REACTIONS OF SOME 1,4-DIAZA-1,3-DIENES

WITH DIELS-ALDER TYPE DIENOPHILES

A THESIS

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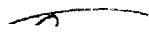
by

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REACTIONS OF SOME 1,4-DIAZA-1,3-DIENES

WITH DIELS-ALDER TYPE DIENOPHILES

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PREFACE

In this work, attempts were made to effect condensations between conjugated dienes containing nitrogen in the one and four positions, and some of the common Diels-Alder type dienophiles. Adducts were obtained from benzoquinone and phenazine, dimethyl acetylenedicarboxylate and 2,3-diphenylquinoxaline (two products), and 2-phenylquinoxaline and dimethyl acetylenedicarboxylate. Of these, only two were investigated, the adduct from the 2-phenylquinoxaline, and one of the adducts from the 2,3-diphenylquinoxaline. The structures of these two compounds have not been unequivocably established, but evidence is presented to support the structures proposed.

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ABSTRACT

2,3-Diphenylquinoxaline condenses with dimethyl acetylenedicarboxylate in methanol solution at room temperature to form two adducts; from 2-phenylquinoxaline, one adduct was obtained. Structures are proposed for the 2-phenylquinoxaline adduct and for the 2,3-diphenylquinoxaline adduct formed in the larger amount. These adducts appear to be formed by a normal 1,4-addition of the ester across the nitrogen-containing diene.

Evidence is presented for a reaction between phenazine and benzoquinone, quinoxaline and maleic anhydride, quinoxaline and dimethyl maleate, quinoxaline or 2-methylquinoxaline and the dimethyl ester of acetylenedicarboxylic acid, methylacridinium chloride and the acetylenic ester, and 2,3-di-p-nitrophenylquinoxaline and diethyl maleate. The structures of the products here have not been determined.

Unsuccessful attempts to effect condensations between the above mentioned dienes and various other dienophiles are described. These and other results are discussed in terms of approximate thermochemical calculations.

CHAPTER I

INTRODUCTION

1,4-Diazabicyclo(2,2,2)octane (triethylene diamine)
was probably first prepared by Hofmann (1) while studying the
reaction between ammonia and ethylene dibromide. Moore and
Doubleday (2) prepared a benz derivative of this bicyclic base
from 6-methyl-tetrahydroquinoxaline and ethylene dibromide,
but the yields were low. Prelog and coworkers (3) were un-
successful in their attempts to prepare triethylene diamine
by heating 1-(beta-bromoethyl)-piperazine hydrobromide in
dilute sodium hydroxide. In 1942, Hromatka (4) obtained a
small amount of triethylene diamine by heating the hydrochlo-
ride salt of diethanolamine at about 220° C for ten hours.
In the following year, Hromatka and Engel (5) described a
better procedure for the preparation of this compound. In
this method, hydrochloride salts of beta-substituted-1-ethyl-
piperazine were heated in closed or open tubes for fifteen
minutes in the temperature range 200-250° C; the product was
isolated as the p-nitrophenyl addition compound in yields as
high as sixty per cent. In 1949, McElvain and Pryde (6) were
unsuccessful in their attempts to convert 1-(beta-hydroxy-
ethyl)-and 1-(beta-haloethyl)-2,2,5,5-tetramethylpyrazines to

tetramethyl-1,4-diazabicyclo(2,2,2)octane.

The Diels-Alder reaction offers another possible synthetic route to the 1,4-diazabicyclo(2,2,2)octanes provided that dienes containing terminal nitrogen atoms add dienophiles in the normal 1,4-manner. A survey of the literature indicated, however, that in most cases nitrogen-containing dienes do not add dienophiles in the usual way.

Diels, Alder, and coworkers have studied the condensation reactions of a series of heterocyclic nitrogen bases in various solvents. Of the bases studied, only acridine (7) adds a dienophile (dimethyl acetylenedicarboxylate) in the same way that anthracene does (8), that is, across the 9,10-positions; and this normal mode of addition occurs only in methanol as solvent. The other nitrogen heterocycles studied, pyrroles (9, 10, 11), indoles (12), imidazoles and pyrazoles (11), pyridine (13, 14, 15, 16, 17), quinoline (13, 15), isoquinoline (13, 18), quinaldine (13, 15, 19), stilbazole (γ-styrylpyridine) (20), α-picoline (21), phenanthridine (22) and acridine (7) add dienophiles in a different manner. The N-methylpyrrole-maleic anhydride adduct was originally assigned (23) a structure analogous to that from furan and maleic anhydride (a normal 1,4-adduct) (24), but later investigations showed this to be incorrect (9).

The reactions of maleic anhydride, a very common dienophile, were found to be abnormal when nitrogen-containing dienes were employed. Barnett and coworkers (25) reported

that no adducts were obtained when attempts were made to condense this dienophile with acridine, 1,2,3,4-dibenzphenazine, or benzalazine ($C_6H_5CH{=}N{-}N{=}CHC_6H_5$). In fact van Alphen stated (26) that none of the groups -C=N-N=C-, -N=C-C=N-, or -C=C-C=N- can add maleic anhydride in the same manner as butadiene does. Anthranil is a possible exception (27). The azines however do react with maleic anhydride. Benzalazine, for example, reacts with two moles of the anhydride to yield an adduct (in very low yield) which appears to have been formed by 1,3- and 2,4- (criss-cross) addition (28, 29). In anhydrous ether solution, benzalazine and maleic anhydride do not react. If water is present, the azine undergoes hydrolysis followed by reaction with the anhydride to form benzaldehyde and benzalmaleinhydrazide ($C_6H_5CH{=}N{-}NH{-}COCH{=}CHCOOH$) (30).

Anils, representative of open chain conjugated systems terminating in nitrogen, also react with maleic anhydride. Cinnamylidene-aniline ($C_6H_5CH{=}CHCH{=}NC_6H_5$) reacts with one mole of maleic anhydride; the unstable intermediate reacts with a mole of water from the air to form cinnamic aldehyde and maleanilic acid ($C_6H_5NHCOCH{=}CHCOOH$). The yield of this acid under highly anhydrous conditions is negligible (31). 2-Ethyl-2-hexenalaniline condenses with maleic anhydride (32) to form an adduct (A) which is more conveniently obtained (33) by heating a mixture of maleanilic acid and 2-ethyl-2-hexenal.

$$CH_3CH_2CH-CH\text{———}C=O$$

with structure showing:

$$\begin{array}{c} CH_3CH_2\underset{|}{C}H-\underset{|}{C}H\text{———}C=O \\ \underset{|}{C}H \quad \underset{|}{C}HCOOH \quad | \\ CH_3CH_2CH-CH\text{———}N-C_6H_5 \end{array}$$

$$\begin{array}{c} R \quad O \\ | \quad \| \\ R-CH-N-C-CH-CHCO_2^- \\ + \end{array}$$

(A)   (B)
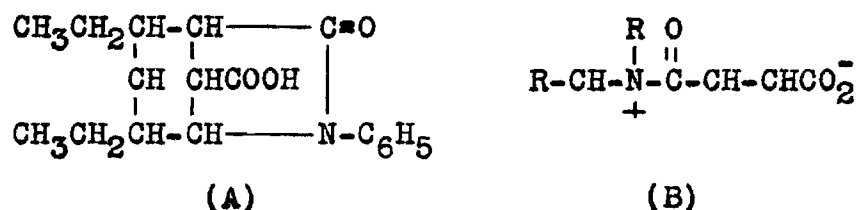
Ordashev and Markova (34) found that maleic anhydride
forms crystalline products (1:1) with a variety of anils, in
benzene or xylene solution. Among the anils investigated
were: $CH_3CH=CH-CH=N-C_6H_5$, $C_6H_5CH=CH-CH=NC_6H_5$, $C_6H_5CH=CH-CH=$
$N-C_6H_4CH_3$(o-, m-, and p-), $C_6H_5CH=CH-CH=N-C_6H_4OCH_3$(p-),
$CH_3CH=N-C_6H_4CH_3$(p-), and $C_6H_5CH=N-C_6H_5$. The products proba-
bly have the structure (B) suggested by van Alphen (26).

As an example of a nitrogen-terminated system which
is not an open chain, may be cited the reaction between 2-
styrylquinoline and maleic anhydride. At 100° C in xylene
solution, a good yield of 2-styrylquinolinium maleate (a salt
from one mole of the quinoxaline compound and one mole of
maleic anhydride) is obtained in a few minutes (31).

The quinoxalines contain a diene system, both ends of
which terminate in nitrogen atoms. 2,3-Dimethylquinoxaline
reacts with maleic anhydride and with benzoquinone (34) but
the addition occurs across the carbon atoms of the methyl
groups. Apparently a rearrangement occurs to form a carbon-
containing diene which includes the methyl carbon atoms (now
methylene groups) and carbon atoms 2 and 3 of the quinoxaline.
A 1,4-addition in this manner is thermodynamically more favor-
able (see part B of the Discussion) than a 1,4-addition across

the nitrogen-containing diene. With benzoquinone, 2,3-di-methylquinoxaline forms an adduct containing two moles of the quinoxaline per mole of quinone. In this case too, the quinoxaline reacts in the methyleneamine form. It has been reported (34) that quinoxaline itself, 2-methylquinoxaline, 2-phenyl-3-methylquinoxaline, and 2,3-diphenylquinoxaline do not give Diels-Alder reactions when heated under the same or more severe conditions, with maleic anhydride or benzoquinone.

One example of a 1,4-diaza-1,3-diene which does add dienophiles in the normal 1,4-manner is dehydroindigo. Although this diene does not add maleic anhydride (35), croton-aldehyde, chlorovinylacetate, allyl mustard oil (allyl iso-thiocyanate), indene, dimethylfulvene, cyclopentadiene, cyclohexene, acrylic acid nitrile or isobutylene, styrene does add when the reactants are heated at 130-140° C, to give a 62 per cent yield of styrene indigo. Dehydroindigo also reacts with methyl acrylate in a sealed tube at 100° (36), as well as with anethole, isoeugenol, safrole, and isosafrole.
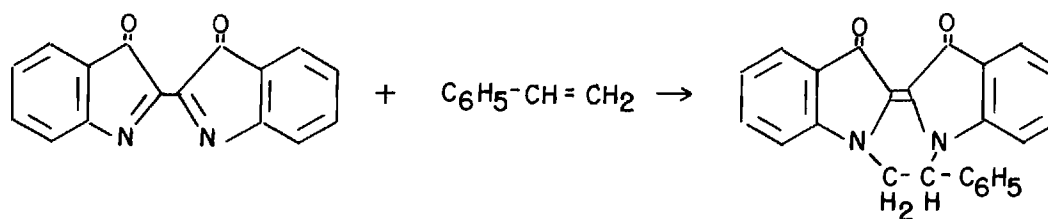
Diels and coworkers have also studied "Polymerization Processes Induced by Pyridine". In two pertinent articles (37,

38), reactions between pyridine, benzoquinone, and anhydrous
formic acid in methanol as solvent are reported. Although
the products obtained can by no means be considered to be
"normal" Diels-Alder adducts, the reactions are interesting
in that they may have been effected in the present work when
attempts were made to condense phenazine and benzoquinone in
the presence of triethylamine. When p-benzoquinone, pyridine,
and anhydrous formic acid are allowed to react in methanol,
hydroquinonepyridinium formate is formed; a betaine
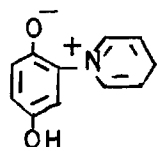
results when this salt is shaken with a
cold saturated solution of sodium carbonate (37). When a
mixture of the quinone and pyridine is treated with the formic
acid in portions, and the product thus obtained is shaken with
methanol, 2,5-dimethoxy-1,4-benzoquinone is obtained. When
water is used in place of the methanol in the above reaction,
2,5-bis(p-hydroxyphenoxy)-1,4-benzoquinone results (37). Thus
in these reactions, the tertiary base pyridine either enters
into the reaction to form a salt, or effects a condensation
reaction of p-benzoquinone. The intermediate products in these
and related reactions have been studied to some extent (38).

The above statements that certain reactions do not occur,
imply, of course, only the limitation that they do not occur
under the reaction conditions attempted. Therefore, additional
attempts were made to synthesize bicyclo octanes containing
nitrogen atoms at the bridgeheads via a Diels-Alder condensa-
tion.

CHAPTER II

DISCUSSION--PART A

EXPERIMENTAL WORK

Phenazine

Phenazine and Benzoquinone

Work was begun by attempting to effect a condensation between phenazine and benzoquinone. Quinone, one of the first dienophiles used in a Diels-Alder type condensation (with isoprene) (39), condenses with anthracene, in xylene as solvent, to form a normal 1,4-adduct (40). In the present work, attempts to condense phenazine and benzoquinone in sealed tubes were unsuccessful.

An attempt to catalyze the reaction by running it in acetic acid as solvent was apparently successful; a small amount of a high-melting compound (204-215° C) was obtained, but at the temperature at which the reaction was run (in refluxing xylene) there was considerable darkening of the mixture. This difficulty was overcome by heating the equimolar quantities of the reactants in a sealed tube, in acetic acid solution, at the temperature of refluxing acetone for 43 hours. When the mixture was heated at the same temperature

for 90 hours, none of the high-melting compound was obtained. Heating for 72 hours in refluxing acetone, then for ten hours in refluxing benzene gave some of the high melting compound (240° C) as well as some unreacted starting material.

In one experiment (No. 6) the effect of a basic catalyst was investigated. Equimolar quantities of phenazine and ben-zoquinone, in xylene as solvent, were heated in a sealed tube with triethylamine, at the temperature of refluxing xylene. Again there was extreme darkening of the reaction mixture, and a product which melted at 197-240° C was isolated. The darkening occurred even at room temperature in the absence of the phenazine.

In the final experiment (No. 7) between phenazine and benzoquinone an attempt was made to effect condensation at a higher temperature without the use of a catalyst. The reac-tants, in solution in nitrobenzene, were heated at 140° C, then at 197° C. This experiment also yielded a product which melted at about 240° C.

From these experiments it appears that a reaction of some type does occur between phenazine and benzoquinone. The nature of the product obtained in these experiments was not determined. The reaction may have been similar in nature to that described by Diels and coworkers (37, 38) between benzo-quinone and pyridine. In our experiments, triethylamine or phenazine could conceivably play the same role that pyridine played in the work reported by Diels.

Phenazine and Maleic Anhydride

Anthracene, a typical diene, smoothly adds maleic anhydride (8). Three experiments were run in an attempt to condense phenazine with maleic anhydride. Glacial acetic acid was not an effective catalyst at the temperature of refluxing xylene; sulfuric acid formed a sulfate with the nitrogen base. In the third experiment a thirty mole excess of the anhydride did not cause the formation of an adduct at 100° C in a sealed tube. These experiments therefore confirm the conclusions of the thermal calculations considered in the second part of the Discussion.

Phenazine and Dimethyl Acetylenedicarboxylate

In one experiment, run at room temperature in methanol as solvent, the only product isolated from the reaction mixture was a small amount of phenazine.

Quinoxaline

Attention was turned next to the more readily available quinoxalines as dienes.

The reaction between quinoxaline and maleic anhydride is complicated by decomposition at about 200° C. The purely thermal decomposition of maleic anhydride is expected to be slow at this temperature since Rice and Murphy (41) reported

that 0.163 mole of maleic anhydride heated alone at 820° C, was 58 per cent decomposed in 0.08 second, the decomposition going quantitatively to carbon monoxide, carbon dioxide, and acetylene. From these data, assuming an activation energy of 35 kilocalories, and that the reaction is first order, the rate constant is found to be 11 sec^{-1} at 820° C, or about 10^{-12} sec^{-1} at 210° C. This rate constant at 210° C is not large enough to account for the explosion which occurred in the present work when 0.01 mole of quinoxaline and 0.05 mole of maleic anhydride were heated together in a sealed tube in a bath of refluxing nitrobenzene. When this reaction was repeated in an open flask fitted with a reflux condenser, gases were evolved, as evidenced by the black molten material which was forced up into the condenser. Maleic anhydride did not decompose when heated alone at 210° C for one hour. Similar decompositions of maleic anhydride, in the presence of $(CH_3)_2$-$C=N-N=C(CH_3)_2$ and $C_6H_5CH=N-CH_2CH_2N=CHC_6H_5$ have been observed by van Alphen (26); with the latter compound, decomposition occurred even at 100° C.

One inconclusive experiment, in which quinoxaline was heated with a 30 mole excess of the anhydride, indicated that under forcing conditions of this nature it may be possible to effect a reaction.

Attempts were also made to condense quinoxaline with dimethyl or diethyl maleate. In both cases isomerization to the fumarate occurred, but in addition, with the methyl ester,

a small amount of a product which melted at 285° C was obtained.

Three attempts were made to effect condensation between quinoxaline and the dimethyl ester of acetylenedicarboxylic acid in methanol solution at room temperature. A reaction of some sort occurred as evidenced by the rapid acquisition of color by the reaction mixture. However, no crystalline products were isolable from any of the experiments. The color observed may have been due either to the formation of an adduct from the reactants, or to polymerization, catalyzed by the nitrogen base, of the ester.

2-Methylquinoxaline

2-Methylquinoxaline with dimethyl acetylenedicarboxylate in methanol solution, exhibited a color change similar to that observed with quinoxaline. The observed color may be attributed to the same causes as were suggested above for quinoxaline.

2,3-Di-p-nitrophenylquinoxaline

The sealed tube experiments run with styrene and this substituted quinoxaline at the temperature of refluxing nitrobenzene were inconclusive, since only about seven per cent of the quinoxaline used was recovered unchanged.

In one experiment, using diethyl maleate as the dienophile, a small amount of a high-melting (255° C) compound was

obtained.

N-Methylacridinium Chloride

Diels and Thiele (7) describe the reaction between acridine and dimethyl acetylenedicarboxylate in methanol solution as occurring in such a manner that one molecule of the ester adds bridge-like across the 9,10-positions of acridine, and one mole of methanol is attached to the nitrogen atom. The structure of the adduct is written as a substituted N-methylammonium hydroxide. These authors give two reasons for believing that the alcohol is attached to the nitrogen atom; it is easily dissociated, and it forms N-methylacridinium chloride under the influence of hydrochloric acid.

If the above structure is correct, it seems reasonable that the adduct, in methanol solution, from methylacridinium chloride and the acetylenic ester, should give the same product as was obtained when Diels and Thiele treated their adduct with hydrochloric acid. Two experiments with methylacridinium chloride and the ester, in methanol, each gave small amounts of a compound which melted at 202-204° C. In addition, small amounts of two other crystalline products were isolated from the first experiment, one which melted at 87-91° C, and one which sublimed in the temperature range 188-191° C. The chloride obtained by Diels and Thiele from heating their adduct with hydrochloric acid melted with decomposition at 122° C;

these authors assigned their product the structural formula
of N-methylacridinium chloride. The carbon, nitrogen, and
chlorine analysis of their product agreed with that of a tri-
hydrate of the compound. However, the hydrogen analysis was
1.18 per cent too low. Furthermore, the dihydrate of N-methyl-
acridinium chloride is reported to melt at 177° C (d) (42)
and this value is confirmed in the present work.

2,3-Diphenylquinoxaline

2,3-Diphenylquinoxaline and Styrene

In one experiment, using an excess of styrene in a
sealed tube at 100° C, a small amount of unreacted 2,3-di-
phenylquinoxaline and some resinous material were recovered.
The resinous material was believed to be polymerized styrene
because it dissolved readily in benzene but was insoluble in
95 per cent ethanol. The experiment was repeated using hydro-
quinone to inhibit polymerization. In this case, 75 per cent
of the quinoxaline used was recovered, and about ten per cent
of the styrene polymerized. Two sealed tube experiments were
run in glacial acetic acid as solvent, to which a small amount
of sulfuric acid was added as a catalyst. The styrene and
quinoxaline were added in the mole ratio two to one, and hydro-
quinone was used to inhibit polymerization. In both of these
experiments, the first run at 56° C, the second at 100° C, a
compound which in water solution turned Congo red paper blue,

and which melted in the range 228-234° C was obtained. A gravimetric sulfate determination on these samples indicated that the compounds were salts, containing one mole of the nitrogen base per mole of sulfuric acid.

2,3-Diphenylquinoxaline and Dimethyl Acetylenedicarboxylate

In methanol solution, at room temperature, these two compounds form two colored adducts. When the reactants, in methanol solution, were mixed in equimolar quantities, a bright yellow, methanol soluble adduct was obtained, but approximately one-half of the slightly soluble quinoxaline remained as unreacted material, even after standing for eighty days at room temperature. When two moles of the ester were mixed with one mole of the 2,3-diphenylquinoxaline, in addition to the yellow adduct, a red compound was also obtained. When equimolar quantities of the 2,3-diphenylquinoxaline and the acetylenic ester were refluxed in methanol for three hours, a low yield of the yellow adduct was obtained.

The yellow adduct, which melted at 153° C, has been tentatively assigned structure I. The higher melting (214° C) red adduct is believed to contain two moles of the ester per mole of quinoxaline.

I   II

Evidence for the Structure of the Yellow Adduct.--The follow-

ing evidence is presented to substantiate the structure of the

yellow adduct:

1. Microchemical analyses for carbon, hydrogen, and nitrogen,

and for methoxyl groups agreed well with formula I, $C_{27}H_{24}N_2O_5$.

2. The molecular weight of the compound agreed with this

formulation.

3. Acid saponification gave a 70 per cent yield of 2,3-di-

phenylquinoxaline.

4. Alkaline saponification yielded 2,3-diphenylquinoxaline

in 45 per cent yield, desoxybenzoin in 16 per cent yield, and

quinoxaline-2-carboxylic acid in 17 per cent yield.

The microchemical analyses indicated that the compound

consisted of one mole each of the ester, the quinoxaline, and

methanol, and showed that it contained three methoxyl groups.

The manner in which these molecules were combined was deduced

from the products of degradation. Attempts to degrade the

molecule by oxidation with potassium permanganate were

unsuccessful. Saponification, however, in both acid and al-
kaline media, did give insight into the problem.

The only product isolated from the acid saponification
was the starting quinoxaline. This represented a reversal of
whatever process was involved in the formation of the compound.
Alkaline saponification gave products which can readily be
explained on the basis of formula I. A reversal of the origi-
nal Diels-Alder 1,4-addition would yield 2,3-diphenylquinoxa-
line and the hydrolyzed ester or its hydrated or alcoholated
product. 2,3-Diphenylquinoxaline was obtained in 45 per cent
yield. Now a compound possessing structure II could be expect-
ed to undergo a reverse Diels-Alder reaction in two ways:
To yield 2,3-diphenylquinoxaline and dimethyl acetylenedicar-
boxylate, or to give quinoxaline 2,3-dicarboxylic acid ester
and tolan. The products obtained from the alkaline saponifi-
cation of the yellow adduct, in addition to the 2,3-diphenyl-
quinoxaline, were quinoxaline-2-carboxylic acid and desoxy-
benzoin. During the isolation of these products, carbon di-
oxide was evolved. The transformations leading to the products
observed may be formulated as follows:

$$C_6H_5C \equiv CC_6H_5 + \text{[adduct]} \longrightarrow \text{[quinoxaline]}-COO^- + CO_2 + {}^-OCH_3$$
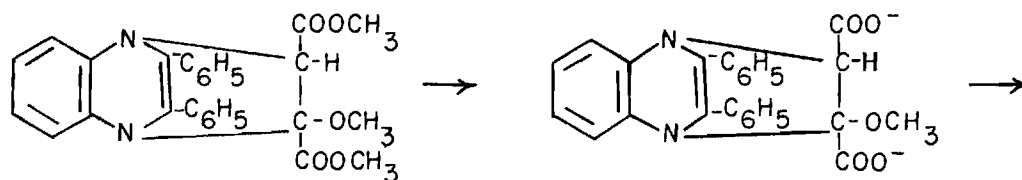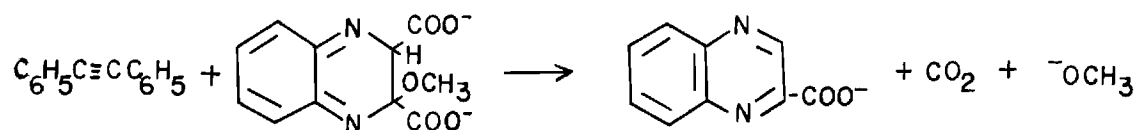
This series of transformations represents a reversal of the Diels-Alder reaction in the second way proposed for a compound having structure II. Although it does explain the formation of the carbon dioxide and the quinoxaline-2-carboxylic acid which were found, it does not account for the formation of the desoxybenzoin. Desoxybenzoin, which is a hydrated form of the tolan expected, was not obtained when an attempt was made to hydrate tolan under the conditions used for the saponification of the adduct. The formation of the hydrated tolan must therefore be explained as due to reactions occurring either before or during its ejection from the adduct.

