KM-70-3 SUBSTITUTED QUINACRINONES FROM SUCCINYLSUCCINIC ESTER AND 2,6-DIETHYLANILINE By: G. R. Aldridge 5/69 - 7/69

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PIGMENT COLOR RESEARCH REPORT

SUBSTITUTED QUINACRIDONES FROM SUCCINYLSUCCINIC ESTER AND 2,6-DIETHYLANILINE

Period Covered May, 1969 to July, 1969 (Part Time)

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SUBMITTED BY: G. R. ALDRIDGE DATE SUBMITTED: 12/15/69

APPROVED BY: F. F. EHRICH DATE RELEASED: 1/30/70

ABSTRACT

The pyrolysis of diethyl 2,5-bis(2,6-diethylanilino)-3,6-dihydroterephthalate in Dowtherm gave a mixture of 4,11-diethyldihydroquinacridone and 4,11-diethylquinacridone. In polyphosphoric acid 2,5-di(2,6-diethylanilino)terephthalic acid gave a mixture of diethy, triethyl, and tetraethyl quinacridones.

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INTRODUCTION

Under conditions that mono-substituted anilines condense with succinylsuccinic ester (SSE) to give substituted dianilinodihydroterephthalate esters, the reaction of 2,6-diethylaniline (I) with SSE was carried out to determine if there was sufficient steric hindrance to prevent the reaction of the amino group in I with SSE. Diethyl 2,5-bis(2,6-diethylanilino)-3,6-dihydroterephthalate (II) was obtained in 90% yield showing there was little, if any, steric hindrance to the reaction of SSE with I.

OBJECT OF INVESTIGATION

To prepare and evaluate substituted quinacridones from II, and its corresponding terephthalic acid, 2,5-di(2,6-diethylanilino) terephthalic acid (III).

PERIOD COVERED BY REPORT

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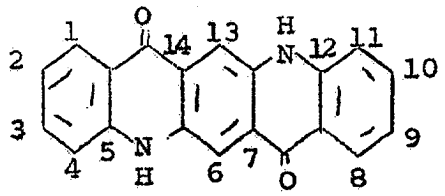
SUMMARY AND CONCLUSIONS

The pyrolysis of diethyl 2,5-bis (2,6-diethylanilino)-3,6-dihydroterephthalate (II) in Dowtherm gave a mixture of 4,11-diethyldihydroquinacridone (4,11-diethyl DQA), and 4,11-diethylquinacridone (4,11-diethyl QA) (see diagram below for numbering in quinacridone system).



QUINACRIDONE (QA)

On oxidation with Sitol, this mixture gave 4,11-diethylQA as shown by its analysis, infrared spectrum, and X-ray crystallographic pattern. The cyclization of II to 4,11-diethylDQA (25-38% yield) requires the displacement of two ethyl groups either in the form of ethylene or diethyl ether (ethyl group in terminal ring combines with ethoxy group from ester group). Tests on the gas mixture from the pyrolysis reaction proved the presence of ethylene.

In polyphosphoric acid at 140-60°, 2,5-di(2,6-diethylanilino) terephthalic acid gave a red pigment (IV), presumably a triethylquinacridone based on its elemental analysis. The mass spectrum of IV showed it to be a mixture of triethylquinacridone (3 parts), tetraethylquinacridone (2 parts), and diethylquinacridone (1 part). The formation of tri- and tetraethylquinacridones requires that the displaced ethyl groups migrate to new positions in the quinacridone ring.

The considerably greater solubility of IV in dimethylformamide and its extremely poor lightfastness (tint faded completely after

24 hours. Fadeometer exposure, slight fading in 4,11-diethyl QA tint after 120 hrs. Fadeometer exposure) in lithographic varnish versus 4,11-diethylQA suggest that the tri- and tetraethylquinacridones in IV may be substituted in the 1 and/or 5 and/or 6 positions. The assumption that 3,10- and 2,9-diethylquinacridones would have lightfastness as good as or better than 4,11-diethyl-QA is a reasonable one.

The lightfastness of 4,11-diethylQA (scarlet in color) is inferior to that of quinacridone.

PATENT STATUS

No filing action is planned.

