

Another point of interest that develops from this work is the difference between the very alkali labile hydrolytic-type dextrans from the continued attack of the aqueous acid and the very alkali stable yellow dextrans from long roasting of starch. The two types of "dextrans" are obviously not the same chemically.

Summary

1. When a given starch, amylose or dextrin is heated with dilute or concentrated alkali, only a very definite fraction is destroyed by the alkali with a corresponding increase in the reducing value of the system as measured by the hypiodite method.
2. Starch or amylose which has not been degraded is substantially unaffected by hot aqueous alkali.
3. Two methods are given for quantitatively estimating the portion of starch which is stable toward alkali.
4. Aqueous acid, certain heat treatment or grinding in the presence of moisture are capable of producing a high alkali unstable fraction from a given starch or amylose.
5. Yellow dextrin made by roasting starch contains a large amount of material stable toward alkali.

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The Interaction of Ketene with Aromatic Aldehydes and its Bearing on the Perkin Reaction

BY CHARLES D. HURD AND CHARLES L. THOMAS¹

Shortly after discovering diphenylketene Staudinger² found that it would add to quinone and produce a β -lactone. Ketene itself failed to do this. Hence, this property of addition at carbonyl groups was ascribed to the disubstituted ketenes.

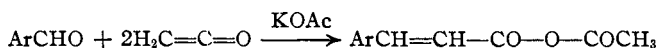
The present work concerns itself with the reaction of ketenes with aromatic aldehydes. From Staudinger's work it would be anticipated that no reaction should occur when ketene was passed into benzaldehyde. None was observed. If, however, a little anhydrous potassium acetate was present, ketene then reacted vigorously with benzaldehyde or furfural or *m*-nitrobenzaldehyde to produce dark colored, viscid liquids.

If the mechanism of the reaction consisted merely in direct addition, β -lactones should have been the major products. They were formed but the chief reaction products were mixed acid anhydrides, namely, cinnamic

(1) Holder of a Quaker Oats Fellowship, 1929-1930, administered through the Miner Laboratories, Chicago.

(2) Staudinger, *Ber.*, **41**, 1355 (1908).

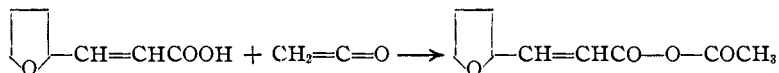
acetic anhydride, furylacrylic acetic anhydride and *m*-nitrocinnamic acetic anhydride. Such an effect may be summarized in the equation



Considering the reagents which are taken, this reaction with aromatic aldehydes, potassium acetate and ketene resembles the Perkin reaction which employs aromatic aldehydes, potassium acetate and acetic anhydride. This is obvious since both ketene and acetic anhydride give rise to acetic acid when treated with water.

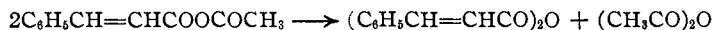
Beta Lactones in the Reaction Product.—The presence of the β -lactones was established by pyrolysis. Styrene distilled from the benzaldehyde material and furylethylene³ from the furfural material. The styrene could not have come from cinnamic acetic anhydride or from cinnamic anhydride for they were shown to pyrolyze differently. Furthermore, its forerunner could not have been cinnamic acid since it was not present and since the decomposition temperature was lower than that required for cinnamic acid. Even milder conditions (steam distillation) were found to suffice in the production of furylethylene. In the case of the *m*-nitrobenzaldehyde reaction product, a small amount of liquid was formed as a product of pyrolysis. This may have contained *m*-nitrostyrene but it could not be established with certainty. Nor was it possible to isolate the β -lactone which, in this case, is known⁴ to be fairly stable.

Synthesis and Reactions of Mixed Acetic Anhydrides.—Prior to the search for the mixed anhydrides in the reaction mixture they were prepared for study. The general method of Hurd and Dull⁵ was used. Acetic cinnamic anhydride was prepared by passing ketene into a solution of cinnamic acid in ether. Acetic furylacrylic anhydride was prepared similarly from ketene and furylacrylic acid



Acetic furylacrylic anhydride is new and but little information exists regarding acetic cinnamic anhydride. Gerhart,⁶ who prepared it from sodium cinnamate and acetyl chloride, reported it to be a very unstable oil. Using cinnamic acid and acetic anhydride, Autenrieth⁷ obtained cinnamic anhydride but not the mixed anhydride.

