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HETEROCYCLIC ANALOGS OF PLEIADIENE

XXXII.* SPIROPYRANS OF THE PERIMIDINE SERIES†

V. A. Anisimova, A. F. Pozharskii,
L. E. Nivorozhkin, and V. I. Minkin

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Colorless spiropyrans were obtained by the reaction of 1,2,3-trimethyl and 1,3-dimethyl-2-ethylperimidinium iodides with salicylaldehyde and 2-hydroxy-1-naphthaldehyde in the presence of piperidine. When 5-nitrosalicylaldehyde is used, the reaction stops with the formation of a bright-orange merocyanine. The spiropyrans obtained have weakly expressed thermochromism; the spiropyrans obtained from 2-hydroxy-1-naphthaldehyde also have photochromic properties.

The formation of spiropyrans by the action of alkaline agents on o-hydroxystyryl derivatives of heterocyclic cations proceeds in two steps: the formation of a deeply colored merocyanine and its conversion to a usually colorless spiropyran as a result of intramolecular attack by the phenoxide oxygen atom on the carbon atom of the heterocyclic cation to which the styryl group is attached. The ease with which the second step occurs depends to a great degree on the effective positive charge on this carbon atom [3]. It has previously been shown that the perimidine molecule and especially its cation have one of the highest (in the diazole series) positive charges on the μ-carbon atom and a localization energy that is extremely favorable for spirocyclization [4, 5]. It therefore might have been expected that, in contrast to, for example, 2-(o-hydroxystyryl)benzimidazolium salts [6], the corresponding perimidinium salts would readily undergo conversion to spiropyrans.

Spiroyrans of the perimidine series were heretofore unknown. In the present research to synthesize them we used the condensation of perimidinium iodides (I, II) with salicylaldehyde, 5-nitrosalicylaldehyde, and 2-hydroxy-1-naphthaldehyde. Bright-red 1-methyl-2-(o-hydroxystyryl)perimidinium methiodide (III) is formed in 68% yield after a few minutes when salt I is heated with salicylaldehyde in alcohol in the presence of a catalytic amount of piperidine. It is very slightly soluble in water and organic solvents and therefore evidently does not lose a molecule of HI when it is treated with an aqueous solution of sodium carbonate or ammonium hydroxide. However, salt III gradually dissolves when it is refluxed in dimethylformamide (DMF) and is converted to colorless spiropyran IV. Spiropyran IV can be obtained immediately in 55% yield if the reaction of iodide I with salicylaldehyde is carried out in alcohol in the presence of excess piperidine. Spiropyran VI is formed very readily under the same conditions in the reaction of I with 2-hydroxy-1-naphthaldehyde. On the other hand, salt II does not react with aldehydes in alcohol solution, evidently because of the inductive and steric effects of the additional CH_3 group, which reduces the lability of the methylene hydrogen atoms. We were able to obtain spiropyrans V and VII only by refluxing salt II with the corresponding aldehydes in pyridine for many hours. (See Scheme on following page).

The structures of the spiropyrans are confirmed by the results of elementary analysis, the PMR and IR spectra, their lack of color, and their high solubility in organic solvents. Thus, for example, the PMR spectrum of spiropyran IV contains a quartet of signals at 6.3 ppm with an intensity of two proton units; this signal is

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*See [1] for communication XXXI.

†Communication VIII from the series "Photochromic and Thermochromic Spirans." See [2] for communication VII.

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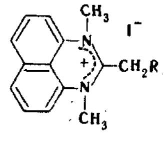
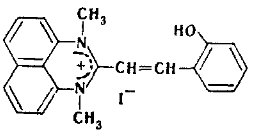
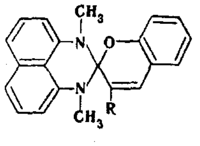


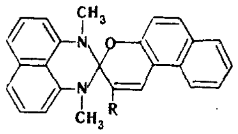
I, II



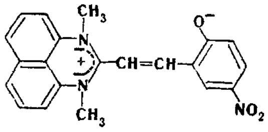
III



IV, V



VI, VII



VIII

I, IV, VI R=H; II, V, VII R=CH_3

characteristic for equivalent 4-H and 9-H protons of the perimidine ring [7]. The 3'-H proton of the vinyl group gives a doublet at δ 5.61 ppm (J = 12 Hz). The doublet from the 4'-H proton is overlapped by a multiplet from the absorption of the other aromatic protons (δ ~6.9 ppm). The PMR spectrum of spiropyran V is similar to the spectrum of IV but does not contain the doublet of a 3'-H proton, since this position is occupied by a CH_3 group, which is characterized by absorption at δ 1.85 ppm. The IR spectra of the spiropyrans do not contain any absorption above 3100 cm^{-1}; at 1500-1700 cm^{-1} the spectra remind one very much of the spectra of the structurally related 2-substituted 1,3-dimethyl-2,3-dihydroperimidines but differ from the IR spectra of the 2-(o-hydroxystyryl)perimidinium salt (III, Fig. 1).

