KN-69-13 PYRIDONOQUINOLONE - INTERIM REPORT By: R. J. North 9/68 - 5/69

1/79 (4)

(19) ~~Alan Jackson 1/29/80~~
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E. I. DU PONT DE NEMOURS & COMPANY

PIGMENTS DEPARTMENT

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NEWPORT PLANT

PIGMENT COLORS RESEARCH REPORT

SUBJECT: PYRIDONOQUINOLONE - INTERIM REPORT

PERIOD COVERED: September, 1968 - May, 1969

Date: 11/6/69

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NEWPORT PLANT

PIGMENT COLORS RESEARCH REPORT

SUBJECT: PYRIDONOQUINOLONE - INTERIM REPORT

PERIOD COVERED: September, 1968 - May, 1969

SUBMITTED BY: R. J. NORTH DATE SUBMITTED: 9/26/69

APPROVED BY: W. A. WEST DATE RELEASED: 11/6/69

ABSTRACT: The synthesis of pyridonoquinolone and related compounds was undertaken to evaluate their potential as lightfast yellow pigments.

TABLE OF CONTENTS

PYRIDONOQUINOLONE - INTERIM REPORT

I. INTRODUCTION

To completely round out the DuPont pigment product line a strong, lightfast yellow is required. Many areas of synthetic organic chemistry have been explored in an attempt to obtain a suitable candidate, particularly the area of pyridone chemistry, in which the lightfast red pigment, quinacridone, was discovered. One approach, which has not been attempted and is the objective of this program is to synthesize an analog of quinacridone possessing no peripheral benzene rings. This compound, pyridonoquinolone (PQ), should possess the same hydrogen-bonding characteristics as quinacridone, which are known to be essential for lightfastness, and hopefully might exhibit color in the desirable yellow region of the spectrum. To this end, the synthesis of pyridonoquinolone and some related derivatives was undertaken.

II. SUMMARY AND CONCLUSIONS

Pyridonoquinolone (PQ) has been synthesized and found to be a tinctorially weak, relatively insoluble, greenish-yellow pigment, the lightfastness of which is presently being determined. It is concluded that in order to obtain the desired color in the reddish-yellow reason, auxochromic substitution is necessary on the pyridone rings.

The N,N'-dibenzylimide of PQ tetracarboxylic acid was synthesized and found to be a tinctorially attractive yellow-orange compound being too soluble, however, for use as a pigment. To decrease the solubility and yet retain the desired color characteristics, the unsubstituted diimide is being prepared.

A yellow-orange diacenaphthyl derivative of PQ was also synthesized. Additional material is being prepared for complete pigment evaluation studies.

III. PATENT SITUATION

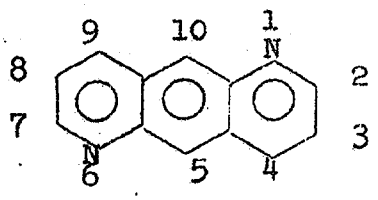
No patent applications based upon this work is warranted at present.

IV. HISTORY

References to the diazaanthracene ring system first appeared in the literature in 1939[1]. The common name used for the ring system is 1,5-anthrazoline but Chem. Abstracts prefers pyrido (2,3-g) quinoline and this nomenclature and numbering system is used throughout this report. Only

IV. HISTORY (Cont'd)

a small number of derivatives have been reported[2],



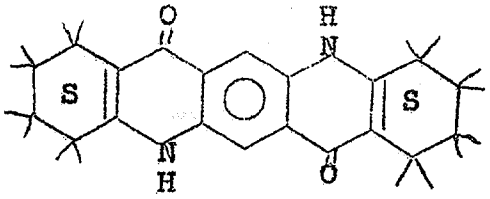
pyrido (2,3-g) quinoline

but it appears that the 4,9-diketo derivatives which are the subject of the present study are unknown in the literature and thus represent a new class of compounds.

V. DISCUSSION

1. Synthesis of Pyridonoquinolone

Two main factors made the synthesis of pyridonoquinolone an attractive project. One, Nelson[3] synthesized octahydroquinacridone (I) and found it to be a fairly strong yellow, non-lightfast compound; the lack of lightfastness is probably a function of the

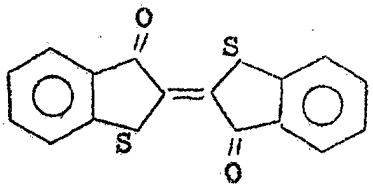


I

non-coplanarity of the fused cyclohexene rings which adversely affect efficient intermolecular hydrogen bonding. Since the cyclohexene rings are not chromophores, but probably act as auxochromes, their removal was expected to cause a very slight hypsochromic shift in the absorption spectrum and thus retain the desired yellow color in the resulting pyridonoquinolone molecule.

