

POLYMERIZATION OF MALEIC ANHYDRIDE
INDUCED BY PYRIDINE

By

SUN CHUN CHOW
"

Bachelor of Science

National Central University

Nanking, China

1939

Submitted to the Department of Chemistry
Oklahoma Agricultural and Mechanical College
In Partial Fulfillment of the Requirements
for the Degree of
MASTER OF SCIENCE
1950

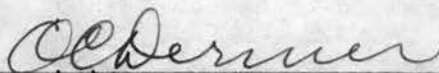
OKLAHOMA
AGRICULTURAL & MECHANICAL COLLEGE
LIBRARY
SEP 30 1950

iii

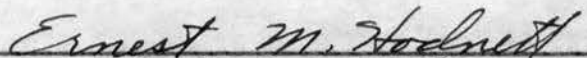
POLYMERIZATION OF MALEIC ANHYDRIDE
INDUCED BY PYRIDINE

SUN CHUN CHOW
MASTER OF SCIENCE
1950

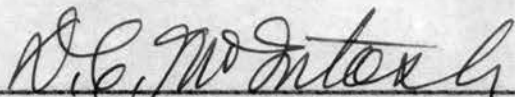
THESIS AND ABSTRACT APPROVED:



Thesis Adviser



Faculty Representative



Dean of the Graduate School

259573

A C K N O W L E D G M E N T

The author wishes to express his sincere thanks to Dr. O. C. Dermer under whose direction and with whose help this work has been done.

He also wishes to express his appreciation for the financial aid rendered by Oklahoma A. and M. College in the form of a graduate fellowship in the Chemistry Department.

TABLE OF CONTENTS

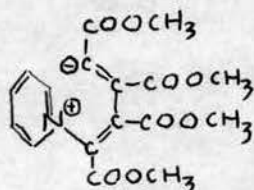
Historical	1
Scope of Reaction	4
Preparative Work	5
Quantitative Data	10
Discussion of Results	17
Summary	23
Bibliography	24

HISTORICAL

Since tertiary amines do not ordinarily combine with anhydrides of carboxylic acids, the observation in these laboratories that a vigorous exothermic reaction takes place between pyridine and maleic anhydride was unexpected and theoretically interesting. A search of the literature showed that the phenomenon had been previously noted but little studied. Both Smith, Bryant, and Mitchell (1) and Mullen and Pacsu (2) observed that the reaction is violent, almost explosive; the former authors suggested that a Diels-Alder reaction was involved. 4-Vinylquinoline, lepidine, and pyridine were all found to react with maleic anhydride at 100° C. with rapid evolution of carbon dioxide (3); this was taken as evidence that the reaction of 4-vinylquinoline involves the quinoline nucleus rather than the conjugated system ending in the unsaturated side chain. Salminen (4) was unable to obtain a crystalline compound from dry pyridine and an equimolar amount of maleic anhydride let stand overnight in benzene at room temperature. In ether, the reaction gave a white precipitate that proved to be pyridinium hydrogen maleate, m.p. 95° C. and 172° C. Quinoline and quinaldine gave similar salts. Hutcheson (5) made a few trials with pyridine and maleic anhydride in various organic solvents but likewise could obtain no definite product.

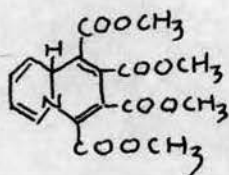
Since the possibility that the reaction is of Diels-Alder type has been mentioned, and acetylenedicarboxylic acid derivatives often act like those of maleic acid, the description of reactions (6) between dimethyl acetylenedicarboxylate and such heterocyclic substances as pyridine, α -picoline, quinoline, isoquinoline, and quinaldine is of interest. Very remarkable

dipolar structures, with a tricovalent carbon atom as anion, have been suggested for some of these products. These products can either change into polynuclear heterocyclic addition products or split out the heterocyclic molecule, add another unsaturated unit, and end as trimers. Thus dimethyl acetylenedicarboxylate with pyridine yields an unstable product (I),

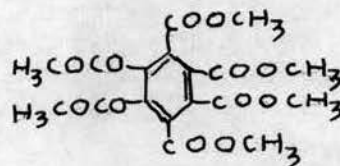


(I)

which can go to either the quinizoline (II) or the mellitic ester (III).



