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Pre-molecular association in the Diels-Alder reaction

Nathaniel Shelton

Atlanta University

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PRE-MOLECULAR ASSOCIATION IN THE DIELS-ALDER REACTION

A THESIS
SUBMITTED TO THE FACULTY OF ATLANTA UNIVERSITY
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BY
NATHANIEL SHELTON

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INTRODUCTION

The reaction involving the addition of a conjugated diene at the 1,4-positions to the 1,2-positions of an olefin or alkyne was first studied by Zincke in 1893\textsuperscript{1} and 1897.\textsuperscript{2} He formulated the reactions as additions.

In 1928, Otto Diels and Kurt Alder published a series of papers characterizing and describing the versatility of the same general reaction scheme.\textsuperscript{3} Because of their work in utilizing and describing this reaction, it is known as the Diels-Alder reaction.\textsuperscript{3a}

The reaction is characterized by the redistribution of electrons to create two new bonds between the termini of a conjugated diene and the unsaturated center of the dienophile. One double bond is formed in the diene. It has not been established exclusively whether the electrons shift one by one or in pairs; hence, two general mechanisms are indicated.

The following are some examples of the types of compounds which undergo the Diels-Alder reaction:

\[
\begin{align*}
\text{C=C} & \quad + \quad \text{C=C} & \quad \rightarrow & \quad \text{C=C} & \quad + \quad \text{C=C} \\
\text{C=C} & \quad + \quad \text{C=C} & \quad \rightarrow & \quad \text{C=C} & \quad + \quad \text{C=C}
\end{align*}
\]
Observations have shown that cisoid dienes react relatively quickly with dienophiles, while transoid dienes reacts to give polymers rather than Diels-Alder adduct. Therefore, Diels-Alder adducts can only be obtained from cyclic cis dienes or from acyclic dienes that are convertible into the cis conformation. The trans configuration is more stable than the cis. Repulsive forces prevent the close approach of the 1- and 4-hydrogens and appear to be responsible for the greater stability of the trans form. It is generally known that the trans conformation is more stable than the cis form because only in the
transoid conformation can maximum overlap of p-orbitals be achieved.

From results obtained from a study of the 1,4-addition of many dienes to several dienophiles, the following three general principles have been advanced to account for the stereospecificity of the Diels-Alder reaction: 3

1. The addition of a dienophile to a diene is purely cis addition. The relative position of substituents in the dienophile are retained in the adduct. This is shown in the following reaction of 1,3-butadiene with maleic acid.

2. When a cyclic diene (e.g., cyclopentadiene) react with a dienophile (e.g., maleic anhydride), two Diels-Alder adducts are possible, endo (13) and exo (14). The endo configuration is produced exclusively. 6
The exclusive formation of the endo adduct has been explained on the basis of maximum accumulation of double bonds in the transition state\(^6\) (the double bonds of the carbonyl groups are included). In the case where the dienophile has no activating unsaturation (such as allyl alcohol) it is not completely valid to refer to 'maximum accumulation of double bonds.' The orientation of the components to give an endo configuration must be due to other factors. According to Alder,\(^7\) the unshared electrons on an oxygen, nitrogen or halogen may be considered equivalent to unsaturation, and in a sense the existence of unshared electrons governs the unique arrangement of the components before addition.

Woodward and Hoffmann\(^8\) have provided a theoretical basis for Alder's rule of maximum accumulation of double bonds. They approached their theoretical study from orbital symmetry relations. Their theory predicts that the endo product would be the preferred product for a concerted (4 + 2) \(\pi\)-electron cycloaddition reaction.

The third general rule of Diels-Alder cycloaddition is that electron-donating groups in the diene and/or electron withdrawing groups in the dienophile generally enhance cycloaddition rates. A study was made in the reaction of tetracyclone and phenylacetylenes where
substituents were introduced into the para positions of tetracyclone (15) and in the substituted phenylacetylene (17).

\[
\begin{align*}
\text{p-X}_{2}\phi & + \phi\text{-C} = \text{C-C} \text{O}_2 \text{C}_2 \text{H}_3 \rightarrow \text{p-X}_{1}\phi \text{p-X}_{2}\phi \text{p-X}_{1}\phi \text{CO}_2 \text{CH}_3 + \text{CO} \quad (1)
\end{align*}
\]

When chlorine is substituted in all X positions (Eq. 1), the rate is increased by a factor of two compared to the unsubstituted tetracyclone (16). Methoxyl groups in all X positions increases the rate by 10 percent.

