²⁹Si chemical shifts but also in the ${}^{1}J_{CH}$ and ${}^{2}J_{SiH}$ constants, which are lower in the case of I than in the case of II. The shift in the resonance of the ${}^{13}C$ atom in the methyl group of I, as compared with II. to weak field is apparently due to the change in the three-dimensional structure of the silicon atom (the silicon atom in sila-tranes has a trigonal-bipyramidal configuration, whereas in silanes it has a tetrahedral configuration). An indirect confirmation of this is afforded by the shift to weak field of the signals of the alkyl substituent in the ${}^{13}C$ NMR spectra of alkyltrichlorostannanes during complexing [3].

We noted similar changes in ${}^{1}J_{CH}$, ${}^{2}J_{SiH}$, and $\delta({}^{13}C)$ during a comparison of the NMR spectra of methyl-triethoxysilane.

EXPERIMENTAL

The synthesis of I and II was described in [1]. The measurements were made from 10% solutions of the compounds in chloroform (with tetramethylsilane as the internal standard) with a Tesla BS 487C NMR spectrometer equipped with an adapter (developed in the Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR) for heteronuclear ${}^{1}H-({}^{29}Si)$ double resonance [4].

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SOME SUBSTITUTION REACTIONS IN A NUMBER OF PHOTOCHROMIC INDOLINESPIROCHROMENES

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UDC 547.754'814.07:542.944'958

The corresponding 5-substituted compounds are formed in the halogenation, nitration, and diazo coupling of 1,3,3-trimethyl-6'-nitroindoline-2-spiro-2'-[2H]chromene.

A large amount of research has been devoted to synthetic and photochemical studies in the series of photochromic spirochromenes, but very little study has been devoted to the chemical properties of these compounds, which are of importance in both a theoretical and practical respect. Continuing our research on the reactivities of indolinespirochromenes [1], we accomplished the halogenation, nitration, and diazo coupling of spirochromene I.



II a $R = NO_2$; b R = Br; c R = CI; d $R = 4 - NO_2C_6H_4N = N$

The nitration of spirochromene I by the action of nitric acid in acetic anhydride or in concentrated sulfuric acid and by treatment with sodium nitrite in acetic acid and subsequent oxidation of the resulting nitroso compound by air oxidation lead smoothly to the corresponding 5-nitro-substituted spirochromene (IIa). We confirmed the structure of the spirochromene by alternative synthesis from 5-nitro-1,3,3-trimethyl-2-methyleneindoline (V) and 5-nitrosalicylaldehyde:

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1065-1068, August, 1977. Original article submitted March 30, 1976; revision submitted November 22, 1976.



Bromo-substituted spirochromene IIb is formed in good yield in the bromination of I by the action of bromine in chloroform without a catalyst or in the presence of aluminum bromide or boron trifluoride etherate, as well as by reaction with cupric bromide in acetonitrile. The chlorination of spirochromene I by the action of chlorine in chloroform or with cupric chloride in acetonitrile leads smoothly to chlorine-substituted IIc. The resulting spirochromenes IIb,c, were found to be identical to genuine samples of the compounds [2].

We also carried out the diazo coupling of spirochromene I with the double salt of p-nitrobenzenediazonium chloride and mercuric chloride [3] and isolated the p-nitrophenylazo-substituted spiran in high yield. Considering that electrophilic substitution reactions, including diazo coupling, are directed exclusively to the para position relative to the nitrogen atom, i.e., to the 5 position [4], and taking into account the fact that the diazo coupling of anilines proceeds almost completely in the para position [5-7], we assigned the 5- (p-nitrophenylazo)spirochromene structure (IId) to the product.

The reaction of bromo-substituted spirochromene Πb with cuprous cyanide in the presence of pyridine at 150-160°C leads to 5-cyano-substituted spirochromene Πe :



The orientation of the entering substituents and the ease of the investigated substitution reactions evidently make it possible to conclude that in the indicated transformations the spirochromenes react in the closed spiro form.

EXPERIMENTAL

<u>1,3,3-Trimethyl-5,6'-dinitroindoline-2-spiro-2'-[2H]chromene (IIa).</u> A) A 1.61-g (5 mmole) sample of spirochromene I was dissolved in 50 ml of acetic anhydride at room temperature, and 0.56 g (5 mmole) of 57% nitric acid (sp. gr. 1.35) was added. The mixture was stirred at 60° for 2 h, after which it was poured into 100 ml of 40% solution of sodium carbonate and 100 ml of chloroform. The mixture was stirred for 40 min, after which the organic layer was separated, and the aqueous layer was extracted with chloroform. The combined extracts were evaporated, and the residue was chromatographed with a column filled with aluminum oxide with successive elution with heptane, benzene-heptane (1:1), and chloroform. The chloroform fraction was evaporated, and the residue was crystallized from heptane to give 0.8 g (43%) of spirochromene IIa with mp 208-210° and R_f (in a thin layer of Al₂O₃) 0.048 (heptane), 0.35 (benzene), and 0.73 (chloroform). According to the data in [4], this compound had mp 175-177°C. Found: C 62.0; H 4.7; N 11.2%. C₁₉H₁₇N₃O₅. Calculated: C 62.1; H 4.7; N 11.4%.