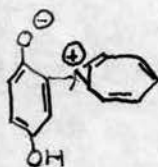
(II)



(III)

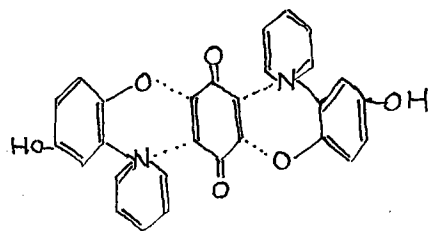
The case of quinones has been studied by Diels and coworkers (7, 8, 9).

The first intermediate here is illustrated by the red pyridine-*p*-benzoquinone complex, hydroquinone pyridinium betaine (IV), which was actually isolated.



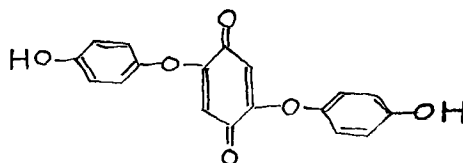
(IV)

Two molecules of this are conceived to associate with another molecule of *p*-benzoquinone, yielding a further intermediate (V).



(V)

Compound (V) yields no nitrogenous derivatives upon stabilization, but only the trimeric *p*-benzoquinone, 2,5-bis(*p*-hydroxyphenoxy)-*p*-benzoquinone (VI); this structure is well established.



(VI)

SCOPE OF REACTION

Studies were first instituted to determine what compounds could replace maleic anhydride in this reaction. Phthalic anhydride, which has structure similar to that of maleic anhydride, was tried, but gave no such reaction as maleic anhydride did. Maleic acid, phthalic acid, succinic acid, and succinic anhydride also did not give the reaction with pyridine. Methyl maleate was tested for reaction with pyridine in methyl alcohol, benzene, or excess methyl maleate solution, in the hope of avoiding decarboxylation which evidently complicates the reaction when the anhydride is used. The only significant reaction was found to be the change of the configuration of methyl maleate into methyl fumarate. A search of the literature showed that pyridine does catalyze the isomerization of methyl maleate into methyl fumarate (10).

Efforts were also made to find out what compounds could be used instead of pyridine as catalysts for the polymerization of maleic anhydride. α -Picoline, 4-ethylpyridine, quinoline, isoquinoline, quinaldine, and nicotine could replace pyridine, but quinoline, isoquinoline, and quinaldine were not as effective as pyridine. Nicotinic acid, a compound having the pyridine nucleus but no basicity, pyrrole, a heterocyclic but neutral nitrogen compound, dimethylaniline, a tertiary but non-heterocyclic amine, and nitrobenzene and *m*-dinitrobenzene, compounds having behavior like pyridine toward ring substitution, were found not effective at all in polymerizing maleic anhydride. Near the close of the experimental work, it became quite certain that the reaction between maleic anhydride and pyridine is a polymerization of maleic anhydride itself, the pyridine serving only as a catalyst.

PREPARATIVE WORK

Preparation and purification of reagents.

Pyridine. Ordinary pyridine was dried over quicklime for a week and distilled. The portion boiling at 114-6° C. was collected and used.

Maleic anhydride. Eastman Kodak white-label maleic anhydride was used. It melted at 56-7° C. and was 99.4% pure as shown by a titration with standard sodium hydroxide solution using phenolphthalein as indicator.

Methyl maleate. Two hundred forty-five grams of maleic anhydride and 300 g. (375 ml.) of methyl alcohol were refluxed for four hours with a small amount of concentrated sulfuric acid. The reaction mixture was washed with several liters of water, then with 10% sodium carbonate solution, and then with water again. The ester thus obtained was dried with anhydrous calcium chloride overnight and distilled under ordinary pressure. The portion which boiled at 203-5° C. was collected. It weighed 177 g., which corresponds to 49% of the theoretical yield.

α -Picoline. Eastman Kodak yellow-label α -picoline was distilled under ordinary pressure until a constant boiling temperature of 128° C. was reached. The last few drops of the distillate were used.

4-Ethylpyridine. 4-Ethylpyridine used in the experiment was prepared by Mr. T. B. Rice in Chem. 620. It had a boiling point of 160-3° C.

Quinoline. Technical-grade quinoline was distilled under ordinary pressure. The portion boiling at 235-6° C. was used.

Dimethylaniline. Technical-grade dimethylaniline was distilled under ordinary pressure. The portion boiling at 190-2° C. was collected and used.