In a parallel study, the rate of the reaction of substituted phenylacetylene in which \( Y = \text{H, CH}_3, \text{CH}_2\text{OH, CHO, CO}_2\text{H and CO}_2\text{CH}_3 \) (Eq. 2) with tetracyclone in refluxing cymene were measured.\(^{10}\) The following rates were observed: \( Y = \text{CH}_3, 1; \text{CH}_2\text{OH, 2; CO}_2\text{CH}_3, 6.7; \text{CHO, 8.9; CO}_2\text{H, 35; and H, 40.} \)

Wasserman and coworkers\(^{11}\) made one of the earliest reports on catalytic effects. This report was made on the dimerization of cyclopentadiene and the addition of benzoquinone to cyclopentadiene. In both reactions it was shown that acetic acid, chloroacetic acid, and hydrochloric acid increased the rates of reaction. Kinetic analysis
indicated that protonation of benzoquinone rather than cyclopentadiene in the quinone reaction is the more favored process. The following mechanism was suggested by Wasserman:

\[ \text{HB} + \text{P} \xrightarrow{\text{H}^+} \text{HP}^+ \ldots \text{B}^- \]
\[ \text{HP}^+ \ldots \text{B}^- + \text{C} \rightarrow \text{HP-C}^+ \ldots \text{B}^- \]
\[ \text{HP-C}^+ \ldots \text{B}^- \xrightarrow{\text{P-C} + \text{HB}} \]

where \( \text{P} \) is the dienophile; \( \text{C} \), cyclopentadiene; \( \text{HB} \), acid; and \( \text{HP}^+ \ldots \text{B}^- \) indicates ion pairs formed by protolytic fission of the acid.

Other acid catalyzed reactions have been reported by Fray and Robinson. They found that in the presence of Lewis acids the addition of substituted vinyl ketones to butadiene can be carried out at room temperature instead of the usual high temperature employed. Yates and Eaton found an enormous rate enhancement for the reaction of anthracene with maleic anhydride and aluminum chloride. They found that when reacting equimolar amounts of anthracene, maleic anhydride and aluminum chloride dissolved in dichloromethane at room temperature the reaction was completed in 1.5 min giving a quantitative yield of Diels-Alder adduct. From extrapolation of the rate curve for the reaction under equivalent conditions of temperature and concentration in the absence of aluminum chloride they estimated that 4800 hrs would be required for 95 per cent completion.

Wasserman compared the experimental evidence of thermal non-catalyzed, one-step and two-step mechanisms. A one-step mechanism involves a concerted bond breaking and bond making process in the transition step. The Woodward-Hoffmann rules require that the reaction be concerted. Considerable evidence has been presented (e.g.
stereospecificity) to support the one-step mechanism. The two-step mechanism is not a concerted reaction and bond formation and breaking do not occur at the same time. The two-step mechanism must proceed as follows:\textsuperscript{4}

\[
a + b \rightleftharpoons x \rightleftharpoons e
\]

where the intermediate \( x \) is a diradical. If diradicals are produced, oxygen or peroxide would produce a marked change in the course of the overall reaction. Since an effect of this kind has not been observed,\textsuperscript{14} it appears that the two-step mechanism of uncatalyzed Diels-Alder reaction is unsatisfactory.

Many aspects of the Diels-Alder reaction have been studied to determine the mechanism. In addition to the ones previously mentioned, studies involving electronic effects,\textsuperscript{15} theoretical predictions of relative rates,\textsuperscript{16} solvent effects,\textsuperscript{17} isomerization studies,\textsuperscript{18} kinetic pressure effects,\textsuperscript{19} and kinetic isotopic effect\textsuperscript{20} have been reported.

The mixing of dienophile and diene often results in rapid appearance of a color as in the case of tetracyanoethylene and isoprene or tetracyanoethylene and anthracene. It has been postulated that the appearance of a color implies the formation of a complex held together by polarization or charge-transfer forces.\textsuperscript{21} This suggests 'pre-molecular association.' Steric, substituent and catalytic effects may contribute to a large degree, to the 'pre-molecular association.'

Pre-molecular association is here defined as the attraction between a diene and dienophile in which no sigma bonds are formed and each component can be separated by physical means before the chemical reaction occurs. At this point in the reaction scheme, an acyclic
transoid diene will have already been converted to the cisoid conformation.

\[
\text{C + P} \xrightarrow{\text{(complex)}} \text{C-P} \xrightarrow{\text{(transition)}} \text{C-P}
\]

The symbol C represent the diene; P the dienophile and C-P the product. Reviews have appeared concerning the mechanism of the Diels-Alder reaction, as mentioned previously, but to our knowledge no work has been done exclusively with pre-molecular association in the reaction.*

*The concept of "pre-molecular association" in the Diels Alder reaction was introduced in informal conversation with Dr. Henry C. McBay.
DISCUSSION AND RESULTS

This study of Pre-Molecular Association in the Diels-Alder reaction was done using the Beckman IR-9 spectrometer and sodium chloride infrared cells (reference and sample; 0.1 mm path length) and two specially made sodium chloride double cells, path length 0.025 mm (see Fig. 1).

