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CONDENSATION REACTIONS OF 2,6-LUTIDINE AND AN ESTROGENIC 2,6-DISTYRYLPYRIDINE DERIVATIVE

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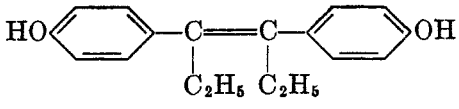
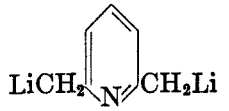
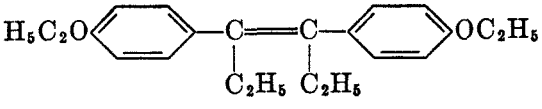
I. In the studies on synthetic estrogens [for a review, see (1)], no attention appears to have been paid to the possibility of introducing heterocyclic radicals in suitable positions into the active molecule of stilbestrol (I). In connection with other experiments, the reaction of the dilithium derivative (II) of 2,6-lutidine with *p*-ethoxypropiophenone (2, 3, 4) (as a model experiment, the reaction of 2,6-lutidine with 1 mole of benzaldehyde was investigated; see Experimental Part), and conversely the condensation by means of acetic anhydride,



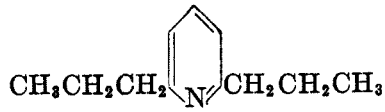
I



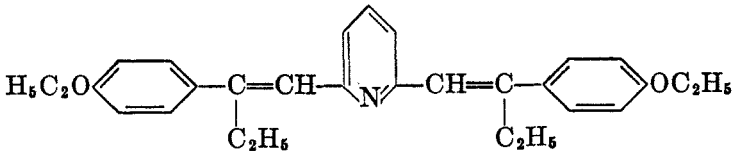
II



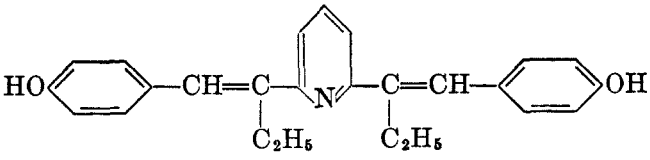
Ia



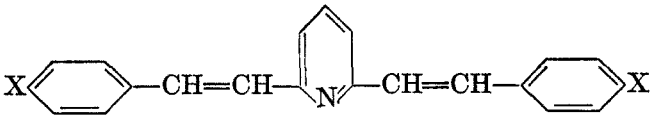
III



IV



V

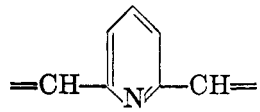


VI, X = OH
VII, X = CN

[1] Part of a thesis presented by S. Pinchas to the Hebrew University in partial fulfilment of the requirements for the degree of Ph.D.

of 2,6-dipropylpyridine (III) with *p*-hydroxybenzaldehyde, was studied. In the former instance, IV, in the latter, V was formed. It is interesting that V showed no estrogenic activity, while IV is—very slightly, yet distinctly—active. Its activity is 33 mouse units per gram.[2] Stilbestrol diethyl ether (Ia) is 125 times less active than I (5).

The interposition, in stilbestrol, of the group



does not destroy its activity. Compound IV appears as a higher vinylog of stilbestrol; however, a shift of the ethyl groups in IV gives a completely inactive

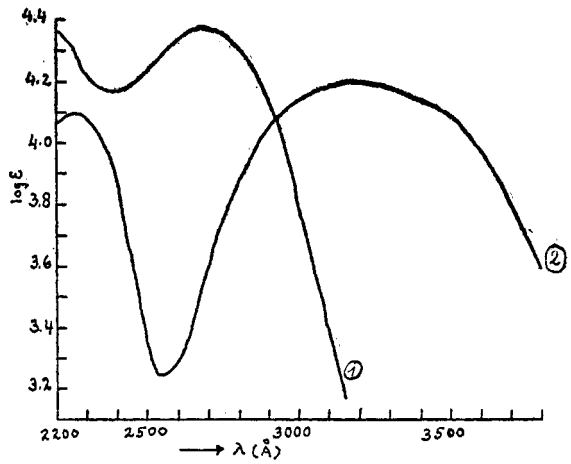


FIG. 1. Ultraviolet absorption (in alcoholic solution) of (1) 2,6-di-(4′-ethoxy-α-ethylstyryl)pyridine (IV) and of (2) 2,6-di-(*p*-hydroxystyryl)pyridine (VI).

substance, as in V. IV corresponds in type to the equally active 3-(*p*-hydroxyphenyl)-4-propyl-7-hydroxycoumarin (6) and to the cinnolines recently described by Kornfeld (7).