The following were used without purification: maleic acid (C.P.), succinic acid (C.P.), phthalic acid (analytical), phthalic anhydride (analytical), succinic anhydride (EKC white-label), isoquinoline (EKC

white-label), nitrobenzene (EKC white-label), quinaldine (EKC yellow-label), nicotinic acid (EKC yellow-label), pyrrole (EKC yellow-label), nicotine (commercial), and m-dinitrobenzene (student preparation).

Reaction of pyridine and substituted pyridines with molten maleic anhydride. Ten to fifty grams of maleic anhydride was melted in a small beaker on a water bath. Pyridine was then dropped in from a medicine dropper while the molten maleic anhydride was stirred vigorously with a glass rod. The molten mass turned deep brown and became viscous after the addition of the first drop of pyridine. After three drops of pyridine had been added, a vigorous reaction started. The reaction mixture boiled and foamed, and gas was evolved. The amount of heat evolved was so large that a considerable part of the material was charred. Similar reactions happened when α -picoline, 4-ethylpyridine, or nicotine was used. Reactions were also obtained when quinoline, isoquinoline, or quinaldine was used instead of pyridine, but the reactions were not so violent. After the addition of 5-7 drops of quinoline, isoquinoline, or quinaldine, the mixture became a thick brown paste, which, upon cooling, became a solid mass and would not crystallize from any solvent. No similar reaction could be detected when nicotinic acid, nitrobenzene, m-dinitrobenzene, dimethylaniline, or pyrrole was used under the same conditions.

Reaction of pyridine with some other dicarboxylic acids and their anhydrides. No reaction happened when pyridine was added to molten phthalic anhydride, succinic anhydride, maleic acid, phthalic acid, or succinic acid.

Reaction of methyl maleate with pyridine. Methyl maleate (56 g.) and pyridine (32 g.) were refluxed in a round-bottom flask for 12 hours. The reaction mixture was cooled. The solid methyl fumarate was filtered off and the filtrate was fractionated. After the removal of pyridine and methyl maleate, only a very small amount of brown, tarry substance was left in the flask. The methyl fumarate was recrystallized from 50% aqueous methyl alcohol. White leaflets were obtained, m.p. 102° C. A part of the methyl fumarate was hydrolyzed by 10% sodium hydroxide solution. The solution was then made acidic with sulfuric acid. Fine crystals of fumaric acid were obtained. They decomposed at a temperature above 280° C. In several trials, methyl alcohol or benzene was used as solvent. Less methyl maleate was then converted into methyl fumarate during the refluxing. After filtration, methyl alcohol or benzene and pyridine was recovered by distillation and the remaining solution was fractionated in a Todd fractionating column. A part of the methyl maleate was recovered but a part of it was converted into methyl fumarate during the fractionation. A little tarry substance was again left in the flask.

Reaction of pyridine with maleic anhydride in benzene. A three-neck round-bottom flask, fitted with a dropping funnel, a mechanical stirrer, and a condenser, was used. Maleic anhydride (80 g.) was dissolved in 250 ml. of benzene by warming over a water bath. A solution of 32 g. of pyridine in 50 ml. of benzene was added to the maleic anhydride solution slowly through the dropping funnel. The solution was refluxed and stirred during the addition of pyridine. After all the pyridine had been added, the solution was refluxed for half an hour or more. Brown amorphous powder formed during the addition of pyridine. After it had been cooled to room temperature,

the solution was filtered and the brown powder collected. The powder was extracted several times with ethyl ether and then dried. A Soxhlet extractor was used sometimes for the extraction. In some runs, the ratio of maleic anhydride and pyridine was different. As little as 3 ml. of pyridine was used with 50 g. of maleic anhydride in one run. The products were always similar. The brown amorphous powders from different runs were slightly different in color and solubility, but in general they were soluble in polar solvents and insoluble in non-polar solvents. The solutions were always fluorescent. The powder melted with decomposition at about 110° C., evolving gas, and changed into a water-insoluble substance when baked at 130° C. It showed no positive test for nitrogen by the sodium fusion method. Its dark-colored aqueous solution, when repeatedly treated with active charcoal, became colorless; but when the colorless solution was evaporated to dryness, only traces of crystals were left. Its aqueous solution decolorized bromine in carbon tetrachloride, and was oxidized by alkaline potassium permanganate solution. Recrystallization from water, alcohol, acetone, ethyl acetate, glacial acetic acid, or a mixture of any of these solvents with benzene or ether always gave a gummy substance. An effort at purification was also made by pouring an alcoholic, acetone, or ethyl acetate solution of the powder into ether or benzene. A brown gelatinous precipitate formed, which upon filtration shrank into a deep-brown gum. A part of the powder was also esterified by boiling with excess alcohol. A small amount of concentrated sulfuric acid was used as catalyst. This treatment did reduce its solubility in water, but attempts to isolate the resultant compound by pouring the alcoholic solution into water or distilling off the alcohol gave only a gummy

