

ADDITION OF ACID ANHYDRIDES
TO OLEFINS

By

DOYLE SIMPSON

Bachelor of Science

Oklahoma Agricultural and Mechanical College

Stillwater, Oklahoma

1951

Submitted to the Faculty of the Graduate School of
the Oklahoma Agricultural and Mechanical College
in Partial Fulfillment of the Requirements
for the Degree of
MASTER OF SCIENCE
August, 1953

OKLAHOMA
AGRICULTURAL & MECHANICAL COLLEGE
LIBRARY
NOV 16 1953

ADDITION OF ACID ANHYDRIDES
TO OLEFINS

Thesis Approved:

A. D. Dermer

Thesis Adviser

H. S. Gentry

W. C. G. Gentry

Dean of the Graduate School

ACKNOWLEDGEMENT

The author is deeply grateful to Dr. O. C. Dermer for suggesting this problem and for his continuous guidance. He is also grateful to the Department of Chemistry for the aid given him in the form of a teaching fellowship during the time this work was being done.

TABLE OF CONTENTS

	Page
Introduction	1
Historical	2
Experimental	5
Discussion	16
Summary	18
Bibliography	20

INTRODUCTION

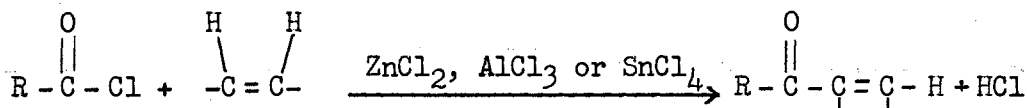
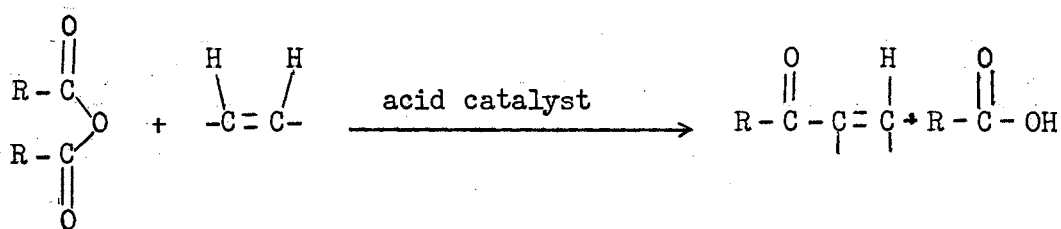
The reaction of monocarboxylic acid anhydrides with olefins to form unsaturated ketones has been known since 1894 when it was reported by Kondakov (13), who showed that the interaction of equimolecular amounts of trimethylethylene and acetic anhydride at room temperature in the presence of zinc chloride gave "methylmesityl oxide", 3,4-dimethyl-3-penten-2-one, along with some of the olefin-anhydride adduct and some tert-amyl acetate. Isobutylene similarly gave tert-butyl acetate and mesityl oxide. Ketones have been produced commercially in this manner from diisobutylene and acetic anhydride (3). These ketones are useful as solvents and plasticizers.

The purpose of this research was to extend this reaction to anhydrides and olefins not previously tried and particularly to effect the reaction of cyclic dicarboxylic acid anhydrides. These cyclic anhydrides should produce unsaturated keto-acids if they react like the monocarboxylic anhydrides.

HISTORICAL

Kondakov (13) showed in 1894 that the interaction of equimolecular amounts of trimethylethylene and acetic anhydride at room temperature in the presence of zinc chloride gave 3,4-dimethyl-3-penten-2-one, along with some 1,1,3-trimethyl-3-oxobutyl acetate and some tert-amyl acetate. Isobutylene similarly gave tert-butyl acetate and mesityl oxide.