In an attempt to gain further insight into the structure of the yellow adduct, oxidative degradation experiments were run. In ether solution, ferric chloride caused the precipitation of a yellow compound believed to be an iron chloride salt of the adduct. Bromine had little effect on the adduct, although the results of the small-scale experiments were inconclusive. The adduct was unaffected by potassium permanganate in acetone or in methanol solution at room temperature. Thirty per cent hydrogen peroxide in glacial acetic acid yielded two new compounds, the identity of which were

not established. The pure white, high-melting (310° C) oxidation product gave a microchemical analysis which agreed with the calculated analysis for the hydrated form of 2,3-diphenylquinoxaline monoxide. The low-melting (124° C) product of the oxidation with hydrogen peroxide was pale yellow in color, and gave analytical results which did not agree well with any calculated whole number empirical formulas.

Since the hydrogen peroxide oxidation experiments were not particularly successful, an attempt was made to degrade the yellow adduct pyrolytically. In a bath at 210° C and at a pressure of 0.1 millimeter, the yellow adduct melted and decomposed, evolving a gas which was condensed in a cold trap; 2,3-diphenylquinoxaline was recovered from the residue left in the reaction vessel. The liquid in the cold trap was believed to be a mixture of methanol and the acetylenic ester, since its index of refraction was intermediate between that of these two possible components. In this experiment, the ability of the yellow adduct to sublime unchanged was also demonstrated.

The yellow 2,3-diphenylquinoxaline adduct did not form a picrate when treated with an alcoholic solution of picric acid. The yellow adduct was not attacked by dilute potassium hydroxide at room temperature in aqueous alcoholic solution. (Compare the behavior of the 2-phenylquinoxaline adduct, below.) Saponification equivalents, run in diethylene glycol, gave values which varied with the time of heating.

Evidence for the Structure of the Red Adduct.--The red adduct
obtained from the reaction of 2,3-diphenylquinoxaline with the
acetylenic ester in methanol solution was submitted for micro-
chemical analysis. The first report received from the analyt-
ical laboratory indicated that this compound contained 16.05
per cent of a non-alkaline ash. Spectroscopic analysis of the
adduct and of the ash failed to indicate the presence of any
of the common elements in significant amount. The ash used
for analysis was obtained by gently heating the adduct in a
porcelain crucible. When this ash was subjected to stronger
heating, essentially all of it disappeared. This information
was submitted to the analytical laboratory which then reana-
lyzed the sample and reported as follows: C,63.51%; H, 4.83%;
N, 5.02%; ash from C-H, 0.44% (non-alkaline). These values,
which agreed well with the original analysis except for the
value for the ash, when corrected for the ash content become:
C, 63.79%; H, 4.85%; and N, 5.04%. A compound containing one
mole of the quinoxaline, two moles of the ester and one mole
of water ($C_{32}H_{28}N_2O_9$) has the following calculated values:
C, 65.74%; H, 4.83%; N, 4.79%. The hydrogen and nitrogen
values agree with those found for the adduct, but the calcu-
lated value for carbon is too high. Other simple combinations
of the reactants give calculated values which are in still
poorer agreement with those reported. The structure of this
compound is therefore still in doubt.

2-Phenylquinoxaline

With Maleic Anhydride

2-Phenylquinoxaline was heated at 100° C under reflux with a large excess of maleic anhydride for 24 hours. A compound believed to be 2-phenylquinoxaline was recovered in 56 per cent yield.

2-Phenylquinoxaline and Dimethyl Acetylenedicarboxylate

A yellow adduct which melted at 136° C and believed to be a compound containing one mole each of the quinoxaline, the ester, and water was obtained when equimolar quantities of the reactants, in methanol solution, were allowed to stand at room temperature for about one week. The structure proposed for this adduct is represented by formula III.

III
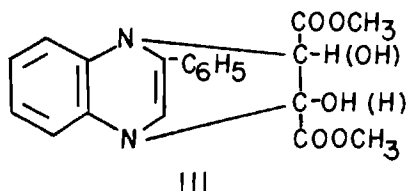
In contrast to the reaction with 2,3-diphenylquinoxaline, solution of the 2-phenylquinoxaline in the methanol and acetylenic ester was complete within four hours after mixing.

Isolation of the 2-phenylquinoxaline adduct proved

difficult, and, when finally effected, very time consuming. In order to obtain a crystalline product, it was necessary to remove all of the solvent by evaporation, dissolve the residue in a suitable solvent (acetonitrile or carbon tetrachloride) and then let the solution evaporate slowly at room temperature. This procedure, which required weeks to effect evaporation of the solvent, may have been necessary to permit the adduct to take up a mole of water from the atmosphere, thus forming a crystalline product. Apparently, oxidation did not occur during this long evaporation period as evidenced by the smiliarity of the ultraviolet absorption curves of the isolated product and of a solution of the reactants before isolation.

In acetonitrile instead of methanol as solvent, no adduct was isolated from an equimolar mixture of 2-phenylquinoxaline and the acetylenic ester; 29 per cent of the quinoxaline charged was recovered unchanged. In ethyl ether as solvent, equimolar quantities of 2-phenylquinoxaline, methyl alcohol, and the ester gave a new compound which melted at 158-160° C. The nature of this product was not determined.

Evidence for Structure III.--Microchemical analysis for carbon, hydrogen, and nitrogen agreed with the values calculated for Structure III, $C_{20}H_{18}N_2O_5$, molecular weight 366. The methoxyl determination, which was a little low (calculated, 16.94%; found, 16.08%), seemed definitely to eliminate the possibility

that the adduct contained a molecule of methanol, as was the case with the 2,3-diphenylquinoxaline adduct. The molecular weight determination gave a result (387 ± 20) which was in agreement with the calculated value. Alkaline saponification of the adduct yielded 2-phenylquinoxaline and a dicarboxylic acid, the identity of which was not established. This acid, which resisted all attempts to purify it by recrystallization, gave a titration curve which showed two definite breaks (Figure 5). The end-points in the titration, estimated from the titration curve, gave calculated neutralization equivalents of 449 and 213. The calculated neutralization equivalent for the dicarboxylic acid obtained on saponification of the two carbomethoxy groups in Structure III, is 338. Although the value obtained from the curve (449) does not agree with this calculated value, this does not eliminate the possibility that this is the acid which was isolated, when it is realized that the sample taken for analysis was impure.

Oxidative degradation of the 2-phenylquinoxaline adduct was more successful. The action of bromine, as in the case of the 2,3-diphenylquinoxaline adduct, was inconclusive. However, the product, in acetone solution, was readily oxidized, at room temperature, by a saturated aqueous solution of potassium permanganate. (2-Phenylquinoxaline itself was not attacked under the same conditions.) Two crystalline products were isolated from the oxidation mixture; 2-phenylquinoxaline (in 24 per cent yield) and 3-phenyl-2-quinoxalinol (1.5 per

cent yield of purified product). The permanganate severed the carbon-nitrogen bonds in III and oxidized the carbon atom at position 2 in the quinoxaline molecule.
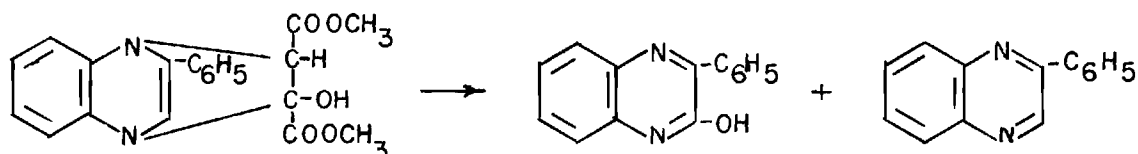
The yellow 2-phenylquinoxaline adduct was found to be slightly soluble in aqueous methanol (1:1) and in dilute aqueous methanolic sodium bicarbonate solution. It dissolved completely however in dilute aqueous solutions of potassium hydroxide or sodium carbonate. This adduct is therefore more readily saponified than the corresponding adduct from 2,3-diphenylquinoxaline.

Failure to isolate a compound containing the quinoxaline nucleus with a carboxyl group attached to one of its carbon atoms is evidence in favor of the structure in which the positions of attachment of the ester do not involve any of the carbon atoms of the 2-phenylquinoxaline molecule.

Attempt to Isolate a Second Adduct from 2-Phenylquinoxaline.--
In one experiment (No. 5) an attempt was made to isolate a second adduct, similar to the red adduct obtained from 2,3 - diphenylquinoxaline. Since the red 2,3-diphenylquinoxaline

adduct was obtained from the mother liquors from which the yellow adduct had been isolated, the crude yellow 2-phenyl-quinoxaline adduct was recrystallized in small portions, and the filtrate from each portion was used to recrystallize subsequent portions. No new adduct was obtained.

Comparison of the Two Yellow Adducts

The structures proposed for the adduct from 2,3-di-phenylquinoxaline (I) and 2-phenylquinoxaline (III) are very similar. The correctness of these formulations is attested to by the similarity of their ultraviolet absorption curves (Figure 2). The position of the methanol in Structure I has not been established. If the methanol adds to the double bond between the two carbomethoxy groups, the symmetry of the molecule makes the position of attachment of the alcohol unambiguous. However, in the 2-phenyl adduct, the water may add to the ester residue as indicated, or in the reverse manner. This question, too, has not been answered.

The bright yellow color observed in both adducts is a little difficult to explain. All of the reactants are colorless in the pure state. Formation of the adducts indicated, results in a loss of conjugation unless one is willing to assume, in defiance of Bredt's rule, that the extra electron pairs on nitrogen are effectively conjugated with the unsaturated system of the molecules. The presence of the electron pairs on nitrogen is evidenced by the increased basicity of

the adduct as compared with that of the starting quinoxaline.

We wish to present two possible explanations for the color observed. If one is willing to assume that in the proposed structures the nitrogen-carbon bonds are p bonds, then the free electron pairs on nitrogen are s electrons. Since s electrons are spherically symetrically located in space, it is conceivable that they are able to react, to some extent, with the p orbitals in the adjacent benzene ring.

The work of Bartlett and Lewis on triptycene (43) offers another possible explanation of the yellow color observed in our adducts. Since triptycene exhibited absorption maxima which were more intense, and which occurred at longer wave lengths than those of triphenylmethane, these authors proposed ionic type structure to account for these facts. Applying this reasoning to our compounds, structures such as the following are proposed: (the dienophile bridge across the nitrogen atoms is omitted, for clarity)
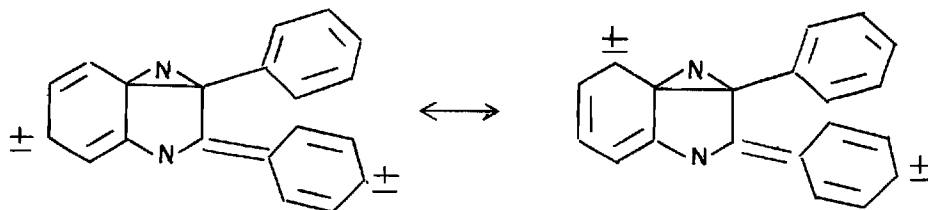
The major difference between the two adducts appears to be the presence, in the diphenyl adduct, of a phenyl group in place of a hydrogen atom. This difference may account for

the ease of oxidation of the 2-phenyl adduct as compared with
the diphenyl adduct. The carbon atom at position 2 in the
quinoxaline containing only one phenyl group is apparently
quite susceptible to the action of permanganate. The addition-
al phenyl group in the diphenylquinoxaline renders this mole-
cule indifferent to attack by this oxidizing agent.

Another factor possibly involved here is the presence
of a hydroxyl group in the 2-phenyl adduct whereas a methoxyl
group exists in the 2,3-diphenyl adduct.

Both yellow adducts appeared to be unstable, as evi-
denced by the decrease (two to three degrees in one week) in
their melting points upon standing.

The equilibrium in the reaction:

2,3-diphenylquinoxaline + ester + methanol = adduct

is such that reaction proceeded to only about fifty per cent
completion when one mole each of the quinoxaline and the es-
ter were allowed to react at room temperature for eighty days.
When two moles of the ester were used, a seventy-five per
cent yield of adduct was obtained in one week.

The equilibrium in the reaction with 2-phenylquinoxaline
is apparently more favorable. In this case, a one to one mix-
ture of the quinoxaline and the ester gave a sixty-six per
cent yield of adduct.

Another outstanding difference between the two adducts
is the procedure required for isolation of a crystalline prod-
uct. With 2,3-diphenylquinoxaline it was necessary merely to
concentrate the methanol solution containing the reactants in
order to obtain the bright yellow crystalline product. With
2-phenylquinoxaline this procedure yielded no crystalline
compound. A crystalline adduct from 2-phenylquinoxaline was
obtained only after dissolving the residue, left after com-
plete removal of the solvent methanol, in carbon tetrachlo-
ride and permitting this solution to evaporate slowly at room
temperature. Since water is believed to be one of the compo-
nents of the adduct from 2-phenylquinoxaline, and all of the
reagents used in its preparation were essentially anhydrous,
it is possible that the water found in the product was taken
up from the atmosphere during this long evaporation period.

For a compound of Structure III, the following equi-
libria might be considered:
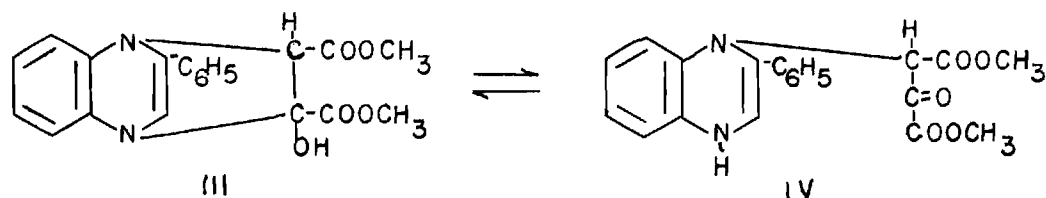
It is rather difficult to estimate ΔH for the above reaction
since the bond strength of the $-C=O$ group varies quite a bit
depending upon substituents. If the value for formaldehyde

is chosen then:

Structure III			Structure IV		
Bond Strength			Bond Strength		
O-H	110.2		N-H	83.7	
C-N	48.6		C=O	142	
C-O	70			225.7	
	228.8				

$$\triangle H = 228.8 - 225.7 = 3.1 \text{ kcal/mole}$$

This calculation suggests that III is probably favored relative to IV and this is confirmed by the known tendency for α-diketones such as phenyl glyoxal and esters such as CH_3CO-CO-$COOC_2H_5$ to form stable crystalline hydrates. (Compare the stable hydrate of chloral). Furthermore, the addition of ammonia to a carbonyl group is favored over that of water or alcohols as is indicated by the calculation:
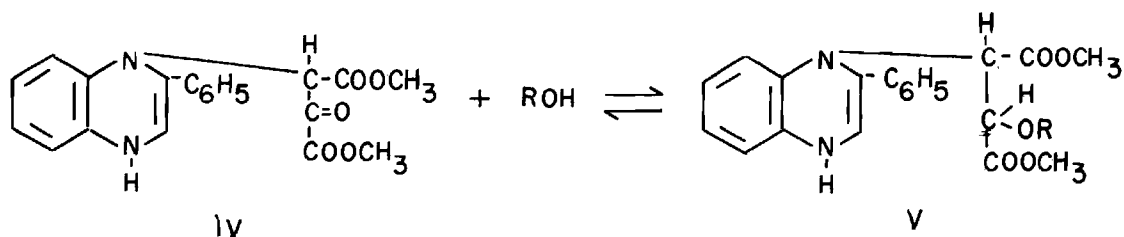
Bond Strength		Bond Strength	
C=O	142 (in CH_2O)	2 C-O	2(70) = 140

$\triangle H = 142 - 140 = 2$ kcal/mole. If the values of C-O for aldehydes and ketones are used then V is even less favored relative to IV.

DISCUSSION--PART B

THEORETICAL CONSIDERATIONS

The choice of diene and dienophile for a Diels-Alder reaction must be such that adduct formation is accompanied by a favorable free energy change. At least to a first approximation, the heat of reaction can serve as an estimate of the free energy change. The error in this assumption should be small when the heat of reaction is large. For a series of dienes and dienophiles of similar rigidity and steric environment, the entropy change should remain approximately constant so that at least relative values of equilibrium constants can be deduced from heats of reaction.

The heat of reaction can be approximated by a consideration of the strengths of the bonds involved in the reaction and the resonance energies of the product and reactants. Calculations of this type are summarized in Table 5 at the end of this section. The data used, and sample calculations are included in the Appendix.

In an attempt to indicate the validity of these calculations, we shall first discuss the results of some well known reactions, data for which are included in Table 5. Butadiene gives a quantitative yield of 1,2,3,6-tetrahydrophthalic anhydride when reacted with maleic anhydride in benzene solution

at 100° C in an autoclave (44). The thermochemical calcula-
tions indicate that this reaction evolves 31 kilocalories of
energy per mole.

The central ring in anthracene, acting as a diene,
readily adds maleic anhydride to form the adduct in 99 per
cent yield.* This reaction is exothermic by about seven kilo-
calories per mole according to the thermochemical calcula-
tions. These same calculations indicate that the reaction
with benzene, which does not go, is endothermic by five kilo-
calories. Thus, based on the theoretical calculations alone,
one would predict that anthracene would add maleic anhydride
and that benzene would not, as is the case.

The theoretical reasons why the present calculations
are approximately valid as far as resonance considerations
are concerned have been given by R. D. Brown (45). Our method
of calculation of resonance energy may seem to be an empirical
way of making Brown's theoretical calculations. In addition,
Brown points out that equilibrium and reaction rates should
and apparently do run parallel for the Diels-Alder Reaction.

Benzoquinone also reacts with anthracene to give a
normal 1,4-adduct (46). The calculations show that this re-
action absorbs about 0.6 kilocalories per mole. However, if
the adduct is assumed to contain an aromatized hydroquinone

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*Reference 44, page 28

ring, the calculations indicate that this reaction is exo-
thermic by 16 kilocalories. Aromatization does occur when
2,3-dimethylbutadiene and methyl-p-benzoquinone are reacted
at 150-170° C (46).

Turning now to some heterocyclic compounds, furan adds
maleic anhydride readily,* as would be predicted from the cal-
culations. These show that this reaction evolves 11.4 kilo-
calories of energy.

Of the nitrogen heterocycles studied by other workers,
only acridine adds a dienophile in the same way that anthra-
cene does. The calculations give a value of 11.8 kilocalories
evolved when this diene reacts with dimethyl acetylenedicar-
boxylate.

Calculations were also made for compounds of the type:
$CH_2=CH-CH=NR$, $RN=CH-CH=NR$, $CH_2=N-CH=CH_2$, and $CH_2=N-N=CH_2$, with
both acetylenic and ethylenic type dienophiles. The first
diene, of the anil type, should, according to the calculations,
readily add dienes. However, cinnamilidineaniline ($C_6H_5CH=$
$CH-CH=N-C_6H_5$) (31) and benzalquinaldine do not give normal
Diels-Alder reactions. The second type of diene should also
add dienophiles according to the calculations. 2,3-Dimethyl-
quinoxaline, which contains the system $-N=C-C=N-$, adds maleic
anhydride, not across the nitrogen-terminated system, but a-
cross the $-C=C-C=C-$ system, formed by rearrangement. The

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*Reference 44, page 28

calculations indicate that the addition to the carbon system
is more favorable (but endothermic by 4.8 kcal.) by about 28
kilocalories. Dehydroindigo, which also contains the system
-N=C-C=N-, does add styrene as well as a number of other
ethylenic dienophiles (35). This result is expected provided
that the adduct is stabilized by resonance to a comparable
or greater extent than the reactants.

The system $CH_2=N-CH=CH_2$ should also add dienophiles.
Pyridine is an example of a heterocyclic system containing
this diene. According to the calculations, the reaction of
pyridine with an acetylenic dienophile should be slightly
(4.2 kcal.) endothermic. Pyridine does not form a normal
adduct with dimethyl acetylenedicarboxylic acid, however.

The thermochemical calculations indicate that azines,
the fourth type of nitrogen-containing diene considered, should
add dienophiles readily. The reactions should be exothermic
by 11.5 and 30 kilocalories per mole respectively, for ethylen-
ic and acetylenic dienophiles. Several examples are available
in the literature. However, in no known case, as was indicated
in the Introduction, does normal 1,4-addition occur.

Nitrogen-containing dienophiles have also been used in
Diels-Alder condensations. Esters of azodicarboxylic acid
combine spontaneously, at moderate temperatures, with various
dienes, as is indicated by the calculations. Among the dienes
may be mentioned cyclopentadiene, which forms N,N'-dicarbethoxy-
endomethylenetetrahydropyridazine in excellent yield (47).

Thus we see that calculations of this type, when applied to reactions for which we have experimental evidence, can serve as useful guides in predicting the possibility of effecting reactions which have not yet been tried. The calculations made for the reactions attempted in this work will now be considered.

Phenazine.--The thermochemical calculations indicate that 9, 10-additions to phenazine by maleic anhydride or benzoquinone should be endothermic by more than 20 kilocalories. The nature of the product obtained from phenazine and benzoquinone was not established. The thermal calculations are supported by the experimental evidence in the case of phenazine and maleic anhydride. The calculations indicate that a reaction between phenazine and an acetylenic dienophile, especially if solvent addition across the residual double bond in the dienophile can occur, is much more favorable. Since only one experiment was attempted with these reactants, the experimental evidence is inconclusive.

Quinoxalines.--The calculations give a value of 29.6 kilocalories per mole as the amount of energy which must be absorbed to effect 1:4-addition of maleic anhydride to the nitrogen atom of quinoxaline. Experiments to effect a condensation of this type appear to uphold the conclusions based on the calculations. Further evidence is supplied by

the failure of 2-methylquinoxaline, 2,3-diphenylquinoxaline, and 2,3-di-p-nitrophenylquinoxaline to react with various ethylenic dienophiles in a normal manner.

The thermochemical calculations indicate that the reaction between quinoxaline and the dimethyl ester of acetylenedicarboxylic acid in methanol solution, with or without the addition of methanol to the adduct, is slightly endothermic, five and eleven kilocalories per mole, respectively.

Dimethyl acetylenedicarboxylate formed colored compounds with 2,3-diphenylquinoxaline and with 2-phenylquinoxaline in methanol solution. The structure of two of these adducts is believed to be that of a true Diels-Alder adduct. The thermochemical calculations indicate that these reactions should be somewhat endothermic even if water (or methanol) adds across the double bond in the dienophile residue. These calculations further indicate that in reactions between dimethyl acetylenedicarboxylate and acridine or quinoxaline, addition across the carbon-containing diene in one of the benzene rings is more favorable than across the diene containing the hetero nitrogen atoms. It therefore becomes necessary to defend the structures of the quinoxaline adducts proposed in this work.