substance. The reaction was also tried successively in acetone, ether, glacial acetic acid and acetic anhydride solutions at the boiling points of these solvents. The boiling points of acetone and ether are apparently too low to cause reaction; a violent reaction occurred only after nearly all of the solvent had been removed. The reaction in glacial acetic acid or acetic anhydride solution gave a deep-brown solution. When the solvent was distilled off, a thick brown paste was left in the flask. If the solution was poured into benzene, a brown gelatinous precipitate formed which, upon filtration, again, shrank and gave deep-brown-colored gum. The amorphous powder gave a positive ketone test with 2,4-dinitrophenylhydrazine reagent in aqueous acid.

QUANTITATIVE DATA

Determination of molecular weight of the amorphous powder. Beckmann's method of determination of molecular weight was used, with water as the solvent. The results are shown in Table I.

Table I

Molecular Weight of the Powder Determined
by Freezing-Point Lowering.

Powder used, g.	0.1197	0.6824	0.2519
Water, ml.	50	50	50
F. P. depression, ° C.	0.015	0.085	0.025
Mol. Wt.	270	300	380

Determination of neutralization equivalent. A weighed sample of the amorphous powder was dissolved in 100 ml. of water by vigorous stirring. Sometimes the solution was warmed to about 50° C. over a water bath. Owing to the deep color of the solution, potentiometric titration was adopted. Standard sodium hydroxide solution was added to the solution a little at a time from a burette. The pH value was measured by a Beckmann pH meter after each addition of the sodium hydroxide. The end point was found by plotting the pH values against the milliliters of sodium hydroxide added. The neutralization equivalent was calculated by the equation:

$$N. E. = \frac{g \times 1000}{ml \times N}$$

where g = weight of the sample in grams

ml = ml. of sodium hydroxide used in the titration

N = normality of the sodium hydroxide used

The results are shown in Table II.

Table II

Neutralization Equivalent of the Powder Determined
by Electrotitration Method

Sample, g.	0.2904	0.2673	0.1197
Sodium hydroxide used, ml.	2.40	2.30	0.95
Sodium hydroxide, normality	1.045	1.045	1.045
Neutralization equivalent	116	111	121

Disappearance of pyridine in the reaction. A weighed amount (0.3-3.6 g.) of maleic anhydride was placed in a 250-ml. round-bottom flask. Pyridine (5-10 g.) was weighed and delivered into the flask through a weighing pipette. The mixture was warmed to start the reaction, and then refluxed for half an hour to one hour after the spontaneous reaction was over. The reaction mixture was then cooled and 150 ml. of water containing 5 g. of sodium hydroxide was introduced into the flask. The solution was immediately distilled Kjeldahl-fashion into a beaker containing excess standard sulfuric acid solution until 100 ml. of distillate was collected. The excess acid was backtitrated with standard sodium hydroxide solution using methyl orange as indicator. Ground-glass-joint apparatus had to be used as rubber stoppers absorb pyridine badly. The results, in Table III, show that the amount of pyridine disappearing in the reaction was fairly constant and was only a little higher than in a blank run, regardless of the amount of maleic anhydride used. This can have only two meanings. First, pyridine was serving only as a catalyst, or second, the reaction product was easily hydrolyzed during the distillation. According to the reaction of pyridine with molten maleic anhydride and the widely different amounts of pyridine used in preparing the brown amorphous powder, the last interpretation seems very improbable.

Table III

Disappearance of Pyridine During Reaction
with Maleic Anhydride at About 114° C.

1 Run Number	2 Maleic anhydride used, g.	3 Maleic anhydride used, milliequiv.	4 Pyridine used, g.	5 Pyridine used, milliequiv.	6 Acid used to titrate recovered pyridine, milliequiv.	7 Pyridine consumed (column 5 minus column 6), milliequiv.
1	0.3320	3.39	6.0805	76.9	69.6	7.3
2	0.2902	2.96	10.1581	128.4	122.3	6.1
3	0.5676	5.79	5.6652	71.6	68.8	2.8
4	0.4927	5.02	7.0141	88.7	82.6	6.1
5	1.0634	10.48	8.7416	110.4	104.8	5.6
6	1.5724	16.03	9.6753	122.3	115.4	6.9
7	3.6363	37.08	8.2943	104.8	98.4	6.4
8	0.0000	0.00	6.0784	76.8	74.4	2.4