2,6-Dipropylpyridine was obtained from II and ethyl bromide, in analogy to Wibaut and Beets' synthesis of β-(2-pyridyl)propionaldehyde acetal (8). Its ability to condense with *p*-hydroxybenzaldehyde is considerably greater than that of 2,6-lutidine, to judge from the relatively good yield of V (see below).

The absorption spectrum of IV is significantly different from that of 2,6-di-(*p*-hydroxystyryl)pyridine (VI) (Fig. 1). This difference cannot be ascribed to the presence of the *p*-ethoxy groups in IV; it must be connected with the ethyl groups and recalls the difference in ultraviolet absorption between stilbene and α, β-dialkylstilbenes (9, 9a, 10, 10a).

[2]For the biological evaluation, we are indebted to Prof. B. Zondek, Hadassah Hospital, Jerusalem.

II. In the presence of acetic anhydride as condensing agent, *p*-hydroxybenzaldehyde (which is converted into its acetyl derivative) undergoes condensation with 2,6-lutidine to VI only with difficulty; the best yield obtained was 23%. The slowness of the reaction expresses itself in contradistinction with other benzaldehydes (11), in the formation of considerable quantities of *p*-acetoxybenzaldiacetate which is no longer capable of easy condensation. Also in the reaction with malonic acid (12), *p*-hydroxybenzaldehyde gives the smallest yield of all aldehydes investigated. As in the case of benzaldehyde (13), the second molecule of the aldehyde reacts more easily than the first: even if a molar ratio of the two components is used, the distyryl compound prevails in the product.

III. In connection with these experiments, 2,6-di-(*p*-cyanostyryl)pyridine (VII) was synthesized. For its preparation, two possibilities were envisaged: the reduction of the easily available 2,6-di-(*p*-nitrostyryl)pyridine to the corresponding diamino compound and subsequent replacement of the amino groups, or the condensation of 2,6-lutidine with *p*-cyanobenzaldehyde. The first method failed, as the replacement of the amino groups by nitrile radicals gave a most unsatisfactory yield. Also an attempt to condense *p*-aminobenzaldehyde (in form of its sulfate) with 2,6-lutidine, met with no success. As to the second method, it was to be expected that *p*-cyanobenzaldehyde would behave like *p*-nitrobenzaldehyde, in view of the general similarity between the NO_2 and the CN groups. This prediction is borne out by the facts. The two aldehydes resemble each other also in that respect, that they are not converted into the benzaldiacetates under the influence of boiling acetic anhydride [for *p*-nitrobenzaldehyde, see Shaw and Wagstaff (11)].

Difficulties were encountered in the preparation of *p*-cyanobenzaldehyde. Neither the oxidation of *p*-cyanobenzyl alcohol nor that of *p*-cyanobenzyl chloride (with cupric nitrate) (14) nor the Sandmeyer reaction of *p*-aminobenzaldehyde gave satisfactory yields (15). The method of choice was the oxidation of *p*-tolunitrile with chromic acid anhydride in presence of acetic anhydride, and subsequent hydrolysis of the *p*-cyanobenzaldiacetate obtained. However, even in this method, the desired aldehyde was always accompanied by *p*-carbamidobenzaldehyde (16); the methods of its isolation and transformation into the *p*-cyano compound are described in the Experimental Part. Surprisingly, the presence of traces of *p*-carbamidobenzaldehyde has an adverse effect on the reaction of 2,6-lutidine with the *p*-cyano derivative.