DISCUSSION

The cyclization of II to 4,11-diethylDQA requires the displacement of either ethylene (2 moles) and ethanol (2 moles) or diethyl ether (2 moles). Similarly, the cyclization of di(n)butyl 2,5-di-(2,6-diethylanilino)-3,6-dihydroterephthalate ($C_{36}H_{50}N_2O_4$) to 4,11-diethylDQA requires the displacement of either ethylene (2 moles) and n-butanol (2 moles) or n-butyl ethyl ether (2 moles)., i. i.e.,

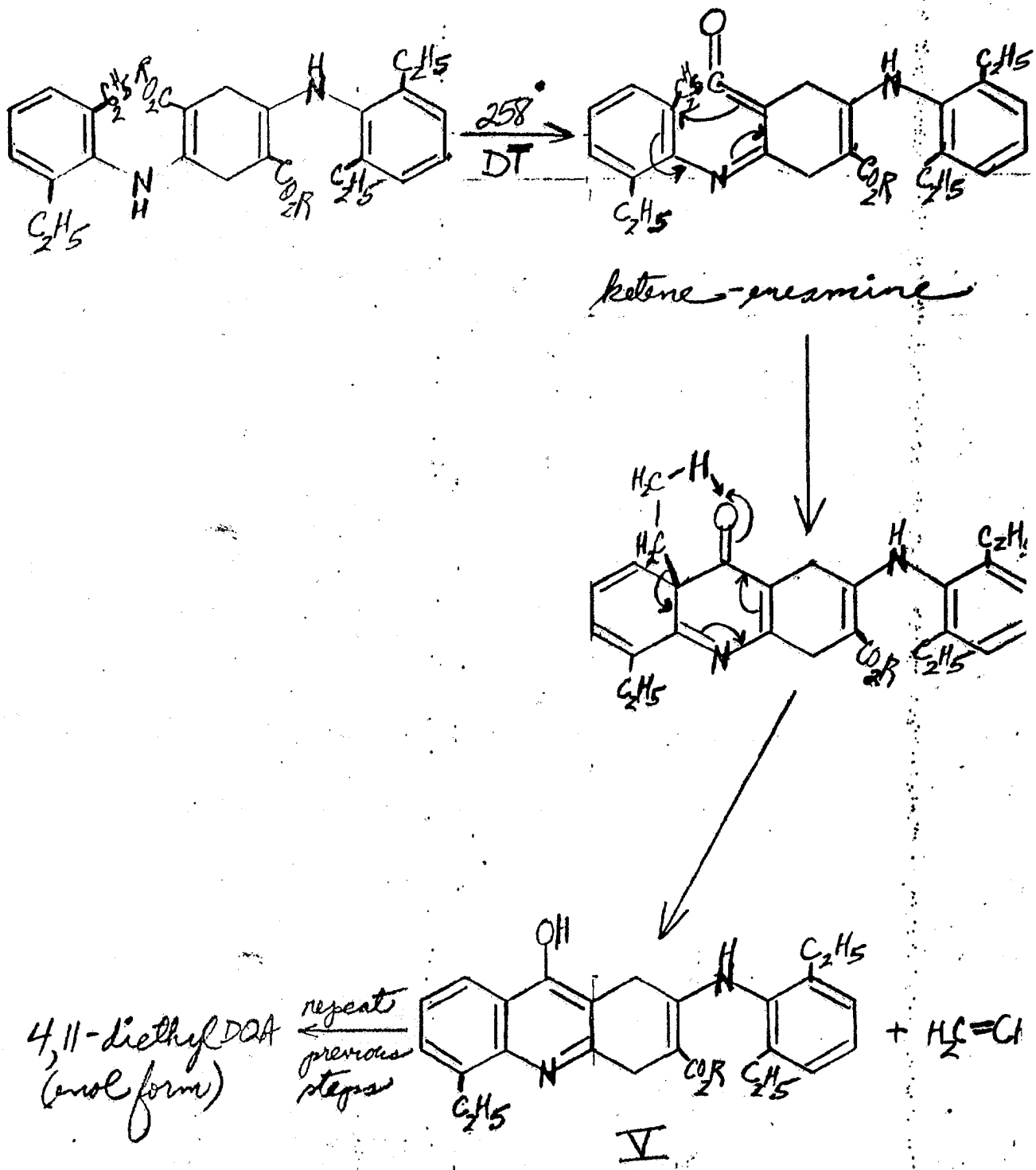
$$C_{36}H_{50}N_2O_4 \rightarrow C_{24}H_{22}N_2O_2 + 2\ H_2C\ CH_2 + 2\ n\text{-}C_4H_9OH$$
(4,11-diethylDQA; ethylene; n-butanol)

$$C_{36}H_{50}N_2O_4 \rightarrow C_{24}H_{22}N_2O_2 + 2\ n\text{-}C_4H_9\text{-}O\text{-}C_2H_5$$
(n-butyl ethyl ether)

The following evidence indicates that ethylene is formed in the pyrolysis of $C_{36}H_{50}N_2O_4$ (II-di(n)butyl ester): the gases from the pyrolysis reaction on passage through a bromine in carbon tetrachloride solution discharge the bromine color without the evolution of hydrogen bromide, and the addition product, ethylene bromide, was shown to be present in the carbon tetrachloride solution by its conversion to a solid derivative, 1,2-di(2-naphthoxy) ethane. The presence of n-butanol in the distillate from the pyrolysis of $C_{36}H_{50}N_2O_4$ was confirmed by olfactory tests.