We believe that the experimental evidence obtained by oxidation of the 2-phenylquinoxaline adduct, and hydrolysis of the 2,3-diphenylquinoxaline adduct quite clearly indicates that addition did occur across the nitrogen-containing diene.

Alkaline saponification of the 2,3-diphenylquinoxaline

adduct yielded three compounds which were positively identi-

fied: 2,3-diphenylquinoxaline, desoxybenzoin, and quinoxaline-

2-carboxylic acid. If addition across the carbon containing

diene in the benzene portion of the quinoxaline had occurred,

forming two carbon-carbon bonds to give (VI), it does not seem

likely that these bonds would have been broken again by alka-

line saponification. However, breaking the two carbon-nitro-

gen bonds in the proposed structure is quite feasible.
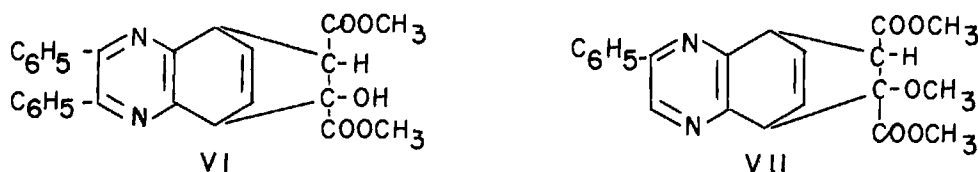
The formation of desoxybenzoin and quinoxaline-2-

carboxylic acid in essentially equal amounts, lends credence

to the assumption that these two compounds were formed together

as the result of degradation of the adduct via one of several

possible routes. The adduct obtained by 1,4-addition across

the carbon-containing diene in the molecule could yield quin-

oxaline-2-carboxylic acid and desoxybenzoin in equal amounts

only if decomposition of the molecule proceeded in a complex

manner.

The adduct obtained from 2-phenylquinoxaline yielded

2-phenylquinoxaline and 3-phenyl-2-quinoxalinol when treated

with aqueous permanganate at room temperature. If the adduct

had structure (VII), oxidation of the carbon-carbon bonds formed by 1,4-addition across the benzene portion of the molecule would not yield the products obtained. It is difficult to visualize severance of carbon-carbon bonds under such mild oxidizing conditions.

Table 5

Energy Changes in Condensation Reactions
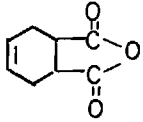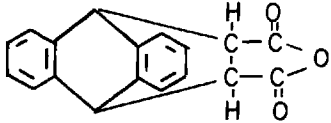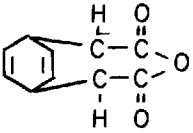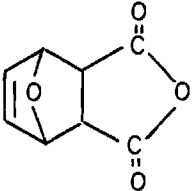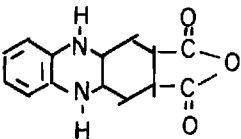
Dieno-phile	Diene	Adduct	ΔH bond kcal/ mole	ΔH reso-nance kcal/ mole	net ΔH kcal/ mole
Maleic Anhy-dride	Buta-diene		- 34.4	3.5	- 30.9
	Anthra-cene		- 34.4	27	- 7.4
	Benzene		- 34.4	39	5
	Furan		- 34.4	23	- 11.4
	2,3-Di-Me-Quin-oxaline		- 19.2	24	4.8

Table 5--Continued
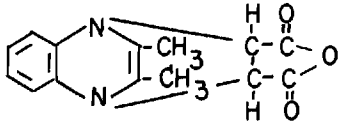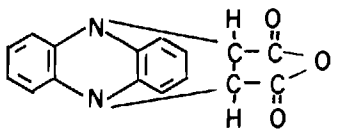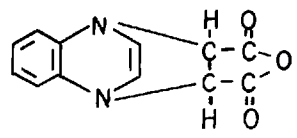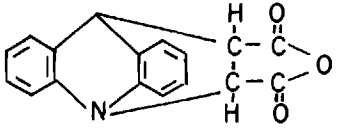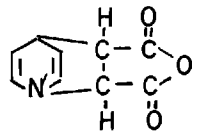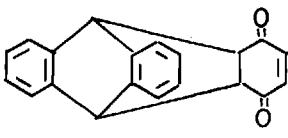
Maleic Anhydride	2,3-Di-Me-Quinoxaline		-	6.4	36	29.6
	Phenazine		-	6.4	27	20.6
	Quinoxaline		-	6.4	36	29.6
	Acridine		-	20.4	28	5.6
	Pyridine		-	20.4	43	22.6
Benzoquinone	Anthracene		-	34.4	35	0.6

Table 5--Continued
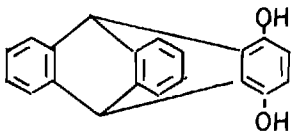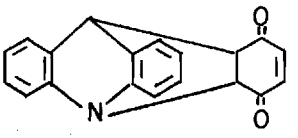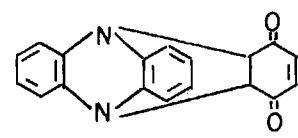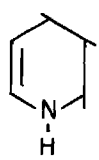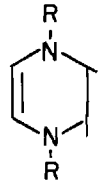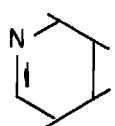
Benzo-quinone	Anthra-cene		1.0	-17	- 16
	Acridine		- 20.4	36	15.6
	Phenazine		- 6.4	35	28.6
Ethyl-enic Dieno-philes	$CH_2=CH-CH=NH$		- 20.4	3.5	- 16.9
	$R-N=CH-CH=NR$		- 6.4	3.5	- 2.9
	$CH_2=N-CH=CH_2$		- 34.4	3.5	- 30.9

Table 5--Continued
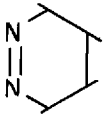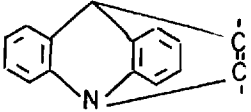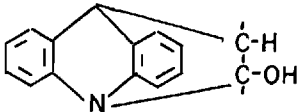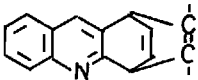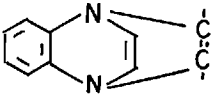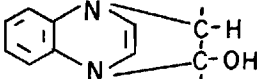
Ethyl-enic Dieno-philes	CH₂=N- N=CH₂	[structure: diazine ring]	− 15	3.5	− 11.5
Acetyl-enic Dieno-philes	Acridine	[acridine bridged structure, C≡C]	− 38.8	28	− 10.8
	Acridine	[acridine bridged structure, Ċ-H Ċ-OH]	− 44.7	28	− 16.7
	Acridine	[acridine structure, C≡C]	− 52.8	31	− 21.8
	Quinoxaline	[quinoxaline structure, C≡C]	− 24.8	36	11.2
	Quinox-aline	[quinoxaline structure, Ċ-H Ċ-OH]	− 30.7	36	5.3

Table 5--Continued
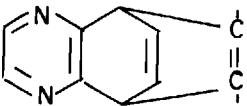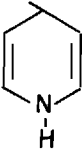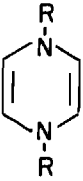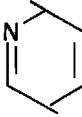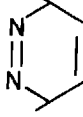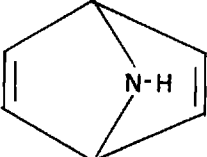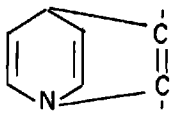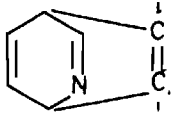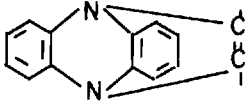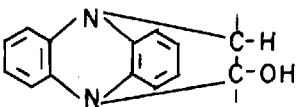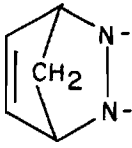
Acetyl-enic Dieno-philes	Quinox-aline		- 52.8	36	- 16.8
	$CH_2=CH-CH=NH$		- 38.8	3.5	- 35.3
	$R-N=CH-CH=NR$		- 24.8	3.5	- 21.3
	$CH_2=N-CH-CH_2$		- 52.8	3.5	- 49.3
	$CH_2=N-N=CH_2$		- 33.4	3.5	- 29.9
	Pyrrole		- 52.8	31	- 21.8

Table 5--Continued

Acetyl- enic Dieno- philes	Pyridine		- 38.8	43	4.2
	Pyridine		- 52.8	43	- 9.8
	Phena- zine		- 24.8	27	2.2
	Phena- zine		- 30.7	27	- 3.7
-N=N-	Cyclo- penta- diene		- 25.8	2.9	- 22.9

CHAPTER III

RECOMMENDATIONS FOR FUTURE WORK

The work reported in this dissertation has left many questions unanswered, and indicates the desirability for additional evidence to either confirm or reject the proposed structural formulas for the two new adducts investigated. In addition, the possibilities for forming new adducts have been revealed.

Phenazine and benzoquinone form a product which melts at about 240° C.* On the basis of the thermodynamic calculations and the experience obtained with quinone, phenazine should condense quite readily with dimethyl acetylenedicarboxylate; it may be possible to effect this condensation by using two moles of the ester per mole of phenazine.

Although quinoxaline catalyzes the decomposition of maleic anhydride at about 205° C, a high melting reaction product may be obtained by heating quinoxaline with a thirty mole excess of the anhydride at 100° C. The nature of the yellow crystals formed when quinoxaline was reacted with dimethyl maleate should be investigated. It seems likely that an adduct was formed between quinoxaline and the dimethyl ester of

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*Thermodynamic calculations do not favor a normal adduct here (15 kcal. endothermic even if hydroquinone is formed).

acetylenedicarboxylic acid; it will be necessary to devise means to isolate the product, if formed, in a pure state. If this work is successful, the reaction of 2-methylquinoxaline with the ester is probably similar in nature.

The experiments with methylacridinium chloride and dimethyl acetylenedicarboxylate in methanol are incomplete. While it has been assumed in this work that methanol, when found to be a constituent of the adduct, adds across the double bond in the ester portion of the adduct, the results obtained do not disprove the structure which Diels and Thiele assigned to the adduct from acridine and the acetylenic ester in methanol. Evidence as to the mode of attachment of the methanol to the acridine-ester adduct may be obtainable from ultraviolet absorption curves. If the acridine-ester-methanol adduct is of the type indicated by Diels and Thiele, no significant change in the absorption should be observed when the ultraviolet absorption curve for the adduct is run in acid.

The evidence for the structure of the 2,3-diphenylquinoxaline-acetylenic ester-methanol adduct seems quite conclusive for everything but the position of the methanol. However, the position of attachment of the methanol, which is not based upon direct experimental evidence, is difficult to determine in an unequivocal manner. Formation of the same adduct from 2,3-diphenylquinoxaline and methyl methoxymaleate is probably not thermodynamically feasible.

The nature of the products obtained on oxidation of the yellow 2,3-diphenylquinoxaline adduct with hydrogen peroxide was not determined. If the high melting compound is a hydrated form of 2,3-diphenylquinoxaline-N-oxide as suspected, reduction with zinc in alcoholic hydrochloric acid solution should yield the starting quinoxaline.

The structure of the red 2,3-diphenylquinoxaline-acetylenic ester adduct has not been investigated. If it were desired to study this adduct further, work should be done in an attempt to determine the optimum conditions for its formation.

Only one adduct was obtained from the ester and 2-phenylquinoxaline; and the position of the water molecule in this adduct was not established. An attempt should be made to isolate a compound corresponding to the red 2,3-diphenylquinoxaline adduct, by reacting 2-phenylquinoxaline with two moles of the ester.

A possible method for more completely elucidating the structure of the adduct from 2-phenylquinoxaline is as follows: Catalytic reduction of the adduct, to saturate the double bond in the quinoxaline residue without affecting the aromatic ring, should yield a compound which on degradation by heat or hydrolysis should yield quinoxaline-2-carboxylic acid (or the 2,3-dicarboxylic acid) without the formation of the 2-phenylquinoxaline which was obtained from the degradation experiments reported.

Additional work should be done to confirm the identity of the dicarboxylic acid obtained on alkaline saponification of the 2-phenylquinoxaline adduct.

The nature of the adduct obtained from 2-phenylquinoxaline, methanol, and the ester, in ether solution, should be investigated.

CHAPTER IV

EXPERIMENTAL DETAILS

Preparation of Dienes

Phenazine (48)

Preparation of o-Nitrodiphenylamine.-- One hundred grams
(0.635 mole) of o-nitrochlorobenzene, 140 grams (1.504 moles)
of aniline (freshly distilled from zinc dust), and 52 grams
of fused sodium acetate were placed in a 500 milliliter three-
neck flask fitted with a thermometer, and a reflux condenser
topped with a calcium chloride drying tube. The mixture was
heated to 180° C with a Glas-col heating mantle and maintained
at 175-185° C for seventeen hours.

The contents of the flask were then distilled with
steam for nine hours, (approximately 60 milliliters of aniline
were collected), made slightly acid to Congo red paper by the
addition of thirty milliliters of concentrated hydrochloric
acid, and steam distilled for an additional 40 minutes. The
resulting mixture was transferred to a beaker in which it was
allowed to cool. The liquid layer was decanted from the black
oil; the oil crystallized on further cooling. The dark brown
crystals thus obtained were filtered and washed thoroughly

with water, then dried in a vacuum desiccator over calcium chloride. The yield of crude product, 105 grams, was 77.2 per cent of theory. The reported yield was 88 grams (48).

Reduction to o-Aminodiphenylamine.--Seventy-seven grams of the crude o-nitro compound were dissolved in 400 milliliters of hot 95 per cent ethanol, then cooled to room temperature. The alcohol solution was diluted with water (with vigorous stirring) to about 1800 milliliters, and the product which separated was filtered, washed with water, and dried in a vacuum desiccator over calcium chloride.

The 54 grams of purified material which melted at 74° C* (reported melting point, 75° C, (49)) were refluxed for thirteen and one-half hours with 54 grams of iron filings, 1080 milliliters of water, and 64 milliliters of glacial acetic acid. After cooling to room temperature, the mixture was filtered and washed thoroughly with water. The residue on the funnel was then heated with 400 milliliters of 95 per cent ethyl alcohol, and the solution was decanted through a Buchner funnel. The extraction with hot alcohol was repeated three times, using an additional 100 milliliters of alcohol

*All melting points are uncorrected and were taken with the same uncalibrated thermometer. In the earlier work (prior to the investigation of the structure of the adducts) the melting points were taken in an aluminum block. Then an electrically heated and stirred oil bath was used. Melting points in the bath were found to be 3° C higher than those obtained with the block. Therefore, all melting points were corrected to agree with the readings in the electrically heated bath.

for each extraction. Finally, the residue was transferred to
the funnel and washed with 200 milliliters of hot alcohol.
The combined alcohol filtrates were diluted (with stirring)
with four liters of water, then left in the dark for three
hours. The product was filtered, washed thoroughly with water,
and dried in a vacuum desiccator over calcium chloride. The
yield of o-aminodiphenylamine, which melted at 78° C (report-
ed (50) melting point 79-80° C), was 38 grams or 82 per cent
of the theoretical. The expected yield from 54 grams of o-
nitro compound was 40 grams of o-aminodiphenylamine (50).

Ring Closure to Phenazine.--Small (five or ten grams) portions
of the o-aminodiphenylamine were mixed thoroughly with ten
times their weight of litharge (PbO), and the mixture was
heated to effect ring closure and subsequent sublimation of
the phenazine formed. No completely satisfactory method for
effecting this sublimation was devised. The methods tried
were: 1) Heating the mixture with a Bunsen burner in a pyrex
retort; 2) Heating the mixture (Bunsen burner) in the center
of a pyrex tube two feet long and one and one-half inches in
diameter, open at both ends; 3) Heating the mixture in the
closed end of a one-inch pyrex tube two feet long, (with a
Bunsen burner) in which the original charge was covered with
a layer of litharge; 4) Heating the mixture with a Bunsen
burner in a shallow glass vessel covered with an inverted
Buchner funnel, in the bottom of which was a piece of card-
board through which several small holes had been punched, and

to which gentle suction was applied with an aspirator pump; and 5) Heating the mixture in the closed end of a combustion tube by slowly introducing the closed end of the tube into a combustion furnace, the center section of which was maintained at a temperature of about 500° C.

By the use of these various procedures, a total of 7.5 grams (20 per cent of the theoretical amount based on o-amino-diphenylamine) of phenazine were collected. This was re-crystallized from 95 per cent ethanol, yielding 3.75 grams of product which melted at $174\text{-}174.5^{\circ}$ C. The reported melting point is $170\text{-}171^{\circ}$ C (51).

2,3-Diphenylquinoxaline

This compound was prepared in 81 per cent yield by con-densing equimolar quantities of o-phenylenediamine and benzil in refluxing glacial acetic acid by the method of Bost and Towell (52).

2,3-Di-p-nitrophenylquinoxaline

This compound was prepared by the procedure described by Chattaway and Coulson (53). Benzoin and urea were con-densed in glacial acetic acid to 4,5-diphenylglyoxalone, which was nitrated, in cold concentrated sulfuric acid solution, with fuming nitric acid, to 4,4'-dinitrobenzil. This was then condensed with o-phenylenediamine in glacial acetic acid. The

glyoxalone was obtained in 56 and 58 per cent of theory yield (based on benzoin; 80 per cent of the reported yield); the dinitrobenzil in 26 per cent yield (based on glyoxalone; 113 per cent of the reported yield); and the final product, which melted at 202-203° C (reported melting point, 201° C), in 75 per cent yield (based on the dinitrobenzil).

Preparation of Quinoxaline

Quinoxaline was prepared by a method similar to that described in Organic Syntheses (54). The yellow oil obtained was fractionated at reduced pressure through a Todd still. The fraction boiling at 108-109° C at a pressure of 16-17 millimeters of mercury was collected. This water-white liquid had an index of refraction (n_D^{48}) of 1.6162 compared with 1.62311 at 48° C reported in the literature (55).

2-Phenylquinoxaline

Preparation of Phenylglyoxal Hydrate.--This compound was prepared as described in Organic Syntheses (56).

Condensation to 2-Phenylquinoxaline.--In a typical experiment, 1.1 moles (147 grams) of phenylglyoxal (as the hydrate) were refluxed in 700 milliliters of 95 per cent ethyl alcohol with 1.1 moles (119 grams) of o-phenylenediamine for two and one-half hours. After cooling in an ice-water bath, the product

was filtered and dried in a vacuum desiccator. The yield of
crude product (177 grams) was 78 per cent of the theoretical.
Recrystallization from 800 milliliters of 95 per cent alcohol,
using animal charcoal to decolorize the crude material, gave
131 grams of a product which melted at 76-77° C. The reported
melting point is 78° C (57).

2-Methylquinoxaline

This compound was made by the procedure described in
Organic Syntheses (58).

Methylacridinium Chloride

Purification of Acridine.--Ten grams of acridine (practical,
Paragon Division, Matheson Co., Inc.) which melted at 108-
112° C were dissolved in 75 ml of hot 95% alcohol, clarified
hot, then diluted with 135 ml of hot water. The resulting
cloudy solution was immediately cooled in an ice-water bath,
with vigorous shaking. After filtration and drying in a
vacuum desiccator over calcium chloride, 9.5 grams of product
melting at 111-115° C were obtained. The reported melting
points are: 110-110.5, 110-111, and 111° C (59, 60, 61).

Purification of Dimethyl Sulfate.--Eastman practical methyl
sulfate was distilled at ten millimeters pressure. The water-
white fraction boiling at 69-70° C was collected and used in

these experiments.

Preparation of Methylacridinium Chloride.--Acridine (4.75 g;
0.0265 mole) and dimethyl sulfate (3.45 g; 0.0274 mole) were
heated under reflux in a bath held at 100° C for one hour.
After cooling, the contents of the flask were removed with a
minimum amount of water, and the dark brown water solution
was neutralized with sodium bicarbonate. This solution, after
clarification (total volume 20 ml) was treated with 25 ml of
a saturated solution of sodium chloride. This caused the
separation of shiny crystals which were filtered, and combined
with the crystals which separated from the mother liquor on
standing overnight. This crude product was dissolved in ten
milliliters of 95% ethyl alcohol at the boil, cooled to room
temperature, and 35 ml of ethyl ether were added. The prod-
uct thus obtained (which melted with decomposition at 165-175°
C) was recrystallized again, using 15 ml of alcohol and 40 ml
of ether. The final product, which melted with decomposition
at 176-178° C, weighed only 0.73 g. Reported melting point,
177° C (42).

Purification of Solvents

Xylene

Eastman technical xylene was washed with concentrated
sulfuric acid until the acid layer was only slightly colored,

then with water, followed by two washes with saturated sodium
bicarbonate solution, and finally with water again. The
washed product was dried over calcium chloride, then stored
over sodium wire.

Benzene

Benzene was purified using the procedure described
above for xylene except that magnesium sulfate trihydrate
was used in place of the calcium chloride.

Acetic Acid

Glacial acetic acid was purified by fractional freezing
in a stoppered flask. The process was repeated until the
freezing point of the product remained constant at 17^0 C.

Methyl Alcohol

All of the methyl alcohol used was purified by reflux-
ing over magnesium turnings, followed by distillation from a
Claisen flask.

Preparation and Purification of Dienophiles

Benzoquinone

Eastman practical quinone was recrystallized from

ligroin. The purified product melted at 111-113° C.

Dimethyl Acetylenedicarboxylate (62).*

Five hundred and ten milliliters of methanol, in a two liter round bottom flask, were cooled in an ice-water bath. One hundred and ten milliliters of concentrated sulfuric acid were added in small portions, with continued cooling. One hundred grams of the acid potassium salt of acetylenedicar- boxylic acid were then added, and the flask, fitted with a calcium chloride drying tube, was left at room temperature, with occasional swirling, for four days.

The solution was decanted from the inorganic salts, which were washed four times with a total of 200 ml of ether. The solution and ether washes, combined in a separatory funnel, were diluted with 500 ml of ice water, and extracted with 500 ml of ether. The combined ether extracts were washed with 200 ml of ice water, 150 ml of a cold saturated solution of sodium bicarbonate, then with 200 ml of ice water, and dried over magnesium sulfate trihydrate.

The ether was removed by distillation at atmospheric pressure, and the product was distilled from a Claisen flask. The fraction boiling at 93-95° C at 19 mm pressure had an index of refraction (n_D^{25}) of 1.4452. The reported index of

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*We are indebted to the authors for supplying us with these directions before their publication.

refraction at this temperature is 1.4452 (62). Yields of about 50% of the theoretical were obtained.

Styrene

Eastman (White label) styrene was distilled from a Claisen flask at 72.5-73° C at 66.5 mm pressure. The product, which was stored under nitrogen in the refrigerator, had an index of refraction (n_D^{25}) of 1.5426. The reported index of refraction is 1.5439 at 25° C (63).

Ethyl Maleate

Eastman (White label) ethyl maleate ($n_D^{19.9} = 1.4396$) was distilled from a Claisen flask. The product collected at 98° C at 14 mm had an index of refraction at 19.9° C of 1.4402. (Reported $n_D^{19.9} = 1.4415$) (64).

