DICHLOROMALEIC ANHYDRIDE AS A REAGENT FOR THE DETERMINATION OF CONJUGATED DIOLEFINS

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A THESIS

Submitted to the College of Science and Arts
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ABSTRACT

The use of dichloromaleic anhydride as a replacement for chloromaleic anhydride in the quantitative determination of conjugated diolefins was investigated. The proposed method is based on the Diels-Alder reaction of dichloromaleic anhydride with only the conjugated olefin, even in the presence of other saturated and unsaturated hydrocarbons. Chlorine on the adduct is then converted to chloride by refluxing in silver nitrate solution. The chloride is determined by the Volhard method. Chlorine on the unreacted anhydride should not be removed by this procedure.

Results indicate dichloromaleic anhydride reacts with numerous conjugated diolefins; however, the reaction did not appear to be quantitative for the systems studied. Both Volhard and gravimetric determination of chloride after refluxing the purified adduct of 2,3-dimethyl-1,3-butadiene in silver nitrate solution indicated only one of the two available chlorine atoms was removed by refluxing. Recovery of chlorine was neither quantitative nor stoichiometric.

Steric hindrance and inductive effects of the chlorine atoms of the dichloromaleic anhydride adducts were considered. The addition of the second chlorine atom vastly alters the chemical behavior of dichloromaleic anhydride as compared to chloromaleic anhydride. It is concluded that dichloromaleic anhydride is not a suitable replacement for chloromaleic anhydride in this type of determination.

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INTRODUCTION

The Diels-Alder reaction offers a unique method for quantitatively determining conjugated diolefins. Since the reaction is specific for conjugated systems, it is possible to analyze for the conjugated olefins in the presence of both saturated and unsaturated hydrocarbons. Numerous analytical methods have been developed using both maleic and chloromaleic anhydride as the dienophile.

Maleic anhydride was first utilized for the estimation of isoprene by Bassett and Williams (1) in 1932. After allowing maleic anhydride to react with the sample at 100°C, the gain in weight of the crystalline anhydride represented the amount of isoprene present.

Birch and Scott (2) utilized the same reaction for the identification of various gasoline fractions. In this procedure the melting points of the crystalline adducts with maleic anhydride identified the various diolefins present.

Another variation of the same reaction was developed by Tropsch and Mattox (8) for the determination of butadiene in gases. A measured volume of gaseous sample was passed over molten maleic anhydride. The loss of volume due to absorption of the butadiene by maleic anhydride thus indicated the amount of diene present in the sample.

Putnam, Moss and Hall (7) developed a method in which chloromaleic anhydride was used as the dienophile in the Diels-Alder reaction. Since the chloro group of the adduct is attached to a tertiary carbon,

it is possible to remove the group as chloride by simple refluxing with silver nitrate. The chlorine in the excess chloromaleic anhydride in the reaction mixture, however, is a vinyl chloride; therefore, silver nitrate does not attack the excess reagent. The quantity of silver nitrate consumed represents the amount of diolefin present.

Although titrating chloride removed from a tertiary carbon in the presence of vinyl chloride offers many analytical possibilities, chloromaleic anhydride is not ideally suited for the Diels-Alder reaction. Disadvantages are:

(1) Purified chloromaleic anhydride has a melting point of 32-34°C; slight impurities cause the material to liquify.

(2) Purification is difficult, requiring vacuum distillation and yields are low.

(3) The product is easily hydrated; therefore, it must be handled under nitrogen or carbon dioxide and stored in sealed ampoules.

(4) Small amounts of chloromaleic acid catalyze polymerization of the diolefins.

Dichloromaleic anhydride is a likely alternative reagent for a quantitative Diels-Alder reaction with conjugated diolefins. This reagent offers the same possibilities as chloromaleic anhydride, but has additional advantages.

(1) Dichloromaleic anhydride is a crystalline compound melting at 117-120°C.

(2) Impurities of dichloromaleic acid are easily removed by sublimation, recovering the anhydride from the acid.

(3) Two chlorine atoms should be available for titration, thus increasing the sensitivity of the method.

The purpose of this investigation was, therefore, to study the use of dichloromaleic anhydride as a reagent for the quantitative determination of conjugated olefins and develop a method utilizing this reagent for the determination of butadiene and related compounds.

EXPERIMENTAL

The course of this study was directed at three main objectives.

(1) Does dichloromaleic anhydride undergo a Diels-Alder reaction with the common conjugated olefins?

(2) Is the reaction with dichloromaleic anhydride quantitative, or can the reaction be made quantitative?

(3) What conditions are necessary for the quantitative removal of chlorine from the adduct without affecting the chlorine of the unreacted anhydride?

In order to answer these questions a series of compounds was synthesized using dichloromaleic anhydride as the dienophile for reaction with various dienes. The most suitable of these adducts was then prepared in quantity and used for the systematic study of conditions necessary for complete removal of chlorine from the adduct.

Preparation of Adducts

Diels and Thiele (4) were the first to perform a Diels-Alder reaction with dichloromaleic anhydride. They obtained quantitative yields of the adduct when anthracene and dichloromaleic anhydride were heated together at 170°C. More recently, Clifford and Gleim (3) formed adducts of dichloromaleic anhydride with butadiene, cyclopentadiene, dicyclopentadiene, cis-piperylene, 2-methyl-1,3-pentadiene and dipentene. In each case they used benzene as the solvent and performed the reaction in an autoclave at 300-500 pounds pressure. Reaction

temperatures varied from room temperature for cyclopentadiene to 210°C for butadiene.

