[CONTRIBUTION FROM THE SCHOOL OF CHEMICAL TECHNOLOGY OF THE NORTH DAKOTA AGRICULTURAL COLLEGE]

THE DIELS-ALDER REACTIONS OF QUINONIMINE AND QUINONEDIIMINE HYDROCHLORIDES WITH CYCLOPENTADIENE[1]

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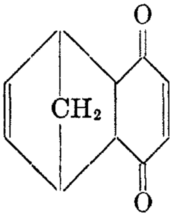
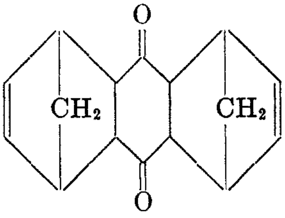
One of the first Diels-Alder reactions to be reported was that discovered by Albrecht (1), who found that quinone will react with cyclopentadiene to give "cyclopentadienequinone" and "dicyclopentadienequinone." Albrecht did not assign the correct structures to his products. Some twenty years later, Diels and Alder (2) showed "cyclopentadienequinone" to be 1,4,4a,5,8,8a-hexahydro-1,4-methanonaphthalene-5,8-dione (I) and "dicyclopentadienequinone" to be 1,4,4a,5,8,8a,9,9a,10,10a-decahydro-1,4,5,8-dimethanoanthracene-9,10-dione (II):

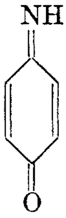


I

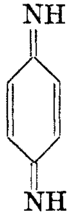


II

Following the elucidation by Diels and Alder of the general nature of the reactions of 1,3-dienes with activated double bonds, reactions of this type have been found to take place with a variety of 1,3-dienes and with compounds containing double bonds activated by a wide variety of groups, besides carbonyl groups (3). This paper reports the results of a study of the reactions of cyclopentadiene with quinonimine (III) and quinonediimine (IV), where one or both of the carbonyl groups of quinone have been replaced by imine groups. For the sake of brevity, Albrecht's nomenclature will be used in the discussion which follows.



III



IV

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[1] Abstracted from the M. S. theses of J. G. E. (June, 1940) and E. K. R. (May, 1942).

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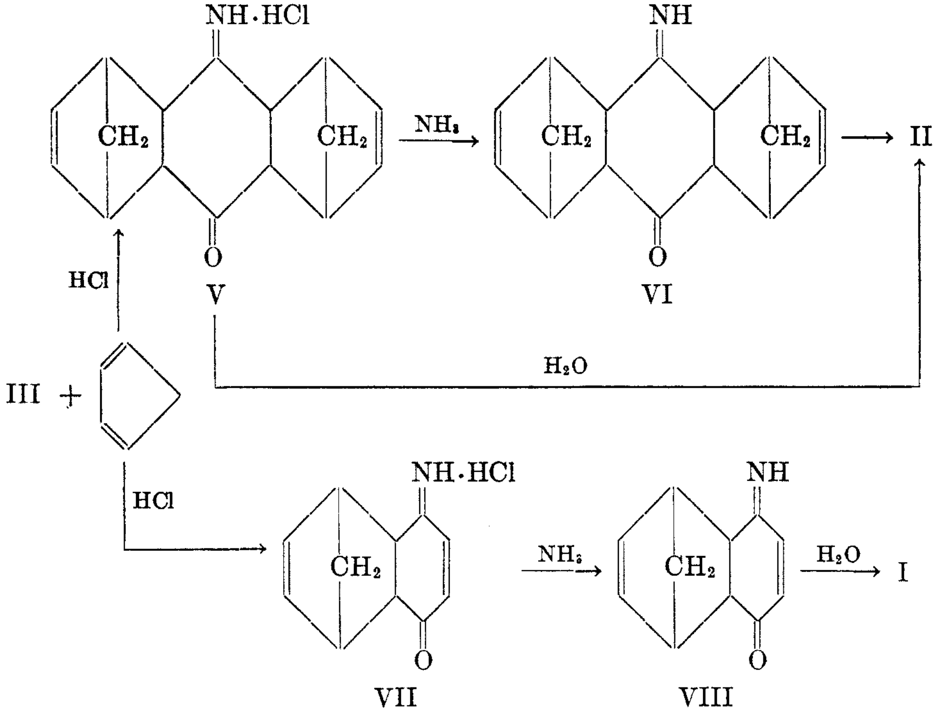
Quinonimine was prepared in ethereal solution by the silver oxide oxidation of *p*-aminophenol. Treated with an excess of cyclopentadiene, quinonimine does not react except to polymerize to a cokelike mass. When chloroacetic acid was added as a catalyst to a solution of quinonimine and cyclopentadiene in ether, a product resembling an indophenol was formed but there was no evidence of a Diels-Alder reaction having occurred. However, when concentrated hydrochloric acid was used as catalyst in place of chloroacetic acid, a rapid reaction took place between the cyclopentadiene and quinonimine (used in a molar ratio of 2.4:1) to yield a solid product (V) which, after crystallization from alcohol-ether, was a nearly colorless solid, melting with decomposition at 126–127°. Compound V possesses the general properties of an imine hydrochloride. It contains chlorine and is soluble in water and alcohol but is insoluble in ether. It was shown to be dicyclopentadienequinonimine hydrochloride by its ready hydrolysis to dicyclopentadienequinone (II), which was identified by its melting point and mixed melting point with an authentic sample of II. Compound V is stable and will stand without change for years.