Dimethyl Maleate

This compound was prepared from maleic anhydride and methanol, in the presence of sulfuric acid, by the method of Schmidt (65). The water-white product was collected by distillation at 15 mm at 97° C. Its index of refraction at 15° C was 1.4440. (Reported, 1.44407)

Phenazine

Phenazine and Benzoquinone

Seven experiments (summarized in Table 1) were run in an attempt to effect condensation between benzoquinone and phenazine. In each case, 0.001 mole of each of the reactants plus one milliliter of solvent were sealed in a glass tube about six inches in length (sealed) having an inside diameter of ten millimeters. The tube and its contents were then placed in a bath of organic liquid (which could be heated under reflux) which boiled at the temperature desired for the reaction. The reaction temperatures given in the table were obtained with the following liquids: xylene (140°), acetone (56°), benzene (80°), and ethylene glycol (197°).

Experiment 1.--The reactants, in xylene as solvent, were heated in a bath of refluxing xylene for 23 hours. No pronounced color change occurred in the reaction mixture. The long needles which separated on cooling were found (by melting point and mixed melting point) to be phenazine.

Experiment 2.--Acetic acid was used as the solvent, and the tube was heated in refluxing xylene for two hours. The reaction mixture turned very dark brown in color, and some black insoluble material separated on cooling. This insoluble product was filtered, washed with three milliliters of a

ten per cent sodium bicarbonate solution, then recrystallized from 95% ethanol with the aid of animal charcoal, using water to reprecipitate the product. The recrystallized compound, which was dark yellow in color, melted with decomposition at 204-215° C.

Quinone, heated as above with acetic acid in the absence of any phenazine turned dark brown, but no crystalline material separated when the mixture was cooled. When quinone and glacial acetic acid were heated together in a sealed tube, in a bath of refluxing acetone (56° C) there was no noticeable color change after five hours.

Experiment 3.--The reactants in acetic acid solution were heated in refluxing acetone for 43 hours. The yellow needles which separated from the reaction mixture on cooling to room temperature were filtered, washed with water, and dried. The product melted with decomposition at 240-243° C.

Experiment 4.--Experiment 3 was repeated but this time heating was continued for ninety hours. At the end of this time, the reaction mixture was not as dark in color as were the runs made in refluxing xylene. The yellow needles which separated on cooling (0.112 g) melted at 174° C. (The melting point of phenazine is 174° C.) Dilution of the mother liquor with water caused the separation of a small amount of product which melted at 135-170° C.

Experiment 5.--Experiment 3 was repeated for a second time.
In this experiment the reactants, in solution in acetic acid,
were heated for 72 hours in refluxing acetone, then for ten
hours in refluxing benzene (80° C). The insoluble material
which separated on cooling to room temperature consisted of
two types of crystals, long yellow needles which melted at
173-174° C, and dark brown crystals which melted at 239-241°
C. These two compounds, which weighed a total of 0.094 g,
were separated mechanically for the melting point determina-
tions. Dilution of the filtrate with water caused the separa-
tion of 0.043 g of a brown product which melted with decompo-
sition at 173° C.

Experiment 6.--The reactants (0.001 mole each of phenazine
and quinone), one mole of xylene, and 0.3 ml (0.00216 mole)
of triethylamine were heated in a sealed tube in refluxing
xylene (140° C) for one and one-quarter hours. After cooling
to room temperature, the liquid in the tube was poured off,
and the solids, very dark brown in color, were extracted five
times, each with about one milliliter of 95% ethyl alcohol.
The dark brown alcohol solution was treated with nuchar,
clarified, then diluted with water. The dark yellow precipi-
tate which separated melted at 197-240° C.

Quinone, triethylamine, and xylene, mixed together at
room temperature, rapidly acquired a dark brown color.

Experiment 7.--The reactants, in solution in nitrobenzene,

were heated for eight and one-half hours in refluxing xylene,
then for five hours in refluxing ethylene glycol (197° C).
After cooling, the contents of the tube were filtered, and
the residue was slurried in four milliliters of 95% ethanol
at room temperature. The material insoluble in the ethanol,
after filtration and drying, weighed 0.03 g, and melted with
decomposition at 238-240° C.

The nitrobenzene mother liquor was subjected to steam
distillation. The residue in the distilling flask was filter-
ed, and the insoluble material was washed with 95% ethanol
to remove the pale yellow-green needles, leaving 0.01 g of
shiny black plates which did not melt at 280° C.

Phenazine and Maleic Anhydride

Three sealed tube experiments (numbers 8, 9, and 10
in Table 1) were run in an attempt to effect condensation
between phenazine and maleic anhydride.

Experiment 8.--Phenazine (0.180 g; 0.0010 mole), maleic an-
hydride (0.098 g; 0.0010 mole), and glacial acetic acid (one
ml) were heated in a sealed tube for six hours in a bath of
refluxing xylene. After cooling in the refrigerator over-
night, the yellow crystals which separated melted at 168-
171° C. (The phenazine used in this experiment melted at
174° C).

Experiment 9.--Experiment 8 was repeated, this time adding
0.027 ml (0.00050 mole) of concentrated sulfuric acid to the
mixture in the sealed tube. The mixture, after heating in
a bath of refluxing xylene for four and one-half hours, was
brown in color, and on cooling, dark yellow needles separated.
The needles, after filtration and drying, in a vacuum desic-
cator, weighed 0.125 g and melted with decomposition at 195-
205° C. Recrystallization from acetic acid gave 0.07 g of a
light yellow product which melted at 226-227° C with decompo-
sition. A portion of these yellow crystals, when slurried
in water, turned Congo red paper blue.

A neutralization equivalent and a sulfate determina-
tion were run on the light yellow compound. The sulfate de-
termination indicated that the compound contained one mole
of sulfuric acid per mole of phenazine. 0.050 g of the sam-
ple, after drying in the oven at 100° C, was slurried in 50
ml of boiled and cooled distilled water. An excess of
0.00790 N sodium hydroxide solution was added, the mixture
was boiled for ten minutes, cooled, and back titrated to a
phenophthalein end point with 0.00790 N hydrochloric acid.
A gravimetric sulfate determination was then run on the
titrated solution.

Sample	ml std. NaOH	ml std. HCl	net ml NaOH	N.E.
Blank	37.3	35.6	1.7	
Exp. 9	46.1	4.0	40.4	157

0.042 g of $BaSO_4$, equivalent to 0.018 g of H_2SO_4, was obtained. 0.032 g (0.050 - 0.018 g) of the original sample was therefore nitrogen base (0.00018 mole) and this was combined with 0.00018 mole of sulfuric acid.

Experiment 10.--Phenazine (0.180 g; 0.0010 mole) and maleic anhydride (2.94 g; 0.030 mole) were heated in a sealed tube in a boiling water bath for eight hours. After cooling, the tube was broken open and its contents were removed with the aid of hot water, and filtered. The green crystals obtained weighed 0.037 g, and melted at 165-175° C.

Phenazine and Dimethyl Acetylenedicarboxylate

Experiment 11.--0.330 g (0.00183 mole) of phenazine, five milliliters of methanol, and 0.260 g (0.00183 mole) of the dimethyl ester of acetylenedicarboxylic acid were mixed together in a glass-stoppered flask, which was agitated in a "shaking machine" overnight. The dark purple reaction mixture was filtered, and the 0.25 g of purple residue, on recrystallization from acetonitrile, melted at 167-169° C. The mother liquor was evaporated to dryness in the filter flask with the aid of an aspirator pump. The residue left in the flask, after two recrystallizations from acetonitrile, yielded 0.04 g of light tan crystals which melted at 174-175° C.

Table 1. Summary of Sealed Tube Experiments with Phenazine

Exp. No.	Diene moles	Dieno-phile	moles	Solvent	ml. of Sol-vent	Temp. ^{o}C	Time Hrs.	
1.	0.001	Benzo-quinone	0.001	Xylene	1	140	23	Phenazine recovered
2.	0.001	Benzo-quinone	0.001	Acetic acid	1	140	2	Dark yellow cpd., m.p. 204-215° C (d)
3.	0.001	Benzo-quinone	0.001	Acetic acid	1	56	43	Dark yellow cpd., m.p. 240-243° C (d)
4.	0.001	Benzo-quinone	0.001	Acetic acid	1	56	90	62% of the phenazine recovered
5.	0.001	Benzo-quinone	0.001	Acetic acid	1	56 80	72 10	Phenazine and a cpd. m.p. 239-241
6.	0.001	Benzo-quinone	0.001	Xylene	1	140	1¼	Cat.: Et$_3$N Yellow cpd. m.p. 197-240° C.
7.	0.001	Benzo-quinone	0.001	Nitro-benzene	1	140 197	8½ 5	cpd. m.p. 238-240° C
8.	0.001	Maleic Anhyd.	0.001	Acetic acid	1	140	6	Phenazine recovered
9.	0.001	Maleic Anhyd.	0.001	Acetic acid	1	140	4½	0.0005 mole H_2SO_4; phenazine sulfate (?)
10.	0.001	Maleic Anhyd	0.03	----	-	100	8	ca. 20% of the phena-zine recov-ered

Quinoxaline

Quinoxaline and Maleic Anhydride

The three experiments run with quinoxaline and maleic anhydride are summarized in Table 2.

Experiment 1.--1.30 grams (0.010 mole) of quinoxaline and 4.9 grams (0.050 mole) of maleic anhydride, in a sealed tube, were placed in a bath of nitrobenzene and heated. The mixture in the tube exploded when the nitrobenzene reached the boiling point!

Experiment 2.--Quinoxaline (1.343 g; 0.01032 mole) and maleic anhydride (30.5 g; 0.311 mole) were heated under reflux, in an atmosphere of nitrogen, in a wax bath held at 205-210° C for one hour. After heating for forty minutes, black molten material was observed in the condenser. The black material remaining in the flask, which solidified on cooling to room temperature, was found to be essentially completely soluble in boiling water, but insoluble in benzene at room temperature. Attempts to decolorize the aqueous solution with the aid of animal charcoal were unsuccessful.

Ten grams of maleic anhydride, when heated alone as above, acquired a slight brown color. The melting point of the material after heating was 57-61° C. (The melting point

of maleic anhydride is 57-61° C.)

Experiment 3.--Quinoxaline (1.30 g; 0.010 mole) and maleic
anhydride (29.4 g; 0.300 mole) were heated in a flask fitted
with a reflux condenser, in a bath held at about 100° C for
twenty-two hours. After cooling to room temperature, the
dark brown residue was transferred to a Claisen flask with
the aid of ether and 95% ethanol. After removal of the sol-
vents at reduced pressure, the mixture was distilled at 104°
C and 10 mm pressure until no more distillate collected in
the receiver. The ether used to remove the residue from the
distilling flask caused the separation of brown insoluble
material which was filtered and washed with ether. The ma-
terial on the funnel, which became tarry when exposed to the
air, was slurried in 50 ml of water, and the aqueous slurry
was decanted through a Buchner funnel. This washing and de-
cantation were repeated several times, using a total of 200
ml of water; with the final wash, all of the insoluble ma-
terial was transferred to the funnel. This dark colored proc-
uct weighed about one gram. A portion of it, recrystallized
from 95% ethanol, gave a positive qualitative test for nitro-
gen. The recrystallized material did not melt at 287° C,
but when dropped into a hot crucible, burned away, leaving
a small amount of a water insoluble residue.

Quinoxaline and Ethyl Maleate

Experiment 4.--Quinoxaline (1.425 g; 0.0110 mole) and di-
ethyl maleate (1.80 ml; 1.93 g; 0.0112 mole) were heated to-
gether in a sealed tube in refluxing ethylene glycol (197°
C) for six hours. No insoluble material separated from the
brown reaction mixture when the tube, open to the atmosphere,
was cooled in an ice-water bath. After washing with water,
the reaction mixture was made acid to Congo red paper by the
addition of dilute (1:1) hydrochloric acid, and extracted with
ether. The combined ether extracts, after evaporation of the
solvent, deposited 1.0 gram of a red sweet-smelling liquid.
The residue left after extraction with ether was made alka-
line with potassium hydroxide solution, and again extracted
with ether. These combined ether extracts, on evaporation,
deposited a residue having the odor of quinoxaline.

Experiment 5.--Five milliliters (5.65 g; 0.043 mole) of
quinoxaline and twenty milliliters (21.4 g; 0.124 mole) of
ethyl maleate were refluxed together in a nitrogen atmosphere
for six and one-quarter hours. The dark red liquid obtained
was then distilled at seven to nine millimeters pressure, and
two fractions of distillate, boiling at 92-94° C were collect-
ed. The first fraction (20 ml) was pale yellow in color and
had an index of refraction ($n_D^{25.5}$) of 1.4740. The second
fraction (1.0 ml) was darker yellow in color and had an index
of refraction of 1.4851 at the same temperature. The index

of refraction of the ethyl maleate used in this experiment
was 1.4372 at 25.5° C.

The dark red viscous oil (2.2 g) left in the distilling
flask did not crystallize in the refrigerator overnight. A
portion (1.6 g) of this oil was refluxed for five hours with
90 ml of aqueous-alcoholic sodium hydroxide solution, cooled
in an ice-water bath, and filtered. The brown insoluble ma-
terial thus obtained (0.6 g) was dissolved in water, clari-
fied to remove the small amount of insoluble, and the aqueous
solution was acidified with dilute (1:1) hydrochloric acid.
The yellow-green precipitate which separated was filtered
and recrystallized from 95% ethanol. The recrystallized prod-
uct, which was pale green in color, melted at about 275° C.
(The melting point of fumaric acid, in a sealed tube, is
286-287° C.)

Both quinoxaline and ethyl maleate were treated (sepa-
rately) in the same manner as the mixture of these two com-
pounds described in this experiment. The quinoxaline, after
refluxing, solidified to a dark red-brown mass, from which
no volatile components were obtained on distillation at nine
millimeters pressure at a bath temperature of 225° C. The
ester, after refluxing, acquired a brown color. From 10 ml
of starting material, 5.4 ml of distillate, having an index
of refraction at 20° C of 1.4770, were collected at 96-98°
C at a pressure of nine millimeters.

Quinoxaline and Dimethyl Maleate

The diene (4.67 g; 0.0359 mole) and the dienophile
(9.0 ml; 10.4 g; 0.0722 mole) were heated under reflux in a
bath at 195° C for four and one-half hours. The dark red
crystals in the reaction flask were removed with the aid of
25 ml of ether in which they were only partially soluble,
filtered, washed with ether, and sucked dry on the funnel.
The residue consisted of 0.2 g of light tan plates which
melted with decomposition at about 105° C. (The melting
point of dimethyl fumarate is 102° C.)

The ether solution and washes were evaporated on the
steam bath, then distilled at nine millimeters pressure from
a Claisen flask from a bath, the final temperature of which
was 145° C. The distillate consisted of a mixture of white
crystals, and liquid. The crystals were filtered but were
lost in the oven at about 75° C.

The blood-red, semi-solid residue in the distilling
flask was removed with the aid of ether and 95% ethanol, and
the solvents were evaporated on the steam bath. The dark
red residue (2.5 g) was washed several times by decantation
with five milliliter portions of ether. Evaporation of the
combined ether washes left 1.5 grams of a dark red viscous
material. The remainder of the dark red residue (1.0 g)
which had been washed with the ether was rubbed with several
two to three milliliter portions of ether in a small mortar.

This caused the separation of some crystalline material which was filtered off as it was formed, then extracted with ether in a small Soxhlet extractor. The residue in the extractor was sucked dry on a Buchner funnel, leaving 9.27 g of dark red material which was slurried in five milliliters of dioxane at room temperature and filtered. Addition of ether to the dioxane filtrate caused the separation of some insoluble, difficultly filterable material. The residue on the funnel was again slurried in dioxane (four ml), filtered and washed thoroughly with dioxane and ether. An attempt was then made to determine the melting point of this residue. No change was noted in the appearance of the sample in the melting point tube until the temperature of the bath reached 260° C. At this temperature, light crystals began to collect above the dark brown sample in the tube. These yellow crystals melted at 285° C.

About one-half (0.02 g) of the dark brown product was transferred to a porcelain crucible covered with a watch glass and the crucible was heated gently with a micro burner. Pale yellow crystals sublimed from the dark brown sample and collected on the sides of the crucible. These yellow crystals also melted at 285° C.

Quinoxaline and Dimethyl Acetylenedicarboxylate

Three experiments (numbers 7, 8, and 9 in Table 2)

were run in methanol as solvent. Only tarry products were
isolated in each case.

Experiment 7.--Equimolar quantities of the ester (0.71 g;
0.0050 mole) and quinoxaline (0.65 g; 0.0050 mole) were mixed
in five milliliters of methanol in a glass-stoppered flask
and left at room temperature for two days. Addition of the
ester to the solution of the quinoxaline in the alcohol caused
a color change to yellow almost immediately. Within one hour
the reaction mixture had acquired a bright orange-red color.

At the end of the two-day reaction period, the dark
red solution was evaporated in a filter flask with the aid
of an aspirator pump. The concentrated solution was then
placed in the refrigerator where it remained for two weeks.
No solid material separated. The mixture was evaporated
further until only a rubbery mass remained. This was dis-
solved in two milliliters of acetonitrile, and the dark red
solution was left in the refrigerator for eight days. Again
no crystals were obtained.

Experiment 8.--The reactants were mixed as described in Experi-
ment 7 and left at room temperature in a stoppered flask for
one week. The solvent was removed by evaporation in a stop-
pered filter flask, the dark red non-crystalline residue was
dissolved in four milliliters of carbon tetrachloride, and
the solution was placed on a watch glass from which the sol-
vent was allowed to evaporate at room temperature. The

residue left after evaporation of the solvent was a clear, very viscous red-brown oil which was readily and completely soluble in ether. The ether solution was extracted ten times with water, dried over anhydrous sodium sulfate, and left at room temperature to permit evaporation of the solvent. Again a dark red tarry residue was obtained.

Experiment 9.--In this experiment 1.42 g (0.010 mole) of the ester were added to a solution of 0.0050 mole of quinoxaline in five milliliters of methanol, and the mixture was left at room temperature in a stoppered flask for six days. An attempt to isolate a pure product by the method described in Experiment 8 again gave only tar.

2-Methylquinoxaline

2-Methylquinoxaline and Dimethyl Acetylenedicarboxylate

Equimolar quantities of 2-methylquinoxaline (3.74 g; 0.0260 mole) and the dimethyl ester of acetylenedicarboxylic acid (3.69 g; 0.0260 mole) were dissolved in 42 ml of methanol. The yellow color of the methanolic solution of the quinoxaline began to darken almost immediately after addition of the ester. After standing for one hour in a stoppered flask at room temperature, the reaction mixture was red-brown in color. At the end of 24 hours, the mixture had deposited a very small amount of some pale tan crystals which

Table 2. Experiments with Quinoxaline

(* Sealed Tube Experiments)

Exp. No.	Diene Moles	Dieno-phile	Moles	Solvent	Temp. $^{\circ}C$	Time	
1.*	0.010	Maleic Anhyd.	0.05	----	210	--	Explosion
2.	0.010	Maleic Anhyd.	0.311	----	205-210	1 hr.	Black resi-due; gas evolved
3.	0.010	Maleic Anhyd.	0.30	----	100	22 hrs.	cpd. with high m.p.
4.*	0.011	Ethyl Maleate	0.0112	----	197	6 hrs.	No crystal-line products
5.	0.043	Ethyl Maleate	0.124	----	re-flux	$6\frac{1}{4}$ hrs.	Fumaric acid (?)
6.	0.036	Di-methyl maleate	0.072	----	195	$4\frac{1}{2}$ hra.	Dimethyl fu-marate (?); cpd. m.p. ca. 285^b C
7.	0.005	Acetyl-enic ester	0.005	5 ml. methanol	room	2 days	Tar
8.	0.005	Acetyl-enic ester	0.005	5 ml. methanol	room	1 week	Tar
9.	0.005	Acetyl-enic ester	0.010	5 ml. methanol	room	6 days	Tar

were filtered and sucked dry on the funnel, while evaporating
the filtrate in the filter flask. No further work was done
on this experiment.

2,3-Di-p-nitrophenylquinoxaline

2,3-Di-p-nitrophenylquinoxaline and Styrene (See Table 3)

Experiment 1.--0.0025 mole (0.93 g) of 2,3-di-p-nitrophenyl-
quinoxaline, 0.01875 mole (1.95 g) of styrene, and 0.01 g of
hydroquinone were heated in a bath of refluxing water for
three and one-half hours. At the end of this time, the quin-
oxaline had formed a solid mass at the bottom of the tube,
the surface of which was yellow in color, while the main por-
tion still maintained its pale grey-green appearance. The
tube was broken open and an additional 0.01875 mole of styrene
and 0.01 g of hydroquinone were added. This new mixture was
again heated in the sealed tube for an additional two and
three-quarters hours at 100° C. There appeared to be two
types of crystals in the tube, yellow ones at the interface
between the unreacted quinoxaline and the styrene, and the
main portion of the quinoxaline. This mixture was filtered,
and the yellow crystals were separated mechanically. After
drying in the oven at 70° C, they weighed 0.107 g and melted
at 155-190° C. The remainder of the residue on the funnel,
which was pure white in color, weighed 0.797 g dry, and melted

at 203-204° C. This 0.797 g of material, which had the same melting point as 2,3-di-p-nitrophenylquinoxaline was 86 per cent of the starting quinoxaline.

Experiment 2.--A glass tube was again filled with 0.0025 mole of 2,3-di-p-nitrophenylquinoxaline, 0.0375 mole of styrene, and 0.02 g of hydroquinone, sealed, and heated in a bath of refluxing nitrobenzene (211° C) for three hours. After cooling, the tube was broken open and the very viscous dark red mixture was steam distilled. The residue in the distilling flask was extracted four times, each with about ten milliliters of hot glacial acetic acid. The combined extracts were evaporated to about ten milliliters, then treated with four milliliters of water. The tarry material which separated from the water-acid mixture was extracted six times, each with five to ten milliliters of absolute ethyl alcohol. The combined alcohol extracts were clarified hot, and the clear filtrate was cooled in the refrigerator. The dark yellow crystals which separated weighed 0.412 g and melted at 155-160° C. This impure sample was extracted with three two-milliliter portions of ether. The ether insoluble residue, which weighed 0.065 g, melted at 185-195° C. Recrystallization of this small sample from glacial acetic acid gave yellow crystals which melted at 201-203° C; a mixed melting point with 2,3-di-p-nitrophenylquinoxaline showed no depression.

Experiment 3.--The quinoxaline (0.0025 mole), styrene (0.0375
mole), and 0.05 g of hydroquinone were heated together in a
sealed tube in a bath of refluxing nitrobenzene for one and
one-quarter hours. The clear deep red homogeneous mixture
in the tube was transferred to a distilling flask and distil-
led with steam. The residue in the distilling flask was ex-
tracted with four ten-milliliter portions of hot (100° C)
acetic acid. The combined acid extracts were clarified hot,
the clear filtrate was heated to boiling, water was added
until the solution became cloudy, then the mixture was cooled
to room temperature and filtered. The residue on the funnel,
which consisted of dark yellow crystals and some dark red
non-crystalline material, was not investigated further. The
aqueous acetic acid filtrate was evaporated to a volume of
about ten milliliters and cooled. The clear red-brown liquid
which remained was dried in a vacuum oven at 60° C, dissolved
in 20 ml of acetone, evaporated to a volume of five milli-
liters, and diluted with ether. The brown crystalline ma-
terial which separated was filtered and dried in an oven at
40° C. The 0.07 g of product obtained melted at 195-200° C;
a mixed melting point with 2,3-di-p-nitrophenylquinoxaline
melted at 197-201° C.