The first step in the postulated mechanism (page2a) is the formation of a ketene-eneamine intermediate and ethanol (or butanol). The second step involves an intramolecular addition of the -N=C-C=C- unit associated with the center ring to the adjacent 2,6-diethylphenyl ring to form a pseudo-quinolone, which eliminates ethylene to form the substituted quinolone, V (enol form). V, then repeats the preceding steps to form 4,11-diethylDQA (enol form).

Unlike II, the pyrolysis of diethyl 2,5-bis(2,6-dimethylanilino)-3,6-dihydroterephthalate (VI) did not yield any 4,11-dimethyl-dihydroquinacridone or any Dowtherm-insoluble product. The failure of VI to form 4,11-dimethylDQA or related dihydroquinacridones is not surprising in view of the greater energy required to displace methyl groups than that required to displace ethyl groups from pseudo-aromatic systems.



In polyphosphoric acid at 140-60°, 2,5-di(2,6-dimethylanilino) terephthalic acid (VII) gave a red pigment whose infrared spectrum was similar to, but not identical with, 4,11-dimethylquinacridone. The migration of ethyl or methyl groups during the ring closure of III or VII to tri- or tetraalkylquinacridones in polyphosphoric acid at 140-60° is not surprising in view of the rearrangement of 1,2,3,5-tetramethyl or 1,2,4,5-tetramethyl benzenes to 1,2,3,4-tetramethyl benzene in cold concentrated sulfuric acid (Jacobsen rearrangement).

EXPERIMENTAL

The sample of 2,6-diethylaniline (I) used to prepare the 2,5-di-(2,6-diethylanilino)dihydroterephthalate esters (diethyl and di-n-butyl) was a high quality sample since vapor phase chromatography of I on two different columns showed it to be substantially free of impurities. The supplier (Matheson, Coleman and Bell) affirmed its minimum purity to be 98%.

Preparation of Diethyl 2,5-Di(2,6-diethylanilino)-3,6-dihydroterephthalate 1914/31F

Charge to 3 liter flask:
76.8 g (0.30 mole) diethyl succinylsuccinate
1500 cc 2B alcohol
Blanket with nitrogen, and heat to 70° (incomplete solution).
Add:
7.5 ml trifluoroacetic acid
134 g (0.90 mole) 2,6-diethylaniline
The water formed in the reaction was removed by codistillation with ethanol (1200 cc in 3 hrs.). Cool, filter, slurry presscake with a sodium carbonate solution (10.8 g Na_2CO_3 in 60 cc H_2O), stir, filter, wash with water until brilliant yellow free, and dry.

Yield: 140 g (90%) mp 169-70°

Found:		$C_{32}H_{42}N_2O_4$ req.	
	C, 75.40		C, 74.2
	H, 8.30		H, 8.1
	N, 5.68		N, 5.4

Preparation of Di-n-Butyl 2,5-Di(2,6-diethylanilino)3,6-dihydrophthalate 1914/50A

Found;		$C_{36}H_{50}N_2O_4$ req.	
	C, 75.32		C, 75.2
	H, 8.82		H, 8.72
	N, 4.77		N, 4.88

Preparation of Diethyl 2,5-Di(2,6-dimethylanilino)-3,6-dihydroterephthalate 1914/41A

Found:		$C_{28}H_{34}N_2O_4$ req.	
	C, 72.95		C, 72.8
	H, 7.57		H, 7.36
	N, 6.10		N, 6.06

Preparation of Diethyl 2,5-Di(2-ethylanilino)-3,6-dihydroterephthalate 1914/46F

Found:	C, 74.09	$C_{28}H_{34}N_2O_4$ req.	C, 72.8
	H, 7.55		H, 7.36
	N, 6.45		N, 6.06

Preparation of 2,5-Di(2,6-diethylanilino)terephthalic Acid 1914/31B

Charge to 1 liter flask
21.4 g (.041 mole) diethyl 2,5-di(2,6-diethylanilino)-3,6-dihydroterephthalate
250 ml 2B alcohol
21.4 g Sitol
Stir. Add dilute sodium hydroxide solution (10 g in 100 cc H_2O), reflux 90', dilute with hot water to 1 liter, and filter. Adjust pH of filtrate of 1-2 with 55 cc 5N HCl, filter, wash chloride ion free, and dry.