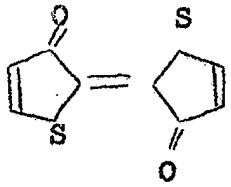
Secondly, Luttke and Hermann's[4] molecular orbital (MO) calculations showed that removal of the peripheral benzene rings in thioindigo, should cause the longest wavelength visible band at 543 mμ to undergo a hypsochromic shift of about 50 mμ in the resulting bisthiophen indigo (II). Experimentally, II was actually

V. DISCUSSION (Cont'd)



thioindigo

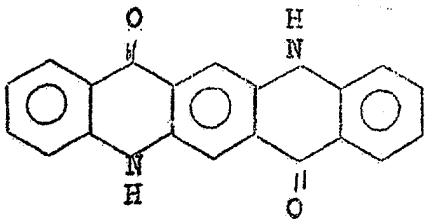
$\lambda_{max.}$ 543 mμ



$\lambda_{max.}$ 502 mμ

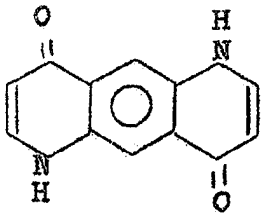
shown to exhibit long wavelength absorption at 502 mμ in excellent agreement with the MO calculations.

If both of the above considerations were applicable in the pyridone system, removal of the two peripheral benzene rings in quinacridone should result in a hypsochromic shift from 515 mμ (QA) to 470 mμ, a desirable red-yellow region for PQ. The synthesis was accomplished



QA

$\lambda_{max.}$ 515 mμ



PQ

$\lambda_{max.}$ 412 mμ

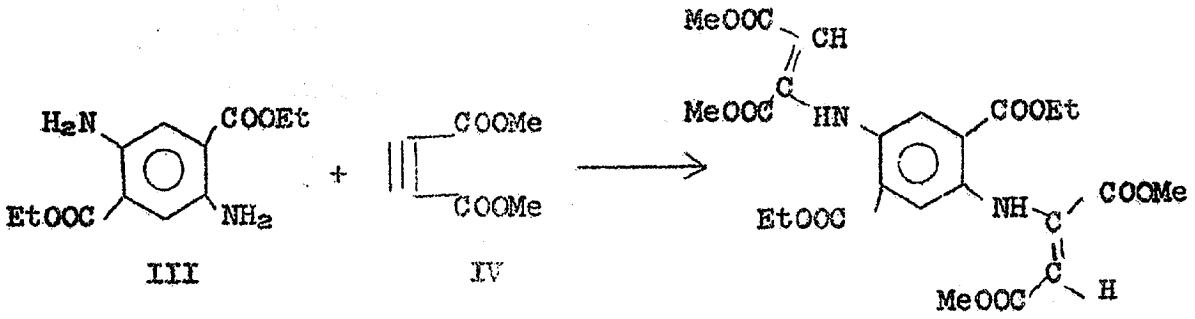
and it was found that the long wavelength absorption of PQ occurred at 412 mμ in the greenish-yellow region indicating that an unexpectedly large hypsochromic shift of ~100 mμ had occurred. A reasonable interpretation of this result is that the peripheral benzene rings in QA contribute to a greater extent to the chromophore than is the case in thioindigo; in other words, the benzo substituents exert a greater auxochromic influence on the electron deficient six-membered pyridone rings than on the electron rich five-membered thiazolone system.

The synthesis of PQ was accomplished in four steps starting with a 1,2-Michael addition of diethyl-2,5-diaminoterephthalate (III) to dimethyl acetylene-dicarboxylate (IV).

V. DISCUSSION (Cont'd)

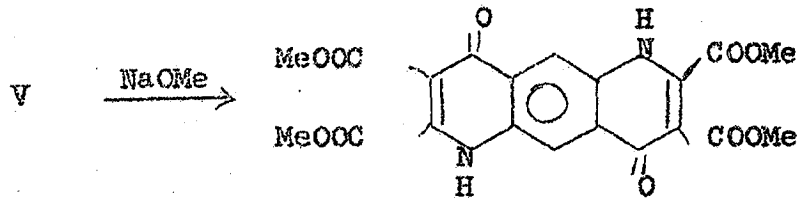
1. Synthesis of Pyridonoquinolone (Cont'd)

The product (V), a bis-fumarate adduct, was obtained in



III IV V

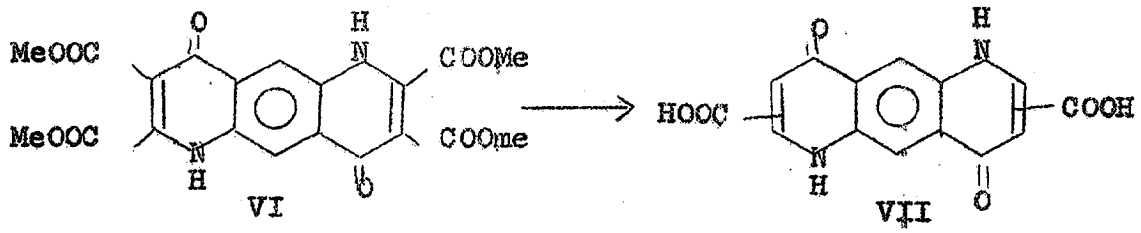
good yield, and was characterized by its ir and nmr spectra. The transoid geometry of the molecule was demonstrated by its single vinyl C-H absorption in the nmr at 5.52 ppm., in good agreement with other work[5] published on anilino-fumarates.