2,3-Di-p-nitrophenylquinoxaline and Diethyl Maleate

Experiment 4.--2,3-Di-p-nitrophenylquinoxaline (0.93 g;

0.0025 mole) and diethyl maleate (8.0 ml; 8.56 g; 0.050 mole) were heated under refulx, in a nitrogen atmosphere, for twenty and three-quarters hours. The dark brown liquid in the reaction vessel was distilled at nine millimeters pressure from a bath held at 165-170° C. Five milliliters of distillate were collected at 97-100° C. Addition of ether to the dark brown liquid residue in the distilling flask caused the separation of a brown precipitate which was filtered and dried on the funnel. The 0.12 g of product thus obtained was boiled with 15 ml of carbon tetrachloride (solution was not complete) and the mixture was filtered hot. The material insoluble in the carbon tetrachloride weighed 0.07 g and melted at about 255° C with decomposition. The carbon tetrachloride filtrate was evaporated, cooled, and filtered to give a product which melted with decomposition at 175-190° C.

The ether filtrate (above) from which the 0.12 g of crude product had separated was evaporated to dryness at room temperature, then placed in a vacuum oven at 55° C for six and one-half hours. The brick red crystalline residue was slurried in 12 ml of 95% ethanol and filtered. The 0.5 g of tan insoluble material on the funnel melted at 195-196° C. The alcohol filtrate was evaporated to dryness on a steam bath. The 1.35 g of dark red oily residue which remained did not crystallize on cooling in an acetone-dry ice bath.

Table 3. Condensation Experiments with

2,3-Di-p-nitrophenylquinoxaline

(* Sealed Tube Experiments)

Exp. No.	Diene moles	Dieno-phile	Moles	Temp. ^{o}C	Time hrs.	
1.*	0.0025	Styrene	0.0375	100	$6\frac{1}{4}$	0.02 g hydroquinone added; 86% of the quinox. recovered
2.*	0.0025	Styrene	0.0375	211	3	0.02 g hydroquinone added; 7% of the quinox. recovered
3.*	0.0025	Styrene	0.0375	211	$1\frac{1}{4}$	0.05 g hydroquinone added; 7.6% of the quinox. recovered
4.	0.0025	Diethyl maleate	0.050	reflux	20 3/4	heated in nitrogen atm.; no pure products

N-Methylacridinium Chloride

N-Methylacridinium Chloride and Dimethyl Acetylenedicarboxylate

Experiment 1.--Purified methylacridinium chloride (2.12 g; 0.00923 mole), methanol (7.4 ml), and the acetylenic ester (1.15 ml) were mixed in a glass-stoppered flask and left in the refrigerator at two degrees C for eleven days. The crystalline material which separated from the reaction mixture was filtered and the two types of crystals on the funnel were separated mechanically. The pale yellow crystals (Sample A, 0.36 g) were mostly inorganic in nature, as evidenced by the large residue left on heating in a porcelain crucible, and their complete water solubility. (A qualitative test for chloride ion on the water solution was positive, and indicated the presence of large amounts of this ion.) The light brown crystalline material (Sample B, 0.22 g), which melted with decomposition at 192-203° C, was extracted three times with five milliliter portions of 95 per cent ethyl alcohol. The alcohol insoluble residue (Sample D), weighed 0.04 g and melted at 202-204° C. The combined alcohol extracts were evaporated, cooled, and filtered; 0.06 g of pale yellow crystals (Sample C) which also melted at 202-204° C were obtained. The mother liquor from Sample C was evaporated to dryness on the steam bath. The mixed red and yellow crystalline residue

was washed several times with water at room temperature. The
very small amount of water-insoluble material remaining sub-
limed in a melting-point tube at 188-190° C.

The solubilities of Samples C and D were tested by shak-
ing small portions with water at room temperature. Sample C
was found to be slightly soluble, and a test for chloride ion
on the aqueous layer was negative. Sample D was apparently
insoluble in water, and the aqueous portion also gave a nega-
tive test for chloride ion.

At the end of thirteen days, the filtrate from Samples
A and B, which had been returned to the refrigerator, had
deposited more insoluble material which was filtered. Again
two types of crystals were obtained, pale yellow (Sample L)
and nearly colorless irregularly shaped glassy crystals
(Sample K), which weighed a total of 0.4 g. Sample K, re-
crystallized from five milliliters of 95 per cent ethyl al-
cohol, gave 0.1 g of a compound which melted at 87-91° C.
This compound, which was light yellow in color when first re-
crystallized, acquired a brown surface color when stored in
a desiccator overnight. Sample L yielded 0.12 g of a sub-
stance which melted at 202-204° C when recrystallized from
ethanol.

The mother liquor from Samples K and L was allowed to
evaporate to dryness at room temperature. Recrystallization
of the dark red residue from ethanol gave a small amount of
a compound which sublimed in a melting-point tube at 191-198°
C.

Experiment 2.--12.2 grams (0.0531 mole) of methylacridinium chloride, 41.7 milliliters of methanol, and 15.2 grams (0.107 mole) of the acetylenic ester were left at room temperature in a glass-stoppered flask for ten days. The insoluble material which separated (5.4 g), after recrystallization from methanol was tan in color and melted at 205-206° C with decomposition. After standing at room temperature for an additional sixteen days, the mother liquor from which the 5.4 g sample had been isolated, deposited an additional 0.88 g of crude material which melted at 204-205° C.

2,3-Diphenylquinoxaline

2,3-Diphenylquinoxaline and Styrene

Four sealed tube experiments were run in an attempt to condense styrene and 2,3-diphenylquinoxaline. Data for these experiments are summarized in Table 4.

Experiment 1.--2,3-Diphenylquinoxaline (0.706 g; 0.0025 mole) was heated in a sealed tube in a boiling water bath with 2.16 ml (1.95 g; 0.0187 mole) of styrene for three hours, then left to cool overnight. The white needles which separated were filtered, washed with a little 95 per cent ethanol, and dried. The 0.1 g of material thus obtained melted at 118° C; a mixed melting point with 2,3-diphenylquinoxaline (melting point 126° C) melted at 123-126° C. The viscous mother

liquor from which the white needles had separated was distilled with steam for one and one-half hours. The resinous residue in the distilling flask, which weighed 0.6 g, was insoluble in hot 95 per cent ethanol, but dissolved readily in warm benzene.

Styrene (2.2 ml) and hydroquinone (0.1 g) were heated together in a sealed tube in a boiling water bath for three hours. Only a very small amount of the hydroquinone dissolved in the hydrocarbon. After cooling to room temperature, the contents of the tube were much more fluid than was the reaction mixture in Experiment 1.

Experiment 2.--2,3-Diphenylquinoxaline and styrene (as in Experiment 1) and 0.01 g of hydroquinone were heated in a sealed tube in a boiling water bath for five and one-half hours. The mixture was transferred to a 25 ml distilling flask with ten milliliters of water, and steam distilled until a total of 83 ml of distillate had been collected. The residue in the distilling flask, which weighed 0.811 g (dry) was extracted three times, each with ten milliliters of hot 95 per cent ethanol. The combined alcohol extracts were evaporated to about ten milliliters, cooled and filtered. The white crystals obtained (0.528 g) melted at 124-127° C. The extracted non-crystalline residue, from which the 0.528 g of white crystals had been obtained, weighed 0.212 g, and was

readily soluble in benzene at room temperature.

Experiment 3.--0.706 g (0.0025 mole) of 2,3-diphenylquinoxaline, 0.521 g (0.00500 mole) of styrene, 0.068 ml (0.12 g; 0.0012 mole) of concentrated sulfuric acid, 0.005 g of hydroquinone, and four milliliters of glacial acetic acid were sealed in a glass tube and heated in a bath of refluxing acetone for five and three-quarters hours. The yellow-green crystalline material which separated from the reaction mixture on cooling was filtered and dried at 70° C. This 0.24 g of product melted with decomposition at 228-232° C.

Experiment 4.--Experiment 3 was repeated, but this time the reactants were heated at 100° C for five and one-half hours. No crystalline material separated from this reaction mixture, even after cooling in an ice-salt bath. The tube was broken open and the contents were seeded with a crystal of the product obtained from Experiment 3. Cooling was continued for one hour, and the bright yellow-green crystals which separated were filtered and dried. The product, which weighed 0.313 g, melted with decomposition at 229-234° C.

Sulfate, and the neutralization equivalent were determined on 0.05 g samples of the yellow-green crystals obtained from Experiments 3 and 4, using the same method described above for these determinations on the phenazine sulfate (Experiment 9).

Exp. No.	ml 0.00790 N NaOH added	ml 0.00790 N HCl consumed	net ml NaOH	N.E.
Blank	37.3	35.6	1.7	
3	36.7	8.2	26.8	236
4	35.0	4.8	28.5	222

The combined titrated solutions gave 0.060 g of barium sulfate, equivalent to 0.025 g of sulfuric acid, or 0.013 g of sulfuric acid from each 0.050 g of sample taken for analysis. Thus each sample contained 0.037 g (0.0500 - 0.013 g) or 0.00013 mole of nitrogen base per 0.00013 mole of sulfuric acid.

2,3-Diphenylquinoxaline and Dimethyl Acetylenedicarboxylate

Experiment 1.--In a preliminary experiment, 2.82 grams (0.010 mole) of 2,3-diphenylquinoxaline and 1.72 grams (0.0120 mole) of the acetylenic ester were mixed with 20 ml of methanol in a glass-stoppered flask and left at room temperature for five days. The quinoxaline was not completely soluble in the liquid portion of the reactants. At the end of the five-day period, the liquid layer, which was bright orange in color, was separated from the undissolved pale yellow solids by filtration, and evaporated in the filter flask with suction. The bright yellow crystals which separated from the concentrated solution were filtered and dried on the funnel. These crystals weighed 1.05 grams and melted at 99-117° C. The melting point of this product was raised to 149-150° C by

Table 4.   Sealed Tube Experiments with

2,3-Diphenylquinoxaline and Styrene

Exp. No.	Quinox. moles	Styrene moles	Solvent	Ml. Sol- vent	Temp. ^{o}C	Time Hrs.	
1.	0.0025	0.0187	--	--	100	3	14% of the Quinox. recovered; styrene polymerized
2.	0.0025	0.0187	--	--	100	$5\frac{1}{2}$	0.01 g hydroquinone added; 75% of the quinoxaline recovered
3.	0.0025	0.005	acetic acid	4	56	5 3/4	0.00124 mole H_2SO_4 as cat.; 0.005 g hydroquinone added; cpd. m.p. 228-232° C
4.	0.0025	0.005	acetic acid	4	100	$5\frac{1}{2}$	0.00124 mole H_2SO_4 as cat.; 0.005 g hydroquinone added; cpd. m.p. 229-234° C.

washing with ether.

The solids which were removed from the original reaction mixture weighed 1.75 grams. After recrystallization from 95 per cent ethanol, the essentially colorless compound melted at 127-28° C. (The melting point of the 2,3-diphenylquinoxaline used in this experiment was 124° C.)

Experiment 2.--2.73 grams (0.00968 mole) of 2,3-diphenylquinoxaline was allowed to react in 19 milliliters of methanol with 1.67 g (0.0118 mole) of the ester for one week. At the end of this time, the solid material remaining in the reaction flask was filtered and sucked dry on the funnel. (Evaporation of the bright orange filtrate yielded some of the yellow crystals obtained in the first experiment.) The 2.30 grams of material thus obtained (0.00815 mole, assuming it all to be unreacted 2,3-diphenylquinoxaline) was mixed with an additional 16 ml of methanol and 1.16 grams (0.00817 mole) of the ester and left at room temperature in a stoppered flask for sixteen days. This mixture was filtered (evaporation of the orange filtrate gave more of the bright yellow product obtained previously) to remove the crystalline insoluble material, which was washed with five milliliters of methanol and recrystallized from 35 ml of ether. 1.27 grams of a product which melted at about 150° C were obtained. Three recrystallizations from methanol caused the melting point of this product to increase to 155-159°, then to 159-161°, and finally to 162-165° C.

Experiment 3.--Experiment 2 was repeated on a larger scale.
The 2,3-diphenylquinoxaline (21.2 g; 0.0752 mole) and the
ester (13.0 g; 0.0915 mole) were mixed in a glass-stoppered
flask with 150 milliliters of methanol and left at room tem-
perature for eleven days. The unreacted material was filter-
ed, mixed with 125 ml of methanol and 9.0 g (0.0634 mole) of
the ester, and this new mixture was left at room temperature
in a glass-stoppered flask for 17 days.

The alcoholic filtrate from the original reaction mix-
ture was evaporated in a closed filter flask with the aid of
a water aspirator. The yellow crystals which separated were
filtered, washed with ether, and sucked dry on the funnel.
(Sample A; 2.7 grams). Sample A, which melted at 147-148° C
was recrystallized from methyl ethyl ketone; the recrystal-
lized product melted at 151-152° C.

The reaction mixture containing the unreacted starting
material and additional quantities of ester and methanol had
deposited some more of the yellow crystals, which were filter-
ed and washed with ether. (Sample C; 14.5 grams). Sample C
which melted at 148-153° C was recrystallized from carbon
tetrachloride; the recrystallized product melted at 152-155°
C. An additional 11.4 grams of the yellow adduct were ob-
tained from the filtrate from Sample C by evaporation in a
stoppered filter flask at reduced pressure.

The yield of yellow adduct from this experiment (28.6
grams) was 83% of theory, assuming the adduct to have a

molecular weight of 456 and to be composed of one mole each of the ester, the quinoxaline and methanol.

Experiment 4.--2,3-Diphenylquinoxaline (2.82 g; 0.010 mole), 15 ml of methanol, and 1.42 grams (0.010 mole) of the acetylenic ester were heated under reflux on a steam bath for three hours. The insoluble material which separated from this reaction mixture on cooling to room temperature was filtered, washed with ether, and sucked dry on the funnel. The 2.0 grams of product melted at about 118° C. Everything (including the residue left after evaporation of the ether used to wash the product) was returned to the reaction flask, a few milliliters of methanol were added, and refluxing was continued for an additional 20 hours. The insoluble material in the reaction flask was filtered at room temperature, washed with ether, and sucked dry on the funnel. The 1.7 grams of product (37.3% of theory) melted at 152-160° C.

Experiment 5.--2,3-Diphenylquinoxaline (14.1 g; 0.050 mole) and the acetylenic ester (7.1 g; 0.050 mole) were mixed in 100 ml of methanol and allowed to react at room temperature in a stoppered flask for 80 days. At the end of this time, the reaction mixture contained a considerable amount of insoluble material which was filtered and dried. This insoluble material, which weighed 12.0 grams, was mixed with an additional 7.1 grams of ester and 100 milliliters of methanol and left at room temperature for nine days. This mixture

then contained a considerable amount of yellow insoluble material, which, after filtration and drying, weighed 11.56 grams and melted at 158-161° C. The filtrates from both reaction mixtures were evaporated, and the yellow adduct which separated was purified by recrystallization from carbon tetrachloride. A total of 14.3 grams (62.7% of theory) of the yellow adduct was obtained from this experiment.

Experiment 6.--In this experiment two moles of the acetylenic ester (34.25 g; 0.2410 mole) per mole of 2,3-diphenylquinoxaline (34.0 g; 0.121 mole) were mixed in methanol (240 ml) and left at room temperature in a stoppered flask for six days. At the end of this time, the yellow insoluble material which had separated was filtered and sucked dry on the funnel. (Sample A). Sample A weighed 33.2 grams and melted at 142-146° C. Sample A, recrystallized from 165 milliliters of carbon tetrachloride, gave 28.2 grams of product (Sample AR) which melted at 149-151° C. Sample AR, recrystallized from 85 milliliters of acetonitrile, gave Sample D which melted at 152-154° C.

The filtrate from Sample A was evaporated in the filter flask. The precipitate which separated (Sample B; 5.7 grams) was filtered and recrystallized from 50 milliliters of the carbon tetrachloride filtrate from Sample AR. The hot solution was clarified, and a small amount of red insoluble material collected on the funnel. This red insoluble

(Sample R) weighed 0.1 gram and melted at 210-212° C with gas evolution. The filtrate from Sample R was placed in the refrigerator where it remained for three days. The precipitate which separated was filtered and recrystallized from a portion of the acetonitrile mother liquor from Sample D. An additional 3.0 grams of the yellow adduct were thus obtained.

The yield of yellow adduct from this experiment (41.9 grams) was 76 per cent of the theoretical, based on a molecular weight for the adduct of 456.

Experiment 7.--Experiment 6 was repeated. The reaction mixture was allowed to react at room temperature for eight days, and then filtered. The yellow crystals (Sample A; 40.1 grams) were recrystallized from 200 milliliters of carbon tetrachloride, then from 120 milliliters of acetonitrile; 29.66 grams of purified yellow adduct were obtained. The mother liquor from Sample A was evaporated with suction in a stoppered filter flask, and the insoluble material which separated (Sample B; 2.5 grams) was recrystallized from some of the carbon tetrachloride filtrate from the recrystallization of Sample A. None of the red adduct was obtained in this recrystallization. The yellow adduct obtained (Sample BR) weighed 1.68 grams. The filtrate from Sample B was evaporated with suction in a stoppered filter flask. The concentrated solution deposited some of the red product which was filtered (Sample E; 1.6 grams) and recrystallized from 45

milliliters of acetonitrile. The recrystallized product melted at 214.5-215° C; gas was evolved at 215.5° C.

The yield of yellow adduct from this experiment, 42.6 grams, was 75 per cent of the theoretical.

Analysis of the Red 2,3-Diphenylquinoxaline-acetylenic Ester Adduct

A portion of the red adduct (Sample E, Experiment 7) was submitted for microchemical analysis. The following results were obtained: C, 63.70%; H, 5.11%; N, 5.13% ash from carbon-hydrogen determination, 16.05% (non-alkaline). On re-analysis, the results were: %C, 63.51; %H, 4.83; %N, 5.02; % ash from the carbon-hydrogen determination, 0.44 (non-alkaline). Corrected for the ash, these values become: %C, 63.79; %H, 4.85; %N, 5.04. These values do not correspond to any simple combination of the reactants. The calculated values for a compound containing one mole of the quinoxaline, two moles of the ester, and one mole of water, $C_{32}H_{28}N_2O_9$ are: %C, 65.74; %H, 4.83; %N, 4.79. Other calculated values for molar combinations of the reactants are included in the following table:

moles quinoxaline	moles ester	moles methanol	moles water	% C (63.79)	% H (4.85)	% N (5.04)
1	1	--	--	73.59	4.75	6.60
1	1	1	--	71.04	5.30	6.14
1	1	--	1	70.57	5.01	6.33
1	2	--	--	67.83	4.62	4.95
1	2	1	--	66.20	5.05	4.68
1	2	--	1	65.74	4.83	4.79

Analysis of the Yellow 2,3-Diphenylquinoxaline-acetylenic Ester Adduct

Titration of the Yellow Adduct.--0.106 gram of the yellow adduct was dissolved in 50 milliliters of anhydrous methanol and titrated with 0.0936 N hydrochloric acid solution. The titration was followed with the aid of a pH meter. A plot of pH versus milliliters of acid gave a smooth curve with no definite break. The apparent pH of the solution of the compound, before addition of any acid, was 6.0.

Titration of 2,3-Diphenylquinoxaline.--0.067 gram of 2,3-diphenylquinoxaline was titrated as described above for the yellow adduct. The same result was obtained, except that in this case the apparent pH of the solution before addition of the acid was 5.22.

Microchemical Analysis.--A sample of the yellow 2,3-diphenylquinoxaline adduct which had been recrystallized from carbon

tetrachloride (m.p. 151-152° C) was submitted for carbon, hydrogen, nitrogen, and methoxyl determinations. Results were as follows: C, 71.45, 71.28% (duplicate determinations); H, 5.21, 5.01% (duplicate determinations); N, 5.94%; CH_3O, 20.24%. The values calculated for a compound containing one mole each of the quinoxaline, the ester, and methanol ($C_{27}H_{24}N_2O_5$, M. W. 456) were: C, 71.04%; H, 5.30%; N, 6.14%; CH_3O, 20.41%.

A second sample of this adduct (m.p. 153-154° C), recrystallized from carbon tetrachloride, acetonitrile and then methyl ethyl ketone was submitted for analysis. The following results were obtained: C, 71.19%; H, 5.58%; N, 6.61%.

A third sample of the yellow adduct (m.p. 155.5-157° C) was submitted for duplicate nitrogen determinations. The values reported were 6.23 and 6.30%.

Ultraviolet Absorption Curves.--The ultraviolet absorption spectra of the yellow adduct and of 2,3-diphenylquinoxaline, in methanol solution, were obtained with a Beckman Model DU Spectrophotometer. The molecular weight of the adduct was assumed to be 456.5 (See Figures 1 and 2).

