added 0.7 g (4 mmole) of N-acetylindoxyl. The mixture was boiled for 15 h, then cooled, and the precipitate was filtered off and washed with alcohol. Yield 0.4 g (32%), mp > 360°C (from DMFA). IR spectrum: 3400, 3370, 3310 (NH_2), 1690, 1650 cm^{-1} (C=O). Found, %: C 61.9; H 4.8; N 22.9; M^+ 309. $C_{16}H_{15}N_5O_2$. Calculated, %: C 62.1; H 4.9; N 22.6; M 309.

LITERATURE CITED

1. G. N. Kurilo, S. Yu. Ryabova, and A. N. Grinev, Khim. Geterotsikl. Soedin., No. 6, 832 (1979).
2. A. N. Grinev, N. N. Suvorov, S. Yu. Ryabova, G. N. Kurilo, K. F. Turchin, and V. S. Velezheva, Khim. Geterotsikl. Soedin., No. 11, 1486 (1979).

SYNTHESIS OF 4-CHLOROSUBSTITUTED SPIROPYRANES OF THE INDOLE SERIES

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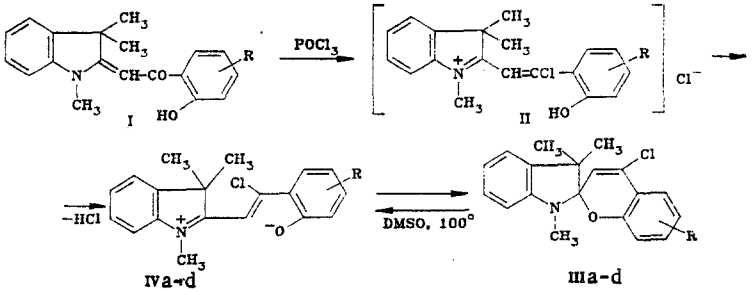
UDC 547.754'814:542.944.1'953:541.651

Enaminohydroxyketones, formed from 1,3,3-trimethyl-2-methyleneindoline and ortho-acetoxyaromatic acid chlorides, are converted by heating with phosphorus oxychloride in dichloroethane and subsequent treatment with alkali to 4-chlorosubstituted spiropyranes of the indole series; these, in contrast to the unsubstituted analogs, do not show photochromic properties.

The search for new photochromic compounds is intimately related to the structure—property problem. In the field of indoline spirobenzopyranes this problem has been solved, as evidence by the regularities already established of the effect of substituents in the indoline and benzopyrane segments on the spectral kinetic properties of photochromic compounds [1]. In spite of the large number of such investigations the problem of the relation between photochromic properties and chemical structure is far from its final solution. A substantial difficulty in this field is the absence of data on the photochromic properties of compounds with a substituent at position 4 of the pyrane ring. The method of Wizinger and Wenning [2] comprising condensation of a Fischer base with a salicyclic aldehyde is not applicable in this case.

The present work proposes a new synthesis of indoline spiropyranes with simultaneous introduction of a chlorine atom at position 4. It consists of heating an enaminohydroxyketone such as compound I with phosphorus oxychloride and cyclization of the resulting indolinium salt II by alkali to the spiro compound III.



III a R=H; b R=8-CH_3; c R=6-NO_2; d R=6,7-benzo

By means of this scheme we obtained the previously unknown indoline 4-chlorospiropyranes containing various substituents in the benzopyrane segment (IIIa-d). The structures were confirmed by PMR and mass spectra and elemental analysis. The chemical shifts of the most characteristic groups of the 4-chlorospiropyranes are shown in Table 1. Analysis of the

D. I. Mendeleev Moscow Institute of Chemical Technology. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1346-1349, October, 1987. Original article submitted September 9, 1986.

0009-3122/87/2310-1078 $12.50

TABLE 1. PMR Spectra of 4-Chlorosubstituted Spiropyranes (III) and Merocyanines (IV) of the Indoline Series

Compound	Solvent	T, °C	δ, ppm			
			3′,3′-$(CH_3)_2$	1′-CH_3	3-H	other protons
IIIa	$CDCl_3$	20	1,19, 1,31	2,73	5,87	6,50—7,85 (8H)
IIIb	$CDCl_3$	20	1,19, 1,32	2,66	5,83	6,40—7,39 (7H); 1,96 (8-CH_3)
IIIc	$CDCl_3$	20	1,22, 1,31	2,75	6,06	6,55—8,48 (7H)
IVc	$(CD_3)_2SO$	100	1,73	3,48	—	6,98—8,73 (8H)
IIId	$CDCl_3$	20	1,24, 1,35	2,69	5,86	6,45—7,90 (10H)
IIId	$(CD_3)_2SO$	20	1,23, 1,34	2,64	6,04	6,69—8,23 (10H)
IVd	$(CD_3)_2SO$	120	1,75	3,44	—	6,75—8,19 (11H)