EXPERIMENTAL

2,6-Di-(4'-ethoxy-α-ethylstyryl)pyridine (IV). In a slow current of nitrogen, and with stirring, a solution of bromobenzene (63 g., 0.4 mole) in ether (100 cc.) was quickly added to a suspension of lithium turnings (5.5 g., 0.8 atom) in the same solvent (150 cc.). In an exothermic reaction, practically all the lithium disappeared within two hours. The addition of 2,6-lutidine (16 g., 0.15 mole) in ether (50 cc.) caused a renewed exothermic reaction, and the solution turned dark red. After one hour, 4-ethoxypropiophenone (54 g., 0.30 mole, b.p. 140–145°/3 mm.) (17) was slowly added and the reaction product hydrolyzed by careful addition of water (100 cc.) and dilute hydrochloric acid (300 cc.). The top layer was dried

and concentrated in the vacuum of the suction pump, and the residue subjected to fractionation under 0.1 mm. pressure. The fraction (20 g.) boiling at 120–160° was re-distilled; b.p. 110°/0.22 mm.; b.p. 125°/0.2 mm. It formed a slightly yellowish, viscous oil, which gave a hygroscopic and very unstable hydrochloride. Yield, 30% of theory.

Anal. Calc'd for $C_{29}H_{33}NO_2$: C, 81.5; H, 7.7.

Found: C, 82.0; H, 7.8.

2,6-Dipropylpyridine. A solution of dilithio-2,6-lutidine was prepared, as above, from lithium (11 g., 1.6 atoms) and bromobenzene (125 g., 0.8 mole) in ether (500 cc.) with 2,6-lutidine (32 g., 0.3 mole). Upon slow addition of ethyl bromide (75 g., 0.7 mole), dissolved in ether (100 cc.), the solution began to boil and the color disappeared. After addition of 300 cc. of water, the ethereal layer was separated and the aqueous layer extracted with fresh ether (50 cc.). The reaction product showed, after repeated fractionation, the b.p. 54–56°/4 mm.; it was an almost colorless, mobile oil, insoluble in water, but soluble in acids, and had a characteristic, not at all lutidine-like odor. Yield, 28 g.

Anal. Calc'd for $C_{11}H_{17}N$: C, 81.0; H, 10.4; N, 8.6.

Found: C, 81.5; H, 10.9; N, 8.7.

2,6-Di-(4'-hydroxy-β-ethylstyryl)pyridine (*V*). A mixture of 2,6-dipropylpyridine (4.5 g., 0.028 mole), *p*-hydroxybenzaldehyde (10.0 g., 0.08 mole) and acetic anhydride (23 cc., 0.25 mole) was refluxed for thirty hours and poured into an excess of water. The reaction product which precipitated as a dark resin, was triturated with concentrated hydrochloric acid and thus converted (hydrolysis of the acetoxy to hydroxy groups) into the *hydrochloride* which crystallized from the solution. It was filtered and recrystallized repeatedly from nitrobenzene and glacial acetic acid and finally from 75% acetic acid. Yellow, prismatic crystals of m.p. 282°; yield, 5 g. The substance is insoluble in water and hydrocarbons, but dissolves in pyridine, aqueous alkali and alcohol.

Anal. Calc'd for $C_{25}H_{26}ClNO_2$: C, 73.6; H, 6.4.

Found: C, 73.0; H, 6.3.

The *free base* was prepared by addition of aqueous ammonia to the solution of the hydrochloride in dilute acetic acid; from a mixture of acetic acid and water (6:1), its *dihydrate* crystallized as a yellow, microcrystalline powder, m.p. 146°. It is very soluble in alcohols, acetone, acetic acid and its esters, insoluble in water and hydrocarbon solvents. The analysis was none too satisfactory, but the *picrate* of the base was well-defined and homogeneous; it formed orange-red crystals of m.p. 236°.

Anal. Calc'd for $C_{25}H_{25}NO_2 \cdot 2H_2O$: C, 73.7; H, 7.1; N, 3.4.

Found: C, 74.3; H, 6.2; N, 3.7.

2-Methyl-6-(2'-phenyl-2'-hydroxyethyl)pyridine. To a solution of phenyllithium (from 0.5 g. of lithium turnings and 5 g. of bromobenzene in 50 cc. of ether), there was added 2.8 cc. of 2,6-lutidine and, after some standing, 2.7 g. of benzaldehyde in ethereal solution. The reaction product was decomposed with a solution of ammonium chloride (5 g.) in water (100 cc.) and purified by repeated distillation *in vacuo*; b.p. 133°/0.01 mm.; yield, 2 g.