Molecular Weight.--The molecular weight of the 2,3-diphenyl-quinoxaline adduct, as determined on a semi-micro scale, in triphenylmethane as solvent, was 465 ± 50. The method was taken from Schneider's Qualitative Organic Microanalysis (66). Triphenylmethane was chosen as solvent because of its
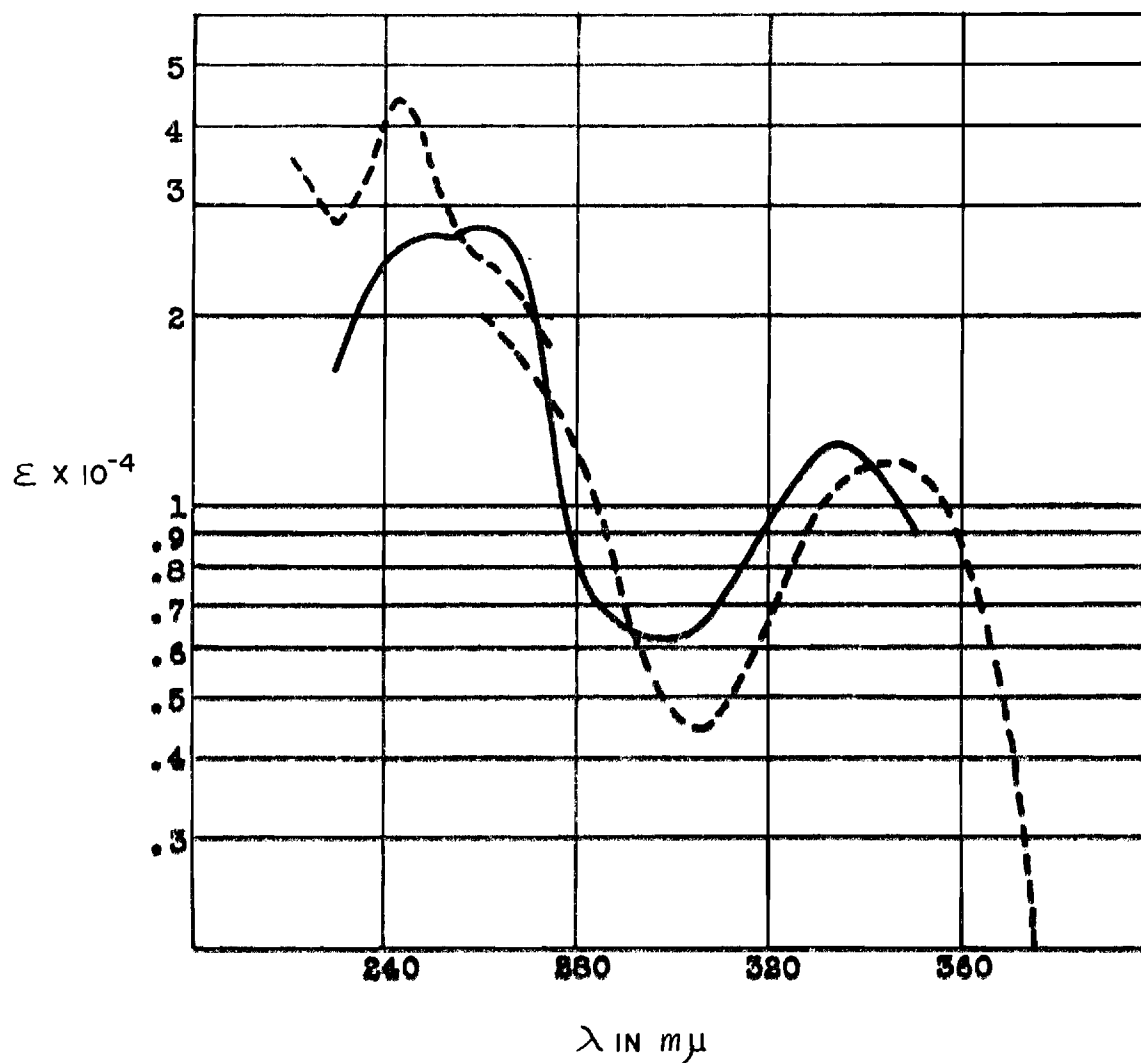
Ultraviolet Absorption Spectra (in Methanol Solution) of

2-Phenylquinoxaline ____

2,3-Diphenylquinoxaline - - -
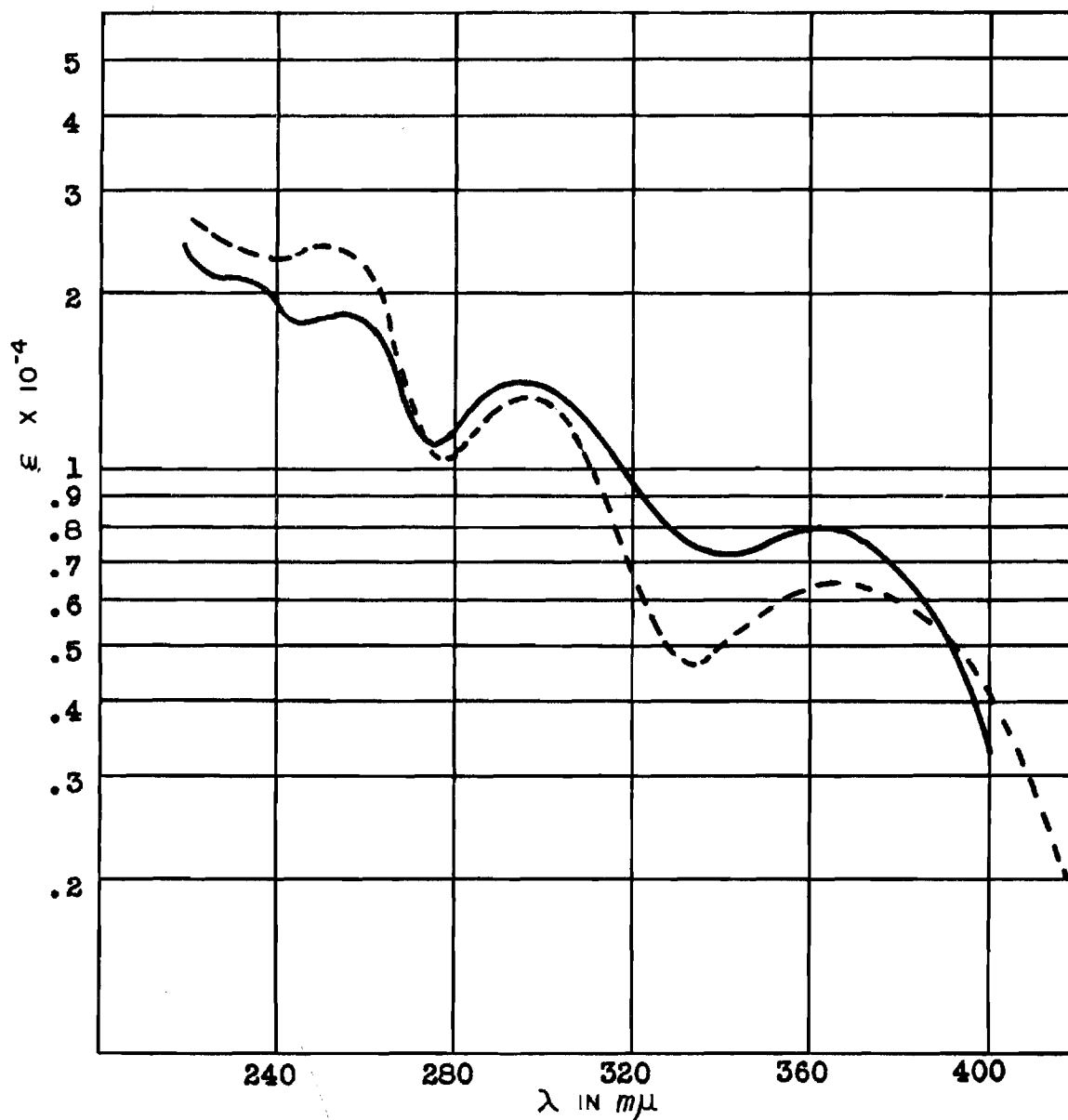
Figure 1

Ultraviolet Absorption Spectra (in Methanol Solution) of

2-Phenylquinoxaline-Acetylenic Ester Aaduot ____

Yellow 2,3-Diphenylquinoxaline-Acetylenic Ester Adduot - - -

Figure 2

convenient melting point, its inertness to the compounds
under investigation, and its rather large cryoscopic constant.
The constant used for the solvent was checked by determining
the molecular weight of a highly purified sample of 1,1,1-
triphenylethane (M.W. 258). The actual values obtained in
checking the cryoscopic constant of the solvent and in de-
termining the molecular weight of the compound are included
in the following table:

wt. of sample (g) (adduct)	wt. of solvent (g)	m.p. of mixture (^{o}C)	m.p. of pure sol- vent (^{o}C)
0.0238	0.2443		
		90.05	92.95
		90.25	92.70
		90.15	93.15
	ave.	90.15	92.80
			92.70
(triphenyl- ethane)			92.80
			92.90
0.0197	0.3477	89.85	92.70
		90.15	93.10
		90.00	92.70
		90.01	92.95
	ave.	90.01	93.00
		ave.	92.87

The molecular weight of triphenylethane, using a value of
13.0 for the cryoscopic constant, was 258. The molecular
weight of the adduct, using the same constant, was 465.

A 0 to 100° C thermometer calibrated in 0.1° C, was
used in all molecular weight determinations.

Saponification Equivalent.--Saponification equivalents were
determined by the method given in Shriner and Fuson (67). A
value of 196 was obtained in diethylene glycol solution by
the method referred to above. When the mixture was heated
for five minutes instead of for two minutes, a value of 172.5
was obtained. The method gave a value of 167 when the mixture
was heated at 120-130° C for fifteen minutes. The calculated
value for a compound of molecular weight 456 (Structure I),
containing two ester groups, is 228.

Acid Saponification.--2.0 grams (0.0044 mole; M.W. 456) of
the 2,3-diphenylquinoxaline adduct were slurried in ten milli-
liters of 95% ethanol, 1.0 milliliter (0.012 mole) of con-
centrated hydrochloric acid was added, and the mixture was
heated under reflux on a steam bath for one hour. The sol-
vent was allowed to evaporate at room temperature, and the
long needles which separated were filtered and dried. The
0.87 gram of compound obtained, which melted at 105° C, was
recrystallized from 95% ethyl alcohol. The recrystallized
product melted at 124.5-125.5° C; a mixed melting point with
2,3-diphenylquinoxaline showed no depression. Assuming the
adduct to be a 1:1:1 molar combination of the quinoxaline,
the ester, and methanol (M.W. 456), the yield (0.87 g) of
crude 2,3-diphenylquinoxaline obtained amounted to 70 per
cent of the quinoxaline in the adduct.

Alkaline Saponification.--20.0 grams (0.0439 mole) of the

2,3-diphenylquinoxaline-acetylenic ester-methanol adduct were refluxed on a steam bath for two hours in 125 milliliters of 95 per cent ethanol with 53.0 milliliters (0.0881 mole) of a 1.663 N solution of potassium hydroxide. The mixture was then cooled in an ice-water bath and filtered. The pale yellow needles on the funnel (Sample A), which weighed 6.69 grams, were slurried in 50 milliliters of water, and the material which did not dissolve was filtered, washed with water, and sucked dry on the funnel. (Sample B). Sample B, which weighed 5.61 grams, was recrystallized from 95 per cent ethanol. The recrystallized product (Sample BR; 4.44 g) melted at 125.8-126.6° C; a mixed melting point with 2,3-diphenylquinoxaline showed no depression. The 5.61 grams of Sample B accounted for 45.3 per cent of the 2,3-diphenylquinoxaline in the original adduct.

The aqueous mother liquor from Sample B (81 ml), i.e. the water-soluble portion of Sample A, was acidified with ten milliliters of dilute (1:3) hydrochloric acid, and the gases evolved were collected over a solution made by dissolving 800 grams of sodium sulfate in four liters of water, then acidifying with 200 milliliters of concentrated sulfuric acid. The flask containing the acidified filtrate was swept out with nitrogen, and the gases collected were analyzed for carbon dioxide in an Orsat apparatus. The total volume of gases collected, including the nitrogen, (562 ml at 33° C and 737.7 mm) was found to contain 21.8% or 106 ml

(S.T.P.) of carbon dioxide. This 106 milliliters of carbon dioxide was obtained from 1.08 grams (6.69 grams of Sample A minus 5.61 grams of Sample B) of the water soluble compound. The potassium hydroxide used in the saponification may have contained as much as three per cent of potassium carbonate; this would have evolved a total (at S.T.P.) of only 59 milliliters of carbon dioxide.

The filtrate from Sample A was evaporated with suction in a stoppered filter flask. The concentrated solution, which had deposited a considerable amount of insoluble material, was cooled in an ice-water bath, and filtered. The brown insoluble material thus obtained (Sample D; 3.34 g) was recrystallized from 95 per cent ethanol. This yielded Sample J, 1.41 grams of pale yellow crystals which melted at 47-50° C. Sample J was recrystallized from a ten volume per cent solution of benzene in cyclohexane, then from normal hexane, and finally two times from 95% ethanol. The final product, which weighed 0.02 gram and was pure white in color, melted at 55-56° C. This product was identified as desoxybenzoin by melting point, mixed melting point, and by a comparison of its ultraviolet absorption curve with that of an authentic sample, (Figure 3), prepared by the method in Organic Syntheses (68). The 1.41 grams of Sample J represented 0.00719 mole of desoxybenzoin or a yield of 16.4 per cent.

The mother liquor from Sample D was evaporated further on the steam bath, cooled, and filtered. This yielded Sample
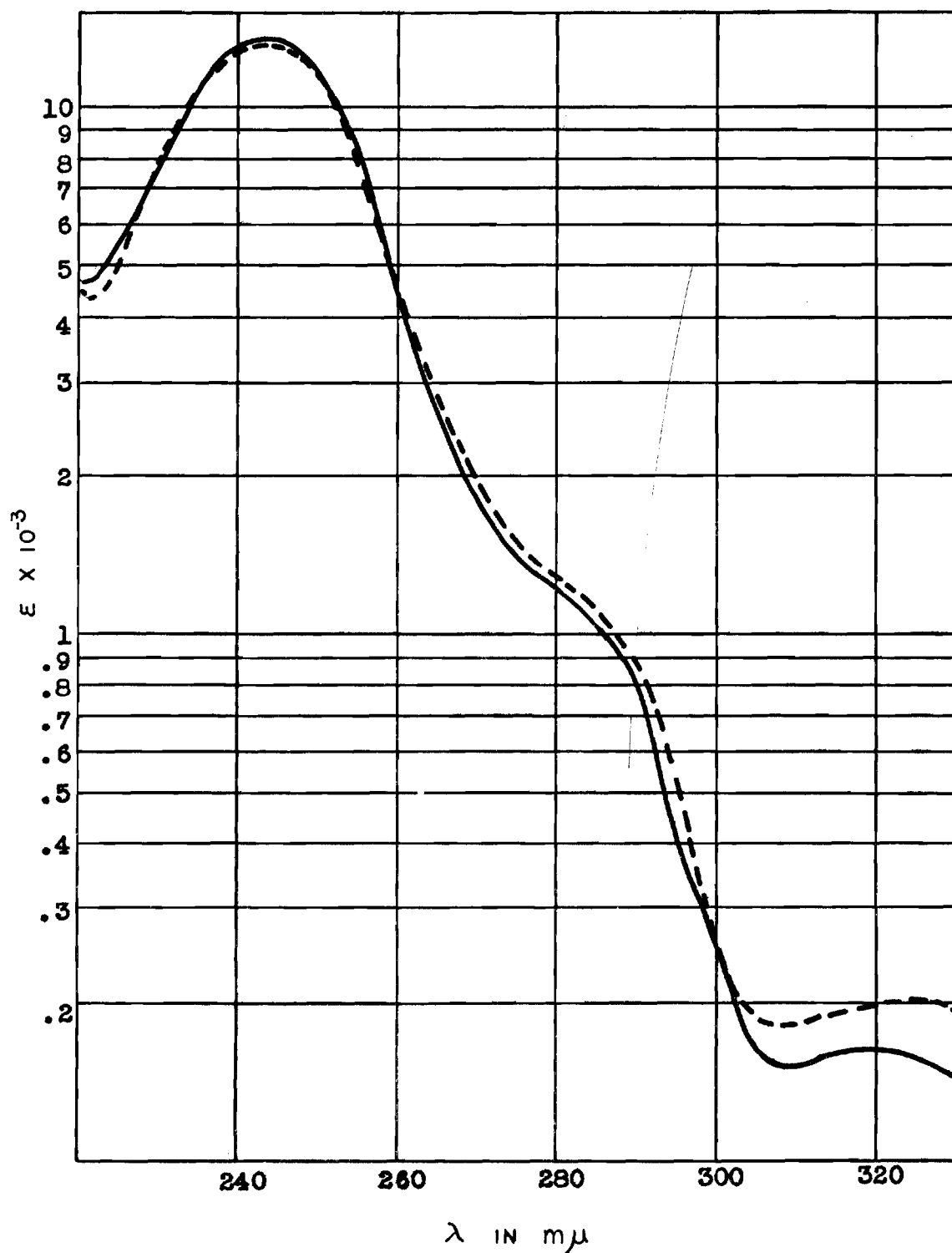
Ultraviolet Absorption Curves for Desoxybenzoin _____

Product from Alkaline Saponification of 2,3-Diphenylquinoxaline
Ester Adduct - - - - in 95% Ethanol

Figure 3

N, 3.03 grams of a dark yellow compound, which was slurried in 25 ml of water and filtered. The filtrate was made strongly acid with hydrochloric acid, and the tan insoluble material which separated (Sample R) was filtered, washed with water, and dried. Sample R, which weighed 1.30 grams and melted at about 204° C, was recrystallized three times from 95% ethanol with the aid of charcoal. The pure white product, which weighed 0.28 gram and melted at 212° C, was identified as quinoxaline-2-carboxylic acid by melting point, mixed melting point, and a comparison of its ultraviolet absorption curve with that of an authentic sample (Figure 4) which was prepared by the method of D. L. Hammick (69). The yield of crude quinoxaline-2-carboxylic acid, as represented by Sample R(1.30 g) was 0.00747 mole, or 17 per cent.

An attempt was made to hydrate tolan, the product expected in conjunction with the quinoxaline-2-carboxylic acid, to desoxybenzoin under the same conditions which effected saponification of the adduct. 1.28 grams (0.00719 mole) of tolan, in solution in 125 ml of 95% ethanol, were refluxed with 5.90 ml (0.0090 mole) of a 1.51 N potassium hydroxide solution and 47 ml of water, for two hours. The mixture was cooled in an ice-water bath, then filtered to remove the white insoluble material which separated (Sample A). Sample A weighed 0.70 gram and melted at 55-62° C. After recrystallization from methanol, the sample did not depress the
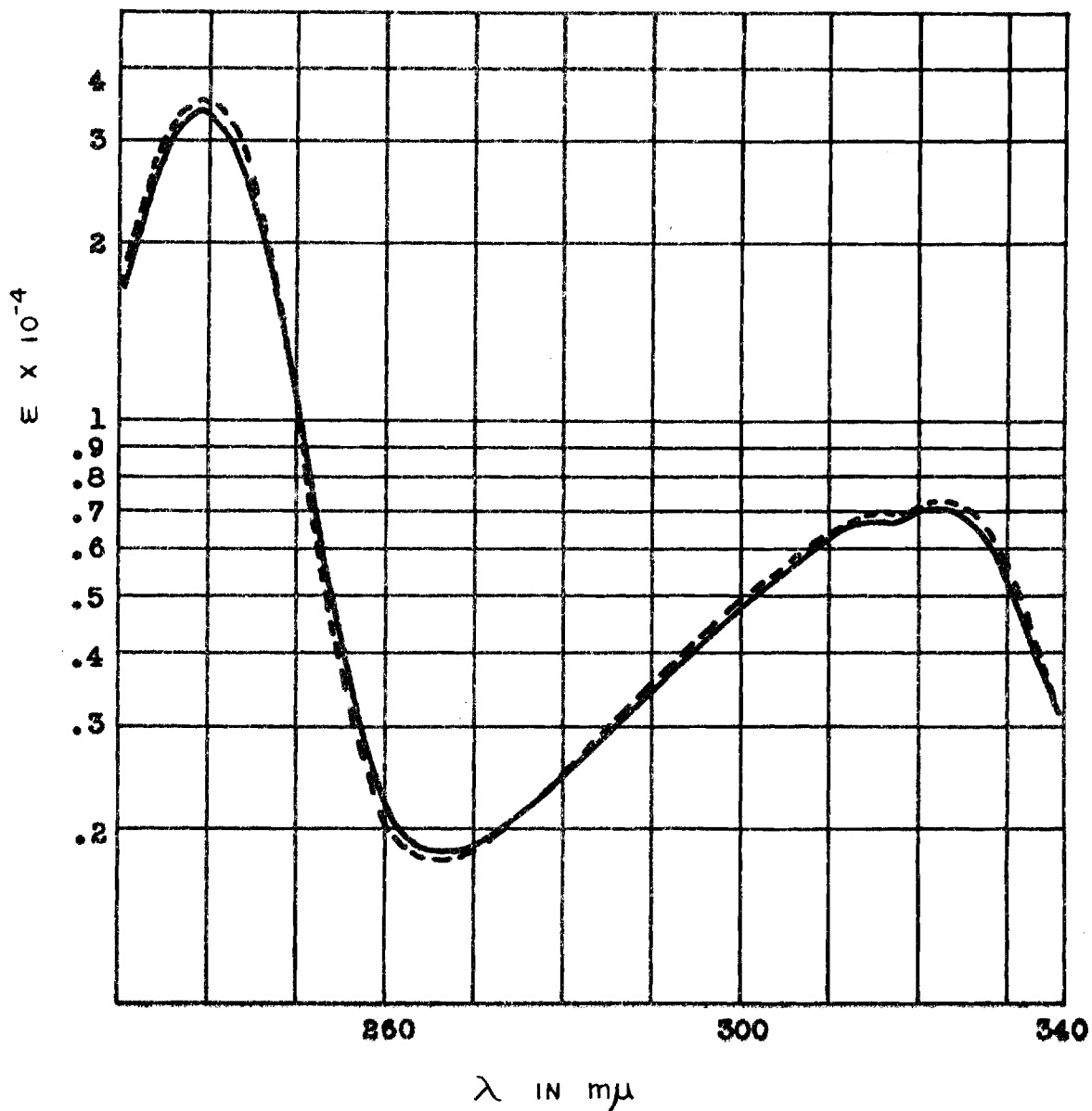
Ultraviolet Absorption Spectra (in 95% Ethanol)

Quinoxaline-2-Carboxylic Acid ____

Alkaline Saponification Product from the Yellow

2,3-diphenylquinoxaline Adduct - - - -

Figure 4

melting point (62-64° C) of an authentic sample of tolan,
prepared by the method given in Organic Syntheses (70).

The mother liquor from Sample A was evaporated with
suction in a stoppered filter flask. The precipitate which
separated was filtered and dried (Sample B). Sample B,
which weighed 0.30 gram, was recrystallized from methanol.
The recrystallized product melted at 61.5-63° C. The melt-
ing point of desoxybenzoin is 55-56° C.

Oxidation

Attempted Oxidation with Ferric Chloride.--0.500 gram (0.00110
mole) of the yellow 2,3-diphenylquinoxaline adduct, in solu-
tion in 50 milliliters of ether, was treated with a slurry
of 0.890 gram (0.00330 mole) of ferric chloride hexahydrate
in 100 milliliters of ehter. The yellow precipitate which
separated as soon as the ferric salt was added to the ether
solution of the adduct was filtered and dried. The 0.65
gram of product, after recrystallization from a 1:1 mixture
of dioxane and benzene, melted at 183-184° C. A portion of
the recrystallized product gave positive qualitative tests
for ferric iron and for chloride ion. A dilute hydrochloric
acid solution of the recrystallized product gave a red
gelatinous precipitate when made alkaline with pyridine. A
similar red precipitate was obtained when a dilute hydrochlor-
ic acid solution of ferric chloride was treated with pyridine.

Attempted Oxidation with Bromine.--A small sample of the yel-

low 2,3-diphenylquinoxaline adduct was dissolved in carbon tetrachloride and treated with a five per cent solution of bromine in carbon tetrachloride. A small amount (2-3 drops) of bromine was taken up by the solution, which then acquired a yellow turbidity. When more of the bromine solution was added, the solution cleared up and acquired the characteristic color of bromine.

Attempted Oxidation with Potassium Permanganate.--Solutions of the yellow adduct in methanol or in acetone, when treated with a dilute aqueous solution of potassium permanganate showed no reaction at room temperature.

2,3-Diphenylquinoxaline was not attacked by potassium permanganate in methanol solution at room temperature.

Sodium Dichromate.--3.0 grams (0.0066 mole) of the yellow 2,3-diphenylquinoxaline adduct were dissolved in 15 milliliters of hot glacial acetic acid. A solution of three grams (0.011 mole) of sodium dichromate in six milliliters of glacial acetic acid was added, and the mixture was refluxed for fifteen minutes. The green solution was poured over cracked ice, then extracted with ether. The combined ether extracts were evaporated, and the residue (1.1 grams) was slurried in a few milliliters of methanol. The crystals which separated were filtered and recrystallized from methanol. The purified white product, which melted at 122-123° C did not depress the melting point of a sample of 2,3-di-

phenylquinoxaline. The 1.1 grams of crude product represented 0.0039 mole of 2,3-diphenylquinoxaline or 59 per cent of the quinoxaline in the three grams of adduct taken for analysis.

Hydrogen Peroxide.--In a typical experiment, 8.0 grams (0.018 mole) of the yellow adduct were slurried in 27 milliliters of glacial acetic acid. To this was added a solution of 67 milliliters of 30 per cent hydrogen peroxide in 40 milliliters of glacial acetic acid. The mixture was heated under reflux on a steam bath for two hours, cooled to room temperature, and filtered. The insoluble material on the funnel (Sample F), which weighed 0.57 gram, was recrystallized two times, from acetophenone. The recrystallized product was pure white in color and melted at 309-310° C with decomposition. A portion of this sample, submitted for a microchemical determination of carbon, hydrogen and nitrogen gave the following results: C, 75.78%; H, 5.38%; N, 9.06%. The identity of this compound was not established but the analysis agrees with that of the hydrated form of 2,3-diphenylquinoxaline monoxide, $C_{20}H_{16}O_2N_2$: C, 75.9%, H, 5.06%, N, 8.86%.