The reaction is a Friedel-Crafts-type synthesis similar to the reaction of acid halides with olefins, as illustrated below:



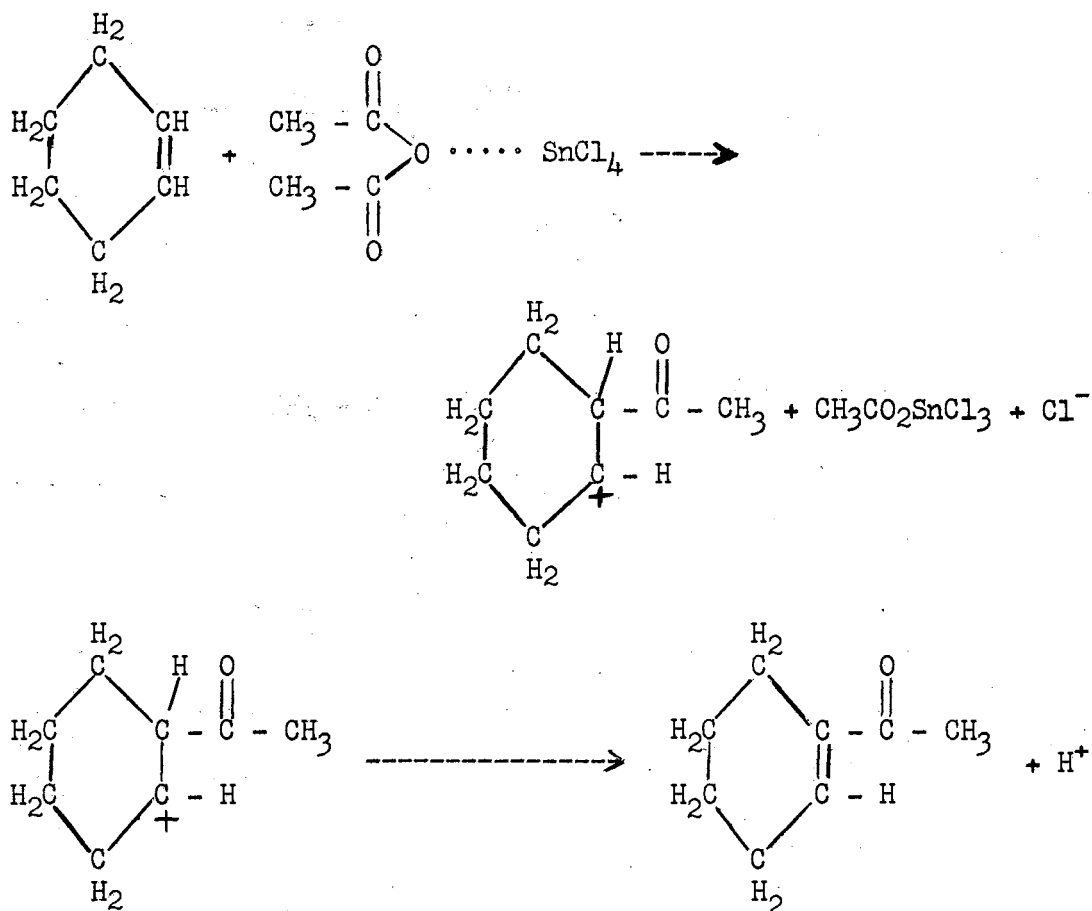
Ebel and Goldbert (7) treated cyclohexene with acetic anhydride containing acetylsulfoacetic acid, $\text{CH}_3\text{CO}_2\text{SO}_2\text{CH}_2\text{CO}_2\text{H}$, the latter being formed by treating acetic anhydride with concentrated sulfuric acid. A thirty per cent yield of 1-acetylcyclohexene was reported. Attempts by the same workers to acetylate ethylene, methyl cinnamate, safrole, and pinene in the same manner were unsuccessful.