Decrease in acidity during the reaction. Maleic anhydride (0.2 g.) was weighed and dissolved in 10 ml. of benzene in a test tube, and a small amount (0.05-0.7 ml.) of pyridine was added. The test tube was fitted with a small reflux condenser. After refluxing for a measured time, the solution was cooled and poured into 100 ml. of water. The mixture was vigorously stirred for five minutes and then titrated against standard sodium hydroxide solution with continued stirring. A Beckmann pH meter was used. The end point was again found by plotting the pH values against milliliters of sodium hydroxide solution used. In one case, 4 g. of maleic anhydride was dissolved in 200 ml. of benzene, and a 10 ml. aliquot was used for each determination, along with 0.1 ml. of pyridine, added from a Mohr pipette. The results were calculated as the percentage of maleic anhydride remaining after reaction. The results are shown in Table IV.

Appearance of carbon dioxide during the reaction. A 200-ml. three-neck round-bottom flask was fitted with a soda-lime tube, a dropping funnel, and a condenser. The condenser was connected successively to two washing towers, a U-tube, a suction flask and a water pump. The washing towers were filled with concentrated sulfuric acid while the U-tube was filled with Ascarite. A weighed sample of maleic anhydride was dissolved in 50 ml. of toluene in the flask. Pyridine was also dissolved in 10 ml. of toluene and added to the maleic anhydride solution slowly through the dropping funnel. The whole mixture was kept refluxing gently. Gentle suction was applied so that any carbon dioxide evolved would be absorbed by Ascarite in the U-tube. In several runs, aliquots of maleic anhydride in benzene like those prepared for the determination of decrease of acidity were used. One-tenth of a milliliter of pyridine

Table IV

Decrease of Acidity During Reaction of Pyridine
and Maleic Anhydride at 80° C. in Boiling Benzene

Run Number	Maleic anhydride used, g.	Pyridine used, ml.	Time, min.	Acid left after reaction (calculated as maleic anhydride), %
1	0.3100	0.00	0	100.8
2	0.2241	0.05	15	102.5
3	0.2853	0.05	30	97.0
4	0.1964	0.05	60	97.0
5	0.2588	0.05	120	93.2
6	0.1938	0.05	240	82.4
7	0.2034	0.10	15	97.8
8	0.2387	0.10	30	92.4
9	0.2812	0.10	60	88.3
10	0.2196	0.10	120	85.0
11	0.2255	0.10	240	74.6
12	0.2501	0.15	5	97.3
13	0.2077	0.15	15	98.7
14	0.2082	0.15	30	93.5
15	0.2435	0.15	45	88.4
16	0.1596	0.15	75	83.7
17	0.1573	0.15	105	81.2
18	0.2238	0.15	135	78.0
19	0.2932	0.15	165	74.4
20	0.2132	0.15	215	75.7
21	0.2030	0.15	240	74.4
22	0.2840	0.00	240	99.0
23	0.2463	0.15	360	74.5
24	0.1832	0.15	600	75.5
25	0.3012	0.15	1290	74.0
26	0.1989	0.30	15	92.7
27	0.3361	0.30	30	87.7
28	0.3032	0.30	60	76.0
29	0.2868	0.30	180	61.6
30	0.4076	0.30	1260	56.3
31	0.2237	0.50	30	81.1
32	0.2127	0.50	60	75.4
33	0.2082	0.50	120	63.7
34	0.2362	0.70	30	77.9
35	0.2154	0.70	60	71.6
36	0.2303	0.70	120	64.3
37	0.2032	0.10	15	95.3
38	0.2032	0.10	30	91.4
39	0.2032	0.10	60	85.6
40	0.2032	0.10	120	73.1
41	0.2032	0.10	240	62.7

was added from a Mohr pipette. The flask was heated with a water bath. After refluxing for a certain time the flask was cooled but suction was continued for five more minutes to assure that all carbon dioxide evolved during the reaction was absorbed by the Ascarite in the U-tube. The amount of carbon dioxide evolved was found by weighing the U-tube before and after the reaction. The results were again converted into percentage of maleic anhydride unreacted and are shown in Table V. The percentages of maleic anhydride left, found by the titration and the amount of carbon dioxide evolved, agree fairly well. Therefore it is believed that the decrease of acidity during the reaction is due only to the decarboxylation.