Yield: 9.3 g (bright red) mp approx. 325°

Found:	C, 72.97	$C_{28}H_{32}N_2O_4$ req.	C, 73.0
	H, 7.38		H, 6.96
	N, 6.17		N, 6.09

Preparation of 2,5-Di(2,6-dimethylanilino)terephthalic Acid 1914/41C

Found: 202 Neutralization Equivalent Calc. for $C_{24}H_{24}N_2O_4$: 202

Preparation of 2,5-Di(2-ethylanilino)terephthalic Acid 1914/53A

Found:	C, 70.48	$C_{24}H_{24}N_2O_4$ req.	C, 71.3
	H, 5.83		H, 5.94
	N, 7.02		N, 6.93

Preparation of 4,11-Diethyldihydroquinacridone 1914/46F

Diethyl 2,5-di(2-ethylanilino-3,6-dihydroterephthalate ⟶ 4,11-$(C_2H_5)_2$DQA

Found:	C, 78.10	$C_{24}H_{22}N_2O_2$ req.	C, 77.8
	H, 5.91		H, 5.95
	H, 7.46		N, 7.57

Preparation of 4,11-diethylquinacridone 1914/53D2

2,5-Di(2-ethylanilino)terephthalic Acid $\xrightarrow[PPA]{}$ 4,11-diethylQA

The product was acid recrystallized, and then recrystallized from dimethylformamide.

Found:	C, 75.88	$C_{24}H_{20}H_2O_2$ req.	C, 78.2
	H, 5.43		H, 5.44
	N, 7.60		N, 7.61

Preparation of 4,11-Diethylquinacridone 1914/57B

4,11-Diethyl DQA $\xrightarrow[\text{Sitol}]{}$ 4,11-diethyl QA

Found:	C, 77.16	$C_{24}H_{20}N_2O_2$ req.	C, 78.2
	H, 5.73		H, 5.44
	N, 7.67		N, 7.61

Ir spectra of 57B and 53D2 are identical except for peak at 6.55μ in 57B which is absent from 53D2. The location of this peak suggests the presence of some 4,11-diethyl DQA in 57B.

Pyrolysis of II-diethyl ester 1914/40A

250 cc Dowtherm (under N_2)
Heated to reflux. Add portionwise
21.4 g II-diethyl ester
Refluxed 1 hr., cooled red-brown suspension to 30°, filtered, washed Dowtherm free with methanol, and dried.

Yield: 3.8 g Color: red

% Yield of 4,11-diethyl DQA = 25

Oxidation of this product with Sitol-C_2H_5OH-NaOH-H_2O followed by two acid recrystallizations gave 4,11-diethyl QA. Recrystallization of this product from dimethylformamide gave an analytically pure sample.

Found:	C, 78.10	$C_{24}H_{20}N_2O_2$ req.	C, 78.2
	H, 5.42		H, 5.44
	N, 7.61		N, 7.61

The infrared spectrum and X-ray pattern of this product are identical with the spectrum and crystallographic pattern of 4,11-diethyl QA (1914/53D2) prepared from 2,5-di(2-ethylanilino)terephthalic acid by ring closure in polyphosphoric acid.

Ring Closure of 2,5-Di(2,6-diethylanilino)terephthalic Acid 1914/31C

4.6 g (.01 mole)	III
92 g.	polyphosphoric acid

Heated at 140-60° for 2 hrs., cooled to 70°, added water (180 cc) at 70-90° drowned in 1 l water, filtered, washed with water, slurried with 0.1 N sodium hydroxide solution, filtered, washed brilliant yellow free, and dried.

Yield: 3.6 g Color: red

This product was acid recrystallized twice and then recrystallized from dimethylformamide.

Found: C, 78.40
H, 6.23
N, 6.94

$C_{26}H_{24}N_2O_2$ req. (triethyl QA)	C, 78.8 H, 6.06 N, 7.07	$C_{24}N_{20}N_2O_2$ req. (diethyl QA)	C, 78.2 H, 5.44 N, 7.61

The mass spectrum of this product shows it to be a mixture of triethylquinacridone (3 parts), tetraethylquinacridone (2 parts), and diethylquinacridone (1 part).

SUGGESTIONS FOR ADDITIONAL WORK

The solubility of the mixture of tri- and tetraethylquinacridones is believed to be greater than that of any other quinacridone. Quinacridone photochemical studies in organic solvents that require solutions and not suspensions are a possibility.

NOTEBOOK REFERENCES

1914

dc