Acetic anhydride reacts with diisobutylene to produce isomeric methyl octenyl ketones. A number of condensing agents have been found to be effective. These include zinc chloride (1,3), aluminum chloride (8), boron trifluoride (2,3), hydrogen fluoride (2), and sulfuric acid (1,3). Sulfonated fatty acids, aromatic sulfonic acids, and alkane-sulfonic acids have also been reported as good catalysts. The following compounds and yields have been claimed: acetylsulfoacetic acid, 88% (5,7), 30% (7); ethanesulfonic acid, 42.8%; m-benzenedisulfonic acid 40.6%; p,p'-diphenyldisulfonic acid, 28.4%; and a dichlorobenzene-sulfonic acid, 28% (14). Para-toluenesulfonic acid, chlorosulfonic acid, and a mixture of acetic acid and sulfamic acid have also been used (14).

Acetic anhydride with ethanesulfonic acid reacts with "polypropylene" to give a 42.8% yield of ketones (12).

Acetic anhydride and diisobutylene react in the vapor phase over activated alumina impregnated with ferric chloride to give a forty per cent yield per pass of the unsaturated ketone (6).

The reaction between acetic anhydride and cyclohexene has been well studied. Royals and Hendry (17) have made a study of the factors influencing the yield of 1-acetylcyclohexene in the presence of aluminum chloride, zinc chloride, and stannic chloride. The best results were obtained with stannic chloride when the acetic anhydride was added dropwise. A 54% yield of ketone was reported for this procedure. The following mechanism was given for the reaction:



Petrov and Kaplan (16) obtained a 33% yield of 3-tert-butyl-6,6-dimethyl-3-hepten-2-one from acetic anhydride, zinc chloride and 2,2,7-trimethyl-4-octene.

Cook, Krimmel, and Whitmore (4) have apparently successfully used the reaction of acid anhydrides with olefins to prepare ketones, but the work has not been published.

To become familiar with technique the known reaction between acetic anhydride and diisobutylene was undertaken.

EXPERIMENTAL

Preparation of Methyl Octenyl Ketones:

One hundred and twelve grams (1 mole) of diisobutylene and 102 grams (1 mole) of acetic anhydride were placed in a three-necked flask fitted with a thermometer and an electric stirrer. Sixty-eight grams (0.5 moles) of granular zinc chloride was added slowly with stirring. The temperature rose immediately. The flask was cooled in an ice bath so that the temperature remained between 20-30° during the addition of the zinc chloride. A yellow color developed which gradually darkened to brown. A fine white solid was suspended in the mixture.

The mixture was stirred for three hours and the solid was filtered out. This weighed 24.2 grams and was assumed to be a complex between the zinc chloride and the ketone. No attempt was made to decompose it since Byrns and Doumani (3) reported that they were unsuccessful in obtaining the free ketone from this complex. The filtrate was washed with three 200-ml. portions of water. This removed some of the brown color. The acetic acid formed in the reaction was removed by washing with a dilute solution of sodium hydroxide. Water was used to remove any sodium hydroxide.

The oil (107.4 grams) was distilled at atmospheric pressure in a Todd column. Twenty-four grams of diisobutylene was recovered. A yield of 59 grams (36.7%) of methyl octenyl ketones (b.p. 186-196°)

was obtained. This fraction gave a 2,4-dinitrophenylhydrazone but no attempt was made to determine the melting point of the derivative because commercial diisobutylene is a mixture of isomers and so at least two products are possible.

Preparation of 1-Acetylcyclohexene:

This was first attempted using sulfuric acid as a catalyst. Fifty-one grams (0.5 moles) of acetic anhydride was placed in a three-necked flask equipped with a stirrer and a thermometer. The flask was cooled in an ice bath. One milliliter of concentrated sulfuric acid was added and then forty grams (0.5 moles) of cyclohexene was added in small portions with stirring. A small temperature rise was noted.

The stirring was discontinued after 4 hours and the mixture was steam-distilled. A vigorous reaction began with the first addition of steam and some product was lost. The oil that was distilled gave no solid derivative with semicarbazide hydrochloride.