Table V

Rate of Appearance of Carbon Dioxide During Reaction
of Maleic Anhydride with Pyridine

Runs in Boiling Toluene*					
1	2	3	4	5	6
Run Number	Maleic anhydride used, g.	Pyridine used, g.	Time, hrs.	Carbon dioxide evolved, g.	Maleic anhydride left after reaction (calculated from column 5), %
1	0.7721	3.505	3	0.0086	97.5
2	1.4493	4.265	4	0.0551	91.5
3	5.0366	7.980	7	0.4225	81.3
Runs in Boiling Benzene					
1	2	3	4	5	6
Run Number	Maleic anhydride used, g.	Pyridine used, g.	Time, min.	Carbon dioxide evolved, g.	Maleic anhydride left after reaction (calculated from column 5), %
1	0.2032	0.10	15	0.0030	96.7
2	0.2032	0.10	30	0.0057	93.7
3	0.2032	0.10	60	0.0087	90.5
4	0.2032	0.10	120	0.0227	75.1
5	0.2032	0.10	240	0.0348	61.8

* Results of these runs are considered less reliable.

DISCUSSION OF RESULTS

Polymeric nature of the reaction. We know that:

1. A vigorous reaction occurs when only two or three drops of pyridine is added to as much as 50 grams of molten maleic anhydride.
2. Regardless of how much pyridine is used to react with maleic anhydride in benzene solution, the products are always similar.
3. Regardless of how much maleic anhydride is used, the amount of pyridine lost through the reaction is nearly constant and is only a little higher than in a blank run.
4. The amorphous powder gives a negative test for nitrogen by the sodium fusion method.

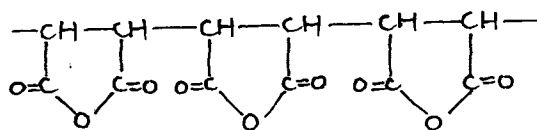
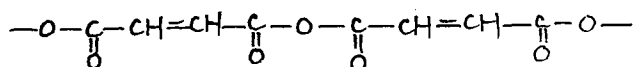
Hence the main reaction is not between maleic anhydride and pyridine as has been suggested (1, 3). It is almost certain that it is essentially a polymerization of maleic anhydride itself. The homopolymerization of maleic anhydride is unusual although copolymerization with various other unsaturated substances is well known (11-18). Nevertheless, maleic anhydride has been polymerized by benzoyl peroxide (19, 20); the product was not described. Maleic anhydride was also reported to give a dark-red compound when reacted with 2,4-dimethylbenzo(g)quinoline in benzene solution (21). The product melted with decomposition at 110-30° C., and could not be purified. From this method of preparation and these properties it is very likely that it was the same type of polymer of maleic anhydride that we have obtained. The brown color of copolymers rich in maleic anhydride was noted by Tong and Kenyon (22), and fluorescence is reported as a property of products resulting from the addition of maleic anhydride to diarylethylenes (23).

Structure of the polymer. The neutralization equivalents of different preparations of the amorphous powder vary somewhat. This can be due to:

1. variation in the amounts of maleic anhydride left unreacted and unseparated in different products,
2. the difference in degree of decarboxylation, due in turn to the difference in amount of pyridine used and the time of reaction, or
3. experimental error due to the small titers involved.

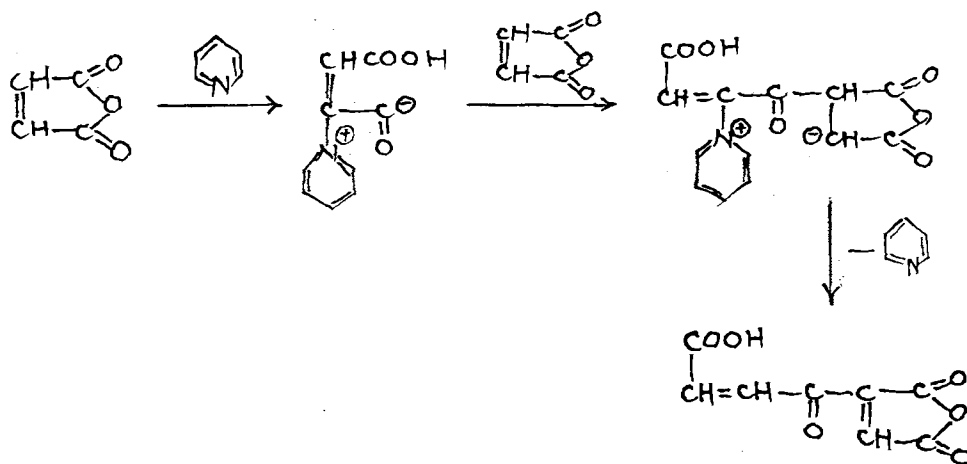
Molecular-weight determination should give some idea of the size of the molecule of the polymer. But it is also complicated by the presence of unreacted maleic anhydride and furthermore by the ionization of the acid groups (already present or produced by hydrolysis) of the polymer in aqueous solution. Such a difficulty was noted by Bartlett and Nozaki (19) in the determination of molecular weight in water of a copolymer of maleic anhydride and allyl acetate. They overcame the problem by determining the molecular weight in acetone solution; some such procedure is desirable for our polymers also.