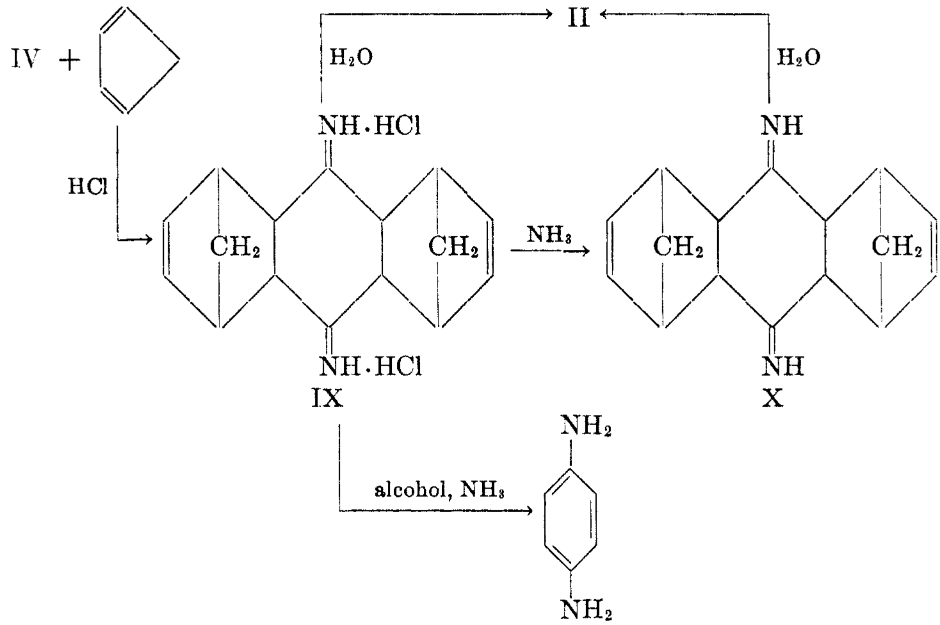
Free dicyclopentadienequinonimine (VI) itself was obtained by treatment of a suspension of V in absolute ether with dry gaseous ammonia. It is a colorless solid, melting at 119–122°. Its identity was shown by carbon-hydrogen analyses and by hydrolysis with dilute sulfuric acid to give dicyclopentadienequinone and one mole of ammonia. Compound VI will stand without decomposition for months but eventually changes to a black tar.