The reaction of salt I with 5-nitrosalicylaldehyde in the presence of excess piperidine leads to the formation of bright-orange merocyanine VIII, which could not be converted to the corresponding spiropyran. This is evidently explained by the reduced nucleophilicity of the phenoxide oxygen atom in VIII because of the electron-acceptor effect of the nitro group. The merocyanine structure of this compound is confirmed by the results of elementary analysis, its deep color, its very low solubility, and its IR spectrum. In the region of the stretching vibrations of the aromatic C—C and C—N bonds the spectrum of merocyanine VIII is similar to the spectrum of the cation of III but differs appreciably from the spectra of the spiropyrans (Fig. 1).

Spiorpyrans IV and VI have thermochromic properties. When solutions of VI in DMF and DMSO are heated, they turn crimson (as compared with crimson-red in nitrobenzene and pink in chlorobenzene and benzene). The color vanishes when the solutions are cooled. Solutions of spiropyran IV in the solvents indicated above remain practically colorless when they are heated, but fused spiropyran IV has a violet color. When the melt is cooled, it gives colorless crystals. Compound VI undergoes decomposition when it is melted. We were unable to observe thermochromism for the other spiropyrans: V and VII form colorless melts and colorless solutions in hot xylene, DMF, and DMSO.

Of all the synthesized compounds, only spiropyran VII has photochromic properties. Irradiation of an alcohol solution of VII at 163°K leads to the appearance in the visible portion of the spectrum at 470 nm of a broad absorption band (Fig. 2) associated with the formation of the corresponding open valence-tautomeric structure as a result of electrocyclic opening of the pyran ring. The reverse transition is observed when the solution is warmed.

EXPERIMENTAL

The IR spectra of mineral oil suspensions or chloroform solutions of the compounds were recorded with a UR-10 spectrometer. The PMR spectra of CCl_4 solutions of the compounds were recorded with a Tesla BC-487 C spectrometer (80 MHz) at 50°C with hexamethyldisiloxane as the internal standard. The electronic absorption spectra were recorded with a Specord UV-vis spectrophotometer with a cryostat for low-temperature measurements. Irradiation was accomplished with a DRSh-250 mercury lamp with a light filter that isolates light with λ_{max} 313 nm.

2-Ethylperimidine and 1,8-Bis(propionylamine)naphthalene. A 5-ml (40 mmole) sample of freshly distilled propionic anhydride was added to 5 g (32 mmole) of finely ground naphthalenediamine, as a result of which we observed a vigorous exothermic reaction, the product of which was a viscous orange oil that crystallized when it was cooled. The solid product was treated with ether, and the undissolved 1,8-bis(propionylamine)naphthalene was removed by filtration and washed with ether to give 0.35 g (4.1%) of fine snow-white needles that were insoluble in water and chloroform but soluble in hot DMF. The needles were crystallized from alcohol (1:200) to give a product with mp 298-299°C (dec.). IR spectrum (mineral oil): 1660 (C=O); 1545, 3270 cm^{-1} (NH). Found: C 71.3; H 6.5; N 10.4%. $C_{16}H_{18}N_2O_2$. Calculated: C 71.1; H 6.7; N 10.4%.

The ether solution from the separation of the precipitate was diluted with alcohol, and the precipitated bright-yellow salt of 2-ethylperimidine with propionic acid was removed by filtration. The salt is soluble in alcohol, ether, acetone, chloroform, and water. Crystallization from benzene gave light-yellow plates with mp 61-62°C. IR spectrum ($CHCl_3$): 1715 (C=O), 3435 (NH), and 3700 cm^{-1} (OH). Found: N 10.6%. $C_{13}H_{12}N_2 \cdot C_2H_5COOH$. Calculated: N 10.4%. The salt was dissolved in water, the solution was neutralized with 22% ammonium hydroxide, and the precipitated lettuce-green crystals (3.1 g) were separated. The mother liquor was evaporated, and the residue was treated with dilute ammonium hydroxide. The mixture was extracted with chloroform, and the chloroform was removed from the extract to give 2.8 g of 2-ethylperimidine for an overall yield of 5.9 g (95%). The product was purified by chromatography or crystallization from aqueous alcohol and had mp 172-173°C (dec.) (mp 161°C [8]). IR spectrum ($CHCl_3$): 1600, 1620, 1640 (C=C, C=N); 3430 cm^{-1} (NH). Found: C 79.5; H 6.3; N 14.2%. $C_{13}H_{12}N_2$. Calculated: C 79.6; H 6.1; N 14.3%.