TABLE 2. PMR Spectra of Enaminohydroxyketones (I) in $CDCl_3$

Compound	δ, ppm				
	3,3-$(CH_3)_2$	1-CH_3	=C—H	O—H	aromatic protons
E-Ia	1,83	3,34	6,05	13,84	6,80—7,84 (8H)
Z-Ia	1,45	3,54	5,86	13,64	
E-Ib	1,81	3,30	6,03	14,00	2,26 (3′-CH_3)
Z-Ib	1,40	3,50	5,76	13,80	6,58—7,65 (7H);
E-Ic	1,83	3,45	6,03	15,06	6,92—8,70 (7H)
Z-Ic	1,50	3,60	5,86	14,91	
E-Id	1,84	3,28	6,06	15,75	6,70—8,48 (10)
Z-Id	1,45	3,54	5,88	15,42	

shifts shows that in deuterochloroform all the compounds are present in the closed (spiropyrane) form. This is evidenced by the signals of the nonequivalent gem-dimethyl groups (~1.2 and 1.3 ppm) and the N-methyl group (~2.7 ppm). Similar values of chemical shift of the corresponding protons have been observed in the spectra of other indoline spiro(2H-chromenes) [3]. The singlet of the 3-H proton is located in the 5.9-6.1 ppm region, which is ~0.25 ppm larger than that for spiropyranes that lack a substituent at position 4. The shift of this signal to a stronger field indicates the proximity of the electron-acceptor chlorine atom.

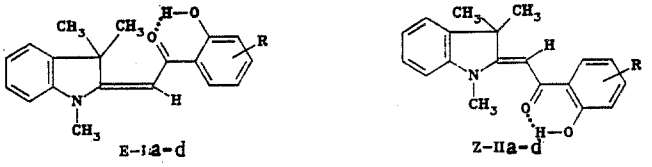
In contrast to the analogs unsubstituted at position 4 [4], the 4-chlorospiropyranes IIIa-d behave the same in both polar and nonpolar solvents and do not show solvatochromic properties. Irreversible thermochromism appears when the compounds are heated in sulfole. Interesting information about the properties of a 4-chlorospiropyrane containing a nitro group (IIIc) was obtained from its PMR spectra in deuteromethyl sulfoxide at various temperatures. The spectrum, obtained at 20°C, is practically the same as in deuterated chloroform. But when the solution is heated to 100°C, there appears in the strong field along with two $(CH_3)_2C$ singlets a singlet with 1.73 ppm chemical shift, while the N-methyl signal shifts to the weaker field (3.48 ppm). These results point to conversion of compound IIIc to the open bipolar structure IVc with symmetrical disposition of methyls relative to the plane of the molecule [3]. It was established by NMR that the transition of spiro compound IIIc to the bipolar open structure IVc is irreversible, because when the solution is cooled to 20° the spectrum does not change. It can be assumed that the chlorine in the molecule provides steric barriers to the reverse transition to the spiro form. Formation of the open form from spiropyrane IIId by an analogous route was recorded (Table 1).

The yields of 4-chlorospiropyranes IIIa-d are low (26, 14, 28, and 39%, respectively). Indolinium salt II (its formation was previously confirmed experimentally [5]) was cyclized under various conditions (in aqueous alkali, salt, and ammonia), but the results could not be improved. It was established that acetylene fragmentation [6], which also lowers the 4-chlorospiropyrane yield, competes with pyrane ring closure.

Compounds IIIa-d were studied by laser photolysis in benzene solution. Photoinduced absorption around 570 nm was observed only for the 4-chlorospiropyrane that contains a nitro group (IIIc). The half life was 50 nsec. For the analogous compound that did not contain chlorine, it was 100 sec. Comparison of the numbers shows that the presence of

chlorine at position 4 of the pyrane ring sharply decreases (by ~10^9-fold) the lifetime of the open form.

The initial enaminohydroxyketones Ia-d were synthesized by the reaction of the respective acid chloride with a Fischer base, followed by removal of the acetyl group with KOH in alcohol. The PMR spectral data for these compounds are shown in Table 2. Enaminohydroxyketones Ia-d, like other Fischer base derivatives with a substituent at the methylene [7], exist as E and Z isomers. Signals are assigned to E or Z configurations on the basis of the assumption that a closer orientation of carbonyl (C=O) to any group should shift the proton signals of that group to the weaker field. The ratio of E to Z forms according to the integral curve is ~4:1. We were unable to separate the isomers.



