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Photodimerization of 2-Styrylpyridine

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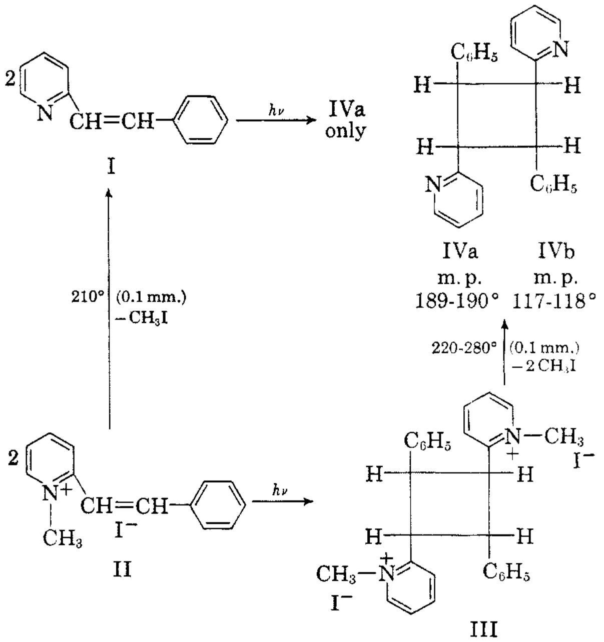
Contrary to previous reports of other investigators, 2-styrylpyridine photodimerizes, though in very low yield, owing to degradation and resinification. Irradiation of 2-styrylpyridinium methiodide produces a high yield of dimeric salt which, when sublimed *in vacuo*, gives two isomeric dimeric bases, one of which is identical with the dimer of 2-styrylpyridine.

Koller[1] reported that ultraviolet irradiation of 2,4-dichloro-3-cyano-6-styrylpyridine produced a high-melting photodimer. By molecular-weight determination and by its inert behavior toward potassium permanganate in acetone, the dimer was shown to be 1,3-bis(phenyl)-2,4-bis[2-(2,4-dichloro-3-cyano)pyridyl]cyclobutane which on pyrolysis reverted to 2,4-dichloro-3-cyano-6-styrylpyridine. Under identical conditions,[1] 2-styrylpyridine (2-stilbazole) (I) did not dimerize. Later, Henze[2] prepared a bis(2-quinolyl)bis(phenyl)-cyclobutane by irradiation of 2-styrylquinoline. It was again reported that 2-styrylpyridine (I) did not photodimerize.

During a study of the ultraviolet spectra of a group of styrylpyridinium salts, it has been found that ultraviolet irradiation of solid 2-styrylpyridinium methiodide (II), m.p. 227–228°, produced a new salt (III), m.p. 310–312°. Irradiation was accompanied by a change of color from yellow to white, with a simultaneous shift of the ultraviolet absorption of 2-styrylpyridinium methiodide (II) from 337 mμ to 265 mμ. Elemental analysis revealed that the empirical formula of the new salt was identical with that of 2-styrylpyridinium methiodide.

Sublimation of styrylpyridinium methiodides produces the corresponding styrylpyridine and methyl iodide. Accordingly, sublimation of the new salt (III) produced a free base (IV) which had elemental analyses and a molecular weight corresponding to that of a dimer of styrylpyridine. The basic dimer obtained from the sublimation melted over the range, 108° to 170°. Fractional crystallization of the basic dimer (IV) has yielded two forms (IVa and IVb) melting at 189–190° and 117–118°. The molecular weights for the two isomers are 364 and 362, respectively. Figure 1 shows that the basic dimers (IVa and IVb) and 2-(β-phenethyl)pyridine (V) are quite similar in ultraviolet spectra. 2-Styrylpyridine (I) differs vastly from both dimers in melting point and in ultraviolet absorption (λ_{max}, 309 mμ). The dimer



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[1] G. Koller, *Ber.*, **60B**, 1920 (1927).

[2] M. Henze, *Ber.*, **70B**, 1273 (1937).

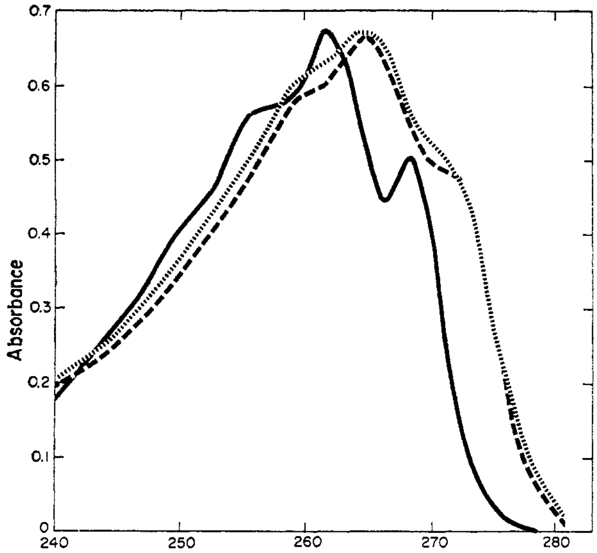

Fig. 1. Ultraviolet spectra in methanol of 2-(β-phenethyl)pyridine, (V), 2×10^{-4} molar, ———; dimer IVa, 1×10^{-4} molar, ---------; dimer IVb, 1×10^{-4} molar, ||||||||||||

salt (III) is similar in ultraviolet spectra to 2-(β-phenethyl)pyridinium methiodide (VI).