The reaction was next attempted using freshly fused zinc chloride. Equimolar quantities of cyclohexene, acetic anhydride and zinc chloride were used. After 8 hours the oil was decanted from a small amount of solid in the flask and placed in a refrigerator overnight. The color became slightly darker and two layers were apparent. Each of these layers was washed in the manner of the previous run. The lower layer emulsified on washing with water and was steam-distilled. Some oil, lighter than water, came over and another layer, heavier than water, remained in the flask. Both these layers were combined with the upper layer from the reaction flask and distilled in a Todd column. A yield of 6.6 grams of material boiling at 203-206° was obtained. This

fraction gave a semicarbazone, m.p. 218-220°. The literature boiling point of 1-acetylcyclohexene is 201-202° and that for the melting point of its semicarbazone is 221° (9).

Attempted Preparation of Acetylcyclohexane:

It has been reported that saturated ketones result from the reaction of acid chlorides with olefins if aluminum chloride is used as a catalyst and the reaction is carried out in cyclohexane (15).

One-half mole of anhydrous aluminum chloride was added to 100 ml. of cyclohexane in a three-necked flask fitted with a stirrer, a buret, and a thermometer. The flask was immersed in an ice bath and 0.5 moles of acetic anhydride was added. One-half mole of cyclohexene was dripped in slowly from the buret with stirring. The mixture became too gummy to stir soon after all the cyclohexene had been added.

The mixture was poured on cracked ice, washed as in the previous runs, and distilled. Only 1 ml. of material boiling at the temperature expected for acetylcyclohexane (179-180°) was obtained, and even this fraction gave tests for active unsaturation. Higher cuts appeared to be 1-acetylcyclohexene. Yields were poor and the product was dark due to some aldol condensation caused by evolved hydrogen chloride.

Preparation of 1-Propanoylcyclohexene:

Eighty-two grams (1 mole) of cyclohexene and 130 grams (1 mole) of propionic anhydride were placed in a three-necked flask fitted with an electric stirrer and a thermometer. Sixty-eight grams (0.5 moles) of anhydrous zinc chloride was added in small portions. The temperature rose immediately from 28° to 42° so the flask was cooled in an ice bath.

A light brown color developed and gradually darkened.

The flask was kept in the ice bath and stirred for 6 hours and then stirred an additional 6 hours at 20°. The mixture was placed in an ice box for one day. It became quite dark.

The contents of the flask were washed in the usual manner and distilled in an ordinary distilling flask. Twenty-three grams of material boiling at 217-220° was obtained. The literature value given in Beilstein for the boiling point of 1-propanoylcyclohexene is "about 218°" but the compound was not certainly identified (18). A large amount of high-boiling material remained in the flask. The 217-220° fraction gave a semicarbazone, m.p. 186-189°. The cut was redistilled and the molar refraction was determined. The observed value was 41.1 and the calculated value was 40.4.

Analytical data: Calculated for $C_9H_{14}O$: C, 78.21; H, 10.21; molecular weight 138. Found. C, 78.18, 78.44; H, 10.12, 10.28; molecular weight (cryoscopically in benzene), 132.

Preparation of Mesityl Oxide:

One-fourth mole of anhydrous zinc chloride was added to one-half mole of acetic anhydride in a three-necked flask fitted with a stirrer and a gas-dispersing tube. Isobutylene was bubbled in for an hour with stirring while the flask was cooled in tap water. There was some heat evolved. The mixture was stirred an additional seven hours and washed as in the previous runs. The oil seemed to be rather soluble in water and some was lost in the washing. The small yield of oil was not distilled. It gave a positive test for a ketone when treated with semicarbazide hydrochloride.

Another attempt to produce the desired reaction was tried using a Parr hydrogenation apparatus. The tank was charged with isobutylene to a pressure of 25 lb./sq. in. One-fourth mole of acetic anhydride and one-eighth mole of anhydrous zinc chloride were used in the reaction bottle. The mixture was shaken for 6 hours during which time there was a pressure drop of only 4 lbs./sq. in. in the tank. The liquid became quite dark. The product was worked up as in the previous runs but no ketone was isolated.