![Diagram of sample inlets and sodium chloride bridge](image)

**Fig. 1**

When using the double-cell the components were placed in opposite sides. This gave a single spectrograph for the uncombined components (ideal mixing). If the double-cell had not been used, separate spectra of each component would have been taken and then the two would be superimposed. This was done in some instances where solubility problems precluded using equimolar concentration of the two components. When the double-cell was used this problem was eliminated and one spectrum was obtained which consisted of all bands produced by each component.
Comparison of spectral data was made by observing shifts, disappearance, appearance and changes in intensities of characteristic absorption bands. These observations were made by comparing the spectra of the ideal mixture (double-cell), actual mixture and the adduct of each pair of components. Changes in spectral bands were used to indicate possible intermolecular association. For example the carbonyl, carbon-hydrogen and conjugated bending and stretching bands might be expected to undergo shifts if there is any perturbation of the \( \pi \)-electrons due to the formation of \( \pi \)-complexes or intermolecular associations. The shifts should probably be more noticeable in the region corresponding to bending vibrations because these require less energy than those vibrations for stretching.

The first pair of coreactants chosen was cyclopentadiene (4) and maleic anhydride (5). Cyclopentadiene reacts with maleic anhydride below room temperature upon mixing. Because of such reactivity it was not possible to obtain a spectrum of the unreacted mixture (see experimental). Attempts were made to obtain a spectrum of the unreacted mixture by cooling each component in a Dry Ice-acetone bath before mixing; but, in each attempt the reaction was too fast to obtain a spectrum of the unreacted starting material. As a result of these difficulties, it was concluded that these components could not be used to determine intermolecular associations. The reaction is too fast! In each attempt a transient color appeared upon mixing, but at room temperature it disappeared rather rapidly. This color might be due to formation of a \( \pi \)-complex.\(^{21}\)
The second pair of coreactants was isoprene (1) and tetracyanoethylene (TCNE, 8). TCNE is one of the most reactive dienophiles. When solutions of 1 and 8 were mixed, the reaction proceeded instantly, even with cooling. Another problem presented by this pair of coreactants is that TCNE is only slightly soluble in chloroform. The solvent was, therefore, changed from chloroform to methylene dichloride. The same procedures used with 4 and 5 for trying to obtain a spectrum was used with these coreactants, but when 8 was placed in an ice bath a solid precipitated. It was noted that when the solutions were mixed in an ice bath the deep transient brown color disappeared with the formation of clear crystals in the bottom of the container. When the mixture was removed from the ice bath, the color again developed and within a short period the solution was clear. The color suggests the formation of a π-complex analogous to the reaction of cyclopentadiene and maleic anhydride.

The spectrum of each component was compared with that of the mixture of 1 and 8 and the adduct 18. The spectrum of the mixture was identical to that of the adduct. It was obvious that the reaction of
the mixed components were too fast to obtain a spectrum of the unreacted mixture. Under the conditions used, this pair of coreactants could not be used to determine intermolecular association in the unreacted mixture.

Another pair of reactants with similar reactivity to that of 1 and 8 was anthracene (7) and tetracyanoethylene 8. The mixture of anthracene and TCNE produced the same problems as did the mixture of 1 and 8. Methylene dichloride was used as a solvent because of aforementioned solubility problems. Upon mixing equal moles of each component a dark green transient color developed and quickly disappeared. The solvent was evaporated. A spectrum of the residue was identical to that of the adduct, 9. These components also reacted too fast to be used as a means of determining pre-molecular association.

\[
\begin{align*}
\text{7} & \quad + \quad \text{8} \\
& \quad \rightarrow \\
& \quad \text{9}
\end{align*}
\]

In all of the examples previously discussed, the reaction between diene and dienophile was too fast to observe any pre-molecular association, if any were present. Slower reaction systems were sought. The maleic anhydride-anthracene pair was the first chosen.