In view of this previous work, no solvent was used in the preparation of the dichloromaleic anhydride adducts and the reaction temperature was varied from 150-180°C.

Furoic Acid Adduct: One gram of furoic acid (Matheson, Coleman and Bell) and 1.8 grams of dichloromaleic anhydride (Westvaco Chlor-Alkali) were heated together in a pressure bottle. The temperature was raised to 170-175°C and maintained there for 30 minutes. As the solution cooled, crystallization occurred at 130°C. The product was recrystallized first from dry ether and then again from carbon tetrachloride. Melting point of the purified material was 129-130°C.

Heating a similar mixture in an oven at 135°C for 3 hours, then 15 minutes at 155°C yielded no product.

2,5-Dimethyl-2,4-hexadiene Adduct: Seven ml. of 2,5-dimethyl-2,4-hexadiene (Monomer-Polymer) and 10 grams of crude dichloromaleic anhydride were heated together in a pressure bottle. The temperature was raised to 160°C and maintained there for 10 minutes. A dark red liquid was obtained that crystallized upon cooling. The product was recrystallized from carbon tetrachloride. The first crop of crystals obtained had a melting point of 100-110°C. After further solvent evaporation crystals were obtained that had a melting point of approximately 75°C.

Since it appeared likely that solvent was still present in both crops of crystals, the products were dried at room temperature under

vacuum for 3 hours. The melting point of the first crop of crystals was raised to 122-125°C. The second crop of crystals still melted at 75°C.

Henne and Turk (6) found that 2,5-dimethyl-2,4-hexadiene did not form a normal Diels-Alder adduct with maleic anhydride, but yielded only an amorphous high melting product. Farmer and Warren (5) found the same to be true of other olefins which had doubly substituted terminal carbons. Therefore, it is possible that the material isolated from the reaction with dichloromaleic anhydride is a polymer of some sort, thus accounting for the inconsistent melting points.

2,5-Dimethyl Furan Adduct: One ml. of 2,5-dimethyl furan (Eastman-white label) and 2 grams crude dichloromaleic anhydride were heated together in a pressure bottle. At 120°C extensive vaporization occurred. Heating was continued to 160°C where the vapors condensed onto the walls of the bottle. After 10 minutes at 160°C a black oil was obtained which was readily soluble in ether. After complete evaporation of the ether, a dark oil remained that did not crystallize even after prolonged standing.

Isoprene Adduct: Three ml. of isoprene (Monomer-Polymer), 4 grams of crude dichloromaleic anhydride and 4 drops of p-(t-butyl)catechol were heated together in a pressure bottle. The temperature was raised to 180°C and maintained there for 15 minutes. The dark oily product obtained was recrystallized from ligroin (60-90°C) after standing overnight. Melting point was 124-126°C.

2,3-Dimethyl-1,3-Butadiene Adduct: Twelve ml. of 2,3-dimethyl-1,3-butadiene (Monomer-Polymer) and 16 grams of crude dichloromaleic

anhydride were heated together in a pressure bottle. The temperature was raised to 150-160°C and maintained there for 15 minutes. A red liquid was obtained that crystallized completely as it cooled. The product was recrystallized from ligroin (60-90°C). An off-white powder was obtained which melted at 134-135°C.

Purification of Dichloromaleic Anhydride

Putnam, Moss and Hall (7) found that small amounts of acid impurities in chloromaleic anhydride catalyzed polymerization of diolefins, introducing significant errors into their method. Some trace of dichloromaleic acid was suspected to be present in the dichloromaleic anhydride obtained from Westvaco Chlor-Alkali. Therefore, two methods of purification were attempted.

Reagent grade carbon tetrachloride was heated to boiling, then saturated with crude dichloromaleic anhydride. After the solution had stood overnight, large needles crystallized out. The crystals were then filtered and washed with carbon tetrachloride. When a melting point was attempted, the material lost solvent at 100°C and then sublimed continuously.

Since dichloromaleic acid is known to lose water upon sublimation to form dichloromaleic anhydride, the crude material was sublimed under reduced pressure at approximately 115°C. Pure white plates were obtained which melted at 117-120°C.

Both the crude and resublimed dichloromaleic anhydride were titrated with an aqueous solution of potassium hydroxide using phenolphthalein indicator. The crude material assayed 99.01 percent

dichloromaleic anhydride. The resublimed product averaged 99.19 percent dichloromaleic anhydride. (Complete data in Appendix.) In both cases the neutralisation equivalent was 84.3; the theoretical neutralisation equivalent for dichloromaleic anhydride is 83.5, for dichloromaleic acid 92.5.

Sublimation was adopted as the standard method of purification of dichloromaleic anhydride. The procedure was not only simple, but also gave high yields of pure dichloromaleic anhydride.

Methods of Chloride Determination

Putnam, Moss and Hall's method utilizes the Volhard procedure to determine the quantity of silver consumed by the chloride present. In their method a measured excess of silver nitrate is refluxed with the reaction mixture, then the excess silver nitrate is back titrated with potassium thiocyanate using ferric alum as the indicator. In this study two methods were used in an attempt to quantitatively remove the chlorine from the adduct. They were: (1) refluxing in sodium bicarbonate solution, and (2) refluxing in silver nitrate solution.