A third attempt was made using acetylsulfoacetic acid. This was prepared by treating one-half mole of acetic anhydride cooled in an ice bath with one-fourth mole of concentrated sulfuric acid. After the initial reaction had slowed this mixture was heated on a steam bath for thirty minutes and added with one-half mole of acetic anhydride to a three-necked flask fitted with a stirrer and a gas-dispersing tube. Isobutylene was bubbled in with stirring while the flask was cooled in an ice bath. One-half mole of isobutylene was dissolved in one hour. The ice bath was removed, the flow of isobutylene was stopped, and the mixture was stirred for six hours. The contents of the flask were dissolved in ether and washed in the customary manner. The ether was stripped off and the residue was distilled in a Todd column. One gram of material boiling at 130-131°, the literature value (10) for the expected product, was obtained.

Preparation of 2-Methyl-2-Hexen-4-one:

One mole of propionic anhydride and one-half mole of anhydrous zinc chloride were placed in a three-necked flask fitted with a

stirrer and a gas-dispersing tube. The flask was placed in a water bath maintained at approximately 18° . Isobutylene produced by passing tert-butyl alcohol over activated alumina at 400° was bubbled in for an hour. A dark brown color developed.

The flask was allowed to stand overnight in a refrigerator and washed in the customary manner. The oil was distilled in a Todd column and yielded 16 grams of material boiling at $148-157^{\circ}$. This fraction gave a semicarbazone, m.p. 162° . The recorded boiling point for 2-methyl-2-hexen-4-one is 148° and the melting point of the semicarbazone is 162° (11).

Preparation of 1-Benzoylcyclohexene:

An attempt was made to combine benzoic anhydride with cyclohexene using boron trifluoride as a catalyst. One-half mole of benzoic anhydride was dissolved in 100 ml. of cyclohexene. The solution was placed in a three-necked flask fitted with a thermometer, a stirrer, and a gas-dispersing tube. The flask was cooled in an ice bath and 25 grams of boron trifluoride was dissolved as determined by the difference in weight of the flask. The contents of the flask were stirred for 3 hours. A large amount of heat was evolved. The material became very viscous and the stirring was discontinued. A slurry of sodium carbonate was used to neutralize the mixture. The solid was filtered and the small amount of oil in the filtrate was separated. It gave no semicarbazone.

A second attempt using anhydrous zinc chloride gave no ketone.

A third attempt was made using anhydrous aluminum chloride. One-half mole of benzoic anhydride was dissolved in 100 ml. of cyclohexene and placed in a flask fitted with a stirrer and a thermometer. One-half mole of anhydrous aluminum chloride was added with stirring over an interval of one hour. A temperature rise followed each addition of aluminum chloride and a dark brown color developed. After 6 hours the stirring had to be discontinued because the contents of the flask became too viscous.

The mixture was neutralized with sodium hydroxide and steam-distilled. An oil, lighter than water, distilled first and then a fraction heavier than water came over. The heavier oil gave a solid derivative when treated with semicarbazide hydrochloride and added bromine. This oil was redistilled. Six grams of material, all boiling above 300° , was obtained.

The same procedure was followed again except that 400 ml. of ether was used as a solvent. No ketone was isolated.

Forty grams of benzoic anhydride was dissolved in 50 ml. of cyclohexene and stirred. Twenty ml. of concentrated sulfuric acid was added. A large amount of heat was liberated and a gummy material was formed in the flask. An additional 50 ml. of cyclohexene was added and the flask was cooled to room temperature in an ice bath.

The mixture was stirred for 6 hours, neutralized with sodium hydroxide and then steam distilled. A large amount of cyclohexene distilled and then 12.3 grams of an oil heavier than water came over. This heavier oil resembled the ketone from the earlier run.

The two yields were combined and distilled in a Todd column. All the material boiled at 130-135° at 8 mm. It was distilled at reduced pressure two additional times. The last time four cuts were taken but they had essentially the same index of refraction. The molar refraction was 53.95 before the last fractionation and 53.88 afterward. The calculated value for 1-benzoylcyclohexene is 50.78. A molecular weight was determined cryoscopically in benzene. The experimental value was 207 while the calculated value is 186.1.