VI

Dieckmann cyclization of V, employing sodium methoxide, produced a symmetrical tetraester (VI), which was characterized by elemental analysis and its nmr spectrum. The ir spectrum did not display characteristic C = O absorption of 4-quinolones. This is analogous to similar observations made with other 4-quinolones substituted in the 2,3 positions with bulky substituents[6].

This particular reaction is of interest since it provides a general facile synthesis of 2,3-dicarboalkoxy-quinolin-4-ones and 2,3,7,8-tetracarboalkoxy pyrido (2,3-g) quinolin-4,9-diones, both new classes of compounds.



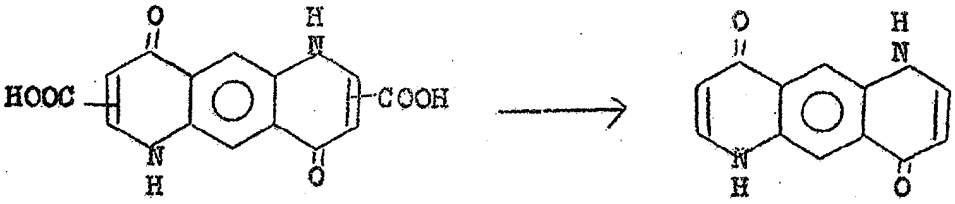
VI VII

V. DISCUSSION (Cont'd)

1. Synthesis of Pyridonoquinolone (Cont'd)

Complete saponification and partial decarboxylation of VI was accomplished by refluxing the ester in ethylene glycol with the theoretical amount of potassium hydroxide. The product (VII) was a diacid, in which the positions of the two carboxy groups has not been unequivocally established.

Finally, thermal decarboxylation of the diacid VII was accomplished by heating at 280°C in tetramethylene sulfone to yield the desired pyridonoquinolone (PQ).

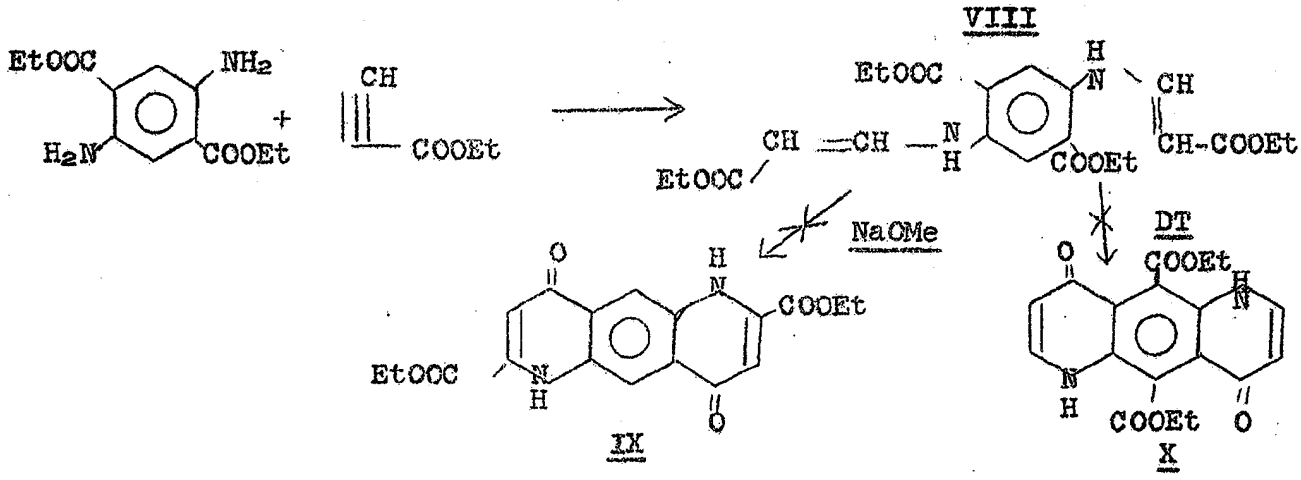


VII PQ

PQ was found to be twice as soluble as QA in boiling DMF, 0.50 g./l. vs. 0.25 g./l., and tinctorially a weak greenish-yellow having a long wavelength absorption at 412 mμ (ε 19,900). The lightfastness is presently being determined, and although the compound does not appear to be of interest as a yellow pigment, it will be evaluated as a UV absorber. In addition, it will be of theoretical interest to see the effect of the absence of the peripheral benzene rings on lightfastness.