Sodium Bicarbonate (0.5N): An approximately 0.5N solution of sodium bicarbonate was prepared by dissolving 42 grams of sodium bicarbonate in 1 liter of distilled water.

Silver Nitrate (0.2N): One hundred twenty grams of reagent grade silver nitrate were dissolved in 3.5 liters of distilled water.

Potassium Thiocyanate (0.1N): Fifty eight grams of reagent grade potassium thiocyanate were dissolved in 6 liters of distilled water.

Ferric Alum Indicator: One hundred twenty five grams of reagent grade ferric ammonium sulfate·dodecahydrate were dissolved in a mixture of 450 ml. water and 50 ml. concentrated nitric acid.

The silver nitrate and potassium thiocyanate solutions were first compared to each other and then the silver nitrate solution was standardized with reagent grade sodium chloride.

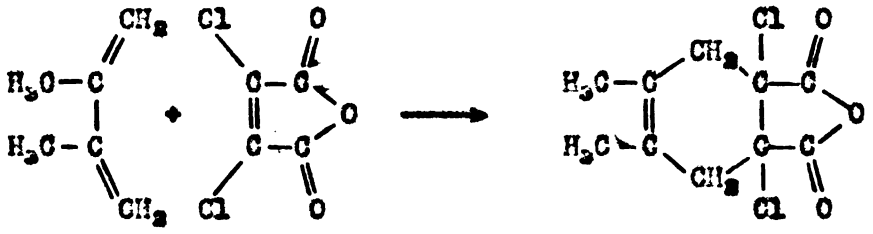
In the sodium bicarbonate method, small samples of adduct were first dissolved in dioxane, then varying amounts of 0.5N sodium bicarbonate solution were added. The solutions were heated to boiling and held just below the boiling point for 1 to 2 hours. After cooling to room temperature, the solutions were acidified with nitric acid and a known excess of silver nitrate solution added. The silver chloride was allowed to settle, then was filtered from the solution. The remaining silver in solution was titrated with potassium thiocyanate using ferric alum indicator.

In the silver nitrate method, samples of adduct were dissolved in acetone. A known excess of silver nitrate solution and varying amounts of water were added, then the solutions were either refluxed for 2 hours or boiled without refluxing, adding water as needed to replace that lost by evaporation. After cooling, the precipitated silver chloride was filtered from the solutions, the solutions were acidified with nitric acid and the excess silver in solution determined by titration with potassium thiocyanate.

Results with 2,3-Dimethyl-1,3-Butadiene Adduct

The adduct of 2,3-dimethyl-1,3-butadiene with dichloromaleic anhydride was found to be most suitable for further study. This adduct was easily obtained and could be recrystallized to yield a product of good purity. In addition, the adduct had a relatively high melting point. Since 2,3-dimethyl-1,3-butadiene is a liquid (boiling point 70°C), it too could be weighed accurately for any work beginning with this compound.

The normal Diels-Alder reaction of dichloromaleic anhydride with 2,3-dimethyl-1,3-butadiene should yield 1,6-dichloro-2,5-dihydro-3,4-dimethyl phthalic anhydride (I).



I

An analysis for carbon, hydrogen and chlorine and the neutralization equivalent of the reaction product of dichloromaleic anhydride and 2,3-dimethyl-1,3-butadiene were obtained. Table I shows analytical results for the adduct.

The neutralization equivalent indicates the adduct is the expected anhydride; however, the elemental analysis checks with the percentages expected if the anhydride were hydrolyzed to its acid. Since the starting material was over 99 percent dichloromaleic anhydride and the

TABLE I

COMPARATIVE RESULTS FOR ANALYSIS OF 2,3-DIMETHYL-1,3-BUTADIENE ADDUCT

Results	Analysis	Theoret. Anhydride	Theoret. Acid
Neutralization Equivalent	124	124.5	133.5
Elemental Analysis			
Carbon	45.00%*	48.2%	45.0%
Hydrogen	4.58%*	4.1%	4.5%
Chlorine	26.40%*	28.5%	26.6%

*Analysis by Micro-Tech Laboratories, Skokie, Illinois.

reaction occurred under anhydrous conditions, it may be assumed that the product obtained was the anhydride. The small sample used for the elemental analysis could have been hydrolyzed in the atmosphere when it was handled and shipped for analysis. The product used in all experimental work was oven dried and kept in a desiccator.

The 2,3-dimethyl-1,3-butadiene adduct was first heated in sodium bicarbonate solution in an attempt to remove the chlorine from the adduct. Results of preliminary experiments are given in Table II.

In all cases the percentage recovery was low. Some correlation is apparent between the relative concentration of bicarbonate and the percentage recovery in that the higher the ratio of bicarbonate to sample, the higher the percentage recovery. The amount of bicarbonate needed for 100 percent recovery on this basis would be 60 milliequivalents of bicarbonate per milliequivalent of chlorine. This required excess of bicarbonate would be impractical for a useful method. Therefore, no further work was done with sodium bicarbonate media.

TABLE II

RECOVERY OF CHLORINE FROM 2,3-DIMETHYL-1,3-BUTADIENE ADDUCT IN SODIUM BICARBONATE

Adduct Wt. grams	Meq.* Adduct Taken	Meq. Cl^- Found	Percent Recovery	Meq. $NaHCO_3$ / Meq. Adduct
0.0621	0.199	0.120	24.1	15
0.0486	0.301	0.120	30.7	19
0.0417	0.335	0.115	34.4	22
0.0568	0.456	0.180	39.5	22

Conditions: Solvent-15 ml. of 1:1 cellosolve:water, heating time-1 hour, heating temperature-130°C.