Careful repetition of the irradiation of 2-styrylpyridine (I), in the manner of Koller[1] and Henze,[2] has shown that dimerization does indeed occur, but in only 2.6% yield. The majority of 2-styrylpyridine (I) is photodegraded to a mixture of resinous and volatile products. The photodimer of 2-styrylpyridine (I) obtained is identical in physical properties with the higher melting isomer (IVa) obtained by the pyrolysis of the photodimer (III) of 2-styrylpyridinium methiodide (II).

In structures IVa, IVb, and III, no attempt is made to fix the configuration of the groups pendant to the cyclobutane ring. It appears reasonable, however, after examination of molecular models, to expect the quaternized rings to dimerize into alternate positions. This would reduce steric as well as charge interference. The configurational aspects of these tetra-substituted cyclobutanes is now under study.

EXPERIMENTAL

Photodimerization of 2-styrylpyridinium methiodide. Twenty-five g. of powdered 2-styrylpyridinium methiodide[3] was irradiated in an open dish for 80 hr. at a distance of 10 in. from a 450-watt, high-pressure, mercury-vapor lamp. The solids were mixed and crushed every 8 hr. to ensure exposure. The color of the solids changed from yellow, m.p. 227–228°, to buff, m.p. 265–269°, during irradiation. Recrystallization of the buff solid from water, after a treatment with Norit, produced a white solid, m.p. 310–312°. The yield was nearly quantitative.

Anal. Calcd. for $C_{28}H_{28}N_2I_2$: C, 51.8; H, 4.7; N, 4.4; I, 39.2. Found: C, 52.0; H, 4.5; N, 4.2; I, 39.1.

Pyrolysis of the photodimer of 2-styrylpyridinium methiodide. Two g. of the photodimer of 2-styrylpyridinium methiodide was placed in an all-glass vacuum sublimation apparatus. The solids were heated at 0.1 mm. for 2 hr. at 220°, followed by 2 hr. at 275–280°. The sublimate (1 g.) was dissolved in a boiling mixture of 100 ml. of benzene and 700 ml. of hexane. After treatment with Norit, the colorless solution was evaporated to dryness on the steam cone. The solids were boiled with 50 ml. of hexane. The undissolved solid (IVa) was separated and dried; weight, 0.2 g.; m.p. 189–190°.

Anal. Calcd. for $C_{26}H_{22}N_2$: C, 85.6; H, 6.1; N, 7.8; mol. wt., 362. Found: C, 85.1; H, 5.7; N, 7.8; mol. wt., 364. The mother liquor, when cooled to 30°, produced 0.1 g. of crystals (IVa), m.p. 185–187°. The mother liquor was then evaporated on the steam cone to 30 ml. and cooled to 30° to produce 0.1 g. of white needles (IVb), m.p. 114–115°.

Anal. Calcd. for $C_{26}H_{22}N_2$: C, 85.6; H, 6.1; N, 7.8; mol. wt., 362. Found: C, 85.7; H, 5.7; N, 7.8; mol. wt., 362.

The mother liquors yield, on evaporation to 15 ml., 0.2 g. of mixed crystals, m.p. 109 to 140°.

Photodimerization of 2-styrylpyridine. Six g. of 2-styrylpyridine[4] was irradiated for 72 hr. at a distance of 10 in. from a 450-watt, high-pressure, mercury-vapor arc. The solids were stirred periodically until they became tacky. During irradiation, a strong aromatic odor was produced. The tacky solids, weighing 4 g., were dissolved in 100 ml. of diethyl ether, and the solution was treated with Norit. The solution was evaporated to dryness, and the solids were boiled with a mixture of 50 ml. of ethyl acetate and 100 ml. of hexane. A considerable portion of the solids were sticky polymers which failed to dissolve and were then removed by filtration. The clear solution was cooled to −10°; white crystals (IVa) separated which, after filtration and drying, weighed 0.4 g., and melted at 185–188°. A sample recrystallized from (4:1) hexane–diethyl ether melted at 189–190°. A mixed melting point with (IVa) obtained from the dimer of 2-styrylpyridine methiodide (III) by pyrolysis was not depressed.

Ultraviolet absorption curves. The ultraviolet spectra were run in 1-cm. quartz cells using a Cary Model 14 instrument.

Molecular weights. Molecular-weight determinations were carried out by Dr. O. E. Schupp, of the Kodak Research Laboratories, using the elegant thermometric method of Neumayer.[5]

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(4) B. D. Shaw and E. A. Wagstaff, *J. Chem. Soc.*, p. 26 (1933).

(5) J. J. Neumayer, *Anal. Chim. Acta*, **20**, 519 (1959).