2. Alternate Attempts to Synthesize PQ

In an effort to obtain a diester rather than tetraester intermediate for subsequent ease of saponification and decarboxylation, diethyl-2,5-

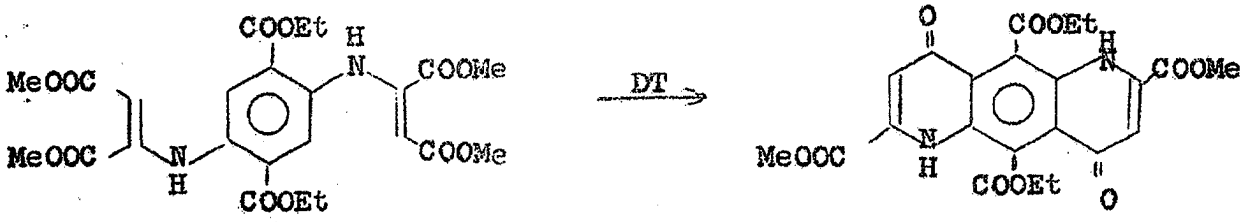


V. DISCUSSION (Cont'd)

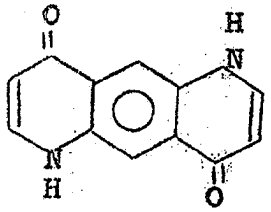
2. Alternate Attempts to Synthesize PQ (Cont'd)

diaminoterephthalate was condensed with ethylpropiolate in a Michael addition to yield the bis-adduct VIII. Attempts were made to cyclize the bis-adduct VIII via a Dieckmann reaction to obtain IX and by a Conrad-Limpach cyclinzation to obtain the diester X; none of the attempts proved successful.

Conrad-Limpach cyclization of the bis-adduct V produced the tetraester XI, which resisted all efforts



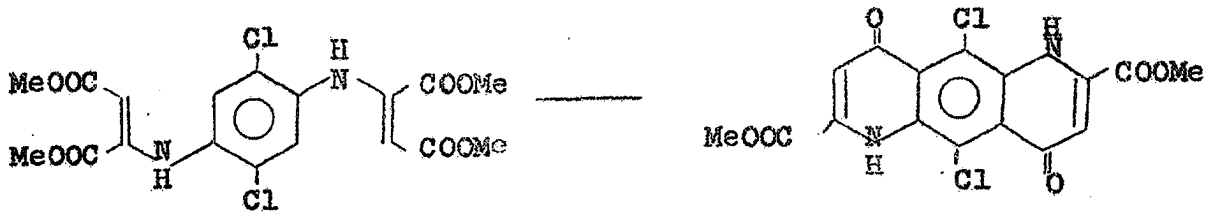
V XI



PQ

of saponification under alkaline and acid conditions. Ring opening may have occurred under these stringent reaction conditions.

A dichloro Michael adduct (XII), prepared by Michael addition of dimethylacetylene dicarboxylate and 2,5-dichloro-p-phenylene diamine, was successfully



XII XIII

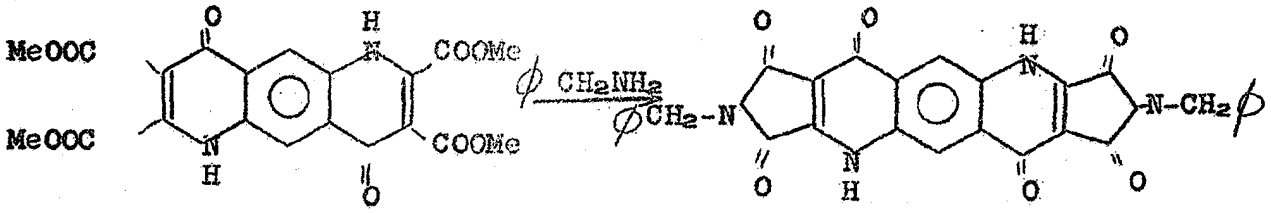
V. DISCUSSION (Cont'd)

2. Alternate Attempts to Synthesize PQ (Cont'd)

cyclized in boiling Dowtherm to yield the 5,10-dichloro - 2,7-dicarbomethoxy derivative of PQ. Further work was interrupted since the desired PQ was obtained concurrently by successful decarboxylation of the diacid VII. However, this approach appears to be another reasonable route for the synthesis of PQ and its 5,10-substituted derivatives.