1-Methyl-2-ethylperimidine. A solution of 3 g (15 mmole) of 2-ethylperimidine and 1.9 ml (30 mmole) of methyl iodide in 10 ml of DMF was heated on a boiling-water bath for 30 min, after which it was cooled and diluted with ether. The precipitate (5.9 g) was removed by filtration, washed with ether, air dried, and dissolved by heating in 50 ml of water. Benzene and 22% ammonium hydroxide (until the odor of ammonia was detectable) were added to the hot solution, the precipitate was removed by filtration, and the benzene layer was separated and evaporated to a small volume. The concentrate was passed through a long broad column filled with Al_2O_3 (elution with benzene). The first light-yellow fraction was collected and worked up to give 1.7 g (54%) of slightly yellowish crystals with mp 107°C. Found: C 80.0; H 6.5; N 13.3%. $C_{14}H_{14}N_3$. Calculated: C 80.0; H 6.7; N 13.3%.

1,3-Dimethyl-2-ethylperimidinium Iodide (II). A mixture of 0.73 g (3.5 mmole) of 1-methyl-2-ethylperimidinium iodide, 1 ml (16 mmole) of methyl iodide, and 4 ml of DMF was heated on a boiling-water bath for 30 min, after which it was cooled, and the precipitate was removed by filtration and washed with a small amount of alcohol to give 1.15 g (94.3%) of bright-yellow needles with mp 236-237°C (dec., from alcohol). Found: C 51.2; H 5.2; I 35.6; N 8.0%. $C_{15}H_{17}IN_2$. Calculated: C 51.2; H 4.9; I 36.0; N 8.0%.

1,3-Dimethyl-2-(2-hydroxystyryl)perimidinium Iodide (III). A 0.11-ml (1 mmole) sample of salicylaldehyde and two drops of piperidine were added to a suspension of 0.34 g (1 mmole) of 1,2,3-trimethylperimidinium iodide [9] in 4 ml of alcohol, and the mixture was heated on a boiling-water bath for 3-4 min. It was then cooled, and the bright-red precipitate was removed by filtration, washed on the filter with water, alcohol, and ether, and dried to give 0.3 g (68%) of a product with mp 227°C. The product was only very slightly soluble in most organic solvents. IR spectrum (mineral oil): 1508, 1550, 1590, 1602, and 1645 (C=C, C=N); 3380 cm^{-1} (OH). Found: N 6.3%. $C_{21}H_{19}IN_2O$. Calculated: N 6.3%.

1,3-Dimethylspiro(2,3-dihydroperimidine-2,2'-[2H]chromene) (IV). A 0.11-ml (1 mmole) sample of salicylaldehyde and 0.25 ml (2.5 mmole) of piperidine were added to a hot solution of 0.34 g (1 mmole) of iodide I in 30 ml of alcohol, and the mixture was refluxed for 2 h. The alcohol was removed by distillation, the residue was treated with water, and the solid material was removed by filtration. It was washed with water and purified by chromatography with a short broad column filled with Al_2O_3 (elution with chloroform) with collection of the light-yellow fraction (the impurities remained at the top of the column). The residue from workup of this fraction was recrystallized from a small amount of benzene to give 0.17 g (55%) of large snow-white crystals with mp 210-211°C. Found: C 80.3; H 5.6; N 9.0%. $C_{21}H_{18}N_2O$. Calculated: C 80.2; H 5.8; N 8.9%. The product was soluble in chloroform, benzene, acetone, alcohol, and CCl_4.