Attempts were made to isolate cyclopentadienequinonimine (VIII) from reaction mixtures of quinonimine and cyclopentadiene. The results of these efforts, while not entirely conclusive, indicate that it was obtained. Cyclopentadiene and quinonimine (in a molar ratio of 1.19:1) reacted in the presence of hydrochloric acid to yield a mixture of two solids which could be separated by hand. One of these was V, the other consisted of greenish flakes, melting at 85°. It seems likely that this latter product was cyclopentadienequinonimine hydrochloride (VII). Unfortunately, attempts to repeat this run and thereby to obtain more of this material were not successful.

When equimolar amounts of cyclopentadiene and quinonimine reacted in the presence of hydrochloric acid, a greenish-black, partially crystalline mass was formed which was probable VII, mixed with tarry by-products. A light yellow solid, melting at 75–78°, was obtained when this greenish-black product was suspended in ether and treated with gaseous ammonia. That this light yellow solid was cyclopentadienequinonimine (VIII) is indicated by fairly good carbon and hydrogen analyses and by its hydrolysis to ammonia and to a white solid, melting at about 80°. Not enough of this white solid was obtained for a mixed melting point but it seems likely that it was cyclopentadienequinone (I) (m.p. 77–78°).

Previous work in this laboratory had shown that quinonediimine will not react with cyclopentadiene in ether solution, either with or without hydrogen chloride as catalyst, nor will these compounds react when ground together in a mortar. In all cases, only polymerization of the quinonediimine was observed.

However, in this study it was found that cyclopentadiene and quinonediimine react readily in ether solution in the presence of hydrochloric acid to yield an orange-red solid. This solid is believed to have been dicyclopentadienequinonediimine dihydrochloride (IX) since, upon standing with water, it gave a 67% yield of dicyclopentadienequinone.



Attempts to purify IX by solution in alcohol and reprecipitation with ether yielded *p*-phenylenediamine. It has been shown by Willstätter and Pfannenstiel (4) that the method of preparing quinonediimine used in this study gives solutions free from unoxidized *p*-phenylenediamine. It seems very likely that there was a reversion of the cyclopentadiene-quinonediimine adduct, during this attempted purification of IX, and that the quinonediimine thus formed was reduced by the alcohol present to *p*-phenylenediamine.

Compound IX was used for further work without purification. It was suspended in ether and treated with dry gaseous ammonia to yield a yellow solid which, after repeated crystallization from benzene and petroleum ether, melted at 110–120°. This yellow solid was shown to be dicyclopentadienequinonediimine (X) by its nitrogen analysis and by its hydrolysis to ammonia and dicyclopentadienequinone.

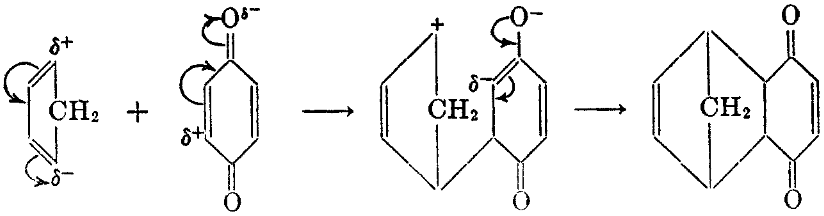
An attempt to prepare cyclopentadienequinonediimine by the reaction of equimolar amounts of cyclopentadiene and quinonediimine in the presence of hydrochloric acid gave a black solid. Treatment of this black solid yielded only *p*-phenylenediamine.

It was observed during this work that all of these imines were so reactive and unstable that, usually, only very low yields of the purified products could be obtained. In all of the hydrolyses of these imines to ammonia and the corresponding carbonyl compounds, side reactions occurred which held part of the nitrogen in non-hydrolyzable forms.