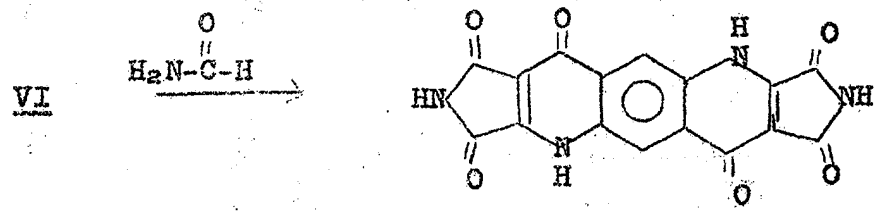
3. Synthesis of the N,N'-Dibenzylimide of PQ - Tetra-Carboxylic Acid

In an effort to enhance the weak yellow absorption exhibited by the symmetrical tetraester VI, the N,N'-dibenzylimide (XIV) was prepared and found to be a



VI XIV

bright yellow-orange solid, with absorption maxima at 485 mμ (ε 16,620) and 455 mμ (ε 17,160). However, due to excessive solubility, the compound is not an attractive pigment candidate. For this reason the unsubstituted diimide (XV) is being prepared in the



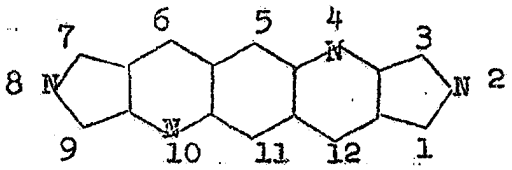
XV

hope of maintaining the desirable visible absorption characteristics while decreasing the solubility.

The diimide represents a new ring system, not listed in Chem. Abstracts or Patterson's Ring Index. A tentative number system and name based upon Chem. Abstracts guidelines for nomenclature is:

V. DISCUSSION (Cont'd)

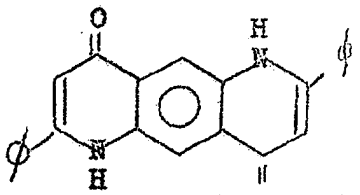
3. Synthesis of the N,N'-Dibenzylimide of PQ - Tetra-Carboxylic Acid (Cont'd)



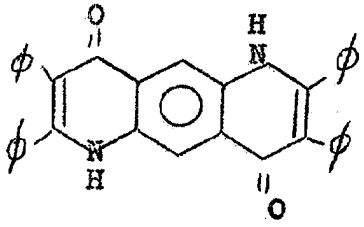
2H,8H-dipyrrolo (3,4-e: 3',4'-e') benzo (1,2-b: 4,5-b') - dipyridine

4. Synthesis of the Diacenaphthyl Derivative of PQ

Two yellow derivatives of the PQ ring system, the 2,7-diphenyl (XVI) and the 2,3,7,8-tetraphenyl (XVII) analogs were synthesized at Newark and both were shown to have poor lightfastness[7]. A reasonable explanation



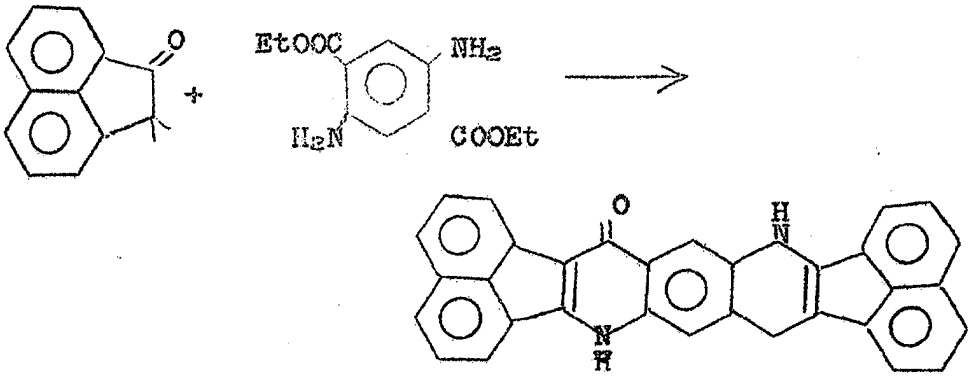
XVI



XVII

for this lightfastness deficiency is based on the assumption that the phenyl rings, which have complete freedom of rotation, interfere with efficient intermolecular hydrogen bonding.

It was thought that by fusing the benzene rings in XVII, keeping symmetry considerations in mind, the resulting coplanarity might favorably affect lightfastness. To this end, the diacenaphthyl derivative (XVIII)



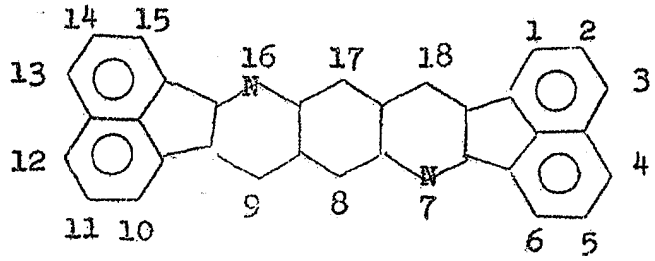
XVIII

V. DISCUSSION (Cont'd)

4. Synthesis of the Diacenaphthyl Derivative of PQ (Cont'd)

by condensing acenapthenone with diethyl - 2,5-diamino-terephthalate followed by pyrolysis in refluxing Dowtherm. A small amount of a yellow-orange solid was obtained which after acid recrystallization showed an ir spectrum suggesting the formation of XVIII. More material is being prepared for a complete characterization and pigment evaluation.