*Meq. wt. = molecular wt. of adduct/2000.

Test tube experiments indicated that, in acetone solution, the chlorine in the 2,3-dimethyl-1,3-butadiene adduct reacted with an aqueous silver nitrate solution. Experiments were undertaken to determine the most favorable conditions for this reaction. Heating time, hydrogen ion concentration, silver ion concentration, and the appearance of an insoluble precipitate other than silver chloride were investigated.

A series of determinations was made in which the silver and hydrogen ion concentrations were kept relatively constant while the heating period was varied from 1 to 3 hours. The results are given in Table III.

In each case the percentage recovery increased when the heating time was extended from 1 to 2 hours. Heating for 3 hours gave no improvement in recovery; therefore, 2 hours was adopted as the heating period for all further work.

In the preliminary work the accumulation of hydrogen ion during the course of the reaction appeared to hinder the reaction and lower

TABLE III

EFFECT OF HEATING TIME

Meq.* Adduct Taken	Meq. Cl⁻ Found	Percent Recovery	Heating Time, hr.	Meq. Ag^+ / Meq. Adduct
0.326	0.245	75.1	3	12.2
0.334	0.294	88.2	2	12.0
0.292	0.170	58.2	1	10.0
0.277	0.220	80.0	3	14.4
0.312	0.250	80.0	2	12.8
0.490	0.260	53.0	2	8.2
0.490	0.220	45.0	1	10.2

*Meq. wt. = molecular wt. of adduct/2000.

the percentage recovery of chlorine. It was found that if the hydrogen ion concentration, based on 100 percent removal of the chlorine, was kept below 0.01N, the recovery of chlorine depended entirely upon the relative concentration of the silver ion.

Early experimental results showed the concentration of silver ion to be the most important factor in improving the recovery of chlorine. Numerous determinations indicated a large excess of silver ion, approximately 20 milliequivalents of silver per milliequivalent of chlorine, would be necessary to obtain 100 percent recovery of chlorine. A series of experiments using an approximate 20:1 ratio of silver to chlorine did give results approaching those calculated theoretically. However, the results were erratic and seemed to show an indeterminate error. Still another series of determinations was run using approximately 30

milliequivalents of silver per milliequivalent of chlorine. Results of these determinations were well above 100 percent of the calculated amount of chlorine present. A somewhat linear relationship, as shown in Figure 1, was found to exist between the silver ion concentration and the percent recovery. (Complete data in Appendix.) Because this relationship was linear above 100 percent, it suggested the possibility that the silver was undergoing another reaction in addition to combining with the chlorine of the adduct.

Careful observation of the reaction as it proceeded revealed that a precipitate formed immediately upon addition of aqueous silver nitrate to the acetone solution of the adduct. This precipitate dissolved as the sample was heated to reflux temperature and the characteristic silver chloride precipitate appeared. After heating, as the solution cooled, an additional precipitate again appeared in some samples. This additional precipitate was filtered from the solution with the silver chloride.

When it became evident that this additional precipitate contained silver, several solvents were tried in an attempt to dissolve the additional precipitate without dissolving the silver chloride. If the nitric acid used in the Volhard determination was added before the filtration, it further decreased the solubility of the precipitate. If nitric acid was added to the filtrate, it sometimes caused further precipitation to occur. Washing the combined residue of silver chloride and the additional precipitate with acetone did dissolve the additional precipitate and a positive test for silver ion was obtained in the