E-Ia-d Z-IIa-d

a R=H,b R=3-CH_3, c R=5-NO_2, d R=4,5-benzo

EXPERIMENTAL

PMR spectra were recorded with a high resolution Bruker WP-200-SY spectrometer (200 MHz) with a superconductive magnet. For column chromatography silica gel grade L 4/100 was used. R_f values were determined on Silufol UV-254 plates, with chloroform eluent. Kinetic properties of synthesized compounds were measured with a laser photolysis instrument. Photoexcitation source was the second harmonic pulse of a ruby laser. Pulse duration was 30 nsec, energy was of the order of 25 mJ, emission wavelength was 347 nm.

1,3,3-Trimethyl-2-(o-hydroxyphenacylidene)indoline (Ia). A mixture of 18 g (0.1 mole) of acetylsalicyclic acid and 17.8 g (0.15 mole) of thionyl chloride in 50 ml of dry benzene was boiled for 2 h, after which excess thionyl chloride and benzene were evaporated in the vacuum of a water aspirator. For complete removal of thionyl chloride two 40-ml portions of petroleum ether were added and evaporated. The resulting acid chloride was dissolved in 50 ml of dry benzene and added with stirring to a mixture of 17.2 g (0.1 mole) of Fischer base and 12.1 g (0.12 mole) of triethylamine in 150 ml of benzene. The mixture was kept at 35°C for 1 h 30 min, then at 20°C overnight. It was washed with 1% HCl, benzene was evaporated, and to the residue were added 20 g (0.35 mole) of KOH, and 40 ml of ethyl alcohol, and the mixture was boiled for 1 h. To the resulting solution was added 200 ml of water. The precipitate that formed was filtered off and washed with water and ethyl alcohol and dried. Yield 21.3 g (73%). Yellow crystals, mp 115-116°C (from alcohol). Found, %: C 78.0; H 6.4; N 4.8. $C_{19}H_{19}NO_2$. Calculated, %: C 77.3; H 6.5; N 4.8.

1,3,3-Trimethyl-2-(2-hydroxy-3-methylphenacylidene)indoline (Ib). Compound Ib was obtained analogously to Ia from 2-acetoxy-3-methylbenzoic acid. Yield 32%. Yellow crystals, mp 144-145°C (from alcohol). Found, %: C 78.0; H 7.3; N 4.5. $C_{20}H_{21}NO_2$. Calculated, %: C 78.2; H 6.9; N 4.6.

1-3,3-Trimethyl-2-(2-hydroxy-5-nitrophenacylidene)indoline (Ic). Ic was obtained analogously to Ia from 5-nitroacetylsalicylic acid. Yield 80%. Yellow crystals, mp 241-243°C (from chloroform). Found, %: C 67.8; H 5.5; N 8.0. $C_{19}H_{18}N_2O_4$. Calculated, %: C 67.4; H 5.4; N 8.3.

1,3,3-Trimethyl-2-(3-hydroxy-2-naphthylacetylidene)indoline (Id). Id was obtained analogously to Ia from 2,3-acetoxynaphthoic acid. Yield 43%. Yellow crystals, mp 160-162°C (from isopropyl alcohol). Found, %: C 80.0; H 5.8; N 4.1. $C_{23}H_{21}NO_2$. Calculated, %: C 80.4; H 6.2; N 4.1.

1',3',3'-Trimethyl-4-chlorospiro(2H-1-benzopyran-2,2'-indoline) (IIIa). A mixture of 1.17 g (4 mmole) of enaminohydroxyketone Ia and 0.92 g (6 mmole) of phosphorus oxychloride in 35 ml of 1,2-dichloroethane was boiled for 4 h, cooled to 20°C, and poured into 150 ml of cold water. The mixture was neutralized with 10% NaOH solution to pH 8. The organic layer was separated, and dried over sodium sulfate, and the solvent was evaporated. The residue was chromatographed on a column. A 1:1 benzene–hexane mixture eluted 0.33 g of colorless material with R_f 0.78, mp 127-129°C. Yield 26%. Found, %: C 73.4; H 6.0; Cl 11.0; N 5.5. $C_{19}H_{18}ClNO$. Calculated, %: C 73.2; H 5.8; Cl 11.4; N 4.5.