1,3-Dimethylspiro(2,3-dihydroperimidine-2,2'-[2H]benzo[h]chromene) (VI). This compound was obtained by refluxing a mixture of 0.34 g (1 mmole) of salt I, 0.17 g (1 mmole) of 2-hydroxy-1-naphthaldehyde, 0.5 ml (5 mmole) of piperidine, and 30 ml of alcohol for 10-15 min. The precipitate was removed from the hot mixture by filtration and washed with cold alcohol, acetone, and ether. The yield was 0.32 g (90%). The small slightly yellowish needles had mp 290-292°C (dec., from DMF). Found: C 82.5; H 5.7; N 7.8%. $C_{25}H_{20}N_2O$. Calculated: C 82.4; H 5.5; N 7.7%. The reaction cannot be allowed to be carried out for a longer time and the reaction mixture cannot be allowed to stand, since side processes that lead to a sharp decrease in the yield of the spiropyran take place under these conditions.

1,3,3'-Trimethylspiro(2,3-dihydroperimidine-2,2'-[2H]chromene) (V). A solution of 0.35 g (1 mmole) of iodide II, 0.11 ml (1 mmole) of salicylaldehyde, and 0.25 ml (2.5 mmole) of piperidine in 4 ml of pyridine was

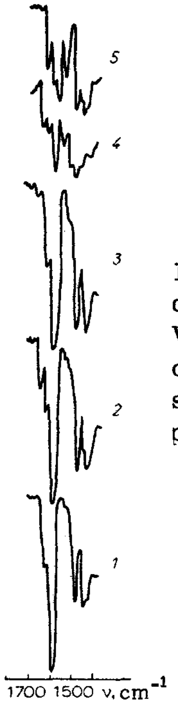


Fig. 1. IR spectra: 1,3-dimethyl-2-phenyl-2,3-dihydroperimidine; 2) spiropyran IV; 3) spiropyran V; 4) merocyanine VIII; 5) salt III (spectra 1-3 were obtained from $CHCl_3$ solutions of the compounds, and spectra 4 and 5 were obtained from mineral oil suspensions of the compounds).

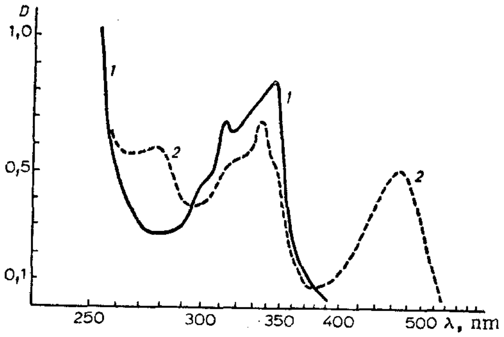


Fig. 2. Electronic absorption spectra of an alcohol solution of spiropyran VII (c $5.28 \cdot 10^{-5}$ mole/liter. l 1 cm): 1) before irradiation; 2) after irradiation.

refluxed for 3.5 h, after which it was cooled and poured into a small volume of water. The resulting precipitate was removed by filtration, washed thoroughly with water, and dried at 100°C to give 0.32 g (97%) of product. The product was soluble in chloroform, acetone, and CCl_4 and was crystallized from benzene to give shiny snow-white needles with mp 174°C. Found: C 80.6; H 6.1; N 8.3%. $C_{22}H_{20}N_2O$. Calculated: C 80.5; H 6.1; N 8.5%.

1,3,3'-Trimethylspiro(2,3-dihydroperimidine-2,2'-[2H]benzo[h]chromene) (VII). A mixture of 0.35 g (1 mmole) of salt II, 0.17 g (1 mmole) of 2-hydroxy-1-naphthaldehyde, 0.3 ml (3 mmole) of piperidine, and 4 ml of pyridine was refluxed for 4.5 h, after which it was worked up as described above to give 0.3 g (80%) of snow-white crystals with mp 269-270°C (from benzene). Found: C 82.7%; H 6.0; N 7.2%. $C_{26}H_{22}N_2O$. Calculated: C 82.5; H 5.9; N 7.4%.

1,3-Dimethyl-2-(2-oxido-5-nitrostyryl)perimidinium (VIII). A solution of 0.34 g (1 mmole) of iodide I, 0.17 g (1 mmole) of 5-nitrosalicylaldehyde, and 0.25 g (2.5 mmole) of piperidine in 40 ml of alcohol was refluxed for 15 min. The precipitate that formed during the reflux period was removed by filtration and washed with acetone to give bright-orange needles that were only slightly soluble in many organic solvents and had mp 289°C (dec., from DMF). The yield was 0.33 g (92%). Found: C 70.0; H 5.0; N 11.7%. $C_{21}H_{17}N_3O_3$. Calculated: C 70.2; H 4.8; N 11.7%. The compound was unaffected by refluxing in benzene, xylene, chlorobenzene, and DMF.

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