B) A 1.61-g (5 mmole) sample of spirochromene I was dissolved in 100 ml of glacial acetic acid, after which 0.69 g (10 mmole) of sodium nitrite was added at room temperature, and the mixture was stirred for 30 min. It was then poured into water, and the aqueous mixture was extracted with benzene. The extract was filtered through a thin layer of aluminum oxide, and the filtrate was worked up to give 1.6 g (87%) of spiro-chromene IIa with mp 208-210° (from heptane).

C) A 1.61-g (5 mmole) sample of spirochromene I was dissolved in 30 ml of concentrated H_2SO_4 , and the solution was cooled to 0° and treated with 0.56 g (5 mmole) of 57% nitric acid (sp. gr. 1.35). The mixture was stirred at 5°C for 1 h, after which it was poured over ice, and the resulting precipitate was removed by filtration and washed with water. The solid was treated with 100 ml of a 40% solution of sodium carbonate and 100 ml of chloroform, and the mixture was worked up as in method A to give 1.1 g (60%) of IIa with mp 208-210° (from heptane).

D) A 1.67-g (10 mmole) sample of 5-nitrosalicylaldehyde was added with stirring to a solution of 2.18 g (10 mmole) of 5-nitro-1,3,3-trimethyl-2-methyleneindoline (V) and 10 ml of ethanol, after which the mixture was refluxed for 3-4 h. It was then cooled, and the precipitate was separated and crystallized from heptane to give 3 g (82%) of spirochromene IIa with mp 208-210°C.

<u>1,3,3-Trimethyl-5-bromo-6'-nitroindoline-2-spiro-2'-[2H]chromene (IIb).</u> A) A 1.66-g (5.1 mmole) sample of spirochromene I was dissolved in 40 ml of chloroform, 0.8 g (5 mmole) of bromine was added to the solution with heating, and the mixture was stirred at 60° for 2.5 h. Sodium carbonate (35 g), 120 ml of chloroform, and 150 ml of water were added, and the mixture was stirred until the precipitate had dissolved completely. The organic layer was separated, washed with water, and filtered through aluminum oxide. The filtrate was evaporated, and the residue was crystallized from heptane to give 1.72 g (84%) of spirochromene IIb with mp 154° (152° according to [2]). Reaction under the same conditions in the presence of 2.67 g (10 mmole) of anhydrous AlBr₃ gave 1.95 g (95%) of IIb with mp 154° and R_f (Silufol) 0.36 (benzene) and 0.48 (chloroform). The product was identical to an authentic sample obtained by the method in [2]. Found: C 56.6; H 4.5; Br 19.5%. C₁₉H₁₇Br-N₂O₂. Calculated: C 56.9; H 4.3; Br 19.9%.

B) A 1.66-g (5.1 mmole) sample of spirochromene I was dissolved in 40 ml of carbon tetrachloride, 0.88 g (5 mmole) of N-bromosuccinimide (NBS) was added, and the precipitated succinimide was separated. The solution was filtered through aluminum oxide, and the filtrate was evaporated. The residue was crystallized from heptane to give 1.91 g (95%) of spirochromene IIb with mp 154°.

C) A mixture of 0.32 g (1 mmole) of spirochromene I, 0.45 g of cuprous bromide, and 50 ml of acetonitrile was heated at 80° for 10 min, after which 20 g of sodium carbonate, 70 ml of chloroform, and 100 ml of water were added, and the mixture was worked up as described above to give 0.35 g (87%) of spirochromene IIb with mp 154°C.

D) Boron trifluoride etherate (3 ml) was added to 3.22 g (10 mmole) of a solution of spirochromene I in 80 ml of chloroform, during which a yellow precipitate formed. Bromine [1.6 g (10 mmole)] was then added with heating and stirring, after which stirring was continued for 1 h. Sodium carbonate (50 g), 150 ml of chloroform, and 200 ml of water were added, and the mixture was stirred until the solid had dissolved completely. The organic layer was washed with water and worked up as described above to give 3.71 g (92.5%) of spirochromene IIb with mp 154°.