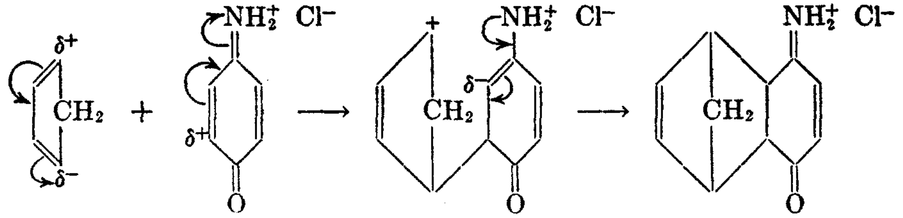
The catalytic effect of hydrochloric acid upon these reactions is of considerable interest. Wassermann (5) has reported a catalytic effect in the addition of cyclopentadiene to benzoquinone and other quinones; acidic substances, such as acetic acid, chloroacetic acid, bromoacetic acid, trichloroacetic acid, phenol and hydrochloric acid, produce a slight increase in the rate of reaction and pyridine produces a slight decrease. Trimethylamine, however, produces an increase. Fairclough and Hinshelwood (6) state that the reaction between cyclopentadiene and quinone takes place approximately five times as fast in highly polar solvents as in non-polar solvents. Despite these findings, however, the Diels-Alder reaction is not generally regarded as being susceptible to catalysis (7).

The work here reported has shown that, with the reaction of cyclopentadiene with quinonimine and quinonediimine, the presence of hydrochloric acid or, possibly, other highly acidic substances is necessary for the reaction to proceed at all. It remains to account for this effect. The following explanation is proposed.

The Diels-Alder reaction is regarded (7, 8) as the addition of a nucleophilic diene to the electrophilic center of the activated double bond system. This may be pictured with quinone and cyclopentadiene:



In quinonimine and quinonediimine, apparently, there exist no carbon atoms whose electrophilic character is great enough to cause reaction with cyclopentadiene. Upon addition of hydrochloric acid, however, the imine groups are converted to imonium groups and, it is suggested, the positive charge carried by these groups bring about electronic displacements which increase the electrophilic character of the carbon atoms adjacent to the carbonyl and imonium groups. The reaction between quinonimine and cyclopentadiene in the presence of hydrochloric acid can be written in the following manner:



Similar effects will produce an added reactivity on the part of quinonediimine. With this compound it is possible that either one or both of the imine groups may be converted to imonium groups; in either case, the electrophilic nature of the reactive carbon atoms in the molecule will be enhanced.

EXPERIMENTAL

Quinonimine and *quinonediimine* were prepared by the method of Willstätter and Pfannenstiel (4).

Preparation of dicyclopentadienequinonimine hydrochloride. A solution of quinonimine was prepared by the silver oxide oxidation of 3.0 g. (0.0275 mole) of *p*-aminophenol in 900 ml. of absolute ether. The dark yellow solution was slowly added, with a swirling motion, to a mixture of 5.5 ml. (4.4 g., 0.0666 mole) of freshly distilled cyclopentadiene, 25 ml. of 95% alcohol and 6 ml. of 12 *N* hydrochloric acid. The mixture became distinctly green at one stage of the addition. The mixture was allowed to stand for five hours in an ice-bath before being filtered. The yield of crude imine hydrochloride, a dark yellow crystalline solid, was 3.9 g. (52%). It was purified by dissolving in small portions in small volumes of 95% alcohol, filtering, and adding two volumes of ether, cooling, and filtering off the precipitated imine hydrochloride. It is a nearly colorless solid, melting with decomposition at 126–127°.

Preparation dicyclopentadienequinonimine. The imine was liberated from its hydrochloride by suspending small portions of the salt in ether, through which was passed dry ammonia gas. The ether solution of the imine was filtered and the free imine obtained by evaporation of the ether solution under reduced pressure. After one crystallization from ether it melted at 119–122°.