Maleic anhydride 5 and anthracene 7 showed less reactivity than the first three pairs of coreactants. The infrared spectra of separate solutions of 5 and 7 were taken. Anthracene was not soluble enough in chloroform to afford a good spectrum with the double cell. When making
the solution for the mixture, 0.001 M (0.49 g) of maleic anhydride was added to 10 ml of a 0.001 M solution of anthracene (see experimental). The purpose of using this method was to obtain a good scan of the mixture. After comparing the spectra of the mixture and separate components, there were no significant changes. However, when compared with the spectrum of the adduct, 19, the carbonyl absorption band at 1852 cm\(^{-1}\) and the one at 1784 cm\(^{-1}\) with a shoulder at 1796 cm\(^{-1}\) in the mixture were replaced by a medium sharp band at 1871 cm\(^{-1}\) and a strong sharp band at 1788 cm\(^{-1}\) with no shoulder respectively in the adduct. This shift is to be expected in going from an alpha-, beta- unsaturated anhydride functional group to a saturated system. There was also a band at 1075 cm\(^{-1}\).

![Chemical structure](image)

Anthracene 7 and p-benzoquinone 2 reacted even slower than did anthracene and maleic anhydride. The spectra of the separate components were compared with the spectrum of the mixture. There were no noticeable changes. The spectrum of the mixture was then compared with that of the adduct, 20. A sharp narrow band appearing at 1595 cm\(^{-1}\) in the mixture was shifted to a broad band at 1615 cm\(^{-1}\) in the adduct. The doublet, characteristic in the mixture, appearing at 1674 and 1659 cm\(^{-1}\) diffused into a strong broad band at 1674 with a shoulder at 1688 cm\(^{-1}\) in the adduct. This reaction was apparently too slow as
indicated by no change in infrared spectrum.

![Chemical structure](image)

p-Benzquinone 2 and isoprene 1 were the next pair of coreactants used. A spectrum of the separate components in chloroform was taken using the double-cell. When the spectrum of the mixed components was compared with that of the separate components, there were no apparent differences. The adduct 3 gave a spectrum which showed a strong broad band at 1692 cm\(^{-1}\), instead of the doublet at 1675 and 1661 cm\(^{-1}\), characteristic in the superimposed spectrum of the separate components. The band at 1598 cm\(^{-1}\) became very weak and shifted to 1605 cm\(^{-1}\). This reaction was also too slow to observe any intermolecular association.

![Chemical structure](image)

Maleic anhydride 5 and isoprene 1 were the only pair of coreactants that gave possible positive results. The separate components, 5 and 1, mixture and adduct 21 gave spectra as shown in Fig. 2, 3, and 4 respectively. Fig. 2 shows the infrared spectrum of the ideal mixture. The following significant spectral observations are evident: (1) A strong characteristic band for the carbonyl stretching vibration, typical of an anhydride, appears in the separate components at 1784 cm\(^{-1}\) with shoulders at 1796 and 1760 cm\(^{-1}\) with another sharp band at 1854 cm\(^{-1}\).
There are other sharp bands appearing at 1055, 992, 892, 905 (sh), and 840 cm\(^{-1}\); (2) Fig. 3 shows the infrared spectrum of the mixture of maleic anhydride and isoprene in chloroform. The carbonyl absorption band in the mixture still appears at 1784 cm\(^{-1}\) with a shoulder at 1796 cm\(^{-1}\). However, the shoulder on the low frequency side of the major carbonyl band is no longer present. The band at 1854 cm\(^{-1}\) has lost its sharpness and split into a doublet. The band at 1055 cm\(^{-1}\) is considerably less intense, if present at all. Several weak bands appear between 1100 and 1000 cm\(^{-1}\). A doublet is visible at 992 and 979 cm\(^{-1}\) instead of a sharp band at 992 cm\(^{-1}\). An additional strong sharp band appears at 929 cm\(^{-1}\). The band at 892 cm\(^{-1}\) in the spectrum of the ideal mixture (shoulder at 905 cm\(^{-1}\)) is still visible but the shoulder is more intense and shifted to 908 cm\(^{-1}\). The band at 840 cm\(^{-1}\) is no longer present; (3) Fig. 4 shows the infrared spectrum of the maleic anhydride-isoprene adduct in chloroform. The carbonyl absorption band occurs in the same position as it did in the spectrum of the mixture (Fig. 3) with the disappearance of the shoulder on the stronger band at 178 cm\(^{-1}\). The two bands at 1650 and 1600 cm\(^{-1}\) seen in the spectrum of the mixture and ideal mixture, characteristic of the conjugated system, have disappeared. Bands between 1100 and 1000 cm\(^{-1}\) gave approximately the same intensity in the adduct as those in the mixture. The band at 992 cm\(^{-1}\) has disappeared but the one at 979 cm\(^{-1}\) is still present and the shoulder has become more intense (968 cm\(^{-1}\)). The band at 892 cm\(^{-1}\) has completely disappeared.
Figure 2. Infrared spectrum of maleic anhydride and isoprene in chloroform in the double cell.