<u>1,3,3-Trimethyl-5-chloro-6'-nitroindoline-2-spiro-2'-[2H]chromene (IIc).</u> A) A 3.22-g (10 mmole) sample of spirochromene I was dissolved in 80 ml of chloroform, and chlorine was bubbled into the mixture at 60°C until the increase in weight was 0.71 g, after which the mixture was stirred at 60° for 2.5 h. It was then cooled, and the precipitate was separated and washed with a small amount of chloroform to remove unchanged spirochromene I. Ethanol (10 ml), 40 g of sodium carbonate, and 150 ml of water were added to the precipitate, and the mixture was heated gently with stirring, after which it was extracted with chloroform. The extract was washed with water and filtered through aluminum oxide, and the filtrate was evaporated. The residue was crystallized from heptane to give 2.9 g (81.2%) of spirochromene IIc with mp 154-155°C (155°, according to [2]). The product was identical to a genuine sample obtained by the method in [2].

B) Spirochromene IIc, with mp 154-156°C, was obtained in 83% yield by the action of cuprous chloride on spirochromene I, as described in the preparation of spirochromene IIb (method C).

 $\frac{1,3,3-\text{Trimethyl-5-}(p-\text{nitrophenylazo})-6'-\text{nitroindoline-2-spiro-2'-}[2H]chromene (IId). A 2.5-g (5.5 mmole) sample of the double salt of p-nitrobenzenediazonium chloride and mercuric chloride [3] was added to 1.5 g (4.6 mmole) of spirochromene I in 30 ml of acetone, and the mixture was stirred for 30 min, after which it was poured into 200 ml of water, and the precipitate was separated, washed with water, and crystallized from heptane to give 1.93 g (89%) of spirochromene IId with mp 257°C. The product was obtained as orange-red powder that was quite soluble in alcohol and acetone to give a red solution, which turned yellow when it was acidified. No photochromic properties could be observed. Found: C 63.5; H 4.4; N 14.6%. C₂₅H₂₁N₅O₅. Calculated: C 63.7; H 4.5; N 14.8%.$

<u>1,3,3-Trimethyl-5-cyano-6'-nitroindoline-2-spiro-2'-[2H]chromene (IIe).</u> Two drops of pyridine was added to a thoroughly ground mixture of 0.8 g (2 mmole) of spirochromene IIb and 0.3 g (3.3 mmole) of cuprous cyanide, after which the mixture was heated at 150-160°C for 6 h. It was then cooled and extracted with chloroform, and the extract was evaporated to a small volume. The residual mixture was chromatographed with a column filled with aluminum oxide with elution by heptane (fraction A), benzene-heptane (1:1) (fraction B), and chloroform (fraction C). Workup of fractions A and B gave 0.3 g of unchanged spirochromene IIb. Fraction C was evaporated, and the residue was crystallized from heptane to give 0.4 g of crude product with mp 105-107°C. For final purification, the product was chromatographed on a plate with a thin fixed layer of silica gel (elution with benzene); the principal spot was extracted with chloroform, and the extract was worked up to give 0.15 g (21.5%) of spirochromene IIe with mp 148-150°C and R_f (Silufol) 0.1 (benzene) and 0.21 (chloroform). IR spectrum: 2200 cm⁻¹ (C=N). The product was obtained in the form of light-yellow crystals that were quite

soluble in ordinary organic solvents. The solutions displayed ordinary photochromic properties. Found: C 69.1; H 5.2; N 12.1%. $C_{20}H_{17}N_3O_3$. Calculated: C 69.2; H 4.9; N 12.1%.

<u>2,3,3</u>-Trimethyl-5-nitroindolenine (III). A mixture of 7 g (45.7 mmole) of p-nitrophenylhydrazine and 5 ml (46.5 mmole) of methyl isopropyl ketone was heated on a water bath for 1 h, after which 100 ml of concentrated HCl was added, and the mixture was refluxed for 4 h. It was then filtered, and the filtrate was made alkaline with sodium carbonate and extracted with benzene. The extract was dried with potassium hydroxide and evaporated, and the residue was recrystallized from alcohol to give 4 g (43%) of a product with mp 128-129°. Found: C 64.5; H 5.6%. C₁₁H₁₂N₂O₂. Calculated: C 64.7; H 5.9%.

1,2,3,3-Tetramethyl-5-nitroindoleninium Iodide (IV). A mixture of 4.1 g (20 mmole) of indolenine III and 6 g ($4\overline{2}$ mmole) of methyl iodide was refluxed for 2 h, after which it was evaporated, and the residue was crystallized from alcohol to give 3 g (43%) of IV with mp 210°. Found: C 41.2; H 4.7; N 7.7%. C₁₂H₁₅IN₂O₂. Calculated: C 41.6; H 4.4; N 8.1%.

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