1',3',3',8-Tetramethyl-4-chlorospiro(2H-1-benzopyran-2,2'-indoline) IIIb was obtained from enaminohydroxyketone Ib analogously to compound IIIa. It was eluted with 1:1 benzene–hexane; colorless crystals, R_f 0.69, mp 115-117°C, 14% yield. Found: C 73.8; H 6.3; Cl 10.6; N 4.8%. $C_{20}H_{20}ClNO$. Calculated: C 73.7; H 6.2; Cl 10.9; N 4.3%.

1',3',3'-Trimethyl-4-chloro-6-nitrospiro(2H-1-benzopyran-2,2'-indoline) (IIIc) was obtained from enaminohydroxyketone Ic analogously to compound IIIa. It was eluted with 2:1 benzene–petroleum ether; R_f 0.62, bright yellow crystals, mp 170-173°C, 28% yield. Found, %: C 64.3; H 4.9; Cl 9.7; N 7.6; M 356. $C_{19}H_{17}ClN_2O_3$. Calculated, %: C 64.0; H 4.8; Cl 9.9; N 7.9; M 356.

1',3',3'-Trimethyl-4-chloro(2H-1-naphtho[2,3-b]pyran-2,2'-indoline) (IIId) was obtained from enaminohydroxyketone Id analogously to compound IIIa. A 1:1 benzene–hexane mixture eluted a colorless material with R_f 0.74, mp 135-137°C. Yield 39%. Found, %: C 76.3; H 5.8; Cl 10.1; N 4.4. $C_{23}H_{20}ClNO$. Calculated, %: C 76.3; H 5.6; Cl 9.8; N 3.9.

LITERATURE CITED

1. É. R. Zakhs, V. P. Martynova, and L. S. Éfros, Khim. Geterotsikl. Soedin., No. 4, 435 (1979).
2. R. Wizinger and H. Wenning, Helv. Chim. Acta, 23, 247 (1940).
3. K. T. Dzhaparidze, I. Ya. Pavlenishvili, V. G. Tsitsishvili, and D. P. Maisuradze, Soobshch. Akad. Nauk Gruz. SSR, 70, 349 (1973).
4. R. C. Bertelson, Photochromism, G. H. Brown (ed.), Wiley-Intersci., New York (1971), p. 49.
5. N. M. Przhiyalgovskaya, L. I. Kon'kov, D. L Tarshits, S. V. Salmina, N. T. Segizova, and N. N. Suvorov, Khim. Geterotsikl. Soedin., No. 7, 915 (1987).
6. L. I. Kon'kov, N. M. Przhiyalgovskaya, and N. N. Suvorov, Dokl. Akad. Nauk SSSR, 278, 1130 (1984).
7. V. N. Zemlyanoi, I. L. Mushkalo, M. Yu. Kornilov, I. E. Boldeskul, and M. L. Dekhtyar', Khim. Geterotsikl. Soedin., No. 3, 361 (1983).

NITRATION OF 4-HALO-1-METHYLPYRAZOLES IN SULFURIC ACID

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UDC 547.772.1.04:542.958.1

The rate of nitration of 4-bromo- and 4-chloro-1-methylpyrazoles with nitric acid in various concentrations of sulfuric acid is higher at position 5 than at position 3.

In the nitration of 4-bromo-1-methylpyrazole (I) with excess nitric acid in sulfuric acid, nitrodebromination takes place to give 1-methyl-4-nitropyrazole (II), and the nitro group enters positions 3 and 5 of the heterocycle to form 4-bromo-1-methyl-3,5-dinitropyrazole (III). It was assumed that compound III is obtained from 4-bromo-1-methyl-3-nitropyrazole (IV) which [like another possible mononitration product, 4-bromo-1-methyl-5-nitropyrazole (V)] was not separated and identified [1].

In order to study the features of nitration of compound I and 1-methyl-4-chloropyrazole (VI) we carried out the reaction at an equimolar ratio of halopyrazole to nitric acid in various concentrations (80, 90, 102.5%) of sulfuric acid. All the assumed nitration products, viz., compounds II-V, 1-methyl-3-nitro-4-chloropyrazole (VII), 1-methyl-5-nitro-4-chloropyrazole (VIII), and 1-methyl-3,5-dinitro-4-chloropyrazole (IX), were obtained individually. They have characteristic differences in the R_f values of TLC and in their PMR spectra (Table 1), which were used in analyzing the nitration of 4-halo-1-methylpyrazoles (Table 2).

When 4-bromo-1-methylpyrazole is nitrated in 80% sulfuric acid, mainly nitrodebromination takes place. The only nitration product at the free heterocycle positions is 4-bromo-

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1350-1352, October, 1987. Original article submitted May 26, 1986.

0009-3122/87/2310-1081 $12.50