Anal. Calc'd for $C_{14}H_{15}NO$: C, 78.8; H, 7.0; N, 6.6.

Found: C, 79.2; H, 7.6; N, 6.8.

2,6-Di-(p-acetoxystyryl)pyridine. A mixture of 2,6-lutidine (27 g.; 0.25 mole), *p*-hydroxybenzaldehyde (92 g.; 0.75 mole), and acetic anhydride (250 cc.; 2.7 moles) was refluxed for twenty-one hours at 150–160° (bath temperature). The reaction mixture was poured into water (1.5 l.) and kept, with occasional shaking, until the excess acetic anhydride was completely hydrolyzed. The brown solid product was filtered, washed with water and recrystallized repeatedly from ethyl alcohol. Thus, 23 g. of colorless prismatic needles of m.p. 183° was obtained; their solution exhibited a violet fluorescence.

Anal. Calc'd for $C_{25}H_{21}NO_4$: C, 75.2; H, 5.3; N, 3.5.

Found: C, 75.2; H, 5.7; N, 3.5.

Concentration of the alcoholic mother liquors gave 37 g. of crystals of m.p. 96°, which were identified as *p*-acetoxybenzaldiacetate (18).

Without condensing agent, no reaction took place in boiling toluene (four hours) or at

120–130° without solvent (six hours). Increase of the amount of acetic anhydride used, reduces the yield, and more *p*-acetoxybenzaldiacetate is formed, which does not condense easily, if at all, with 2,6-lutidine. Even under conditions, which stoichiometrically favor the formation of 2-methyl-6-(*p*-acetoxystyryl)pyridine, the di-(*p*-acetoxystyryl) compound is formed predominantly.

2,6-Di-(p-hydroxystyryl)pyridine (VI). A mixture of the preceding substance (1.5 g.) and of 0.75 *N* alcoholic potassium hydroxide (15 cc.) was refluxed for ninety minutes and the reaction product precipitated from the clear solution as a voluminous powder by a current of carbon dioxide. It was precipitated as the *hydrochloride hydrate* from aqueous sodium hydroxide solution by dilute hydrochloric acid and recrystallized from water (250 cc.). Long yellow needles, which melted above 300° under carbonization, and were slightly soluble in boiling alcohol, easily in pyridine.

Anal. Calc'd for $C_{21}H_{13}ClNO_2 \cdot H_2O$: C, 68.1; H, 5.4; N, 3.8.
Found: C, 68.1; H, 5.5; N, 3.7.

Hydrate formation of such styryl-pyridine derivatives has been observed in a number of instances (13, 19, 20).

The *free base* was obtained from the hydrochloride hydrate, when its solution in 10% aqueous sodium hydroxide solution was acidified with 50% acetic acid. From butyl or ethyl alcohol, light yellow, small needles, m.p. 254° (decomp.). The solution of the base in pyridine, cyclohexanone, acetic acid and alcohols show strong fluorescence; the base is insoluble in hydrocarbon solvents and water.

Anal. Calc'd for $C_{21}H_{17}NO_2$: C, 80.0; H, 5.4; N, 4.4.
Found: C, 80.0; N, 5.5; N, 4.4.

2-Methyl-6-(p-hydroxystyryl)pyridine. A mixture of lutidine (2.2 g.), *p-acetoxy*benzaldehyde (3.6 g.) (b.p. 160–170°/22 mm.) (21), acetic anhydride (5 cc.) and glacial acetic acid (5 cc.) was refluxed for ten hours in a slow current of nitrogen. The dark resin so obtained was washed with water and extracted with 50 cc. of ethyl alcohol. This left 0.8 g. of 2,6-di(*p*-acetoxystyryl)pyridine undissolved. The alcoholic solution was concentrated and the residue hydrolyzed with an excess of concentrated hydrochloric acid. The solution so obtained was brought to dryness *in vacuo*, and the residue dissolved in 10% aqueous sodium hydroxide solution and precipitated by neutralisation. Repeated crystallization from methanol, butyl acetate and aqueous methanol gave colorless needles of m.p. 232° (decomp.), which are soluble in acetic acid and most other organic solvents and fluoresce in solution.

Anal. Calc'd for $C_{14}H_{13}NO$: C, 79.6; H, 6.2; N, 6.6.
Found: C, 80.0; H, 6.4; N, 6.6.