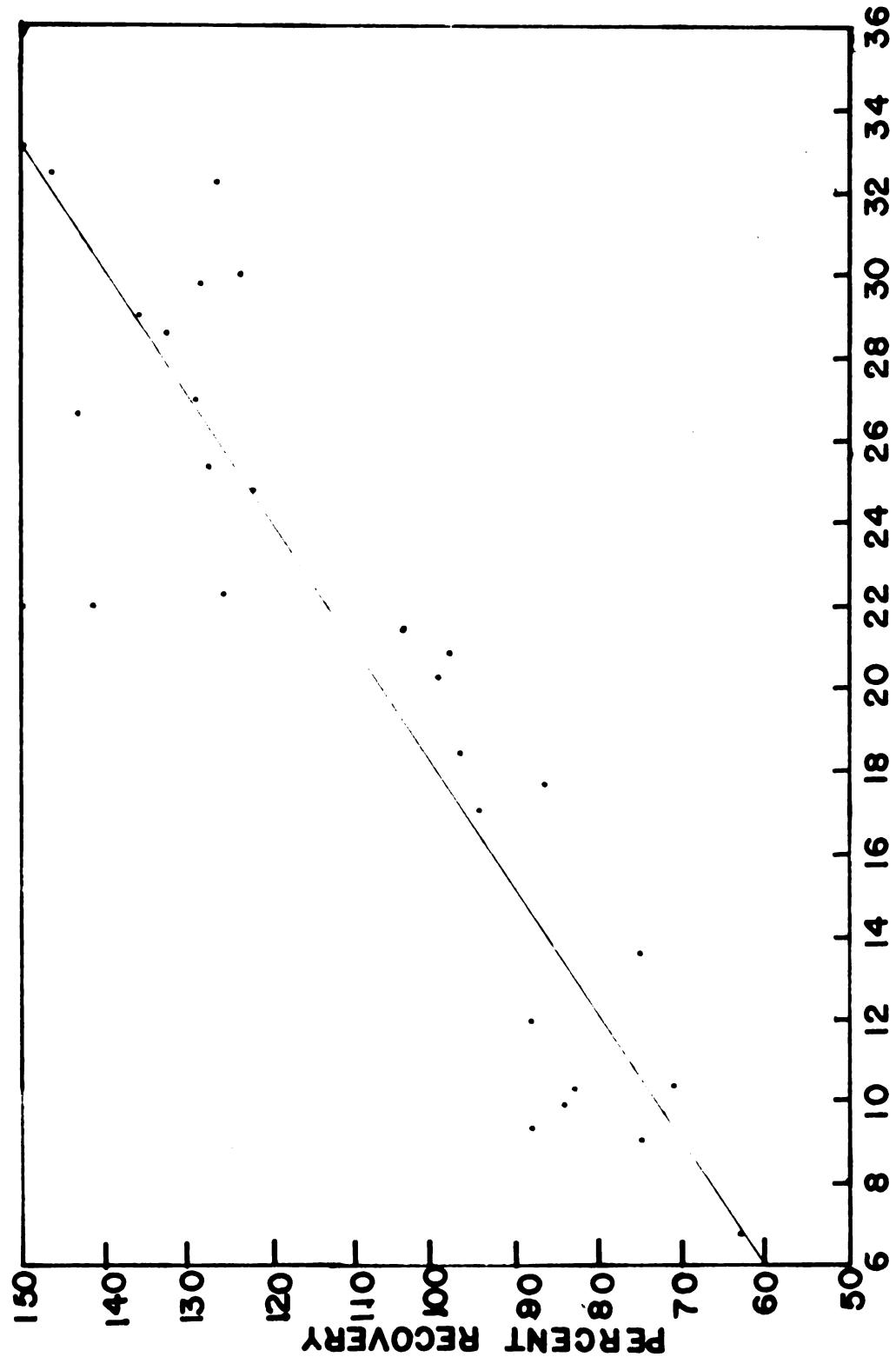


FIG 1 EFFECT OF SILVER ION CONCENTRATION ON PERCENT RECOVERY

acetone wash solution. From the observations made it seems reasonable to suggest that the precipitate was an insoluble silver salt of the organic acid present in solution.

Results obtained by the Volhard method after washing the residue with acetone were still high. It was proposed that the silver might be complexed in some manner in the resulting acetone-water mixture. In a final effort to obtain quantitative results, a series of determinations was made in which the silver chloride obtained was dried and weighed.

For the gravimetric determination of chloride, the sample was dissolved in 20 ml. of acetone, 100 ml. of 0.2N aqueous silver nitrate added, and the solution refluxed for 2 hours. After refluxing the silver chloride formed was filtered from the solution, washed with acetone and water, dried, and weighed. Results for a series of determinations are given in Table IV.

TABLE IV

RECOVERY OF CHLORINE USING GRAVIMETRIC CHLORIDE DETERMINATION

Adduct Wt. grams	Meq.* Adduct Taken	Meq. Cl* Found	Percent Recovery	Meq. Ag* / Meq. Adduct
0.0589	0.473	0.264	55.8	42
0.0657	0.528	0.326	61.8	38
0.0975	0.703	0.394	56.1	28
0.1024	0.742	0.457	61.5	27
0.1032	0.828	0.443	53.5	24
0.1137	1.106	0.592	53.5	18
0.3447	2.768	1.67	60.5	7.2

*Meq. wt. = molecular wt. of adduct/2000.

No correlation is evident between the percentage recovery and the relative concentration of silver ion, thus suggesting the correlation in the previous work could be due almost entirely to the presence of an additional silver compound. In all cases the percentage recovery is slightly above 50 percent, but results vary widely with no apparent reason based on silver ion concentration, hydrogen ion concentration, or heating time. The results suggest that only one chlorine atom is ionized and removed from the adduct entirely, since 50 percent recovery would indicate complete removal of one chlorine. The removal of one chlorine atom, however, is not stoichiometric under the conditions employed.

To determine whether or not the reaction of dichloromaleic anhydride with 2,3-dimethyl-1,3-butadiene was quantitative, accurately weighed samples of 2,3-dimethyl-1,3-butadiene were allowed to react with an excess of dichloromaleic anhydride. After the reaction was completed, the reaction mixture was dissolved in acetone and the chlorine recovered by refluxing in silver nitrate solution and weighing the silver chloride precipitated. Table V shows that under the reaction conditions used, less than 50 percent recovery was obtained. These data indicate, therefore, that the reaction of dichloromaleic anhydride with 2,3-dimethyl-1,3-butadiene is not quantitative under these conditions.

Finally, samples of the adduct were refluxed in 0.5N sodium hydroxide solution for 2 hours, then the chlorine which had ionized was precipitated as silver chloride and weighed. Even under these conditions

TABLE V

RECOVERY OF CHLORINE FROM 2,3-DICHLORO-
1,3-BUTADIENE REACTION MIXTURE

Wt. 2,3-Dimethyl-1,3-Butadiene, grams	Meq.* Sample Taken	Meq. Cl^- Found	Percent Recovery
0.706	17.2	7.21	42
0.505	14.5	6.61	45.5
0.0744	1.81	0.74	41

*Meq. wt. = molecular wt. of 2,3-dimethyl-1,3-butadiene/2000.

it was impossible to obtain 100 percent recovery of the chlorine. Results are shown in Table VI.