As already noted, the decrease of acidity during the reaction as measured by titration and the amount of carbon dioxide evolved agree fairly well. This suggests that the decrease of acidity is due to decarboxylation and not due to polymerization. The possible polymerization of maleic anhydride, without loss of acidity, can lead to the following two structures:



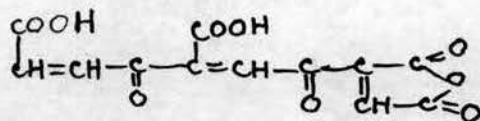
The first structure is bound together in part by anhydride linkages, which should be broken during esterification. Either ethyl maleate or ethyl fumarate would be the product. But the esterification of the amorphous powder only decreased the solubility of the powder and gave a gummy product; no ethyl maleate or ethyl fumarate could be isolated. The second formula agrees with the postulated structure of the maleic anhydride unit in copolymers, and probably is representative of the peroxide-produced polymer of maleic anhydride made by Bartlett and Nozaki (19). But the positive ketone test given by our product, its unsaturation as shown by the alkaline permanganate and the bromine tests, and a neutralization equivalent of about 110, can not be explained by this formula; furthermore the decarboxylation of an anhydride is most unusual.

By analogy with the action of pyridine upon quinones, the following mechanism and products of its reaction with maleic anhydride may be written:



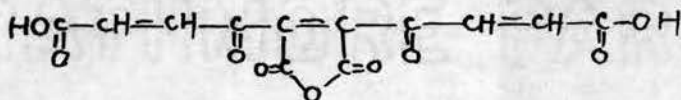
(VII)

By repetition of the above steps, compound (VII) can yield the unsymmetrical trimer (VIII) and higher polymers.



(VIII)

Or compound (VII) may react with the simple betaine in reverse manner giving the symmetrical trimer (IX) which cannot polymerize further, at least not by the same mechanism.



(IX)

All these structures for the polymer, (VII), (VIII), and (IX), account for many of the observed properties of our product. The multi-conjugated double-bond structure explains the color and the unsaturation of the polymer. All these structures are either β -ketonic acids or vinylogs of α -ketonic acids which will give ketone tests and lose carbon dioxide readily. But all these structures would have acidity substantially less than the original maleic anhydride, even without any decarboxylation, and no such loss has been observed, as already mentioned. We must therefore assume that these keto-acid units are cleaved apart by alkali so readily as to be titratable as dibasic acids.

By analogy with the behavior of quinones neither structure (VIII) or (IX) seems very probable, because the polymerization of quinones is not known to go farther than trimers. Yet the molecular weight, the equivalent weight, and the extent of decarboxylation are all too low to suggest structure (VII). The observed molecular weight of about 300 and the equivalent weight of 110 mean roughly three acid groups per molecule.

Even if these are only slightly ionized, the true molecular weight must be definitely in excess of 300. This is evidence for structure (VIII) and higher polymers. Again structure (IX) can lose only one-third of its original acidity through decarboxylation (assuming dibasicity of keto-acid units); while observed loss of acidity (see Table IV) went as high as 44% in 21 hours. Thus the weight of evidence is in favor of compound (VIII) and higher polymers.

Catalytic influence of pyridine bases. We have supposed that pyridine bases catalyze the polymerization of maleic anhydride through the betaine salts. This satisfactorily explains the failure of nicotinic acid as a catalyst because it already exists in betaine structure. The only basic derivative of pyridine that does not polymerize maleic anhydride is 2,4,10-trimethylbenzo(g)quinoline, which undergoes a Diels-Alder reaction instead (21). There is no good explanation of the failure of dimethylaniline, a base of about the same strength as pyridine, to act as a catalyst unless it is the much greater reactivity of some hydrogens on this benzene ring. Certainly, more work should be done to clarify all the points, but the author spent most of his time in fruitless trials of isolation and purification of the powder before he realized that it is a polymer and therefore very difficult to purify by standard organic procedures.