Three reactions of acetic cinnamic anhydride were studied: (a) disproportionation into the symmetrical anhydrides. This occurred on distillation



(3) Moureu, Dufraisse and Johnson, *Ann. chim.*, **7**, 14 (1927); *Bull. soc. chim.*, **43**, 586 (1928).

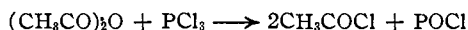
(4) Prausnitz, *Ber.*, **17**, 597 (1884).

(5) Hurd and Dull, *This Journal*, **54**, 3427 (1932).

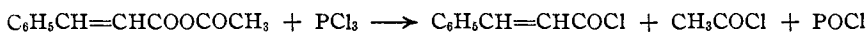
(6) Gerhart, *Ann.*, **87**, 81 (1853).

(7) Autenrieth, *Ber.*, **34**, 186 (1901).

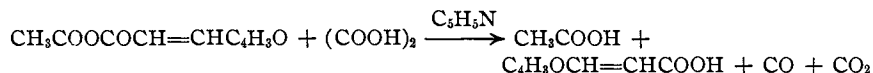
(b) reaction with phosphorus trichloride. Besson⁸ reported the following reaction between acetic anhydride and phosphorus trichloride



Repetition of this reaction showed that an 85% yield of acetyl chloride was formed. Similarly, the mixed anhydride was found to give an 85% yield of acetyl chloride with phosphorus trichloride



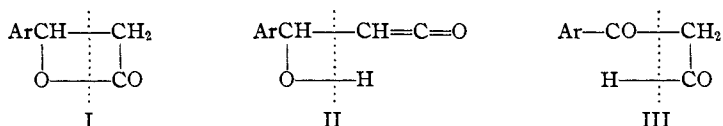
(c) analysis⁵ with dry oxalic acid and pyridine. The reaction seems to hold quantitatively for the mixed anhydrides of the acetic type; *e. g.*



It is not quantitative for all acid anhydrides, however, as cinnamic anhydride gave but nine-tenths of the calculated volume of gas and *m*-nitrocinnamic anhydride did not react at all.

Mixed Anhydrides in the Ketene-Aldehyde Reaction Products.—The reactions just described were applied on the brown, viscous products of the reaction between ketene, aldehydes and potassium acetate. (a) Vacuum distillation of the reaction product from ketene and benzaldehyde produced some crystalline cinnamic anhydride. The corresponding product from *m*-nitrobenzaldehyde gradually deposited crystals of *m*-nitrocinnamic anhydride on standing. (b) When phosphorus trichloride was mixed with the benzaldehyde-ketene product, the yield of acetyl chloride indicated 50% of acetic cinnamic anhydride in the material. (c) Using the oxalic acid and pyridine method of analysis there was found 59% of furylacrylic acetic anhydride and 30% of cinnamic acetic anhydride, respectively. The amounts of furylacrylic and cinnamic acids isolated agreed with these values.

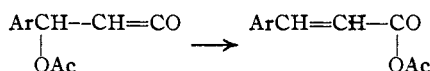
Mechanism of the Reaction.—If one assumes that a molecule each of ketene and aldehyde participate in the first stage of the reaction, there are three modes of addition to be considered:



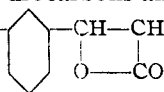
Formula (I) represents a β -lactone. This is undoubtedly formed but whether it is formed directly or by isomerization of (II) is debatable. Formula (II) represents an hydroxyketene, a new type of compound which might isomerize into (I) and concurrently might form an acetic ester with an excess of ketene. In this ester, the acetate radical is at an end of a "three carbon system," with an aryl group at the same end. Hence, a

(8) Besson, *Compt. rend.*, **125**, 771 (1897).

rearrangement⁹ typical of such systems would be anticipated. The resultant compound would be the mixed anhydride