Acetyl derivative, prepared with acetic anhydride and a drop of concentrated sulfuric acid, from very little of dilute alcohol shiny, colorless leaflets of m.p. 95°.

Anal. Calc'd for $C_{16}H_{15}NO_2$: C, 75.9; H, 5.9; N, 5.5.
Found: C, 75.6; H, 6.3; N, 6.1.

2,6-Di-(p-cyanostyryl)pyridine (VII) and 2-methyl-6-(p-cyanostyryl)pridine. A mixture of *p*-cyanobenzaldehyde (4.0 g.), 2,6-lutidine (1.7 cc.) and acetic anhydride (13 cc.) was refluxed for ten hours and diluted with water (200 cc.). After the excess acetic anhydride had undergone hydrolysis, a brown solid remained, which was filtered, washed with water and dissolved in boiling alcohol (75 cc.) in the presence of charcoal. From the filtered solution, 2,6-di-(*p*-cyanostyryl)pyridine crystallized upon cooling (yield, 1.5 g., 25%). Repeated recrystallization from 80% alcohol and glacial acetic acid gave the compound in long, almost colorless prismatic needles of m.p. 175–176°. Its solution in alcohol or benzene shows an intense violet fluorescence.

Anal. Calc'd for $C_{23}H_{15}N_3$: C, 82.9; H, 4.5; N, 12.6.
Found: C, 83.3; H, 4.5; N, 12.5.

The alcoholic mother liquor was cautiously diluted with aqueous ammonia, until turbidity appeared; upon standing, 2-methyl-6-(*p*-cyanostyryl)pryidine crystallized. Repeated recrystallization from 70% alcohol gave colorless prismatic needles of m.p. 131°, in a yield of 0.7 g.

Anal. Calc'd for $C_{15}H_{12}N_2$: C, 81.8; H, 5.5; N, 12.7.
Found: C, 82.2; H, 5.6; N, 12.7.

p-Cyanobenzaldehyde. (a) *p-Carbamidobenzaldehyde.* To a mixture of *p*-tolunitrile (38 g.) (22), glacial acetic acid (450 cc.) and acetic anhydride (450 cc.) which was cooled in an ice-salt mixture, concentrated sulfuric acid (67 cc.) was added slowly with vigorous agitation, so that the temperature did not exceed 25°. The solution was then cooled to 5°, and in the course of ninety minutes, finely ground chromic acid anhydride (72 g.) was added at a temperature of 5–8°. Thirty minutes after the addition, the temperature began to rise slowly. When it reached 10°, the stirring was interrupted and the reaction mixture left overnight. It was then poured out onto 2 kg. of ice, and water (2 l.) was added. The fine colorless precipitate so obtained was washed with water. (From the mother liquors, a small quantity of *p*-cyanobenzaldehyde could be secured by extraction with benzene, hydrolysis and conversion into the bisulfite compound.) The solid was suspended in 2% sodium carbonate solution (400 cc.), filtered, washed, dried (28 g.) and refluxed for thirty minutes with a mixture of concentrated sulfuric acid (7 cc.), ethyl alcohol (75 cc.) and water (100 cc.). From the filtered solution, a mixture of *p*-cyanobenzaldehyde (long white needles of m.p. 92–93°) and an oil separated on standing. The solid was separated and the mother liquor (containing the oil) diluted with an equal volume of water. Thereby, the oil was induced to crystallize: 7 g. of *p*-carbamidobenzaldehyde (14%), m.p. 75–76°. A second small crop of *p*-cyanobenzaldehyde was obtained by concentration of the mother liquor; total yield, 6.3 g. (15%). *p*-Carbamidobenzaldehyde crystallized from dilute alcohol or petroleum ether in colorless needles, m.p. 75–76°.

Anal. Calc'd for $C_8H_7NO_2$: N, 9.4. Found: N, 9.4.

(b) *p-Carbamidobenzaldiacetate.* A mixture of *p*-carbamidobenzaldehyde (2 g.), acetic anhydride (10 cc.) and one drop of conc'd sulfuric acid was refluxed for thirty minutes, and diluted with water (100 cc.). The crystals which separated upon standing, were recrystallized from dilute alcohol or petroleum ether, m.p. 118°.