Figure 3. Infrared spectrum of the mixture of maleic anhydride and isoprene in chloroform.

Figure 4. Infrared spectrum of the maleic anhydride-isoprene adduct in chloroform.
The spectrum of the actual mixture has elements of both the ideal mixture and the adduct. Clearly, none of the spectra are identical. When note is made of the changes of the bands in the mixture and adduct, some type of molecular association is indicated. For example, the carbonyl stretching band in the mixture and adduct are very similar. The bands between 1100 and 1000 cm$^{-1}$ appeared in the mixture and in the adduct. The band at 992 cm$^{-1}$ appeared in the separate components and mixture, but disappeared in the adduct; however, the bands at 979 and 992 cm$^{-1}$ appeared in both the actual mixture and adduct, but not in the ideal mixture.

After the spectrum of the mixture was compared, it was separated into its separate components. The residue was weighed, melting point determined, and also analyzed by infrared spectroscopy (see experimental). The fact that maleic anhydride was recovered quantitatively from the reaction mixture is evidence that no chemical reaction had occurred. Hence, the small but significant shift of the carbonyl stretching vibration toward higher energies (1954 to 1865 cm$^{-1}$) is indicative of a shift from an alpha-, beta- unsaturated system to a more saturated one. One can conclude from this evidence that there is some perturbation of the electron cloud in the diene and dienophile in the maleic anhydride-isoprene system.

When viewing this work one must be cautious of the indications
implied. The results do not necessarily mean that pre-molecular association can or cannot be detected by infrared spectroscopy. The results obtained in the spectra of the maleic anhydride-isoprene system could be due to some sort of perturbation caused by solvent effects or it could be due to a state effect. At room temperature, maleic anhydride and isoprene are in the solid and liquid states, respectively. This was the only pair of coreactants, with the exception of maleic anhydride and cyclopentadiene which reacted too fast, where the diene was a liquid and the dienophile was a solid. Thus there might have been some sort of association caused by the difference of physical state of the coreactants.
EXPERIMENTAL

Infrared spectra were recorded on a Beckman IR-9 spectrometer and calibrated periodically with the automatic wavelength indicator. The double cell was constructed of sodium chloride, path length 0.025 mm, with a sodium chloride bridge between the two cells (see Fig. 1). They were made by the Beckman Manufacturing Company. Chloroform was used as a solvent for all solutions and for infrared spectra except where indicated. A Fisher-John melting point apparatus was used for melting point determinations. Melting points are uncorrected. Removal of solvent by evaporation refers to evaporation using an all glass Büchler rotary evaporator. Activated alumina (Alcoa) was used for chromatographic work.
Cyclopentadiene (4) and Maleic Anhydride (5).-- Cyclopentadiene 4 was prepared from dicyclopentadiene by procedures described by Fieser.\textsuperscript{23} The distilled cyclopentadiene (bp 40-41\deg) was stored in Dry Ice to prevent polymerization.

Cyclopentadiene was diluted to 10 ml (330 mg; 0.5 m) with chloroform. A 0.5 M solution of 5 in chloroform was prepared as previously described. An infrared spectrum of the two components in the double cell showed bands at $\nu_{\text{max}} = 3108, 3078, 3042, 3020, 2900, 2888, 1854, 1784$ with a shoulder at 1795 cm$^{-1}$, 1379 and 1058 cm$^{-1}$.

Ten ml of each component were mixed. A vigorous exothermic reaction occurred. A spectrum of the product showed bands at 3020, broad band at 1865, 1780 cm$^{-1}$ with no shoulder and a band at 1086 cm$^{-1}$. The solvent was evaporated under reduced pressure to give 0.82 g (100\%) of adduct as needle-like crystals. These were taken up in a 2:1 v/v ligroin-benzene mixture, recrystallized, and dried; mp 161\deg (Reported:\textsuperscript{24} 161-162\deg).

Maleic Anhydride-Cyclopentadiene Adduct 6.-- The maleic anhydride-cyclopentadiene adduct 6 (Eastman Organic Chemicals) were recrystallized by dissolving it first in benzene. Ligroin (bp 51-56\deg) was added until the crystals began to precipitate. The solution was warmed until the crystals redissolved and then allowed to cool. The crystals were collected with suction and dried; mp 161\deg. The adduct was identical in every respect to that obtained above.

