SYNTHESIS OF ISOMERIC BENZODIPYRROLENINES AND THEIR DERIVATIVES

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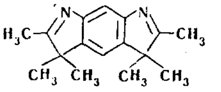
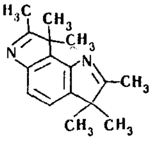
The Fischer reaction was used to synthesize 2,3,3,5,5,6-hexamethyl-3H,5H-benzo[1,2-b:5,4-b']dipyrrole and 2,3,3,7,8,8-hexamethyl-3H,8H-benzo[1,2-b:3,4-b']dipyrrole from the dihydrazone obtained by the action of methyl isopropyl ketone on m-phenylenedihydrazine. Centrosymmetrical 2,3,3,6,7,7-hexamethyl-3H,7H-benzo[1,2-b:4,5-b']dipyrrole was synthesized from p-phenylenediamine and methyl bromoisopropyl ketone. Mono- and diquaternary salts were obtained from the new bases. The diquaternary salts were converted to bismethylene bases.

In [1] we used isomeric benzobisthiazoles and benzobisoxazoles to obtain polymethine dyes with two conjugated chromophores [1]. The dyes from heterocycles of this sort were convenient subjects for a study of the effect of structural factors on the interaction of conjugated chromophores.

This paper is devoted to the preparation of the similarly constructed benzodipyrrolenines (I-IV) and their derivatives, which are suitable for the synthesis of dyes with conjugated chromophores.



I



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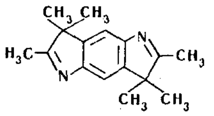

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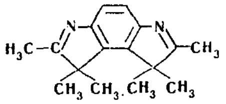

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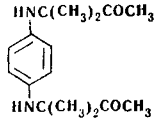

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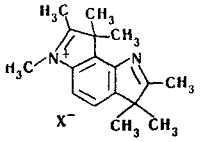

X

The dihydrazone from methyl isopropyl ketone and m-phenylenedihydrazine readily enters into the Fischer reaction in refluxing acetic acid to form a mixture of two isomers of hexamethylbenzodipyrrolenine (I and II). These isomers could be separated by crystallization of their hydrochlorides from water. An isomer with mp 135°C was isolated from the more soluble salt. The IR spectrum of this base contains a band at 855 cm^{-1} which corresponds to the deformation vibrations of the hydrogen atoms in the two adjacent CH groups of the benzene ring [2], which corresponds to the structure of the angular isomer (II). An isomer with mp 148° was isolated from the second salt. The IR spectrum of this base has a band at 895 cm^{-1} due to the deformation vibration of the hydrogen atom in an isolated CH group of a benzene ring [2], which corresponds to the structure of the linear isomer (I). To confirm the structures of both isomers we measured their dipole moments in benzene at 20°. The dipole moment of the base with mp 149° was 4.83D, while the base with mp 135° had a dipole moment of 2.75D. If it is assumed that the moment of the pyrrolenine ring is directed from the isopropyl group to the nitrogen atom, the moments of both pyrrolenine rings in linear isomer I should be close to parallel and be added together, while in angular isomer II they form an obtuse angle, which results in a decrease in the dipole moment of II as compared with that of I.

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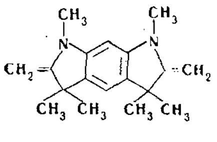
The yield of II is twice that of I. Only products with angular structures are usually obtained in the formation of trinuclear aromatic systems from bifunctional benzene derivatives. However, in our case the nonaromatic pyrrolenine rings are joined, and this results in a mixture of linear and angular isomers.

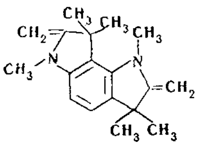
The dihydrazone necessary for the synthesis of bases III and IV via the Fischer reaction could not be obtained from methyl isopropyl ketone and p-phenylenedihydrazine. We therefore attempted to obtain isomers III and IV in a manner similar to that described in [3] for the synthesis of 2,3,3-trimethylindolenines from ring-substituted anilines and methyl bromoisopropyl ketone in pyridine. However, an amino ketone (V) rather than a benzodipyrrolenine (III or IV) was obtained by the reaction of p-phenylenediamine with methyl bromoisopropyl ketone. The structure of V is confirmed by the presence in its IR spectrum of bands at 1715 and 3355 cm^{-1} which are characteristic for the valence vibrations of the ketone and secondary amino groups bonded to an aromatic ring, respectively [2]. It is known [4] that 3-anilino-3-methyl-2-butanone hydrochloride is converted to 2,3,3-trimethylindolenine on heating. The hydrochloride of V also cyclized on heating to 210° with splitting out of water to hexamethylbenzodipyrrolenine with mp 247°. This base has no dipole moment, and its IR spectrum contains a band at 910 cm^{-1} which is characteristic for the deformation vibration of the hydrogen atom in an isolated CH group of a benzene ring [2]. From these data, structure III should be assigned to the hexamethylbenzodipyrrolenine obtained. Isomer IV is not formed, probably as a result of the steric hindrance created by two adjacent isopropyl groups.