The diacenaphthyl derivative also represents a new ring system not listed in Chem. Abstracts or Patterson's Ring Index and a tentative name and numbering system based upon Chem Abstracts guidelines of nomenclature is:



diacenaphtho (1,2-e: 1',2'-e') benzo (1,2-b: 4,5-b') - dipyridine

VI. EXPERIMENTAL

1. Preparation of Diethyl-2,5-bis [1,2-bis (methoxycarbonyl) - vinylamino] terephthalate (V).

NB-1904-9 (RJN)
NB-1847-32 (EEF)

A solution of 12.6 g (0.05 mol) of diethyl - 2,5-diamino-terephthalate and 15.6 g (0.11 mol) of dimethylacetylenedicarboxylate in 125 ml anhydrous methanol was refluxed for five hours. During the reflux period a yellow solid came out of solution. The hot mixture was filtered and the yellow solid washed with methanol to yield 18.5 g (69%) of yellow crystals, mp. 175-178 (EEJ 1847/32, mp. 178-179). Recrystallization from 185 ml methanol and 90 ml DMF yielded 13.5 g yellow solid mp. 178-179; ir (Nujol) 1740 (C=O), 1720 (C=O), 1680 (C=O) and 1600 cm^{-1} (C=C); UV and visible spectra (DMF) λ max. 401 mμ (ε 18,500), 350 (21,300) and 263 (13,500); nmr (DMSO-d^6) δ 1.48 ppm

VI. EXPERIMENTAL (Cont'd)

(t,6,-O-CH_2CH_3), 3.73 (d,12,-OCH_3), 4.37 (q,4,-OCH_2CH_3), 5.52 (5,2, vinyl=C-H), 7.24 (s,2, aromatic C-H), and 10.90 ppm (s,2, N-H).

Anal. Calc'd for $C_{24}H_{28}N_2O_{12}$; C, 53.70; H, 5.22; N, 5.22

Found: C, 53.76; H, 5.33; N, 5.28

2. Preparation of 2,3,7,8-tetracarbomethoxy-pyrido (2,3-g)-quinolin-4,9 (1H, 6H)-dione (VI).

1904-26 (RJN)
1847-37 (EEF)

To a stirred solution of 1.38 g (0.06 mol) sodium metal in 300 ml of anhydrous methanol, 16.08 g (0.03 mol) of diethyl-2,5-bis [1,2-bis (methoxycarbonyl)-vinyl amino] terephthalate (V) was added. Solution occurred at 50° with a yellow solid precipitating at 60°. The mixture was refluxed for four hours and filtered hot. The dry yellow solid was dissolved in water, and acidified with glacial acetic acid to yield 15 g crude yellow solid after drying. Recrystallization from DMF yielded 13 g (97.5%) of a yellow powder, mp. 330-340 (d.) (EEJ 1847/37, mp. 330-340 (d.)); ir (Nujol) 1750 (C=O), 1610 and 1540 cm^{-1} (ring); UV and visible spectra (DMF) λmax. 445 mμ (ε 7600), 424 (8050), 375 (16,100) and 269 (26,000); nmr (DMSO-d^6) δ 3.75 ppm (s,6, NH-C-$COOCH_3$), 3.90 (s,6, O=C-C-$COOCH_3$), 8.70 (s,2, aromatic C-H), and 12.60 ppm (s,2, N-H).

Anal. Calc'd for $C_{20}H_{16}N_2O_{10}$: C, 54.00; h, 3.61; N, 6.31

Found: C, 54.75; H, 3.72; N, 6.24

3. Preparation of Dicarboxypyrido (2,3-g) quinoline-4,9 (1H, 6H)-dione (VII).

1904-42C (RJN)

A mixture of 4.84 g (0.0109 mol) 2,3,7,8-tetracarbomethoxypyrido (2,3-g) quinolin-4,9-dione, 2.96 g (0.0643 mol) potassium hydroxide in 100 ml ethylene glycol was refluxed at 185-190°C for six hours. The yellow-orange solid which had precipitated out during the reflux period was filtered, washed with water and dried. The dry solid was suspended in water, acidified with conc. HCl, filtered, washed acid-free and dried to yield 3 g yellow solid, mp. > 400°C; ir (Nujol) 1695 (C=O) and 1600 cm^{-1} (ring); UV and visible spectra (DMF) λmax. 424 mμ (17,700) and 402 (11,000); neut. eq., 150 (theo. 150).