Isoprene 1 and Tetracyanoethylene 8.-- Isoprene (0.068 g) was diluted to 10 ml (0.001 m) with methylene dichloride (Analyzed Baker’s Reagent Grade). Tetracyanoethylene (TCNE, 0.65 g) was dissolved in
5 ml (0.005 M) of methylene dichloride. (Methylene dichloride is a better solvent for TCNE than chloroform.) The superimposed infrared spectra of these solutions exhibited bands at \( \nu_{\text{max.}} = 3095, 2929, 2860, 2840 \), a doublet at 2250 and 2218, 1608 and 1598, 994, and 895 cm\(^{-1}\) with shoulders at 910 and 932 cm\(^{-1}\).

Five ml of equal moles (0.001 m) of each component were mixed at room temperature. A faint brown color developed immediately and remained for about 30 min; \( \nu_{\text{max.}} = 2920, 2860 \), a weak doublet at 2275, and 2258, doublet at 1131 and 1119 and 874 cm\(^{-1}\).

Five ml of a 0.001 M solution of 1 in chloroform were placed in a volumetric flask and cooled in an ice bath. Five ml of a 0.001 M solution of 2 were added with cooling. This procedure was used to slow down the reaction. The brownish color appeared, remained for about 5 min, and gradually lightened. The faint brown color remained for approximately 15 min while the solution was still in the ice bath. The disappearance of the color was used as an indication of a complete reaction.25 An infrared spectrum of this mixture was no different from that of the previous one.

Several attempts were made to obtain a spectrum of the unreacted mixed components by lowering the reaction temperature, but when the mixture was placed in the cell and a spectrum was taken, the scanning time was too long for the solution to remain unreacted.

The liquid was evaporated from the above mixture under reduced pressure. The crystals (1.33 g; 100%) were recrystallized by dissolving in benzene and adding enough ligroin (bp 51-56°) to cause them to precipitate. The solution was warmed to redissolve the crystals. Upon
cooling, the crystals precipitated. They were then filtered with suction and dried; mp 120-121° (Reported: 120-121°). The infrared spectrum of this product gave the same results as that of the mixture.

**Anthracene 7 and Tetracyanoethylene 8.** A 0.001 M solution of 7 in methylene dichloride (0.178 g diluted to 10 ml) and a 0.001 M solution of 8 (0.165 g diluted to 5 ml in the same solvent) were prepared. The superimposed spectra of the components gave \( \nu_{\text{max.}} = \text{doublet at 2250 and 2218, 1608 and 886 cm}^{-1}. \)

The mixture of the two were prepared by mixing 5 ml of a 0.001 M solution of each component at room temperature. A deep blue-green color developed which became less intense upon standing. It finally became clear. This mixture produced the same problems as that observed for 1 and 8. Attempts made to slow down the reaction enough to obtain a spectrum by cooling the mixture in an ice bath were unsuccessful.

Equal volumes and moles of each component (5 ml and 0.001 M) were mixed again, and the liquid was evaporated under reduced pressure. The residue (0.74 g; 100%) was recrystallized by first dissolving in benzene and adding enough ligroin (bp 51-56°) to initiate precipitation. The solution was warmed slightly to allow the crystals to redissolve. Upon cooling, the crystals precipitated and were then filtered with suction and dried. The infrared spectrum was the same as that of the mixture; \( \nu_{\text{max.}} = 2258, 1475 \) and 1172 cm\(^{-1}. \)

**Anthracene 7 and Maleic Anhydride 5.**— Four hundred mls of a hot saturated solution of anthracene in benzene were treated with 2 g of Norite according to standard procedures. The crystals were filtered with suction and dissolved in a 1:1 v/v ratio benzene-hexane mixture.
This solution was passed through a chromatographic column and eluted with hexane. An ultraviolet light was used to trace the anthracene region (anthracene gave a violet region in the lower part of the column). The column was eluted continuously, first with hexane and finally with a 1:1 v/v ratio of hexane-benzene mixture until the region had passed through.

The solvent was evaporated under reduced pressure. The recrystallized \( \mathcal{Z} \) was collected with suction and dried; mp 217-218°. (Reported:\textsuperscript{22} 217-218°). A spectrum was taken using a single cell (0.1 mm path length); \( \gamma_{\text{max.}} = 886 \text{ cm}^{-1} \). The solution of \( \mathcal{Z} \) and \( \mathcal{Z} \) was not placed in the double cell because \( \mathcal{Z} \) was not soluble enough in chloroform to obtain a solution concentrated enough to give a good spectrum.

Anthracene (0.178 g) was diluted to 10 ml (0.001 M) with chloroform. Maleic anhydride (0.098 g) was dissolved in 10 ml (0.001 M) of the above solution. This mixture showed no change in infrared spectrum from that of the superimposed spectra of the individual components.