The mother liquor from Sample F was poured over crushed ice and neutralized with ammonium hydroxide. Addition of the base caused a vigorous gas evolution which resulted in the loss of some of the mixture. (Ammonium hydroxide

and hydrogen peroxide gave no visible reaction). The pale yellow crystalline material which separated from the ammoniacal solution was filtered, washed with water, and then recrystallized three times from 95 per cent ethanol. The recrystallized product, which was very pale yellow in color and melted at 124-124.5° C, was submitted for carbon, hydrogen, and nitrogen analysis: C, 69.76%; H, 5.27%; N, 6.18%. These data do not give a whole number empirical formula. The calculated formula from these data is $C_{26.4}H_{23.9}N_2O_{5.33}$. No further work was done on this compound. The formula $C_{27}H_{24}N_2O_6$ has the following percentage composition: C, 68.63%; H, 5.12%; N, 5.93%.

Pyrolysis.--A sample of the yellow adduct (2.0 g; 0.0044 mole) was placed in a 50 ml round-bottom flask which was connected through a side-arm tube to another 50 ml flask which served as a receiver. The side arm led, via an acetone-dry ice trap, to a vacuum pump. The system was evacuated to 0.05 to 0.10 mm pressure, and the flask containing the sample was placed in a Wood's metal bath at 100° C. The bath temperature was increased to 255° C. At 210° C, the sample began to boil and the white fumes evolved were collected in the acetone-dry ice trap. The brown liquid which refluxed in the 50 ml flask, condensed in the top of the flask and ran back into the hot reaction mixture.

The pale yellow liquid which collected in the cold

trap was found to have an index of refraction at 20° C of 1.3991. The brown residue in the round-bottom flask was dissolved in alcohol, heated to boiling, charcoal was added, and the mixture was filtered. The tarry residue on the funnel was redissolved in ethanol, refluxed with dilute potassium hydroxide solution for a few minutes, and the resulting solution was cooled in an ice-water bath and filtered to remove the tan insoluble material which separated. The precipitate was washed with water until alkali-free, and dried. The 0.44 g of product, which melted at about 110° C, was recrystallized from 95 per cent ethyl alcohol. The recrystallized product was identified as 2,3-diphenylquinoxaline by melting point and mixed melting point. The 0.44 g of crude 2,3-diphenyl-quinoxaline (0.0016 mole) represented 36% of the quinoxaline in the original two grams of adduct.

An attempt was made to pyrolyze five grams of the yellow adduct in a Hickmann molecular still. The still, containing the sample, was evacuated to 0.05-0.1 mm pressure, then immersed, as far as the side-arm would permit, into a Wood's metal bath held at 250-260° C. In this experiment, only a small portion of the sample was pyrolyzed. Most of it sublimed into the upper portions of the still. The contents of the still were removed with hot 95 per cent ethanol. The yellow alcoholic solution was clarified, then evaporated with suction in the filter flask. The yellow crystals which separated melted at 152-156° C. The melting point of the

original adduct was 155-156° C.

Attempt to Form a Picrate of the 2,3-Diphenyl Adduct.--Approximately ten milliliters of a saturated alcoholic solution of picric acid was added to about ten milliliters of a saturated alcoholic solution of the yellow 2,3-diphenyl adduct. The combined solutions were heated to boiling on a steam bath, then cooled in an ice-water bath. No insoluble material separated from the clear yellow solution which, however, was darker in color than either of the solutions of the reactants.

Reaction with Alkali in Aqueous-Alcoholic Solution.--A small sample of the 2,3-diphenylquinoxaline adduct was slurried in about five milliliters of water in a test tube. Approximately five milliliters of methanol were added, and the mixture was shaken thoroughly. Only a small amount of the sample dissolved, as evidenced by the pale yellow color of the solution. This experiment was repeated in a second test tube, but this time the water was replaced by about five milliliters of a ten per cent aqueous solution of potassium hydroxide. Very little, if any, difference in color was noticeable in the liquid layer in the two test tubes, and no more of the adduct seemed to have dissolved than in the absence of the potassium hydroxide.

2-Phenylquinoxaline

2-Phenylquinoxaline and Maleic Anhydride

2-Phenylquinoxaline (0.95 g; 0.0046 mole) and maleic
anhydride (13.5 g; 0.138 mole) were heated together in a
flask fitted with a reflux condenser, in a bath held at
95-105° C for twenty-four hours. The dark brown residue
in the reaction vessel was dissolved in hot water, trans-
ferred to a separatory funnel, and extracted with 125 milli-
liters of ether. The combined ether extracts were evaporated
on a steam bath, and the dark brown liquid residue was washed
with water, which caused the separation of some very dark
crystalline material. This was filtered, dissolved in 95
per cent ethanol (15 ml), clarified with the aid of animal
charcoal, diluted with 120 ml of water, and filtered. The
pale violet crystals thus obtained weighed 0.53 g and melted
at 74-75° C. (The melting point of 2-phenylquinoxaline is
78° C.)

2-Phenylquinoxaline and Dimethyl Acetylenedicarboxylate

Experiment 1.--2-Phenylquinoxaline (0.90 g; 0.0044 mole),
seven milliliters of methanol, and 0.62 g (0.0044 mole) of
dimethyl acetylenedicarboxylate were mixed in a glass-stop-
pered flask and left at room temperature for two days.

(All of the quinoxaline dissolved, and the solution acquired a yellow color, four hours after mixing the reactants.) The dark yellow solution was evaporated with suction in a filter flask; a yellow oil separated. The two-phase system was placed in the refrigerator where it remained for two days, but no crystalline material was formed. The mixture was warmed to room temperature (the yellow oil dissolved), then evaporated to dryness with suction. The residue was dissolved in three milliliters of acetonitrile and the solution was again cooled in the refrigerator. The yellow crystals which separated weighed 0.25 g and melted, after recrystallization from acetonitrile at 137-140° C. The 0.25 g of product represented a yield of 15.5% of an adduct of molecular weight 366, from one mole each of the quinoxaline, the ester, and water.

Experiment 2.—Experiment 1 was repeated on a larger scale. 15.4 g (0.0748 mole) of the quinoxaline and 10.6 grams (0.0747 mole) of the ester were mixed in 120 milliliters of methanol and left at room temperature in a stoppered flask for three days. The red solution was clarified to remove a small amount of black insoluble material, and the clear filtrate was evaporated to dryness in the stoppered filter flask. Attempts to obtain a crystalline product by crystallizing the extremely viscous red residue in the filter flask from acetonitrile were unsuccessful. In order to obtain a

crystalline product it was necessary to permit an acetonitrile solution of the residue to evaporate at room temperature in an open evaporating dish. The crystals thus obtained were recrystallized from carbon tetrachloride. A total of 15.0 grams (55% of theory for a compound of M. W. 366) of recrystallized product, which melted at 122-128° C was obtained.

Experiment 3.--Experiment 2 was repeated. The mixture was allowed to react for five days at room temperature. The residue left after evaporation of the solvent was dissolved in 25 milliliters of carbon tetrachloride and left to evaporate at room temperature. When evaporation of the solvent was essentially complete, the crystals which had formed were filtered and dried in a vacuum desiccator. The 16.1 grams (59% of the theoretical yield) of product obtained melted at 132.5-135.5° C. A portion of this sample was again recrystallized from carbon tetrachloride. The product melted at 136-137° C.

Experiment 4.--2.06 grams (0.010 mole) of 2-phenylquinoxaline were slurried in 16 milliliters of methanol. To this was added 1.42 grams (0.010 mole) of the acetylenic ester. The glass-stoppered flask containing this reaction mixture was flushed with nitrogen, the stopper, coated with silicone grease, was inserted, and its contents were left at room temperature for six days. An ultraviolet absorption curve, run

on a portion of this solution (Figure 5ʲ was similar to the curve obtained with the isolaʋed adduct (Figure 2). Figure 5 was obtained by assuming the ɽeaction was 100% complete. The molecular weight was assumed ʋo be 380, the same value used in plotting the curve in Figure 2.

Experiment 5.--2-Phenylquinoxaline (97.0 g; 0.471 mole), 66.8 grams (0.470 mole) of the ester, and 760 milliliters of methanol were allowed to reacʋ at room temperature in a one liter glass-stoppered flask for one week. The solvent was evaporated with suction in a stoppered filter flask, the residue was dissolved in 170 milliliters of carbon tetrachloride, and the solution was left in an open evaporating dish at room temperature for three weeks. During this period, the solid material which formed a crust over the solution was broken up from time to time. The residue in the evaporating dish was filtered and washed thoroughly with ether. The insoluble portion, which consisted of yellow crystals, the surface of some of which were red in color, were sucked dry on the funnel while evaporating the filtrate and washings in the filter flask. (This filtrate was not investigated further.) The product, which weighed 114 graɴs, was recrystallized, in 20-gram portions, from carbon tetrachloride. The second 20-gram portion was recrystallized from the filtrate from the first portion, the third from the filtrate from the second, etc. Fresh carbon tetrachloride was used as necessary to effect
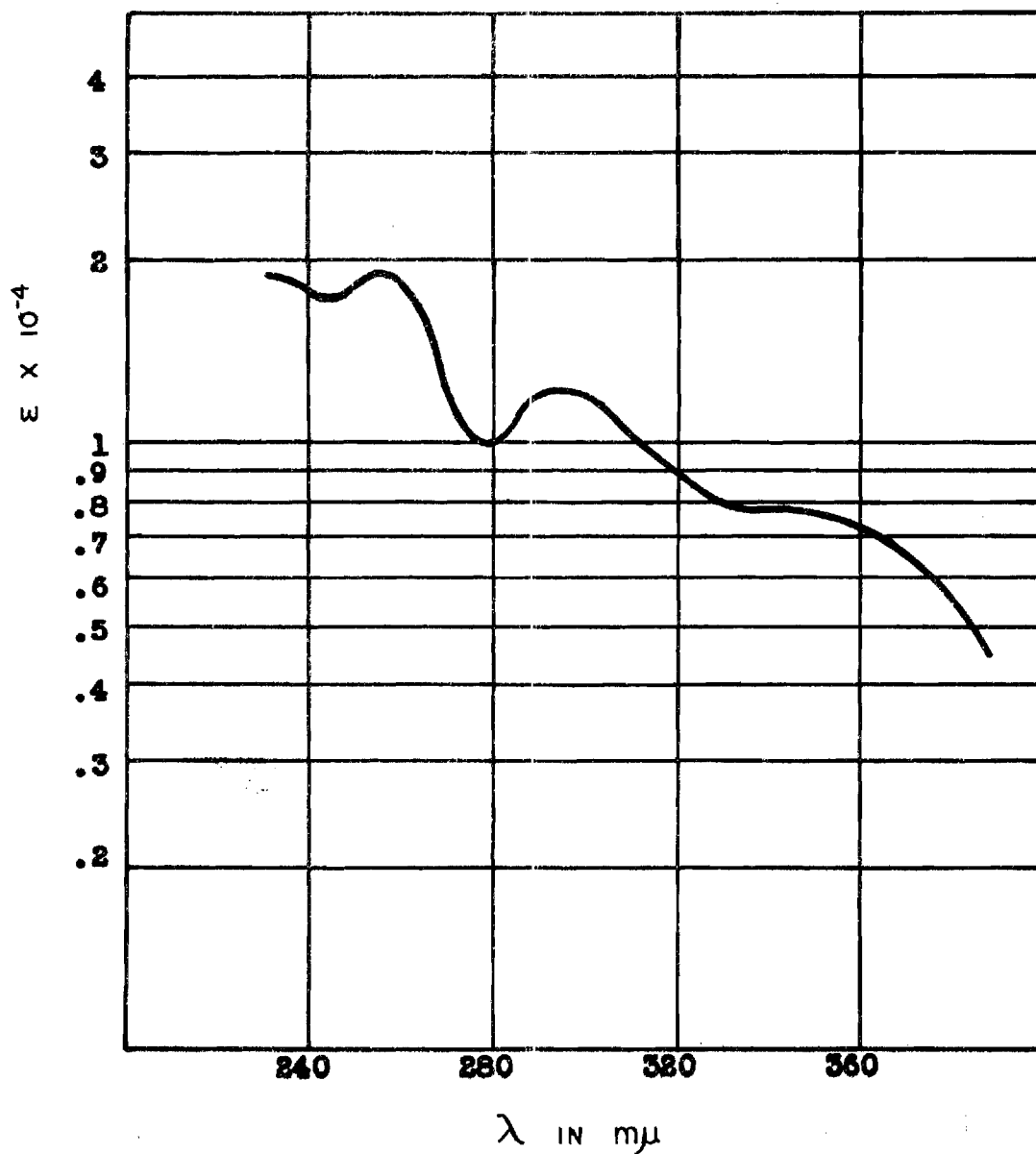
Ultraviolet Absorption Curve for Solution of 2-Phenyl-
quinoxaline Adduct Before Isolation (in Methanol)

Figure 5

complete solution of each portion. The samples recrystallized from carbon tetrachloride were then recrystallized from methyl ethyl ketone in the same manner. The samples recrystallized from the ketone solvent were combined. A portion of this sample was recrystallized again from carbon tetrachloride, then from methyl ethyl ketone. The final product melted at 139.5-140° C.

The 114 grams of crude product obtained in this experiment represented a theoretical yield of 66 per cent of a compound containing one mole each of water, the quinoxaline, and the ester.

Experiment 6.--0.90 gram (0.0044 mole) of 2-phenylquinoxaline was allowed to react at room temperature for three days with 0.62 g (0.0044 mole) of dimethyl acetylenedicarboxylate in five milliliters of acetonitrile. The homogeneous yellow solution was then placed in the refrigerator and left for two days. The yellow crystals which separated were filtered, washed with ether, and sucked dry on the funnel. These yellow crystals, which weighed 0.26 gram, melted at 77-78° C. (The melting point of 2-phenylquinoxaline is 78° C.) The 0.26 gram of product recovered amounted to 29 per cent of the quinoxaline charged.

Experiment 7.--0.0044 mole (0.90 g) of 2-phenylquinoxaline was dissolved in ten milliliters of anhydrous ethyl ether. To this solution were then added 0.0044 mole each of methyl

alcohol (0.14 g) and dimethyl acetylenedicarboxylate (0.62
g). This mixture was left at room temperature in a stopper-
ed flask for three weeks. The dark orange solution, which
contained a small amount of white insoluble material, was
clarified, and the filtrate was evaporated in the filter
flask until yellow crystals separated. The mixture was cool-
ed in an ice-water bath and filtered. The crystals obtained
weighed 0.21 gram and melted at 141-148° C. These crystals
were then slurried in ether, in which they were not complete-
ly soluble, and filtered. The 0.15 g of pale yellow insol-
uble material melted at 158-160° C.

Analysis of the Adduct from 2-Phenylquinoxaline and Dimethyl
Acetylenedicarboxylate

Microchemical Analysis.--A portion of the adduct from Experi-
ment 2 was recrystallized from carbon tetrachloride, then
from acetonitrile, then two more times from carbon tetra-
chloride. The purified product, which melted at 135-137° C
was submitted for carbon, hydrogen, nitrogen and methoxyl
determinations. The analytical results were as follows:
C,63.99%; H, 4.64%; N, 7.68%; CH$_3$O, 37.35%. These results
did not agree well with any simple combination of the re-
actants.

Another sample of the adduct, which had been recrystal-
lized only from carbon tetrachloride, and melted at 136-137°

C (Experiment 3) was analyzed. The following results were obtained: C, 64.46%; H, 4.56%; N, 7.37%; and CH₃O, 16.67%. The carbon, hydrogen, and nitrogen analyses agreed reasonably well with those obtained from the previous sample.

A third sample (from Experiment 5) which melted at 139.5-140° C gave the following analytical results: C, 65.42%; H, 4.87%; N, 7.52%; ash from the C, H determination, 0.68% (non-alkaline); CH₃O, 15.82, 16.08% (duplicate determinations). Corrected for the 0.68% ash, these values became: C, 65.87%; H, 4.90%; N, 7.57%; CH₃O, 16.06% (average for the two results). The calculated values for a compound containing one mole of 2-phenylquinoxaline, one mole of the ester, and one mole of water $C_{20}H_{18}N_2O_5$ (M. W. 366) were: C, 65.56%; H, 4.95%; N, 7.65%; CH₃O, 16.94%.

Ultraviolet Absorption Curves.--The ultraviolet absorption spectra of the adduct (M. W. 366) (Figure 2) and of 2-phenyl-quinoxaline (Figure 1) were obtained with a Beckman Model DU Spectrophotometer.

Molecular Weight.--The molecular weight of the adduct was determined (66) and found to be 387 ± 20. 0.0174 g of the sample, dissolved in 0.1956 g of triphenylmethane, melted at 89.80, 89.95, and 89.90° C, or at an average temperature of 89.88° C. Using the cryoscopic constant (13.0) and the freezing point of the solvent (92.87° C) found during the determination of the molecular weight of the 2,3-diphenyl-

quinoxaline adduct, the molecular weight of this adduct was
387.

Alkaline Saponification.--10.0 grams (0.0273 mole, assuming
a M. W. of 366) of the adduct from 2-phenylquinoxaline were
refluxed for two and one-half hours in 60 milliliters of 95
per cent ethanol with 32.0 ml (0.0552 mole) of 1.725 N aque-
ous potassium hydroxide solution. The reaction mixture was
cooled to room temperature, poured into 250 milliliters of
water, and extracted with 25 ml portions of ether until the
ether extracts acquired only a pale yellow color. The com-
bined ether extracts were evaporated on the steam bath, then
transferred to an evaporating dish and allowed to evaporate
at room temperature. The brown residue in the dish, which
weighed 0.76 gram, was recrystallized from 95% ethanol with
the use of animal charcoal. The product was identified as
2-phenylquinoxaline by melting point (74-76° C) and mixed
melting point (76.5-78° C). The 0.76 gram of 2-phenylquin-
oxaline represented a yield of 13.5 per cent.

The aqueous solution which had been extracted with the
ether was acidified with hydrochloric acid. The brown pre-
cipitate which separated was filtered, slurried in water, re-
filtered, and washed with water. The brown product (Sample
A) weighed 9.2 grams and melted with decomposition and gas
evolution at 143-145° C. All attempts to purify Sample A by
recrystallization were unsuccessful. Benzene, water, glacial

acetic acid, ethanol, methyl ethyl ketone, and ether were tried as solvents, but in all cases a brown, impure product was obtained.

Alkaline Saponification of Sample A.--5.0 grams of Sample A were heated under reflux for one and one-half hours with 30 ml of 95 per cent ethyl alcohol and 25.0 ml of 1.725 N aqueous potassium hydroxide solution. After cooling to room temperature, the mixture was poured into about 100 ml of water, and the aqueous solution was extracted with three 25 ml portions of ether. The combined ether extracts were separated in a steam bath; the red-brown crystals obtained weighed 1.25 grams. Recrystallization of these crystals from 95 per cent ethanol with the aid of charcoal gave orange tinted crystals which melted at 74-76° C. A mixed melting point with 2-phenylquinoxaline showed no depression.

Potentiometric Titration of Sample A.--0.100 gram of Sample A was slurried in 50 ml of 95 per cent ethanol and titrated with 0.1013 N sodium hydroxide solution. The course of the titration was followed with the aid of a pH meter. The titration curve (Figure 6) for this compound showed that it was a dicarboxylic acid. The end-points in the titration, estimated from the curve, occurred at 2.2 ml and at 4.65 ml. These values gave neutralization equivalents of 449 and 213 respectively.

Titration Curve

Sample A

Obtained on Alkaline Saponification

of 2-Phenylquinoxaline Adduct
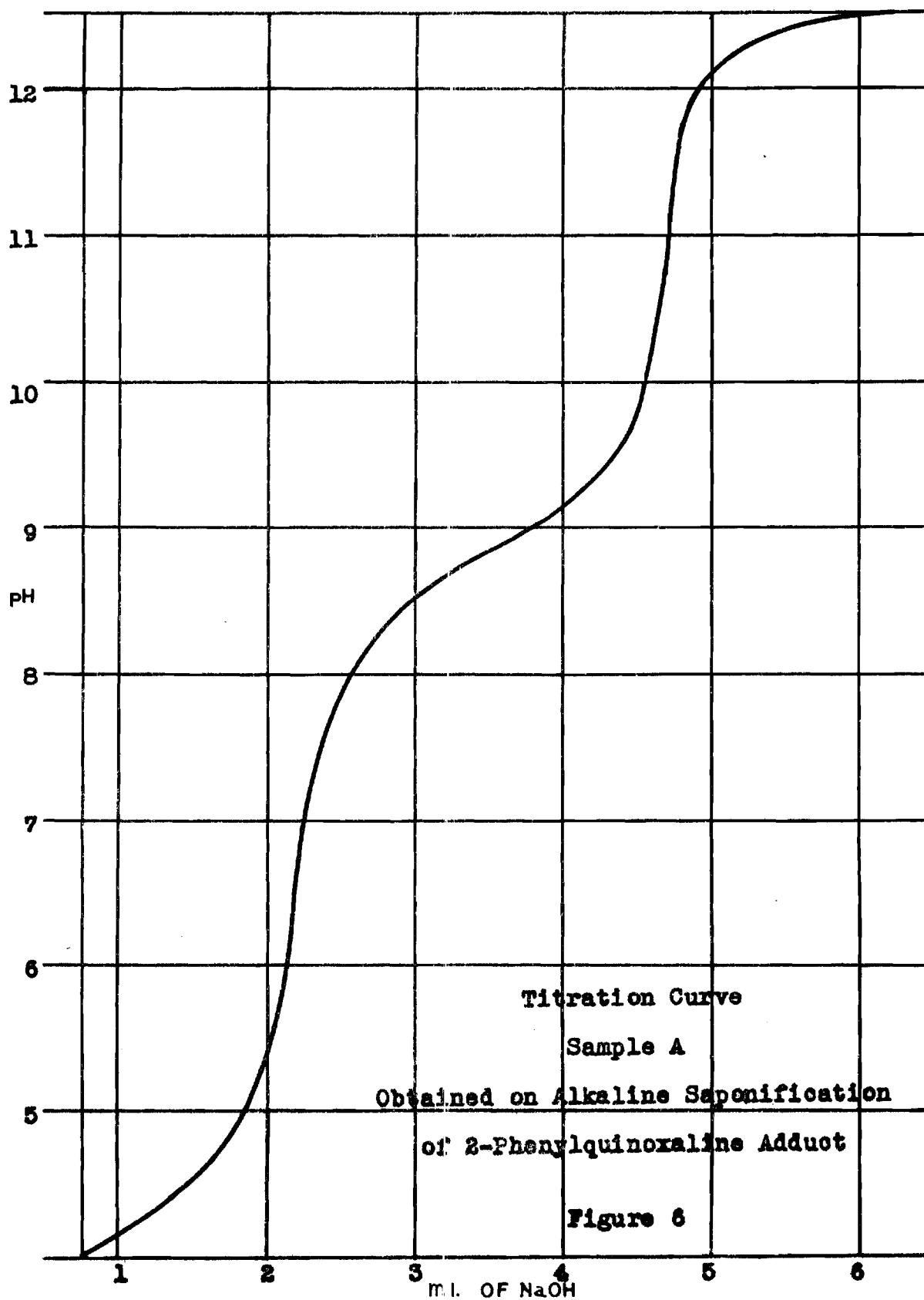
Figure 6

<u>Ultraviolet Absorption Curve for Sample A.</u>--The ultraviolet
absorption spectrum of Sample A was determined. The curve
obtained (Figure 7) was similar to that for the 2-phenyl-
quinoxaline adduct (Figure 2). A molecular weight of 338
(the weight of the adduct) was assumed in plotting the curve.

Oxidation

<u>Attempted Oxidation with Bromine.</u>--A small sample of the 2-
phenyl adduct was dissolved in carbon tetrachloride. When
a few drops of a five per cent solution of bromine in carbon
tetrachloride were added, a yellow precipitate formed. The
mixture was left at room temperature for about five minutes.
There was no evidence for the evolution of HBr. Addition
of more bromine solution caused the solution to acquire the
characteristic red color of bromine.