Anal. Calc'd for $C_{16}H_{17}NO$: C, 80.30; H, 7.15.
Found: C, 79.86; H, 7.06.

The quantitative hydrolysis of the imine was brought about by dissolving a weighed sample of the imine in standard dilute sulfuric acid. The solution was kept at 0° for nine days, then filtered. After another 24 hours no further precipitate had appeared and the solution was warmed on a steam-bath to ensure complete hydrolysis. It was then titrated to a phenolphthalein end-point with standard dilute sodium hydroxide solution. The ammonia obtained was 86% of theoretical. The solid product filtered off during this hydrolysis melted at 156–158°. The mixed melting point of this substance with a known sample of dicyclopentadienequinone was 156–158°.

It was observed that attempts to effect this hydrolysis at higher temperatures or with the use of hydrochloric acid instead of sulfuric acid gave lower yields of ammonia.

Preparation of cyclopentadienequinonimine. A solution of quinonimine was prepared by the oxidation of 1.0 g. (0.0092 mole) of *p*-aminophenol in 300 ml. of absolute ether. It was added with swirling to a mixture of 0.9 ml. (0.72 g., 0.0110 mole) of freshly distilled cyclopentadiene, 25 ml. of 95% alcohol, and 2 ml. of 12 *N* hydrochloric acid, held at 0°. The mixture darkened rapidly. After standing for several hours at 0°, the mixture was filtered to yield a mixture of small yellowish-brown nodules and greenish flakes. The yellowish-brown substances melted with decomposition at 126–127°. The other material, the greenish flakes, melted with decomposition at 85°. It is believed that these greenish flakes were composed of cyclopentadienequinonimine hydrochloride in fairly pure form. Attempts to repeat this experiment were not successful.

In other experiments, solutions of quinonimine prepared by the oxidation of 1.0 g. (0.0092 mole) of *p*-aminophenol were added to mixtures of 0.85 ml. (0.68 g., 0.0104 mole) of cyclopentadiene, 2 ml. of 12 *N* hydrochloric acid, and 25 ml. of alcohol. The products consisted of a greenish-black, partially crystalline material with a melting point of wide range.

This greenish-black material was suspended in ether and treated with dry ammonia gas. After filtration, the ether solution was concentrated under reduced pressure until a resinous material separated. The remaining solution was drained off and the resinous material subjected to reduced pressure. Under this treatment it rapidly puffed up to a spongy yellow solid melting at 75–78°.

Anal. Calc'd for $C_{11}H_{11}NO$: C, 76.27; H, 6.41.
Found: C, 77.29; H, 6.72.

A quantitative hydrolysis of this free imine was attempted. A weighed sample was dissolved in dilute sulfuric acid. The solution was kept at 0°, filtered, and warmed on a steam-bath. It was then made alkaline with sodium hydroxide and the ammonia was distilled into standard hydrochloric acid, which was then titrated to a phenolphthalein end-point. The amount of ammonia obtained was 16% of theoretical. A small amount of white substance was filtered from the hydrolysis mixture before distillation. It was found to melt at 80°. Not enough was available for a mixed melting point with known cyclopentadienequinone.

Preparation of dicyclopentadienequinonediimine dihydrochloride. A solution of quinonediimine, prepared by the oxidation of 1.0 g. (0.0092 mole) of *p*-phenylenediamine in 500 ml. of absolute ether, was added at 0° to a mixture of 5.3 ml. (4.3 g., 0.065 mole) of freshly distilled cyclopentadiene, 2 ml. of 12 *N* hydrochloric acid, and 30 ml. of 95% alcohol. A light tan flocculent precipitate was formed immediately but gradually settled to the bottom of the vessel in a semi-solid mass. Upon standing for an hour in an ice-bath, the semi-solid mass gradually crystallized and became orange-red in color. It was filtered off and washed with acetone and ether. The yield of crude imine hydrochloride was 0.93 g. (32%).