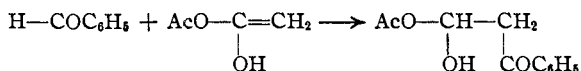


The β -lactone provides a satisfactory explanation for the arylethylenes which were isolated and the hydroxyketene for the mixed anhydrides. It would be conceivable to consider the β -lactones as forerunners of the mixed anhydrides if they could rearrange into unsaturated acids. These acids add ketene normally and give mixed anhydrides. However, β -lactones do not undergo rearrangement by heat to unsaturated acids. They give unsaturated hydrocarbons and carbon dioxide instead. Furthermore, the β -lactone, $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}_2$, is stated⁴ to be stable at the tempera-



tures used. Hence if formed it should not have decomposed into *m*-nitrocinnamic acid, yet *m*-nitrocinnamic acetic anhydride was formed.

Formula (III) lacks support in the present work since benzoylacetaldhyde was not found and since it cannot be regarded as a probable intermediate in the production of either the arylethylenes or the mixed anhydrides. Mention is made of formula (III), however, because of its bearing on Kalnin's recently proposed mechanism¹⁰ for the Perkin reaction. Kalnin assumed the first step to be enolization of acetic anhydride by potassium acetate. Then he postulated addition of benzaldehyde to it with scission of the aldehyde into hydrogen and benzoyl



Because of the structural similarity of ketene to enolized acetic anhydride $\left(\text{CH}_2=\text{C}=\text{O} \text{ and } \text{CH}_2=\text{C} \begin{array}{l} \text{OAc} \\ \text{OH} \end{array} \right)$ it is reasonable to think that benzaldehyde should add to ketene analogously and produce benzoylacetaldhyde, were this equation correct. However, as stated above, this was not found. Furthermore, with this mechanism it is not apparent why potassium acetate is necessary in the ketene-benzaldehyde reaction, for $\text{C}=\text{C}$ exists in ketene (whereas it does not in acetic anhydride).

Other objections to Kalnin's mechanism are these. Phthalic anhydride¹¹ or benzoyl cyanide,¹² with no labile hydrogen, may replace benzaldehyde in the reaction with acetic anhydride and potassium acetate. Also, the fact

(9) Burton and Ingold, *J. Chem. Soc.*, 906 (1928); Burton, *ibid.*, 1650 (1928); 248 (1930); 759 (1931). The wandering of not only the acetate radical but also others such as chloride, bromide, trichloroacetate and *p*-nitrobenzoate is shown and the influence of aryl groups in facilitating the change of $\text{ArCHXCH}=\text{CH}_2$ to $\text{ArCH}=\text{CHCH}_2\text{X}$ is demonstrated.

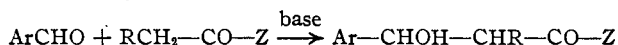
(10) Kalnin, *Helv. Chim. Acta*, 11, 977 (1928).

(11) Michael and Gabriel, *Ber.*, 10, 391 (1877); Gabriel and Michael, *ibid.*, 11, 1007 (1878).

(12) Mueller, *Ann.*, 491, 251 (1931).

that bases induce the condensation of methyl benzoylformate, which contains no labile hydrogen, with methyl cyanacetate¹³ is a similar objection.

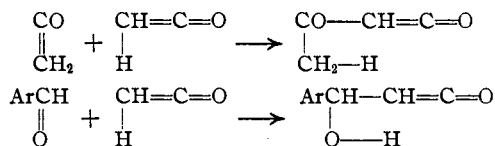
The most satisfactory interpretation of the Perkin reaction is one originally suggested by Michael,¹⁴ which aligns it with well-known condensations of aromatic aldehydes with other aldehydes, ketones and esters, all of which are catalyzed by a base. The general equation becomes



wherein Z represents H, R, OR or OCOR. Whether or not dehydration to ArCH=CR—CO—Z occurs depends on the conditions of the reaction. In such a process, the base may be considered to loosen the C—H bond in $\text{RCH}_2\text{—CO—Z}$. Two carbonyl groups are present to compete for the hydrogen, namely, the one in benzaldehyde and the one in acetic anhydride. The former gives rise to the Perkin reaction (irreversible) and the latter to enolized acetic anhydride (reversible). With this viewpoint, the double bond of enolized acetic anhydride loses the significance ascribed to it by Kalnin.