The mixture was washed with two 20-ml portions of distilled water and the chloroform layer containing \( \mathcal{Z} \) was separated from the water layer containing \( \mathcal{Z} \). The solvent was evaporated under reduced pressure to give 0.178 g of \( \mathcal{Z} \). A spectrum gave identical results as that of the previous one for authentic anthracene.

**Maleic Anhydride-Anthracene Adduct 19.**-- The maleic anhydride-anthracene adduct was prepared according to the procedures of Vogel.\textsuperscript{24} Pure anthracene (1 g), 0.55 g of maleic anhydride and 25 ml of p-xylene (Eastman Kodak; dried over anhydrous sodium sulfate) were placed in a 50-ml round bottom flask fitted with a reflux condenser. The mixture
was heated to reflux for 20 min with frequent shaking during the first
10 min. The hot solution was allowed to cool and 0.5 g of Norite was
added. The resulting solution was heated to reflux for 5 min more and
filtered with suction while still hot. The adduct 19 (1.55 g, 100%)
precipitated on cooling; mp 262° (Reported:22 262-263°). A spectrum
of the adduct showed bands at $\nu_{\text{max.}} = 1871, 1788$ and 1075 cm$^{-1}$.

$p$-Benzoquinone 2 and Anthracene 7.-- Crude $p$-benzoquinone was
purified by heating in a 500 ml round bottom flask fitted with a con-
denser and an adaptor to which another 1 liter round bottom receiving
flask was attached. The adaptor was connected to the water pump and
the crude product was collected under reduced pressure. The yellow
needle-like crystals were dissolved in methanol. This solution was
filtered several times with suction, concentrated by heating, and
allowed to cool. The crystals were collected and taken up in chloro-
form. The solution was filtered with suction three times to remove the
dark particles. The chloroform solution was concentrated by heating
in a water bath at low temperature and under reduced pressure. After
concentrating the solution, it was placed in a Dry Ice-isopropyl alco-
hol bath, the needle-like crystals were collected and dried; mp 115°
(Reported:22 115-116°).

The separate infrared spectrum for each component was used to make
comparisons instead of using the double cell. Anthracene (0.178 g)
was diluted to 10 ml with chloroform. $p$-Benzoquinone (0.54 g) was di-
luted to 5 ml using the above solution as a solvent. One ml of this
solution was diluted to 2 ml and an infrared spectrum of this mixture
gave the same results as that of the superimposed spectrum of the
separate components; \( \nu_{\text{max.}} \) = doublet at 1674 and 1659, 1595, 1308 and 884 cm\(^{-1}\).

\textbf{p-Benzquinone-Anthracene Adduct 20.--} In a 50-ml round bottom flask, equal moles of anthracene (0.178 g; 0.001 m) and p-benzoquinone (0.108 g; 0.001 m) were dissolved in 5 ml of \( p \)-xylene. A reflux condenser was attached, and the mixture was refluxed for 2.5 hr. At the end of the refluxing time the solution was concentrated under reduced pressure. The residue was allowed to cool to room temperature. The greenish precipitate was washed with methanol and the flakey white crystalline substance was poured off. This flakey residue was unreacted anthracene. The greenish solid (0.180 g; 63\%) was recrystallized from methanol and chloroform and dried; mp 231-232\(^{\circ}\) (Reported: \textsuperscript{22} 231-232\(^{\circ}\)). This precipitate afforded a spectrum with \( \nu_{\text{max.}} \) = 1679 with a shoulder at 1694 cm\(^{-1}\), 1615 and 1475 cm\(^{-1}\).

\textbf{p-Benzquinone 2 and Isoprene 1.--} p-Benzoquinone (0.54 g) was diluted to 5 ml with chloroform. Isoprene (4.08 g) was diluted to 10 ml with the same solvent. These solutions were placed in opposite sides of the double cell. The infrared spectrum showed absorptions at \( \nu_{\text{max.}} \) = 3090, 3015, 2988, 2949, doublet at 1675 and 1661, 1598, 1308, 895 with shoulders at 907 and 889 cm\(^{-1}\).