Reactions between the olefins and cyclic anhydrides in Table I were tried with various catalysts. In each case, except where noted, the reaction mixture was extracted with base or sodium carbonate and acidified in an attempt to isolate the keto-acid. No keto-acids were isolated.

In the maleic anhydride runs the product was neutralized with sodium carbonate and then filtered. The filtrate was acidified and any solid filtered out. It was assumed that the keto-acid would precipitate from this acid solution. Products of treating maleic anhydride with cyclohexene and with isobutylene gave identical solids when treated in the described manner. The neutralization equivalents of both products were 144 as compared to 180 for the expected product. An identical run omitting the olefin gave the same product. Ignition of this material left a white residue which was basic in water solution and gave a flame test for sodium. From these results the precipitated acidic product was identified as monosodium maleate.

Table I
Testing of Cyclic Anhydrides

<u>Anhydride</u>	<u>Olefin</u>	<u>Solvent</u>	<u>Catalyst</u>
Phthalic	Isobutylene	Methyl alcohol	Zinc chloride
Phthalic	Isobutylene	Cellosolve	Zinc chloride
Phthalic (molten)	Isobutylene	none	Zinc chloride
Phthalic	Cyclohexene	none	Boron trifluoride
Maleic ^a	Diisobutylene	none	Zinc chloride
Maleic ^a	Diisobutylene	Isopropyl ether	Zinc chloride
Maleic ^b	Styrene	none	Zinc chloride
Maleic	Cyclohexene	Ether	Boron trifluoride
Maleic	Propylene	Ether	Boron trifluoride
Maleic	Isobutylene	Ether	Boron trifluoride
Maleic (molten)	Cyclohexene	none	Zinc chloride
Succinic	Cyclohexene	Dioxane	Boron tribluoride
Succinic	Cyclohexene	none	Zinc chloride

^a Product tested directly for ketones without extracting

^b Polymerized; no attempt to isolate product

Reactions of acetic anhydride with the following reagents were tried. No ketones were formed.

<u>Olefin</u>	<u>Catalyst</u>	<u>Results</u>
α -Pinene	Zinc chloride	Very exothermic; polymerized
Allyl chloride	Aluminum chloride	Some polymerization
Allyl chloride	Zinc chloride	Some polymerization
Vinyl acetate	Sulfuric acid	No sign of reaction
Styrene	Sulfuric acid	Very exothermic; polymerized
Trichloroethylene	Aluminum chloride	No sign of reaction
Propylene	Acetylsulfoacetic acid	Polymerized
Vinyl bromide	Sulfuric acid	No sign of reaction

Thirty-four grams of chloroacetic acid anhydride was dissolved in 50 ml. of cyclohexene and placed in a three-necked flask fitted with a stirrer and a thermometer. The flask was cooled in an ice bath and 20 ml. of concentrated sulfuric acid was added slowly. There was a rapid temperature rise at first. The temperature was kept below 35°.

The mixture was stirred for 9 hours at room temperature. It was washed in the usual manner with sodium hydroxide solution and water. The oil layer was distilled. Sulfur dioxide was evolved during the distillation and a large amount of polymer was left in the flask. The distillate gave only a slight precipitate when treated with semicarbazide hydrochloride.

Another attempt was made to cause chloroacetic acid anhydride to react with cyclohexene using acetylsulfoacetic acid as a catalyst. No ketone was isolated.

Attempts were made to cause acetic anhydride and isobutylene to react in the vapor phase over activated alumina at various temperatures. Acetic anhydride was vaporized by dripping it into a heated flask and then passing it along with isobutylene through the catalyst tube.

The flow rates in all cases were approximately 0.4 ml. (liquid) of acetic anhydride per minute and 150 ml. of isobutylene gas per minute.