TABLE VI

RECOVERY OF CHLORINE FROM ADDUCT AFTER REFLUXING
IN 0.5N SODIUM HYDROXIDE

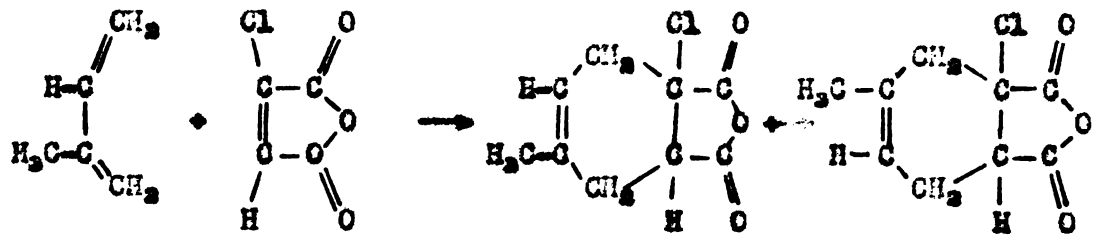
Adduct Wt. grams	Meq.* Adduct Taken	Meq. Cl^- Found	Percent Recovery
0.0777	0.624	0.459	73.6
0.0697	0.530	0.415	74.1

*Meq. wt. = molecular wt. of adduct/2000.

Since the chlorine could not be quantitatively removed from the adduct with aqueous sodium hydroxide, it is unlikely that any procedure using silver nitrate could accomplish this removal.

DISCUSSION

Putnam, Moss and Hall (7) allowed isoprene to react with chloromaleic anhydride to yield a mixture of 1-chloro-2,5-dihydro-4-methyl phthalic anhydride (II) and 1-chloro-2,5-dihydro-3-methyl phthalic anhydride (III).



II III

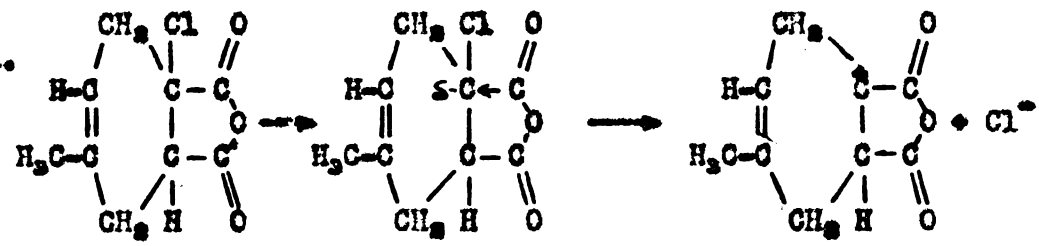
By refluxing this mixture in 0.2N silver nitrate solution using a ratio of 2 milliequivalents of silver ion per milliquivalent of sample they obtained quantitative removal of chlorine. The 1,6-dichloro-2,5-dihydro-3,4-dimethyl phthalic anhydride (I) used in this study has a similar structure except for the replacement of hydrogen by chlorine on the bridgehead carbon. However, the results of this study indicate that only one chlorine atom of the two available in 1,6-dichloro-2,5-dihydro-3,4-dimethyl phthalic anhydride is removed even after extensive refluxing in silver nitrate or sodium hydroxide solution. This decrease in activity must be due in some manner to the additional chlorine atom in the structure.

Scale models were constructed of 1-chloro-2,5-dihydro-4-methyl phthalic anhydride (II) and 1,6-dichloro-2,5-dihydro-3,4-dimethyl phthalic anhydride (I). The models showed both molecules to be completely rigid with the tertiary carbon blocked to attack by a nucleophilic reagent for an SN_2 substitution reaction. The rigidity of the structures also makes inversion at the tertiary carbon impossible. Acid forms of these compounds could not be constructed with models due to steric hindrance of the two hydroxyl groups added in the cis-configuration.

Silver nitrate solution is not basic enough to favor an E_1 or E_2 elimination reaction. An SN_2 reaction is not a reasonable mechanism because of the steric factors involved. Therefore, the reaction apparently proceeds by an SN_1 mechanism, that is, first an ionization step followed by a second step in which the carbonium ion is attacked by a nucleophilic reagent.

For 1-chloro-2,5-dihydro-4-methyl phthalic anhydride (II) in aqueous silver nitrate the reaction may proceed:

1.



