The UV spectra were obtained with an SF-10 spectrophotometer.

Condensation of 4,6-Dihydroxypyrimidines with β-Diketones. A) A mixture of 4 mmole of the appropriate 4,6-dihydroxypyrimidine and 4.4 mmole of the β-diketone was heated on a water bath in 2.2-2.5 ml of a mixture of perchloric and acetic acids (0.24 g of $HClO_4$ per milliliter of the mixture) for 30-40 min. The resulting precipitate was separated and recrystallized from acetic acid (Ic, IIa) or a mixture of acetic and perchloric acids (Ia, d, e and IIf).

B) A mixture of the same composition was heated in 1-1.5 ml of trifluoroacetic acid for 2-3 h, after which it was cooled and diluted with ether. The resulting precipitate was removed by filtration and recrystallized from acetic acid (IIb, d) or from a mixture of acetic and formic acids (IIc).

C) A mixture of 4,6-dihydroxypyrimidine and the β-diketone in 1 ml of 85% phosphoric acid was heated for 1 h. The condensation product (Ib), which was isolated by dilution of the reaction mixture with ether, was obtained in analytically pure form.

2-Amino-5,7-dimethylpyrido[2,3-d]pyrimidin-4(3H)-one. A mixture of 0.2 g of pyrylium salt IIa and 5 ml of 25% ammonium hydroxide was shaken for 30 min, after which the precipitate (0.1 g) was separated and purified by reprecipitation from alkaline solution by the addition of acetic acid as in [3]. Since the compound did not melt below 360 deg C, it was identified by comparison of its IR and PMR spectra with the spectra of the compound obtained from 2,6-diamino-4-hydroxypyrimidine and acetylacetone in phosphoric acid [3].

Reaction of Pyrylium Salts I and II with Aniline. A solution containing 0.5 g of the salt and 0.2 ml of aniline in 10-12 ml of acetic acid was refluxed for 30 min (for Ia), 1.5 h (for IIIa), or 2 h (for IIIb). It was then cooled and treated with excess ether, and the reaction product was removed by filtration and recrystallized from aqueous methanol (IVa) or acetic acid (IIIa, b).

TABLE 1. Characteristics of the Compounds Obtained

Compound	X/Y	R	R′	A	mp, °C (dec.)	Found, %		Empirical formula	Calc., %		Yield, %
						Cl	N		Cl	N	
Ia	O	CH_3	CH_3	ClO_4	249	12,0	9,5	$C_9H_9ClN_2O_7$	12,1	9,6	90
Ib	O	CH_3	CH_3	H_2PO_4	153	—	9,6	$C_9H_{11}N_2O_7P$	—	9,6	67
Ic	O	C_6H_5	C_6H_5	ClO_4	275	8,3	—	$C_{19}H_{13}ClN_2O_7$	8,5	—	37
Id	O	C_6H_5	CH_3	ClO_4	>320	10,3	8,1	$C_{14}H_{11}ClN_2O_7$	10,0	7,9	51
Ie	S	CH_3	CH_3	ClO_4	235	11,6	—	$C_9H_9ClN_2O_6S$	11,5	—	64
If	S	C_6H_5	C_6H_5	ClO_4	229	8,4	—	$C_{19}H_{13}ClN_2O_6S$	8,2	—	18
Ig	S	C_6H_5	CH_3	ClO_4	270	9,9	7,7	$C_{14}H_{11}ClN_2O_6S$	9,6	7,6	56
Ih	O	CH_3	*	ClO_4	>300	8,1	—	$C_{18}H_{18}ClN_3O_7$	8,4	—	96
IIa	NH_2	CH_3	CH_3	ClO_4	226	12,3	14,3	$C_9H_{10}ClN_3O_6$	12,2	14,4	83
IIb	NH_2	CH_3	CH_3	CF_3COO	>300	—	14,1	$C_{11}H_{10}F_3N_3O_4$	—	13,8	50
IIc	NH_2	C_6H_5	C_6H_5	CF_3COO	>300	—	9,7	$C_{21}H_{14}F_3N_3O_4$	—	9,7	90
IId	NH_2	C_6H_5	CH_3	CF_3COO	>300	—	11,6	$C_{16}H_{12}F_3N_3O_4$	—	11,4	79
IIe	NH_2	C_6H_5	CH_3	ClO_4	274	10,0	12,2	$C_{14}H_{12}ClN_3O_6$	10,0	11,9	61
IIf	SCH_3	CH_3	CH_3	ClO_4	232	11,2	—	$C_{10}H_{11}ClN_2O_6S$	11,0	—	57
IIg	SCH_3	C_6H_5	C_6H_5	ClO_4	262	7,9	—	$C_{20}H_{15}ClN_2O_6S$	7,7	—	20
IIh	SCH_3	C_6H_5	CH_3	ClO_4	232	9,2	—	$C_{15}H_{13}ClN_2O_6S$	9,2	—	34
IIIa	O	CH_3	CH_3	ClO_4	266	8,3	—	$C_{15}H_{14}ClN_3O_6 \times$ $\times CH_3COOH$	8,3	—	52
IIIb	O	C_6H_5	C_6H_5	ClO_4	>300	7,2	8,5	$C_{25}H_{18}ClN_3O_6$	7,2	8,5	51
IVa	NH_2	CH_3	CH_3	ClO_4	>300	9,9	15,5	$C_{15}H_{15}ClN_4O_5$	9,7	15,3	75

*p-Dimethylaminostyryl.

5-(p-Dimethylaminostyryl)-7-methylpyrylia[2,3-d]pyrimidin-2,4(1H,3H)dione Perchlorate. A mixture of 0.5 g of salt Ia and 0.25 g of p-dimethylaminobenzaldehyde in 15 ml of acetic anhydride was heated on a water bath for 2 min, after which it was cooled, and the dye crystals were removed by filtration, washed with ether, and recrystallized from acetic anhydride. UV spectrum (in ethanol), λ_{max} (log ε) 570 nm (4.73).

LITERATURE CITED

1. J. Bailey and I. A. Elvidge, J. Chem. Soc., Perkin Trans. I, No. 7, 823 (1973).
2. L. L. Woods, Texas J. Sci., 24, No. 4, 543 (1973).
3. R. K. Robins and G. H. Hitchings, J. Am. Chem. Soc., 80, 3449 (1958).

PREPARATION OF 3-SUBSTITUTED ISOCOUMARINS IN THE REACTIONS OF HOMOPHTHALIC ANHYDRIDE AND ITS DERIVATIVES*

D. Kh. Mutsenietse and Yu. T. Rotberg

UDC 547.81

Acetylation of 4-nitrohomophthalic anhydride gave 4-acetyl-7-nitroisochroman-1,3-dione, which was converted to 3-methyl-7-nitroisocoumarin. 3-Benzylisocoumarin derivatives were synthesized by reaction of homophthalic anhydrides with arylacetic acids in acetic anhydride and triethylamine.

The condensation of homophthalic acids and their esters and anhydrides with compounds containing carbonyl groups is the most important method for the synthesis of isocoumarin derivatives [2]. Since homophthalic acid and its derivatives contain carbonyl and active methylene groups, they are also capable of self-condensation to give 3-(2'carboxybenzyl)isocoumarin derivatives [3-6].

---

*Communication XXVIII from the series "Condensation of Dicarboxylic Acid Anhydrides with Compounds Containing Active Methylene Groups." See [1] for communication XXVII.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Riga Medical Institute, Riga 226047. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1487-1489, November, 1977. Original article submitted October 22, 1976.