<u>Temperature</u>	<u>Results</u>
210° ^a	Only acetic anhydride was recovered
250°	Some acetic acid was formed
280°	Some acetic acid was formed
340°	Some acetone was formed

No ketone except acetone could be identified in the effluent. Acetic anhydride is known to produce acetone on pyrolysis.

At this point it seemed useless to try more reactions with cyclic anhydrides as they did not appear to give the desired reaction. It did not appear profitable to pursue the reaction of monocarboxylic acid anhydrides further since it appeared that only the more reactive olefins and anhydrides could be used. Many of the same compounds could be produced more easily from the acid chlorides and olefins.

^a No alumina was used in this run, only the hot glass tube.

DISCUSSION

It has been pointed out in the Historical part that this reaction is believed to proceed by the formation of a carbonium ion from the anhydride under the influence of the acid catalyst and then the attack of this carbonium ion on the double bond. Anhydrides are not as suitable as acid chlorides as a source of carbonium ions but are used when the acid halide is less accessible.

Olefins themselves are converted to carbonium ion by Lewis acids, and these carbonium ions may then react preferentially. The polymerization of olefins proceeds by such a mechanism and with the same catalysts. The large number of failures and poor yields in this work indicate that the carbonium ion from the olefin either is formed faster or adds to an olefin molecule faster than the one from the acid anhydride does. The cyclic anhydrides are apparently stabilized by the ring structure and do not readily form carbonium ions. Styrene polymerized so rapidly that there was no chance for attack by the acylcarbonium ion. Polymerization of the olefins was worse when no solvent other than excess olefin was used, but it was never completely prevented by change of solvent, catalyst, or temperature. Indeed, more severe conditions and catalysts only appeared to increase the amount of polymer with little effect on the amount of ketone formed. It is, of course possible that part of the observed polymerization is

that of the unsaturated ketones, as suggested by Royals and Hendry (17).

The present results verify those of others for acetic anhydride with diisobutylene and cyclohexene, and supply new examples of the reaction in propionic anhydride and isobutylene, propionic anhydride and cyclohexene, and benzoic anhydride and cyclohexene. Higher anhydrides were not immediately available and were not tried. It appears that only the more reactive olefins can be used successfully. The poor results with the gaseous olefins may be due to the difficulty of keeping them in solution with the anhydride. No explanation is available for the difficulty in purifying the 1-benzoylcyclohexene produced.

Altogether, no more work on this reaction can be recommended. It appears to be less suitable for synthetic work than the better-known acylation of olefins with acid chlorides, in spite of the contrary observation of Royals and Hendry (17) for the one acylation they studied intensively, and of the presumable success of Cook, Kimmel, and Whitman (4).

SUMMARY

Maleic anhydride, succinic anhydride, and phthalic anhydride did not react with olefins to form keto-acids in the presence of Friedel-Crafts-type catalysts. Raising the temperature of the reaction mixture merely resulted in polymerization of the olefins.

Acetic anhydride reacted with diisobutylene in the presence of zinc chloride to form isomeric methyl octenyl ketones, and likewise with cyclohexene to form 1-acetylcyclohexene. Sulfuric acid was not effective as a catalyst for the reaction of acetic anhydride and cyclohexene. Only unsaturated ketones were formed when aluminum chloride was used as a catalyst with cyclohexane as a solvent. Acetic anhydride reacted with isobutylene to form mesityl oxide with either zinc chloride or acetyl sulfoacetic acid as catalyst; however, the yields were poor. Acetic acid did not react with isobutylene in the vapor phase over hot activated alumina.

Acetic anhydride did not react with trichloroethylene, vinyl bromide, vinyl acetate, α -pinene, styrene, propylene, or allyl chloride in the presence of various acid catalysts.

Results with chloroacetic acid anhydride and cyclohexene were inconclusive. However, it appears that no desired ketone was formed. Propionic anhydride reacted like acetic anhydride with isobutylene and cyclohexene.