VI. EXPERIMENTAL (Cont'd)

3. (Cont'd)

Anal. calc'd for $C_{14}H_8N_2O_6$: C, 55.70; H, 2.67; N, 9.32

Found: C, 54.49; H, 2.81; N, 9.11

4. Synthesis of pyrido (2,3-g) quinoline-4,9 (1H, 6H)-dione (pyridonoquinolone).

1904/42D (RJN)

A mixture of 5 g (0.0167 mol) dicarboxypyrido (2,3-g)-quinolin-4,9-dione in 75 ml tetramethylene sulfone was stirred and refluxed for eight hours, the mixture changed color from orange to greenish-yellow. The mixture was filtered hot, the solid washed with ethanol to yield 3 g greenish-yellow solid. Acid recrystallization yielded a greenish-yellow solid, insoluble in dil. $NaHCO_3$, mp.> 400°C; ir (Nujol) 1605 cm^{-1} (C=C) and 1540 (ring); UV and visible spectra (DMF) λ max. 412 mμ (ε 19,100) and 390 (ε 15,800); solubility, 0.50 g/l boiling DMF.

Anal. calc'd for $C_{13}H_8N_2O_2$: C, 67.91; H, 3.79; N, 13.20

Found: C, 68.10; H, 3.85; N, 13.12

5. Preparation of 6,8-Dibenzyl-1,3,7,9-tetrahydro-2H,8H-dipyrrolo (3,4-c; 3',4'-e') benzo (1,2-b; 4,5-b')-dipyridine-1,3,7,9,12 (4H, 10H)-hexaone (XIV)

1904-32 (RJN)

A mixture of 4 g (00.009 mol) 2,3,7,8-tetracarbomethoxypyrido (2,3-g) quinoline-4,9-dione and 0.2 g (0.0037 mol) ammonium chloride in 100 ml benzylamine was refluxed for six hours. The yellow-orange solid which had precipitated during the reflux period was filtered, washed with aqueous ethanol, and dried to yield 4.1 g of solid. Recrystallization from DMF yielded 3.8 g (56.8%) yellow-orange solid, mp. > 400°C; ir (Nujol) 1740 (C=O), 1710 (C=O) and 1630 cm^{-1} (C=O); visible spectrum (DMF) λ max. 485 mμ (ε 16,620) and 455 (17,160).

Anal. calc'd for $C_{28}H_{14}N_4O_6$: C, 67.92; H, 3.42; N, 10.56

Found: C, 68.36; H, 4.17; N, 10.70

6. Preparation of Acenapthenone 1904-31 (RJN)

A mixture of 142.3 g (0.762 mol) 1-naphthylacetic acid in 310 ml thionyl chloride was refluxed for six hours. Excess thionyl chloride was distilled off under water aspirator pressure never allowing pot temperature to exceed 150°. 1-naphthyl acetyl chloride was then distilled at bp. 175-185 at 15-20 mm (lit. bp. 188 at 23 mm.[8]) to yield 78.5 g (50.5%) clear yellow oil.

VI. EXPERIMENTAL (Cont'd)

6. (Cont'd)

Cyclization to yield acenapthenone was accomplished by slowly adding a solution of 78.5 g (0.384 mol) of 1-naphthylacetyl chloride in 75 ml dry nitrobenzene dropwise to a suspension of 56.4 g (0.42 mol) aluminum chloride in 500 ml dry nitrobenzene at 25° with stirring. The addition required 1-1/2 hours and when complete, the brownish mixture was stirred for six hours and allowed to stand overnight. The mixture was poured onto 1000 ml crushed ice and the contents were then steam distilled. After distillation of all the nitrobenzene, acenapthenone distilled over it was filtered and dried to yield 20 g (31%) of white needles, mp. 118-120 (lit. mp. 120-121°); ir (Nujol) 1710 cm^{-1} (C=O).

7. Preparation of Diacenaphtho (1,2-e: 1',2'-e') benzo (1,2-b: 4,5-b') - dipyridine-9,18 (7H,16H)-dione (VXIII).

1904-45 (RJN)

A mixture of 3.36 g (0.02 mol) acenapthenone and 2.52 g (0.01 mol) of diethyl-2,5-diaminoterephthalate in 75 ml Dowtherm was stirred and heated at 170° for one hour. The dark brown solution was then slowly heated to reflux (260°C) and held there for four hours. The orange solid which had precipitated was filtered hot, washed with ethanol and hot DMF to yield 2 g yellow-orange solid. Acid recrystallization from 95% H_2SO_4 yielded 1.2 g yellow-orange solid, mp. >400°C; ir (Nujol) 1660 (C=O), 1645 cm^{-1} (C=C); %N, 4.60 (theo. 6.08).