Bases I and III readily react on heating with excess dimethyl sulfate or methyl iodide to form quantitative yields of the diquaternary salts (VI and VIII). Monoquaternary salts (IX and XI) are obtained from these bases by heating equimolar amounts of the bases and methyl iodide in nitrobenzene. Base II forms only a monoquaternary salt (X) on heating with excess dimethyl sulfate or methyl iodide. The formation of an isomeric quaternary salt of this base with respect to the 1-position is complicated because of steric hindrance. We obtained a diquaternary salt (VII) by heating II with a stronger alkylating agent – methyl o-nitrobenzenesulfonate [5].

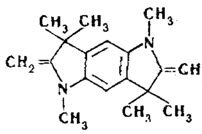
By treatment of the diquaternary salts (VI-VIII) with ammonia, we obtained bismethylene bases (XII-XIV); these were solids which were readily purified by vacuum sublimation.



XII



XIII



XIV

Bases XII and XIII are oxidized and become colored on storage, but at an appreciably lower rate than for 1,3,3-trimethyl-2-methyleneindoline. Methylene base XIV does not change appreciably on storage.

EXPERIMENTAL

2,3,3,5,5,6-Hexamethyl-3H,5H-benzo[1,2-b:5,4-b']dipyrrole (I) and 2,3,3,7,8,8-Hexamethyl-3H,8H-benzo[1,2-b:3,4-b']dipyrrole (II). A total of 28 ml (0.25 mole) of methyl isopropyl ketone and 60 g (0.5 mole) of crystalline sodium acetate were added with stirring to a solution of 43 g (0.1 mole) of the double tin salt of m-phenylenedihydrazine [6] in 300 ml of water. The resulting oil was extracted with chloroform. The solvent was removed in vacuo, 150 ml of acetic acid was added to the residue, and the solution was heated carefully until it began to boil. An exothermic reaction then occurred. After 15 min the acetic acid was removed in vacuo, the residue was neutralized with ammonium hydroxide, and the resulting oil was extracted with chloroform. The chloroform was removed, and the residue was vacuum distilled with collection of the 110-160° (0.5 mm) fraction. Water (220 ml) and 30 ml of 50% perchloric acid were added to the polycrystalline mass obtained (22 g), and the mixture was heated until everything dissolved. The crystals that settled out in cooling were crystallized twice from water and acidified with perchloric acid. The crystals of the diperchlorate of I were dissolved in hot water, and the base was liberated with ammonia. Vacuum sublimation yielded 6.0 g (25%) of I as colorless crystals with mp 149° (from heptane). Found %: N 11.4. $C_{16}H_{20}N_2$. Calculated %: N 11.7. The diperchlorate of I was formed as light-red crystals with mp 262° (decomp., from water) when I was dissolved in dilute perchloric acid. Found %: Cl 15.1. $C_{16}H_{20}N_2 \cdot 2HClO_4$. Calculated %: Cl 16.1. The filtrate after the first crystallization was neutralized with ammonia, and the liberated base (II) was extracted with chloroform. The chloroform was removed, and the residue was crystallized twice from water acidified with perchloric acid. The crystals of the diperchlorate of II obtained were dissolved in water, and the base was liberated with ammonia. Vacuum sublimation yielded 12.3 g (51%) of colorless crystals of II with mp 135° (from hexane). Found %: N 11.4. $C_{16}H_{20}N_2$. Calculated %: N 11.7. Diperchlorate of II was formed as light-rose crystals with mp 288° (decomp., from water) when II was dissolved in dilute perchloric acid. Found %: Cl 15.8. $C_{16}H_{20}N_2 \cdot 2HClO_4$. Calculated %: Cl 16.1.

3,3'-p-Phenylenediaminobis(3-methyl-2-butanone) (V). A total of 18.3 g (0.1 mole) of methyl bromoisopropyl ketone, obtained via the method in [7], was added to a solution of 5.4 g (0.05 mole) of p-phenylenediamine in 25 ml of pyridine at 70°. In the process, a yellow precipitate formed and gave a dark solution on heating for 10 min at 90°. The pyridine was removed in vacuo, and a dark-brown, crystalline product was isolated from the black viscous residue by trituration with ammonium hydroxide. Crystallization from xylene and vacuum sublimation yielded 3 g (22%) of colorless needles of V with mp 182°. Found %: N 10.4; C 69.7; H 8.6. $C_{16}H_{24}N_2O_2$. Calculated %: N 10.3; C 69.6; H 8.7.

