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NEWARK PLANT
CHEMICAL DIVISION - COLORS

JACKSON LABORATORY

PIGMENTS GROUP RESEARCH REPORT

DIHYDROPHENAZINE PIGMENTS

Period Covered NOVEMBER 13, 1951 to APRIL 14, 1952.

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JACKSON LABORATORY

PIGMENTS GROUP RESEARCH REPORT

DIHYDROPHENAZINE PIGMENTS

NOVEMBER 13, 1951 to APRIL 14, 1952.

CHARGE: A-II-C-275

SUBMITTED BY: A. D. Reidinger — DATE SUBMITTED: 4/30/53

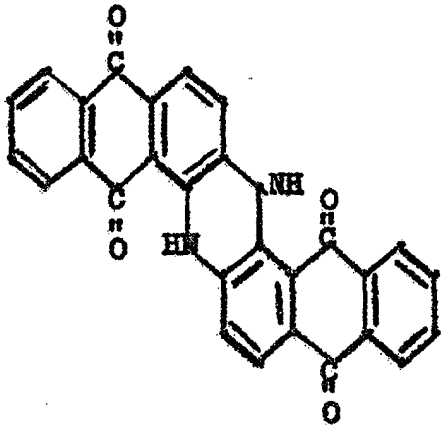
A. D. Reidinger

APPROVED BY: W. S. Struve — DATE ISSUED: 5/7/53

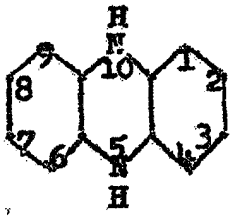
W. S. Struve

INTRODUCTION:

The belief that the excellent lightfastness and bleed resistance of pigments of the Indanthrone class were related to their structure which permits a high degree of charge separation, hydrogen bonding and of resonance, suggested the possibility that new pigments of similar properties might be obtainable by adopting some of the structural characteristics of the Indanthrones. Inspection of the structural formula for the latter showed its resemblance



to substituted dihydrophenazine and it



(Chemical Abstracts numbering)

accordingly appeared that other phenazine derivatives might be found which would be of value as pigments.

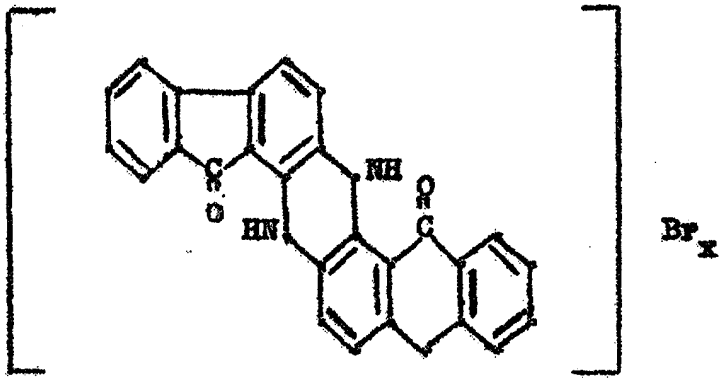
SUMMARY AND CONCLUSIONS:

1,6 Dibenzoyl-5,10 dihydrophenazine was a violet colored substance insoluble in water but quite soluble in benzene. It was unsuitable for pigment use because of instability in the presence of oxygen. When rubbed out in lithographic varnish it was oxidized quite rapidly to the yellow azine form with retardation of drying.

The corresponding 1,4 derivative appears to be even more unstable. The violet product obtained by reducing 1,4 dibenzoyl phenazine with ammonium sulfide is soluble in alcohol and on standing at room temperature soon fades completely.

Two other derivatives in which one of the reactive hydrogen atoms were replaced by a phenyl group and the other bonded by nitro and carbonyl groups (1-nitro-3-chloro-5-phenyl-5,10 dihydrophenazine and 1-benzoyl-5-phenyl-5,10 dihydrophenazine) were red shade blues or violets which were also sensitive to oxygen and soluble in organic solvents. It is of interest that the nitro substituted color was greener and stronger than the benzoyl substituted product.

In view of the difference in stability and in solubility between the dibenzoyl dihydrophenazines and Indanthrone, which was ascribed to the benzoyl groups, attempts were made to prepare a comparable product of the following type by condensation of di- or tribromofluorenone.



However, only small yields of a black product of uncertain composition could be obtained.