The hydrolysis of the crude imine hydrochloride to dicyclopentadienequinone was done as follows: 0.233 g. of the imine hydrochloride was dissolved in 25 ml. of water and the solution was allowed to stand for three days, then was filtered to give 0.12 g. of dicyclopentadienequinone (67%). After one crystallization from 50% alcohol, it melted at 153°.

The attempted purification of this imine hydrochloride was carried out as follows. Approximately 0.5 g. of the hydrochloride was dissolved in 150 ml. of 95% alcohol. The light brown solution was treated with 1.5 g. of decolorizing charcoal and filtered into 400 ml. of ether. The nearly colorless solid thus formed was filtered off and washed with ether. It was then suspended in 50 ml. of absolute ether and treated with dry ammonia gas. The resulting ether solution was filtered and evaporated to dryness, leaving a tan solid as residue. Recrystallization of this residue from benzene gave a light pink solid, melting at 140°. A mixed melting point with *p*-phenylenediamine gave no depression.

Preparation of dicyclopentadienequinonediimine. Approximately 0.8 g. of crude dicyclopentadienequinonediimine dihydrochloride was suspended in 30 ml. of absolute ether and treated with dry ammonia gas. The ether solution was then filtered and evaporated under reduced pressure, giving the crude free imine. Five milliliters of dry benzene was added to this material, which dissolved completely but then began to deposit a tan solid which was filtered off (m.p. 238–239°). The filtrate was poured into 50 ml. of petroleum ether (b.p. 30–60°). A yellow solid, melting at 90–100°, was precipitated. This yellow solid was again dissolved in benzene and the solution again poured into petroleum ether. This treatment gave a light yellow solid, melting gradually between 110° and 120°. Further repetition of this method of purification failed to give a sharper or higher melting point and the use of other solvents was no more effective.

Anal. Calc'd for $C_{16}H_{18}N_2$: N, 11.76. Found: N, 11.73.

Hydrolysis of this imine to dicyclopentadienequinone was done as follows: 0.384 g. of the imine was dissolved in a mixture of 25 ml. of water and 0.5 ml. of 12 *N* hydrochloric acid. The solution was allowed to stand for two days; the dicyclopentadienequinone formed was then filtered off. The yield was 0.064 g. (17%).

Attempted preparation of cyclopentadienequinonediimine. Quinonediimine was prepared by the oxidation of 0.5 g. (0.0046 mole) of *p*-phenylenediamine in 150 ml. of absolute ether. The ether solution was added rapidly and with a swirling motion to a mixture of 0.75 ml. (0.6 g., 0.0091 mole) of cyclopentadiene, 1.5 ml. of 12 *N* hydrochloric acid and 9 ml. of 95% alcohol. A gray precipitate formed immediately. This precipitate darkened rapidly and turned to a sticky resin which, after standing for two hours, solidified somewhat. The solid was filtered and washed with ether. An attempt to hydrolyze this solid to cyclopentadienequinone by dissolving a portion of it in water gave only a very small amount of dark solid.

Another portion of the solid was suspended in ether and treated with dry ammonia gas. The solution resulting from this treatment was treated with decolorizing charcoal and filtered. Evaporation of the ether left a sticky solid which was recrystallized from benzene to give a brownish solid melting at 130–132°. A mixture of this solid with known *p*-phenylenediamine melted at 132–134°. Apparently the major reaction was a reduction of the quinonediimine rather than any appreciable amount of addition to the cyclopentadiene.

SUMMARY

It has been shown that cyclopentadiene will undergo the Diels-Alder reaction with quinonimine and with quinonediimine when hydrochloric acid is present in the reaction mixtures. In the absence of hydrochloric acid, the only reactions which occur appear to be polymerization of the imines.

An explanation has been proposed for the catalytic effect of hydrochloric acid.

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