Benzoic anhydride evidently reacted with cyclohexene to give impure 1-benzoylcyclohexene. The yields utilizing sulfuric acid as a catalyst were much better than those with aluminum chloride, and zinc chloride and boron trifluoride were entirely ineffective.

The reaction offers little promise of any general usefulness for the preparation of unsaturated ketones.

BIBLIOGRAPHY

- (1) Byrns, U. S. Patent 2,355,703, August 15, 1944; via C.A., 39, 87 (1945).
- (2) Byrns, U. S. Patent 2,463,742, March 8, 1949; via C.A., 43, 4685 (1949).
- (3) Byrns and Doumani, Ind. Eng. Chem., 35, 349-53 (1943).
- (4) Cook, Krimmel, and Whitmore, work cited by Brooks, The Chemistry of the Nonbenzenoid Hydrocarbons, 2nd ed., Reinhold, New York, 1950, page 398.
- (5) Doumani and Cuneo, U. S. Patent 2,411,823, November 26, 1946; via C.A., 41, 1234 (1947).
- (6) Doumani and Cuneo, U. S. Patent 2,438,334, March 23, 1948; via C.A., 42, 4602 (1948).
- (7) Ebel and Goldberg, Helv. Chim. Acta., 10, 677-80 (1927); via C. A., 22, 393 (1928).
- (8) Gutsche and Johnson, J. Am. Chem. Soc., 68, 2239-45 (1946).
- (9) Heilbron, Dictionary of Organic Compounds, Oxford University Press, New York, 1943, Vol. I, Revised Edition, page 10.
- (10) Heilbron, Dictionary of Organic Compounds, Oxford University Press, New York, 1936, Vol. II, page 593.
- (11) Heilbron, Dictionary of Organic Compounds, Oxford University Press, New York, 1936, Vol. II, page 731.
- (12) Johnson, U. S. Patent 2,458,603, January 16, 1949; via C.A., 43, 3441 (1949).
- (13) Kondakov, Ber. 27, R 941 (1894).
- (14) Lukes and Swann, U. S. Patent 2,457,696, December 28, 1948; via C.A., 43, 3442 (1949).
- (15) Nenitzescu and Cioranescu, Ber., 69, 1820-1823 (1936).

- (16) Petrov and Kaplan, Izvest. Akad. Nauk. S. S. S. R., Otdel Khim. Nauk, 295-308 (1947); via C.A. 43, 1718 (1949).
- (17) Royals and Hendry, J. Org. Chem., 15, 1147-54 (1950).
- (18) Wallach, Churchill, and Rentschler, Ann., 360, 57 (1908);
via Beilsteins Handbuch der Organischen Chemie, 4th ed.,
Julius Springer, Berlin, 1933, Vol. 7, page 63.

VITA

Doyle Simpson
candidate for the degree of
Master of Science

Thesis: ADDITION OF ACID ANHYDRIDES TO OLEFINS

Major: Organic Chemistry

Biographical and Other Items:

Born: March 12, 1929, Holdenville, Oklahoma

Undergraduate Study: Murray State School of Agriculture,
Tishomingo, Oklahoma, 1947-49; Oklahoma Agricultural
and Mechanical College, 1949-51, B.S. Degree, 1951.

Graduate Study: Oklahoma Agricultural and Mechanical
College, 1951-53

Experiences: Teaching fellowship in Chemistry Department,
Oklahoma Agricultural and Mechanical College, 1951-53.

Member of American Chemical Society, Phi Lambda Upsilon, Phi
Kappa Phi.

THESIS TITLE: ADDITION OF ACID ANHYDRIDES TO OLEFINS

AUTHOR: Doyle Simpson

THESIS ADVISER: Dr. O. C. Dermer

The content and form have been checked and approved by the author and thesis adviser. Changes or corrections in the thesis are not made by the Graduate School office or by any committee. The copies are sent to the bindery just as they are approved by the author and faculty adviser.

TYPIST: Mrs. J. O. Richardson