<u>Potassium Permanganate.</u>--10.0 grams (0.0273 mole) of the 2-
phenylquinoxaline adduct were dissolved in 150 ml of acetone.
A saturated aqueous solution of potassium permanganate was
added in small portions, with shaking, until the color of
the permanganate persisted for a few minutes on continued
mixing of the reactants. A total of 170 ml of the permangan-
ate solution were used. During the addition of the oxidizing
agent, the mixture warmed up (spontaneously) to 35-40° C.
The precipitate which separated was filtered, slurried in
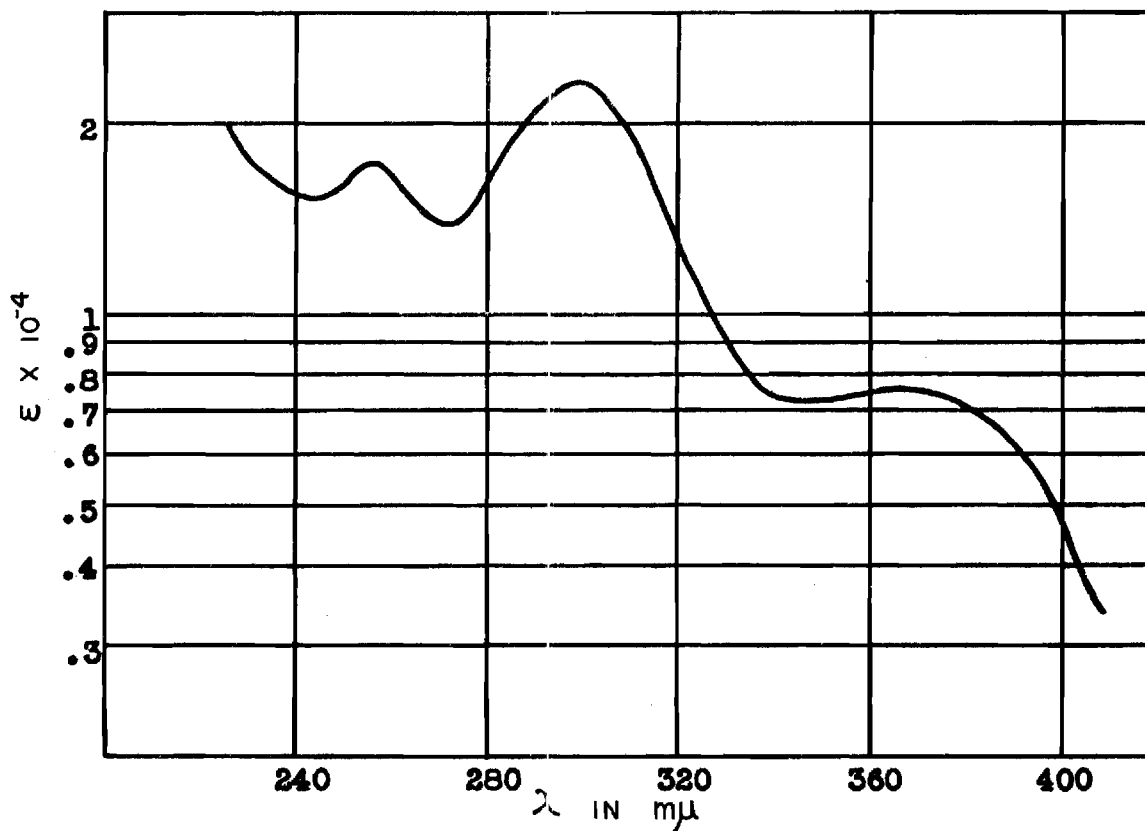
Ultraviolet Absorption Curve (in Methanol Solution)

Sample A

Obtained on Alkaline Saponification of the

2-Phenylquinoxaline Adduct.

Figure 7

water, acidified with hydrochloric acid, then treated with sodium bisulfite until the manganese dioxide dissolved. The clear yellow solution, in which some tan insoluble material was suspended, was filtered, and the insoluble material on the funnel was washed acid-free with water. This residue, which weighed 1.39 grams, was recrystallized from methyl ethyl ketone. The recrystallized product, which was slightly colored, melted at 244-245° C. This sample was recrystallized from 95 per cent ethanol with the aid of animal charcoal (Sample E). Sample E, which was very pale yellow in color, weighed 0.150 g and melted at 248.5-249° C.

The filtrate from which the precipitate had been removed was evaporated in the filter flask. The yellow insoluble material which separated was filtered and sucked dry on the funnel (Sample C). Sample C weighed 2.44 grams and melted at 76-78° C. A mixture of Sample C with 2-phenylquinoxaline melted at 76-78° C. The 2.44 grams of Sample C accounted for 24 per cent of the quinoxaline in the adduct.

Analysis of Sample E gave the following results: %C, 75.62; %H, 4.60; %N, 12.52. These data agree with the empirical formula $C_{14}H_{10}N_2O$, calculated %C, 75.65; %H, 4.54; %N, 12.61. This compound was identified as 2-hydroxy-3-phenylquinoxaline by mixed melting point with an authentic sample. The 2-hydroxy-3-phenylquinoxaline was prepared by condensing 3.56 g (0.0330 mole) of o-phenylenediamine (as

the hydrochloride) in 150 milliliters of water, with 5.00

grams (0.0330 mole) of benzoylformic acid (71) by refluxing

in the presence of 10.0 grams of sodium acetate for 20 hours.

The product which separated, after one recrystallization from

95 per cent ethyl alcohol, melted at 248-248.5° C. The re-

ported melting point was 247° C (72).

2-Phenylquinoxaline was not attacked by permanganate

under the conditions described in the above experiment.

A 0.1983 g portion of Sample E, in 95 per cent ethanol,

was titrated with 0.122 N sodium hydroxide to a thymol blue

end point. The 6.10 milliliters of alkali required, indi-

cated that the sample was acidic, and gave a calculated

neutralization equivalent of 267. The molecular weight of

2-hydroxy-3-phenylquinoxaline is 222.

Reaction with Alkali in Aqueous-Alcoholic Solution.--A small

sample of the 2-phenylquinoxaline adduct was slurried in

about five milliliters of water in a test tube. An approxi-

mately equal volume of methanol was added, and the mixture

was mixed thoroughly. A small amount of the sample dissolved,

as evidenced by the pale yellow color of the liquid layer.

The first experiment was repeated, but in this case a

ten per cent solution of potassium hydroxide was used in

place of the water. Solution of the adduct was complete in

five minutes.

The first experiment was repeated again, using sodium

carbonate solution in place of the water. Solution of the sample was essentially complete.

The first experiment was again repeated, this time with sodium bicarbonate solution. The result approximated that obtained in Experiment 1.

APPENDIX

DATA USED IN THERMODYNAMIC CALCULATIONS

All bond strength and resonance energy values were taken from Pauling (73), unless otherwise noted.

Bond Strengths

C-C	58.6		C-H	110.2	
C=C	100		N-H	83.7	
C≡C	123		N-N	20	
C-H	87.3		N≡N	50	(assumed value)
C-O	70		C=O	142	(formaldehyde)
C-N	48.6		C=O	149	(other aldehydes)
C≡N	94		C=O	152	(ketones)

Resonance Energies

Benzene	39		Quinoline	75		
Butadiene	3.5		Quinoxaline	75	(76)	
Naphthalene	75		Phenazine	105	(75)	
Anthracene	105	(74)	Acridine	106	(75)	
Furan	23	(74)	Pyrrole	31		
Thiophene	29	(74)	Hydroquinone	60	(assumed value)	
Pyridine	43		Benzoquinone	16	(74)	
1,3-Cyclopentadiene	2.9	(74)				

Where no experimental values for resonance energy for alternate aromatic compounds containing hetero nitrogen are available, the values for the corresponding aromatic hydrocarbons are assumed to be valid. This assumption is known to be at least approximately true on the basis of available

data, and Dewar (45) states that there are theoretical justifications for this near equality.

Sample Calculations

The reaction between anthracene and benzoquinone:
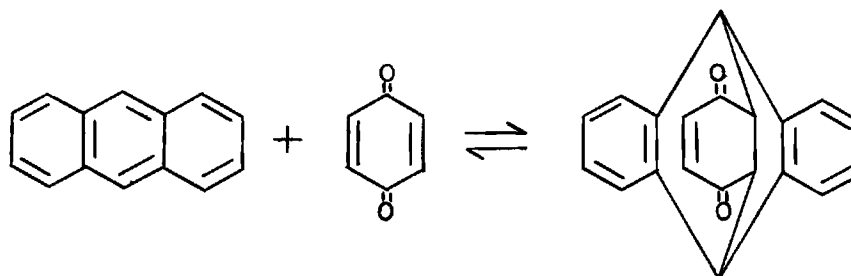
	C-C	C=C
Bond Strength	58.6	100
No. of bonds broken in reactants	1	3
No. of bonds formed in product	5	1

Only the bonds involved in the reaction are considered. In the anthracene molecule this includes the two carbon-carbon double bonds and the carbon-carbon single bond in the diene portion of the molecule (of which carbon atoms 9 and 10 are the number 1 and 4 atoms of the diene). One of the carbon-carbon double bonds in the quinone (carbon atoms 2 and 3) is considered. Thus, in the reactants there is a total of three double bonds and one single bond to be considered. In the product a total of six bonds is considered; the two newly formed carbon-carbon single bonds, the two

carbon-carbon single bonds and the new double bond formed
from the original diene as a result of the 1,4-addition, and
the single bond formed from the original double bond of the
dienophile. Thus the net gain in energy involved is due to
the increase from one to five in the number of carbon-carbon
single bonds or a total of 234.4 (4 x 58.6) kilocalories per
mole. The energy of two (three in the reactants and only
one in the product) double bonds, 200 kilocalories per mole
(2 x 100), is lost. The net change in energy, based on bond
strength alone, is therefore 234.4 minus 200, or 34.4 kilo-
calories per mole gained.

The loss in resonance energy is also included, as
follows: The resonance energy of anthracene is 105 kilo-
caloried per mole. In the adduct, ignoring for the moment
the quinone residue, this energy is reduced to essentially
that of two isolated benzene rings, the resonance energy of
each of which is 39 kilocalories per mole. (Wheland, refer-
ence 74, gives a value of 41 kilocalories per mole for ben-
zene.) Thus the loss in resonance energy from this cause is
105 minus 78 (2 x 39) or 27 kilocalories per mole. The
resonance energy of benzoquinone is 16 kilocalories per mole
(48). Assuming that approximately one-half of this energy
is lost (all or maybe more of the resonance energy of the
quinone may be lost; reference 74, page 61) in the adduct,
an additional eight kilocalories or a total of 35 (27 + 8)
kilocalories per mole of resonance energy is lost in this

reaction.

Therefore the net energy change, according to these calculations, is 34.4 kilocalories per mole gained in bond transformations, 35 kilocalories per mole lost as resonance energy, or a total energy change of essentially zero. ΔH is therefore zero for this reaction and, if we assume no change in entropy, ΔF is also zero.

For the reaction:
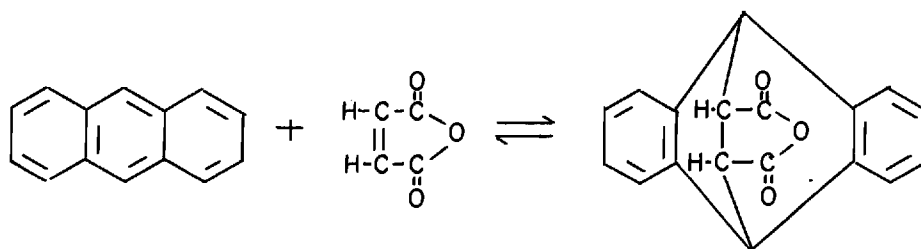
	C-C	C-C
Bond Strength	58.6	100
No. of bonds broken in reactants	1	3
No. of bonds formed in product	5	1

In this example the adduct is more stable by 34.4 kilocalories than the reactants, on the basis of bond strengths. Assuming the resonance energy of maleic anhydride to be zero (Wheland, reference 74, page 61, gives data from heats of hydrogenation which indicate negative resonance energy, -5.4 kilocalories, for ethyl maleate), the net change in resonance energy for this reaction is represented by the

loss of 105 kilocalories from the anthracene, and a gain of only 78 kilocalories in the adduct (from two benzene rings) or a net loss of 27 kilocalories. The overall energy change for this reaction is therefore a gain of about seven kilocalories, or $\Delta H = +7$ kcal/mole.

In the reaction:
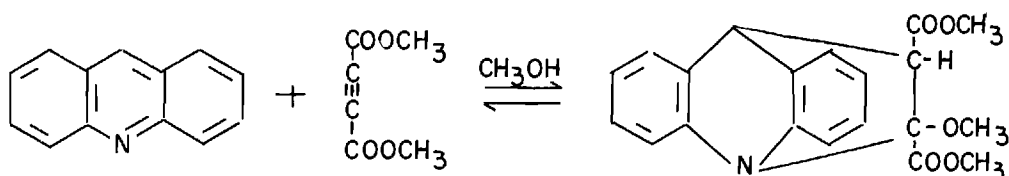
	C-C	C≡C	C≡C	C-N	C≡N	O-H	C-O	C-H
	58.6	100	123	48.6	94	110.2	70.2	87.3
No. of bonds broken in reactants	1	1	1	0	1	1	0	0
No. of bonds formed in products	3	1	0	2	0	0	1	1

The carbon-carbon and carbon-nitrogen bonds are treated as in the previous examples. The O-H bond referred to in the reactants is that in the methanol; it is broken, and the two fragments form two new bonds in the product, one carbon-hydrogen bond and one carbon-oxygen bond. Thus there are three more product bonds (a total of eight) to be considered than reactant bonds (five) in this case. The product is more

stable (based on bond strengths) than the reactants by 44.7 kilocalories. A loss of 27 kilocalories in resonance energy makes the overall energy change for this reaction about 18 kilocalories.

Note that the result in this case is the same whether water or methanol is added to the adduct.

BIBLIOGRAPHY

1. A. W. Hofmann, Proceedings of the Royal Society of London, 9, 153 (1859).

2. T. S. Moore and I. Doubleday, Journal of the Chemical Society, 119, 1170 (1921).

3. V. Prelog, E. Cerkovnikov, and G. Ustricev, Justus Liebig's Annalen der Chemie, 535, 37 (1938).

4. O. Hromatka, Berichte der Deutschen Chemischen Gesell-schaft, 75, 1302 (1942).

5. O. Hromatka and E. Engel, ibid., 76, 712 (1943).

6. S. M. McIlvain and E. H. Pryde, Journal of the American Chemical Society, 71, 326 (1949).

7. O. Diels and W. E. Thiele, Justus Liebig's Annalen der Chemie, 543, 79 (1940).

8. O. Diels, K. Alder, and S. Beckmann, ibid., 486, 191 (1931).

9. O. Diels, K. Alder, and D. Winter, ibid., 486, 211 (1931).

10. O. Diels, K. Alder, and H. Winckler, ibid., 490, 267 (1931).

11. O. Diels and K. Alder, ibid., 498, 1 (1932).

12. O. Diels, K. Alder, and W. Lübbert, ibid., 490, 277 (1931).

13. O. Diels and K. Alder, ibid., 498, 16 (1932).

14. O. Diels, K. Alder, W. Friedrichsen, H. Klare, H. Winckler, and H. Schrum, ibid., 505, 103 (1933).

15. O. Diels, K. Alder, W. Friedrichsen, Petersen, Brodersen, and Kech, ibid., 510, 87 (1934).

16. O. Diels and R. Meyer, ibid., 513, 129 (1934).

17. O. Diels and H. Schrum, *ibid.*, 530, 68 (1937).

18. O. Diels and J. Harms, *ibid.*, 525, 73 (1936).

19. O. Diels and H. Kech, *ibid.*, 519, 140 (1935).

20. O. Diels and F. Möller, *ibid.*, 516, 45 (1935).

21. O. Diels and H. Pistor, *ibid.*, 530, 87 (1937).

22. O. Diels and W. E. Thiele, *Journal für Praktische Chemie*, 156, 195 (1940).

23. O. Diels and K. Alder, *Justus Liebig's Annalen der Chemie*, 470, 62 (1929).

24. O. Diels, K. Alder, and E. Naujoks, *Berichte der Deutschen Chemischen Gesellschaft*, 62, 554 (1929).

25. E. de B. Barnett, N. F. Goodway, A. G. Higgins, and C. A. Lawrence, *Journal of the Chemical Society*, 1934, 1224.

26. J. van Alphen, *Recueil des Travaux Chimiques des Pays-Bas*, 61, 895 (1942).

27. A. Schönberg and A. Mostafa, *Journal of the Chemical Society*, 1943, 654.

28. T. Wagner-Jauregg, *Berichte der Deutschen Chemischen Gesellschaft*, 63, 3219 (1930).

29. J. van Alphen, *op. cit.*, p. 892.

30. H. R. Snyder, R. H. Levin, and P. F. Wiley, *Journal of the American Chemical Society*, 60, 2025 (1938).

31. F. Bergmann, *ibid.*, 60, 2811 (1938).

32. H. R. Snyder, R. B. Hasbrouck, and J. F. Richardson, *ibid.*, 61, 3558 (1939).

33. H. R. Snyder and J. C. Robinson, *ibid.*, 63, 3279 (1941).

34. B. I. Ordashev and Z. D. Markova, *Journal of General Chemistry of the U. S. S. R.*, 21, 1505 (1951).

35. R. Pummerer and H. Fiesselmann, *Justus Liebig's Annalen der Chemie*, 544, 206 (1940).

36. R. Pummerer and E. Stieglitz, *Berichte der Deutschen Chemischen Gesellschaft*, 75, 1072 (1942).

37. O. Diels and R. Kassebart, *Justus Liebig's Annalen der Chemie*, 530, 51 (1937).

38. O. Diels and H. Preiss, *ibid.*, 543, 94 (1940).

39. H. V. Euler and K. O. Josephson, *Berichte der Deutschen Chemischen Gesellschaft*, 53, 822 (1920).

40. P. D. Bartlett, M. J. Ryan, and S. G. Cohen, *Journal of the American Chemical Society*, 64, 2649 (1942).

41. F. O. Rice and M. T. Murphy, *ibid.*, 64, 896 (1942).

42. A. Kaufmann and A. Albertini, *Berichte der Deutschen Chemischen Gesellschaft*, 42, 2003 (1909).

43. P. D. Bartlett and E. S. Lewis, *Journal of the American Chemical Society*, 72, 1005 (1950).

44. M. C. Kloetzel, *Organic Reactions*, John Wiley and Sons, New York (1948), Vol. IV, p. 41.

45. R. D. Brown, *Journal of the Chemical Society*, 1950, 691, 2730; 1951, 1612, 3129.

46. L. W. Butz, *Organic Reactions*, John Wiley and Sons, New York (1949), Vol. V, p. 145.

47. O. Diels, J. H. Blom, and W. Koll, *Justus Liebig's Annalen der Chemie*, 443, 242 (1925).

48. I. G. M. Campbell, C. G. LeFevre, R. J. W. LeFevre, and E. E. Turner, *Journal of the Chemical Society*, 1938, 404.

49. M. Schöpf, *Berichte der Deutschen Chemischen Gesellschaft*, 23, 1840 (1890).

50. M. Schöpf, *ibid.*, 22, 3287 (1889); 23, 1842 (1890).

51. C. H. Browning, J. B. Cohen, R. Gaunt, and R. G. Gulbransen, *Proceedings of the Royal Society of London*, 93B, 329 (1922).

52. R. W. Bost and E. E. Towell, *Journal of the American Chemical Society*, 70, 904 (1948).

53. F. D. Chattaway and E. A. Coulson, *Journal of the Chemical Society*, 1928, 1361.

54. R. G. Jones and K. C. McLaughlin, *Organic Syntheses*, John Wiley and Sons, New York (1950), Vol. 30, p. 86.

55. J. W. Brühl, *Zeitschrift für Physikalische Chemie*, 22, 390 (1897).

56. H. A. Riley and A. R. Gray, *Organic Syntheses*, John Wiley and Sons, New York (1943), Coll. Vol. II, p. 509.

57. O. Hinsberg, *Justus Liebig's Annalen der Chemie*, 292, 246 (1896); O. Fischer and E. Schindler, *Berichte der Deutschen Chemischen Gesellschaft*, 39, 2243 (1906).

58. R. G. Jones and K. C. McLaughlin, *Organic Syntheses*, John Wiley and Sons, New York (1950), Vol. 30, p. 88.

59. A. Albert and J. B. Willis, *Journal of the Society of Chemical Industry*, 65, 26 (1946).

60. O. Fischer and G. Körner, *Berichte der Deutschen Chemischen Gessellschaft*, 17, 102 (1884).

61. G. Blau, *Monatshefte für Chemie*, 18, 125 (1897).

62. E. H. Huntress, T. E. Lesslie, and J. Bornstein, *Organic Syntheses*, John Wiley and Sons, New York (1952), Vol. 32, p. 55.

63. C. E. Schildknecht, *Vinyl and Related Polymers*, John Wiley and Sons, New York (1952), p. 8.

64. C. Knops, *Justus Liebig's Annalen der Chemie*, 248, 192 (1888).

65. O. Schmidt, *Zeitschrift für Physikalische Chemie*, B1, 207 (1928).

66. F. Schneider, *Qualitative Organic Microanalysis*, John Wiley and Sons, New York (1946), p. 112.

67. R. L. Shriner and R. C. Fuson, *Identification of Organic Compounds*, John Wiley and Sons, New York (1940), Second Ed., p. 117.

68. C. F. H. Allen and W. E. Barker, *Organic Syntheses*, John Wiley and Sons, New York (1943), Coll. Vol. II, p. 156.

69. D. L. Hammick, *Journal of the Chemical Society*, 1923, 2883.

70. L. I. Smith and M. M. Falkof, *Organic Syntheses*, John Wiley and Sons, New York (1942), Vol. 22, p. 50.

71. B. B. Corson, R. A. Dodge, S. A. Harris, and R. K. Hazen, *Organic Syntheses*, John Wiley and Sons, New York (1941), Coll. Vol. I, p. 244.

72. J. Buraczewski and L. Marchlewski, *Berichte der Deutschen Chemischen Gesellschaft*, 34, 4009 (1901).

73. L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York (1948).

74. G. W. Wheland, *The Theory of Resonance*, John Wiley and Sons, New York (1944).

75. J. B. Willis, *Transactions of the Faraday Society*, 43, 97 (1943).

76. M. J. S. Dewar, *Annual Reports of the Chemical Society (London)*, XLVIII, p. 114 (1951).

BIOGRAPHICAL SKETCH

The author was raised in the foothills of the Adiron-dack Mountains in New York State, in the glove-manufacturing town (population, 25,000) of Gloversville. After finishing high school in 1935, at the age of 17, he entered the Massachusetts Institute of Technology in Cambridge, Massachusetts. In 1939, he received the S. B. degree in Chemistry from the Institute.

After working at odd jobs in his home town, the author went to New York City (where he was born on March 18, 1918) to seek work in chemistry. In January 1941, he accepted a position at Calco Chemical Division, American Cyanamid Company in Bound Brook, New Jersey. At Calco, he worked as a routine analyst (1941); as a chemist in the laboratory in which analytical methods for the plant were developed (1942-1943); as chief analyst in the azo dyestuff department (1944-1947); and finally as a development chemist in the azo dyestuff department (1947-1948).

The author was married in January, 1945, to Miss Claire Sender of New York City, and has one child.

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