Suggestions for further work. The writing of the thesis in order to fulfill a part of the requirement for a master's degree does not mean that the experimental work is complete. Polymaleic anhydride might be prepared by the method of Bartlett and Nozaki (19) in order to study its properties and compare it with the polymer obtained in the present work. A quantitative determination of carbon and hydrogen will certainly throw some light on the

structure of the polymer, but unfortunately the powder is by no means pure, especially since it has been more or less decarboxylated even when prepared at minimum temperatures. The analogous polymers of p-benzoquinone are of course not subject to decarboxylation. Determination of pyridine liberated (if any is present) from the polymer by sodium hydroxide would measure the amount associated with acid groups, and total nitrogen content less the nitrogen of such pyridine would establish the extent to which the pyridine nucleus is permanently involved in the polymerization. Measurement of carbonyl groups in the polymer, either gravimetrically with 2,4-dinitrophenylhydrazine or volumetrically with hydroxylamine hydrochloride, would contribute further evidence on structure. Reasoning by analogy from the behavior of methyl acetylenedicarboxylate, maleic anhydride, and p-benzoquinone, maleimide and esters of azodicarboxylic acid will undergo this type of polymerization. The chief value in such extension of the reaction would be the possibility of finding polymers easier to purify and characterize than the one from maleic anhydride.

SUMMARY

The reaction between maleic anhydride and pyridine has been studied, and found to be essentially a polymerization of maleic anhydride. Pyridine, 4-ethylpyridine, α -picoline, nicotine, quinoline, isoquinoline, and quinaldine act as catalysts for the polymerization while nicotinic acid, pyrrole, dimethylaniline, nitrobenzene, and m-dinitrobenzene do not. Phthalic anhydride, maleic acid, phthalic acid, succinic acid, and succinic anhydride do not polymerize under the same conditions. Although completely satisfactory purification of the polymer was not achieved, its molecular weight and equivalent weight were determined. The quantitative relationship between decrease of acidity and decarboxylation during the reaction was also studied. A tentative structure for the polymer and mechanism for its formation are proposed.

BIBLIOGRAPHY

1. Smith, Bryant, and Mitchell, J. Am. Chem. Soc. 63, 1700 (1941).
2. Mullen and Pacsu, Ind. Eng. Chem. 34, 1209 (1942).
3. Johnson and Hamilton, J. Am. Chem. Soc. 63, 2864 (1941).
4. Salminen, Master's Thesis, Clark Univ. (1933).
5. Hutcheson, Report in Chem. 620, Okla. A. & M. College (1940).
6. Holmes, Organic Reactions Vol. IV, Chap. II (1948).
7. Diels and Kassebart, Ann. 530, 51 (1937); 536, 78 (1938).
8. Diels and Preiss, Ann. 543, 94 (1939).
9. Diels and Thiele, J. prakt. Chem. 156, 186 (1940).
10. Nozaki, J. Am. Chem. Soc. 63, 2681 (1941).
11. Wagner-Jauregg, Ber. 63, 3213 (1930).
12. Alfrey and Lavin, J. Am. Chem. Soc. 67, 2044 (1945).
13. Unruh and Kenyon, U. S. Pat. 2,452,165 (1948).
14. McDowell and Kenyon, U. S. Pat. 2,313,565 (1947).
15. Simpson, J. Chem. Soc. 94 (1946).
16. Hurdis, U. S. Pat. 2,467,033 (1949).
17. Seymour, Branum, and Hayward, Ind. Eng. Chem. 41, 1482 (1949).
18. Seymour, Harris, and Branum, Ind. Eng. Chem. 41, 1509 (1949).
19. Bartlett and Nozaki, J. Am. Chem. Soc. 68, 1495 (1946).
20. Marvel, Prill, and DeTar, J. Am. Chem. Soc. 69, 52 (1947).
21. Johnson and Mathews, J. Am. Chem. Soc. 66, 210 (1944).
22. Tong and Kenyon, J. Am. Chem. Soc. 71, 1925 (1949).
23. Bergmann and Szmuszkowicz, J. Am. Chem. Soc. 70, 2748 (1948).

Typed by:

Mrs. J. O. Richardson