2,3,3,6,7,7-Hexamethyl-3H,7H-benzo[1,2-b:4,5-b']dipyrrole (III). A total of 7.1 g (0.025 mole) of V was dissolved by heating in 30 ml of concentrated hydrochloric acid. The residue remaining after evaporation of this solution to dryness was heated in a gentle stream of nitrogen for 30 min at 210°. The base was liberated from an aqueous solution of the salt by ammonium hydroxide. Vacuum sublimation yielded 4.1 g (67%) of colorless crystals of III with mp 248° (from benzene–cyclohexane). Found %: N 11.8. $C_{16}H_{20}N_2$. Calculated %: N 11.7.

1,2,3,3,5,5,6,7-Octamethyl-3H,5H-benzo[1,2-b:5,4-b']dipyrrolium Diperchlorate (VI) and 1,2,3,3,5,6,7,7-Octamethyl-3H,7H-benzo[1,2-b:4,5-b']-dipyrrolium Diperchlorate (VIII). A mixture of 0.24 g (1 mmole) of I (or III), 0.5 g (4 mmole) of dimethyl sulfate, and 10 ml of xylene was heated for 1 h at 140°. The precipitated salt was washed with dry ether to give 0.47 g (96%) of product. This was dissolved in water, the hot solution was treated with activated charcoal, and the quaternary salts were precipitated with sodium perchlorate. Compound VI formed colorless crystals with mp 289° (from water). Found %: Cl 14.6. $C_{18}H_{26}Cl_2N_2O_8$. Calculated %: Cl 14.8. Compound VIII formed colorless crystals which melt above 300° (from water). Found %: Cl 14.9. $C_{18}H_{26}Cl_2N_2O_8$. Calculated %: Cl 14.8.

1,2,3,3,6,7,8,8-Octamethyl-3H,8H-benzo[1,2-b:3,4-b']dipyrrolium Diperchlorate (VII). A mixture of 0.24 g (1 mmole) of II and 0.54 g (2.5 mmole) of methyl o-nitrobenzenesulfonate was heated for 1 h at 105°. The salt was washed with dry ether, dissolved in water, and the hot solution was treated with activated charcoal. The salt was precipitated with sodium perchlorate to give 0.36 g (77%) of colorless crystals with mp 282° (from water or methanol). Found %: Cl 14.9. $C_{18}H_{26}Cl_2N_2O_8$. Calculated %: Cl 14.8.

1,2,3,3,5,5,6-Heptamethyl-3H,5H-benzo[1,2-b:5,4-b']dipyrrolium Perchlorate (IX) and 1,2,3,3,6,7,7-Heptamethyl-3H,7H-benzo[1,2-b:4,5-b']dipyrrolium Perchlorate (XI). A mixture of 0.24 g (1 mmole) of I (or III), 0.15 g (1 mmole) of methyl iodide, and 3 ml of nitrobenzene was heated in a sealed ampoule for 4 h at 100°. The addition of dry ether gave a crystalline precipitate which was filtered and washed with ether. The salt obtained was dissolved in chloroform, and the solution was filtered away from the undissolved, admixed diquaternary salt. The filtrate was evaporated, the residue was dissolved in a small amount of water, and the salt was precipitated with sodium perchlorate to give 72% of light-gray crystals of IX with mp 224° (from water). Found %: N 7.6. $C_{17}H_{23}ClN_2O_4$. Calculated %: N 7.9. Compound XI was obtained in 82% yield as light-gray crystals with mp 245° (from water). Found %: Cl 10.0. $C_{17}H_{23}ClN_2O_4$. Calculated %: Cl 10.0.

2,3,3,6,7,8,8-Heptamethyl-3H,8H-benzo[1,2-b:3,4-b']dipyrrolium Iodide (X). This was obtained in quantitative yield by heating II with excess methyl iodide in benzene. The product was light-yellow crystals with mp 244°. Found %: I 33.6. $C_{17}H_{23}IN_2$. Calculated %: I 33.2.

1,3,3,5,5,7-Hexamethyl-2,6-dimethylbenzo[1,2-b:5,4-b']dipyrroline (XII), 1,3,3,6,8,8-Hexamethyl-2,7-dimethylenebenzo[1,2-b:3,4-b']dipyrroline (XIII), and 1,3,3,5,7,7-Hexamethyl-2,6-dimethylenebenzo[1,2-b:4,5-b']dipyrroline (XIV). These were obtained by the action of ammonia on aqueous solutions of VI–VIII. The liberated bismethylene base was extracted with chloroform, and the residue after evaporation of the chloroform was vacuum sublimed. Compound XII was obtained in 73% yield as light-yellow crystals with mp 154°. Found %: N 10.5. $C_{18}H_{24}N_2$. Calculated %: N 10.4. Compound XIII was obtained in 52% yield as crystals with mp 133°. Found %: N 10.9. $C_{18}H_{24}N_2$. Calculated %: N 10.4. Compound XIV was obtained in 89% yield as light-brown crystals with mp 198° (from hexane). Found %: N 10.4. $C_{18}H_{24}N_2$. Calculated %: N 10.4.

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