Some Schiff Bases of N-Methyl-4-carbostyrilcarboxaldehyde

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Several studies have been reported on the preparation and properties of N-substituted-4-methylcarbostyrils (1), (2), (3). We have been interested in the substitution of various groups on the 4 position of 1, 4-dimethylcarbostyril by the conversion of the 4-methyl group to a formyl group with selenium dioxide and the subsequent production of a number of derivatives from this aldehyde.

With the intention of continuing this study, we have prepared a number of Schiff Bases of 1-methyl-4-carbostyrilcarboxaldehyde which we hope to use as intermediates for further study. It is the purpose of this paper to report the preparation and properties of these anils.

Similar compounds produced from quinoline-4-aldehyde and several different aromatic amines have already been reported by Ramsey, Baldwin and Tipson (4). It is interesting to note that compounds prepared by us are quite similar in physical properties to the compounds reported by these authors.

The anils prepared are those obtained by the condensation of 1-methyl-4-carbostyrilcarboxaldehyde with p-aminophenol, p-diethylaminoaniline, p-aminobenzoic acid, p-aminobenzenesulfonamid, and p-aminoazobenzene. These compounds were all obtained in yields of 76-98 percet by condensation of the amine and aldehyde in boiling alcohol for eighteen hours.

One of these compounds, 1-methyl-4-carbostyrilcarboxaldehyde p-phenylazoanil, has the properties of an indicator dye. It has been found to give a brown-red color in acid solution with a definite change to light green when the solution is made basic with ammonium hydroxide or sodium hydroxide. Further study is contemplated to find the pH range of this color change.

These compounds offer a convenient method for the introduction of substituents in the carbostyril nucleus at the 4 position.

Experimental

1-Methyl-4-carbostyrilcarboxaldehyde (I) was prepared as previously described in this journal (3). The necessary substituted anilines were all Organic Chemicals obtained from the Distillation Products Industries, Rochester, New York. The melting points listed for these compounds were all taken on a Fisher-Johns Melting Point Block.

1-Methyl-4-carbostyrilcarboxaldehyde p-Hydroxyanil.—Two and nine-tenths grams (.0265 moles) of p-aminophenol was dissolved in 75 ml. of absolute alcohol with heating. This solution was filtered and a

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solution of 5 g. of I dissolved in 40 ml. of ethanol was added to it. This mixture was refluxed on the steam bath for 18 hours. When cooled in the refrigerator, the crystalline product formed and was recovered by filtration. The product weighed 7.2 g. (98%). A 0.5 g. sample was recrystallized from 30 ml. of ethanol which on cooling gave bronze colored crystals. This product melted at 234-236°.

Anal.

Calc'd for $C_{17}H_{14}N_2O_2$: N, 10.1%
Found: N, 10.5%

1-Methyl-4-carbostyrilcarboxaldehyde p-Diethylaminoanil. — In a manner similar to that described for the preceding preparation, 2.2 g. (.0132 moles) of p-diethylaminoaniline was dissolved in ethanol and treated for 18 hours with 2.5 g. (.0132 moles) of I. Upon cooling small flat red plates were collected. Five tenths of a gram of this substance was recrystallized from 30 ml. of ethanol. Orange crystals were recovered which melted at 171-172°. The total yield was 4.0 g. (91%).

Anal.

Calc'd for $C_{21}H_{23}ON_3$: N, 12.7%
Found: N, 12.6%

1-Methyl-4-carbostyrilcarboxaldehyde p-Carboxyanil.—In a like manner 1.81 g. of p-aminobenzoic acid (.0132 moles) was treated with 2.5 g. of I. After refluxing for 18 hours, the product was obtained as fine pale yellow crystals. The yield was 3.1 g. (76%). This compound was recrystallized from ethanol and gave a m.p. of 263.5-264.5°.

Anal.

Calc'd for $C_{18}H_{14}N_2O_3$: N, 9.15%
Found: N, 8.83%

1-Methyl-4-carbostyrilcarboxaldehyde p-Sulfonamidanil.—Two and two-tenths grams (.0132 moles) of p-aminobenzenesulfonamid was treated with 2.5 g. of I in ethanol as described in the preceding preparations. The product was recovered as yellow crystals which melted at 257-258°. The yield was 4.4 g. (98%). Upon recrystallization the compound melted at 261-262°.

Anal.

Calc'd for $C_{17}H_{15}N_3O_3S$: N, 12.31%
Found: N, 11.98%

1-Methyl-4-carbostyrilcarboxaldehyde p-Phenylazoanil. — The same general procedure was followed as in the preparation of the other anils. Two and six-tenths grams of the p-aminoazobenzene (.0132 moles) was reacted with 2.5 g. of I. After refluxing, a green-brown solid was obtained which weighed 4.7 g. (97%). This substance, when crystallized twice from ethanol, was obtained as orange crystals which had a softening point at 91° and melted at 97-99°.

Anal.

Calc'd for $C_{23}H_{18}N_4O$: N, 15.3%
Found: N, 14.7%

Summary

Several Schiff Bases of 1-Methyl-4-carbostyrilcarboxaldehyde have been prepared and described. These compounds can be used for starting materials in the preparation of 4 substituted carbostyrils.

Literature Cited

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