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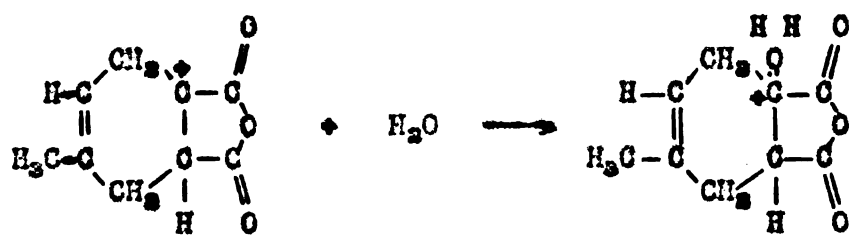
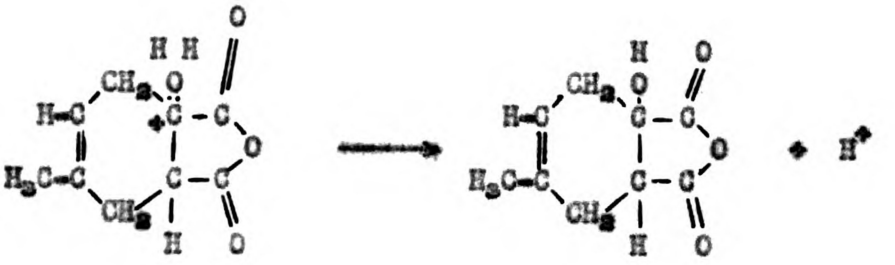


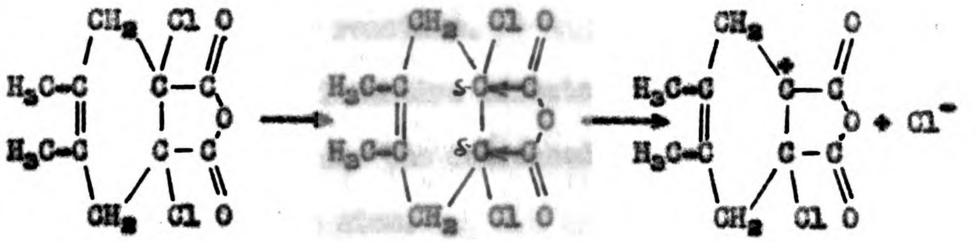
3. 

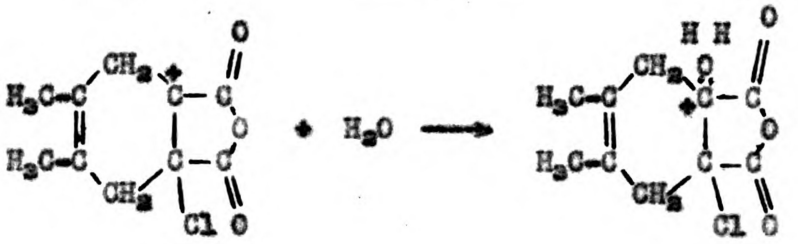
IV

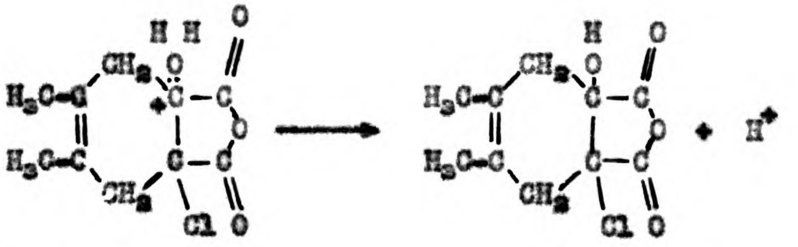
4. $Cl^- + Ag^+ \longrightarrow AgCl$

In this reaction it is possible for the carboxyl group to furnish electrons to the chlorine because of mesomeric effects induced by the presence of silver ions in the solution. The hydrogen on the alpha carbon would probably have little effect towards either hindering or assisting the reaction.

For 1,6-dichloro-2,5-dihydro-3,4-phthalic anhydride a similar series of steps would occur.

1. 

2. 

3. 

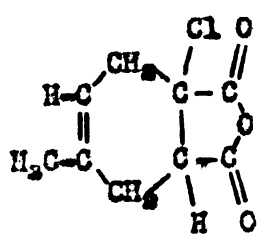
V

4. $Cl^- + Ag^+ \longrightarrow AgCl$

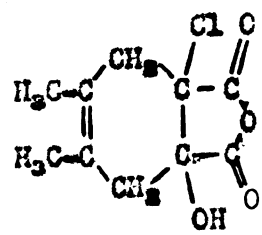
Again in this reaction the carboxyl group could furnish electrons upon demand of the silver ion. However, the effect would be lessened because of the presence of two chlorine atoms each drawing electrons towards itself. The mesomeric effects of chlorine are not transferred through the alpha carbon. Therefore, there would be little contribution of electrons from one chlorine atom to the other. Since two chlorine atoms are available, any shift of the equilibrium would allow one chlorine to ionize and steps 1 through 3 could occur.

Data obtained support the argument that the extent of reaction was decreased by the presence of the second chlorine atom in the molecule, since a much higher silver ion concentration was required to obtain even 50 percent removal of the chlorine. The data show that the extent of removal of the second chlorine is even further decreased, almost to the point of no further reaction.

Comparison of the inductive effects in structures II and V offers a possible explanation for the decreased extent of reaction after the removal of one chlorine atom.



II



V

In structure II the chlorine may draw electrons from the adjacent carboxyl group with perhaps a small contribution from the hydrogen

attached to the alpha carbon. In structure V the hydrogen has been replaced with a hydroxyl group which has a strong attraction for electrons. Mesomeric effects of electron contribution by the hydroxyl group are not transferred through the carbon chain, leaving only the inductive effects of the hydroxyl group. This competition for electrons could decrease the extent of reaction substantially, making quantitative recovery of the second chlorine atom difficult under the reaction conditions employed.