Anal. Calc'd for $C_{12}H_{13}NO_5$: C, 55.2; H, 5.4; N, 5.6; acetyl, 34.0.
Found: C, 55.8; H, 5.2; N, 5.3; acetyl, 32.0.

(c) *p-Cyanobenzaldehyde.* A mixture of the preceding substance (64 g.) and thionyl chloride (100 cc.) was refluxed for two hours aud the excess thionyl chloride distilled off. To the remaining red oil, alcohol (200 cc.), water (200 cc.), and dilute sulfuric acid (40 cc.) was added and the mixture refluxed again for one hour. The filtered solution was diluted with an equal volume of water and cooled at 0°, whereupon *p*-cyanobenzaldehyde (25 g.) crystallized. A small second crop secured by concentration of the mother liquor, brought the yield to 85%.

2,6-Di-(p-nitrostyryl)pyridine and 2-methyl-6-(p-nitrostyryl)pyridine. A mixture of *p*-nitrobenzaldehyde (30.2 g.), 2,6-lutidine (11.2 cc.) and acetic anhydride (60 cc.) was refluxed for six hours and after addition of 2,6-lutidine (5.6 cc.) for further eight hours, and then poured into water (500 cc.). The crystals of the di-nitrostyryl compound which precipitated, were separated from the aqueous mother liquor and some adherent oil; from pyridine (intense green fluorescence), shiny yellow leaflets, m.p. 258° (decomp.); yield, 31% (23). The filtrate was further diluted, and deposited, upon standing, a 50% yield of 2-methyl-6-(*p*-nitrostyryl) pyridine, from water or 50% alcohol, yellow needles, m.p. 135° (24), from 80% alcohol, needles of m.p. 96°. The latter substance is converted into 2,6-di-(*p*-nitrostyryl)pyridine only with difficulty.

2,6-Di-(p-aminostyryl)pyridine. A mixture of 2,6-di-(*p*-nitrostyryl)pyridine (12.5 g.), tin (20 g.) and 10% hydrochloric acid (300 cc.) was gently refluxed until the metal had disappeared completely. The *stannous chloride double salt* of the desired diamine, which precipitated, was collected, washed with water and alcohol and dried (22.0 g.); it was soluble in acetone (as in other solvents, with red color) and crystallized from hydrochloric acid in orange prisms.

The salt was triturated with a mixture of 180 cc. of alcohol and 20 cc. of 33% aqueous sodium hydroxide solution. Filtration and extraction of the solid with boiling alcohol (100 cc.)

gave two extracts, which were combined. The alcohol was removed by distillation and the residue triturated with water, filtered and dried; m.p. 230°; yield, quantitative. Royer's method (25) which used as reducing agent hydrogen and Raney nickel, gave only 49% yield. The base is soluble in pyridine and dilute acids, sparingly soluble in benzene and acetone.

Anal. Calc'd for $C_{21}H_{19}N_3$: C, 80.5; H, 6.1; N, 13.4.

Found: C, 79.9; H, 6.5; N, 13.2.

The transformation of the diamino into the dicyano compound failed.

SUMMARY

1. In the presence of acetic anhydride, *p*-hydroxybenzaldehyde and 2,6-lutidine condense to 2-methyl-6-(*p*-hydroxystyryl)pyridine and 2,6-di-(*p*-hydroxystyryl)pyridine (VI). The same behavior is shown by *p*-nitro- and *p*-cyanobenzaldehyde. The preparation of the latter aldehyde is described in detail.

2. 2,6-Di-(*p*-nitrostyryl)pyridine can be reduced to the diamino compound; the conversion of the latter into 2,6-di-(*p*-cyanostyryl)pyridine failed.

3. The dilithio-compound of 2,6-lutidine (II) gives with ethyl bromide 2,6-dipropylpyridine, and the latter with *p*-hydroxybenzaldehyde 2,6-di-(4′-hydroxy-β-ethylstyryl)pyridine (V).

4. The dilithio-compound (II) gives, with *p*-ethoxypropiophenone, 2,6-di-(4′-ethoxy-α-ethylstyryl)pyridine (IV). IV, a "vinylog" of stilbestrol, has estrogenic activity, V has not.

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