To 10 ml of 2 (0.027 g) in chloroform, 1 (0.017 g) was added. The resulting mixture was placed in a single cell. The infrared spectrum was identical to that of the separate components. An equal molar mixture (0.108 g/10 ml \( p \)-benzoquinone; 0.69 g/10 ml of isoprene) was separated by evaporating the liquid under reduced pressure. Crystals of 2 precipitated as indicated by mp 115\(^{\circ}\) and infrared analysis.
**p-Benzquinone-Isoprene Adduct 3.**— The adduct of 2 and 3 was prepared by placing 0.108 g (0.001 m) of 2 and 0.068 g (0.001 m) of 1 in a clean 10 ml thick-walled glass tube (10 mm diameter). The tube was sealed under reduced pressure (water pump) while the contents were immersed in a Dry Ice-acetone bath. The sealed tube containing the reactants was placed in a steam bath and heated for 4 hrs. After this time, the tube was broken and pale yellow crystals formed (0.16 g; 96.4%). These crystals were recrystallized from a 1:1 v/v chloroform-methanol solution and dried; mp 81° (Reported: 22 81-82°). The infrared spectrum of these crystals showed $\nu_{\text{max}}$ at 2981, 2937, 2900, 1692 and 1605 cm$^{-1}$.

**Isoprene 1 and Maleic Anhydride 5.**— Isoprene 1 (4.08 g) was diluted to 10 ml with chloroform (Analyzed Baker's Reagent Grade). Maleic anhydride 5 (0.49 g) was diluted to 10 ml with chloroform. These two solutions were placed in opposite sides of the double cell and the infrared spectrum was recorded (see Fig. 2). The spectrum of an isoprene-maleic anhydride mixture (1:1 v/v ratio) was taken in a single cell (path length 0.1 mm), Fig. 3. A 2.5 ml solution of 1 (0.85 g; 0.0125 m) in chloroform and a 10 ml solution of 5 (0.49 g; 0.005 m) in the same solvent were mixed. The liquid was evaporated under reduced pressure. The residue remaining (0.490 g) was recrystallized from a 1:1 v/v ratio of ligroin (bp 51-56°) and chloroform mixture; mp 53° (Reported: 22 53-57°). An infrared spectrum of the residue was the same as that of authentic maleic anhydride.

**Isoprene-Maleic anhydride Adduct 21 (3 methyl-$\Delta^4$-tetrahydrophthalic anhydride).**— Isoprene 1 (0.85 g; 0.0123 m) and maleic
anhydride 5 (0.49 g; 0.005 m) were mixed together in a 10 in thick-walled glass tube which was sealed under reduced pressure while the tube and contents were immersed in a Dry Ice-acetone bath. The mixture was heated for 30 hrs on the steam bath. The crude product (0.568 g; 64.4%) was taken up in ligroin (bp 51-56°) and recrystallized; mp 61° (Reported: 22 60-61°). (If an equal molar mixture of the two components is allowed to remain at room temperature for a month, the adduct, 21, will form, as indicated by infrared spectral analysis and melting points).
SUMMARY

Even though some difficulties were encountered during this study, one might be able to obtain more meaningful results if it were possible to control certain reaction conditions. With temperature control of infrared cells, the reaction for the pairs of reactants that were too fast could be retarded and reactions for the pair of reactants that was too slow could be enhanced. For example, it would have been helpful if the infrared spectra of the following pairs of reactants that reacts too fast at room temperature could have been taken below room temperature; isoprene and TCNE; anthracene and TCNE; and maleic anhydride and cyclopentadiene. It would have been equally as helpful if the infrared spectra of the following pairs of reactants that react too slow at room temperature could have been taken above room temperature; (e.g. maleic anhydride and anthracene; anthracene and p-benzoquinone and isoprene and p-benzoquinone).

The aforementioned pairs of reactants were chosen because they represent diene and dienophilic reactivity that extends over a wide temperature range. Isoprene and p-benzoquinone react at 100° (4 hrs), anthracene and p-benzoquinone react in boiling p-xylene (138°; 2.5 hr), maleic anhydride and isoprene require 30 hrs reflux at 100°, cyclopentadiene and maleic anhydride add instantly below room temperature, TCNE and isoprene form an adduct in an ice bath, and anthracene and TCNE react at room temperature.

This was not the most successful method to use because of the
wide temperature ranges and the scan time required on the spectrophotometer for the coreactants mentioned above. However, the method could be improved as mentioned before. Under the conditions employed in this study, infrared spectroscopy was not sensitive enough to measure with consistancy, any potential pre-molecular association of the molecules in the Diels-Alder reaction. In addition to the work done, one might try nuclear magnetic resonance and ultraviolet spectroscopy. Since these methods are sensitive to proton shifts and electronic changes respectively, it might be possible to observe any $\pi$-electron perturbation due to pre-molecular association.

Yates and Eaton\textsuperscript{13} studied the enhancing rates of diene and dienophile addition by using aluminum chloride as a catalyst. They obtained remarkable results. Hence this might be another way to observe pre-molecular association by using catalytic effects on the slow reactions.
REFERENCES


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