Dichloromaleic anhydride proved to be a convenient compound to handle. It was obtained relatively pure from the manufacturer and a single sublimation yielded a product of high purity. Since the compound did not hydrolyse readily in air, no special handling precautions were necessary.

Addition products were obtained when dichloromaleic anhydride was allowed to react with furoic acid, isoprene and 2,3-dimethyl-1,3-butadiene. Reaction products were obtained from 2,5-dimethyl-2,4-hexadiene and 2,5-dimethyl furan, but their behavior would lead to the supposition that the reaction had yielded only polymeric material. Clifford and Gleim (3) obtained reaction products of dichloromaleic anhydride with butadiene, cyclopentadiene, dicyclopentadiene, cis-piperylene, 2-methyl-1,3-pentadiene and dipentene.

The reaction products obtained by Clifford and Gleim and in these experiments were difficult to separate and purify. This would indicate some polymerization, making it difficult to obtain a quantitative reaction. Data for the 2,3-dimethyl-1,3-butadiene adduct show that

although the reaction proceeded smoothly, the addition was not quantitative.

The 1,6-dichloro-2,5-dihydro-3,4-dimethyl phthalic anhydride model also showed that any addition to carbons 2 and 5 of the six membered ring, as in the case of the 2,5-dimethyl-2,4-hexadiene adduct, would make the reaction difficult because of the steric hindrance introduced by the two chlorine atoms on the bridgehead carbons.

The reactivity of dichloromaleic anhydride for the Diels-Alder reaction should also be considered. Since the Diels-Alder reaction is believed to have an ionic mechanism, the addition of a single chlorine atom to the anhydride, as in chloromaleic anhydride, should assist this ionization by inductive effects and increase the reactivity. The two chlorine atoms present in dichloromaleic anhydride would oppose each other and tend to cancel any inductive effects. From this viewpoint, the reactivity of dichloromaleic anhydride would be similar to that of maleic anhydride with the added steric hindrance caused by the chlorine atoms.

CONCLUSIONS

The conclusions of this study may be stated briefly:

(1) Dichloromaleic anhydride is a convenient material to purify and handle.

(2) Dichloromaleic anhydride does form adducts with a number of diolefins, but its addition is restricted to compounds which offer no steric difficulties, i.e., no substitution on the terminal carbon of the conjugated system.

(3) The reaction of dichloromaleic anhydride with the common diolefins is not quantitative under the reaction conditions employed.

(4) The temperature necessary for the reaction of dichloromaleic anhydride with diolefins is in the range of 150-180°C. Butadiene at such elevated temperatures presents a safety hazard.

(5) Recovery of chlorine from the 2,3-dimethyl-1,3-butadiene adduct is not quantitative or stoichiometric using mild reaction conditions.

Although dichloromaleic anhydride offers certain advantages over chloromaleic anhydride as a reagent for the quantitative determination of conjugated diolefins, these results indicate it is not a suitable replacement. The steric factors and inductive effects introduced by the second chlorine atom in the molecule vastly alter the behavior of dichloromaleic anhydride as compared to chloromaleic anhydride.

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APPENDIX

I. Analysis of Dichloromaleic Anhydride

Samples dissolved in water, titrated with 0.8617N potassium hydroxide, phenolphthalein indicator.

Crude Dichloromaleic Anhydride

Sample Weight, grams	2.5212
Ml. of Potassium Hydroxide	34.70
Percent Dichloromaleic Anhydride	99.01
Neutralization Equivalent	84.3

Resublimed Dichloromaleic Anhydride

Sample Weight, grams	2.6818	2.0930
Ml. of Potassium Hydroxide	37.00	28.83
Percent Dichloromaleic Anhydride	99.27	99.11
Neutralization Equivalent	84.2	84.3

Calculations:

Percent Dichloromaleic Anhydride =

$$\frac{(\text{mls. KOH})(0.8617)(0.167)}{(\text{sample weight})(2)}$$

Neutralization Equivalent =

$$\frac{(\text{sample weight})(1000)}{(\text{mls. KOH})(0.8617)}$$

II. Effect of Silver Ion Concentration on Percent Recovery

Meq.* Adduct Taken	Meq. Cl^- Found	Percent Recovery	Meq. Ag^+ / Meq. Adduct
0.305	0.132	43.1	13.1
0.334	0.294	88.2	12.0
0.387	0.274	71.0	10.3
0.398	0.333	84.0	10.1
0.411	0.329	74.5	9.1
0.463	0.393	85.0	8.6
0.600	0.374	62.3	6.7
0.182	0.276	151	33.0
0.184	0.269	146	32.6
0.185	0.233	126	32.4
0.201	0.238	128	29.8
0.206	0.280	136	29.0
0.209	0.276	132	28.7
0.222	0.286	129	27.0
0.224	0.320	143	26.7
0.236	0.300	127	25.4
0.240	0.294	122	25.0
0.268	0.345	125	22.4
0.273	0.410	150	22.0
0.273	0.383	141	22.0
0.278	0.290	104	21.3
0.286	0.280	97.9	20.9
0.292	0.290	99.3	20.4
0.324	0.314	96.9	18.5
0.336	0.288	85.7	17.8
0.348	0.329	94.5	17.2
0.446	0.335	75.1	13.5
0.542	0.408	76.6	11.1
0.580	0.481	83.0	10.4

Heating Time - 2 hours
Hydrogen ion concentration less than 0.01N

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