8. Preparation of 2,7-dicarbomethoxy-5,10-dicarboethoxy-pyrido (2,3-g) quinoline-4,9 (1H,6H)-dione (XI).

1904-23 (RJN)

One gram (0.0018 mol) of well pulverized diethyl-2,5-bis- [1,2-bis(methoxycarbonyl)-vinylamino] terephthalate (V) was added portionwise to 50 ml vigorously refluxing Dowtherm. The resulting solution was refluxed for 30 minutes, and turned light brown during that period. The solution was then cooled and drowned into 100 ml ligroin with stirring. The resulting precipitate was collected, washed with ethanol to yield, after drying, 0.5 g of a tan solid. Recrystallization from DMF/EtOH yielded 0.25 g orange solid, mp. 251-253 (d.);

VI. EXPERIMENTAL (Cont'd)

8. (Cont'd)

ir (Nujol) 1730 (C=O), 1710 (C=O) and 1635 cm^{-1} (C=O); nmr (DMSO-d_6) δ 1.33 ppm (t,6, CH_2-CH_3), 3.94 (5,6,-$COOCH_3$), 4.48 (m,4,-CH_2CH_3) and 7.34 ppm (s,2, aromatic C-H).

Anal. calc'd for $C_{22}H_{20}N_2O_{10}$: C, 56.00; H, 4.26; N, 5.97

Found: C, 56.01; H, 4.06; N, 5.97

9. Preparation of Diethyl 2,5-bis [(2-ethoxycarbonyl) vinyl amino] terephthalate (VIII).

1904-9 (RJN)
1847-67A (EEJ)

A mixture of 12.6 g (0.05 mol) diethyl 2,5-diamino-terephthalate and 10.80 g (0.11 mol) of ethyl propiolate in 125 ml anhydrous methanol was refluxed for five hours. After cooling, the precipitated yellow-orange solid was filtered, washed with cold methanol and dried to yield 14 g (62.5%) yellow solid, mp. 145-165. Recrystallization from DMF/EtOH yielded 10 g orange solid. mp. 150-165 (EEJ 1947/67A, mp. 150-165); broad melting point suggest mixture of geometric isomers; ir (Nujol) 1740 (C=O), 1690 (C=O) and 1615 cm^{-1} (C=C); UV and visible spectra (DMF) λ max. 420 mμ (ϵ 8500) and 351 (46,000).

Anal. calc'd for $C_{22}H_{28}N_2O_8$: C, 59.00; H, 6.25; N, 6.25

Found: C, 59.00; H, 6.41; N, 6.29

10. Preparation of diethyl-3,6-dichloro-2,5-bis [1,2-bis (methoxycarbonyl)-vinylamino] terephthalate (XII).

1904-35 (RJN)
1847-33 (EEF)

A mixture of 3.154 g (0.02 mol) 2,5-dichloro-p-phenylene diamine and 5.68 g (0.04 mol) of dimethyl acetylene dicarboxylate in 120 ml anhydrous methanol was refluxed for five hours. After cooling, the precipitated yellow solid was filtered, washed with cold methanol to yield, after drying, 8 g (66.3%) yellow solid, mp. 183-184 (EEJ 1847/33, mp. 183-184).

VI. EXPERIMENTAL (Cont'd)

11. Preparation of 3,10-dichloro-2,7-dicarbomethoxy-pyrido (2,3-g) quinoline-4,9 (1H,6H)-dione (XIII).

1904-34 (RJN)

Three grams (0.0049 mol) of diethyl-3,6-dichloro-2,5-bis [1,2-bis (methoxycarbonyl)-vinylamino] terephthalate (XII) were added portionwise to 50 ml of vigorously refluxing Dowtherm.

After complete addition, the yellow-brown solution was refluxed and stirred for an additional 15 minutes. The solution was cooled and drowned into 100 ml ligroin. The precipitated yellow solid was collected and washed with methanol to yield, after drying, 2 g of yellow solid, mp. 245-250. Recrystallization from DMF produced a yellow solid, mp. 259-260; ir (Nujol) 1740 (C=O) and 1690 cm^{-1} (C=O); mass spec. molecular ion at 395 ± 2 (MW 397.17).

Anal. calc'd for $C_{16}H_{10}N_2Cl_2O_6$: C, 48.38; H, 2.53; N, 7.06

Found: C, 48.38; H, 2.63; N, 7.36

/mc

VII. BIBLIOGRAPHY

1. Ruggli and Preiswerk, Helv. Chim. Acta. 22, 478 (1939).

2. Ruggli and Brandt, Helv. Chim. Acta 27, 274 (1944).

3. Nelson, Newark KN Report.

4. Littke and Hermanns, Ber. 101, 1708-14 (1968)

5. Heindel, Fish, and Lemke, J. Org. Chem. 33, 3997 (1968).

6. Kay and Taylor, JCS (C), 2656 (1968).

7. Matrick, H., Newark KN Report.

8. Buu-Hoi, Caignant, Compt. Rend. (1942) 214, 315.