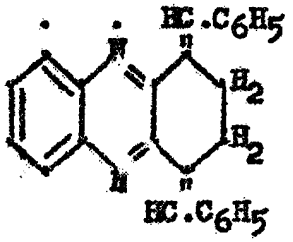
DISCUSSION:

1,6-Dibenzoyl phenazine was obtained in rather low yield by condensation at 210°C in trichlorbenzene of two molecules of 2-brom-3-amino benzophenone. The latter intermediate was prepared by the following route - 3-nitrophthalic acid ⟶ 2-bromo-3-nitrophthalic acid ⟶ 2-bromo-3-nitro-benzophenone ⟶ amino compound. Reduction of 1,6 dibenzoyl phenazine to the 5,10 dihydro form was easily accomplished with sodium hydrosulfite and sodium hydroxide in alcohol. As stated in the summary, re-oxidation to the azine form also occurred readily.

Condensation of 2-brom-3-amino benzophenone with the parent nitro-compound did not proceed satisfactorily in ethylene glycol or in alcohol.

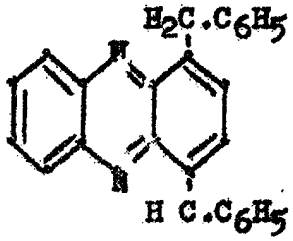
1,4-Dibenzoyl phenazine was prepared in the following steps: cyclohexanone ⟶ cyclohexane-1,2 dione (+ o-phenylenediamine) ⟶ 1,2,3,4-tetrahydrophenazine (+ benzaldehyde) ⟶ 1,4 dibenzal-2,3-dihydrophenazine ⟶ 1,4 dibenzyl phenazine ⟶ product. It is of interest to note that the condensation of 1,2,3,4 tetrahydrophenazine and benzaldehyde is reported in the literature reference (JCS 1937, 1701) to give the dibenzyl derivative II directly, rather than the dibenzal phenazine I.

I



M.P. 152-154° (Lit 158°)

II



M.P. 142-145°

However, the inability to oxidize the initial product to the dibenzoyl derivative, the evidence of ultra-violet absorption curves, and finally the successful isomerization to the desired product, demonstrate the reverse to be the case.

Preparation of 1,4 dibenzoyl phenazine was also attempted by the following route - paraxylidine (+ o-nitro chlorbenzene) ⟶ 1,4 dimethyl-2' nitrodiphenylamine (with iron ⟶ 1,4 dimethyl phenazine ⟶ 1,4 dicarboxy phenazine ⟶ product. However, the oxidation of dimethyl phenazine was unsuccessful and the method was abandoned.

Another route to 1,4 dicarboxy phenazine (pyrocatechol (+ $KHCO_3$) ⟶ 2,3 dihydroxy terephthalic acid (+ o-phenylene diamine) ⟶ product) was not pursued because of low yield and impurity of product resulting from the carbonation step.

Phenazine was obtained in fair yield by heating 2-nitro diphenyl amine with a mixture of iron powder (reduced iron) and iron filings. Use of some reduced iron was necessary to initiate the reaction.

Nitration of phenazine gave the 1,3 dinitro derivative which upon heating with ammonium sulphide was selectively reduced to 1,3 dinitro-5,10 dihydrophenazine. The product was a bluish black substance almost insoluble in organic solvent but which according to the literature also tends to reoxidize and become yellow.

The attempt to make an Indanthrone analog from di- or tri-brom-aminofluorenone involved the following steps: - fluorene → 2-nitrofluorene → 2-nitrofluorenone → 2-aminofluorenone → (1,3) dibrom 2-aminofluorenone → product.

Bromination of 2-aminofluorenone gave a mono-bromo-derivative believed to be 3-bromo-2-aminofluorenone and a dibrom (probably 1,3) derivative. Tribrom-2-amino-fluorenone was made by brominating 2-aminofluorene hydrochloride and then oxidizing to the fluorenone counterpart.

Condensation of these derivatives by the Ullman method did not proceed with the ease exhibited by the comparable bromo-amino-anthraquinones and no products of merit were obtained. This may be explained by the relative inactivity of the bromine atoms in the fluorenone molecule as reported in the literature.

EXPERIMENTAL DETAILS:

Methods of preparation and results are recorded in N.B.1290, and N.B.1430, 1325, 1398.

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MPH