A strictly analogous mechanism best pictures the formation of the hydroxyketene (II) in the ketene-aldehyde reaction.

Finally, it is interesting to call attention to the polymerization of ketene. If the dimer of ketene is regarded as acetylketene, $\text{CH}_3\text{COCH=C=O}$, rather than cyclobutanedione, a preference which seems necessary to account for its polymerization¹⁵ into dehydroacetic acid, then the mechanism for the addition of ketene to itself resembles that of its addition to aldehydes



Experimental Part

Ketene was synthesized from acetone by pyrolysis.¹⁶ In experiments where it was desired to have the ketene completely free from acetone vapor, the latter was removed by passing the gases through a -80° condenser.

Acetyl Chloride from Acetic Anhydride and Phosphorus Trichloride.—Twenty cc. (21.6 g.) of acetic anhydride and 20 cc. (32.3 g.) of phosphorus trichloride were distilled together with a good column. The acetyl chloride which formed distilled between $51-52^\circ$. The yield was 29.5 g. or 89% of the calculated amount. The residue was a yellow, paraffin-like solid.⁸

Mixed Anhydrides from Ketene

Furylacrylic Acetic Anhydride.—Fifteen grams of furylacrylic acid was suspended in 50 cc. of dry, ice-cold ether and ketene was passed in until it was no longer absorbed.

(13) Kohler and Corson, *THIS JOURNAL*, **45**, 1975 (1923).

(14) Michael, *Ber.*, **34**, 918 (1901).

(15) Hurd, Sweet and Thomas, *THIS JOURNAL*, **55**, 335 (1933).

(16) Hurd, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1924, Vol. IV, p. 40.

The ether was then evaporated *in vacuo*. The product was a slightly brown liquid which possessed a sharp odor. On standing it gradually changed into a black jelly, a change which was facilitated by heating. The compound (freshly prepared) was analyzed⁵ with dry oxalic acid and pyridine.

Anal. Anhydride calcd. for $C_9H_8O_4$, 100%. Found: anhydride, 99.5%.

Cinnamic Acetic Anhydride.—Just as in the previous case, 15 g. of cinnamic acid was suspended in 50 cc. of cold, dry ether and treated with ketene. The residue on evaporation of the ether was a slightly colored liquid with a sharp odor.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.5; H, 5.26. Found: C, 69.1; H, 5.22.

On standing at room temperature, cinnamic acetic anhydride slowly deposited cinnamic anhydride.¹⁷ This action was rapid on heating.

Ten grams of cinnamic acetic anhydride was distilled with 11 g. of phosphorus trichloride. There was formed 3.5 g. (84.5%) of acetyl chloride, b. p. 52°, which gave acetanilide, m. p. 114°, on reaction with aniline.

Cinnamic Anhydride.—Cinnamic anhydride, prepared by pyrolysis of the acetic cinnamic anhydride and recrystallized from xylene, melted at 134°. It was found to distil practically unchanged at 23 mm. at a bath temperature of 270°. Search was made for styrene as a decomposition product without success.

When pure cinnamic anhydride was analyzed by the oxalic acid and pyridine method the reaction was not quantitative. Thus, in one experiment 0.2778 g. of anhydride gave rise to 40.2 cc. (corr.) of gas which represents a conversion of 89.5%. In three similar runs the values were 87.0, 88.8 and 91.1%. Since the purity of the cinnamic anhydride was not in question, the method evidently is not a quantitative one in this case.

Reaction of Aldehydes with Ketene and Potassium Acetate

Ketene-Furfural Reaction Product.—Fifty cc. (58 g. or 0.6 mole) of furfural and 3.3 g. of freshly fused potassium acetate were placed in a flask and 0.8 mole of ketene passed in. The furfural warmed up to about 60° and turned dark rapidly. It required about three hours to generate this amount of ketene and the furfural was quite warm until the last half hour of the reaction. The total increase in weight was 27 g. and the product was a thick, dark brown liquid having an odor of furfural. It was analyzed for its acetic furylacrylic anhydride content by the oxalic acid and pyridine method. A molecular weight determination was also made on this material.

Anal. Subs. 0.4358: cc. of gas (corr.), 64.3. Anhydride content calcd. as $C_4H_2OCH=CHCOOCOCH_3$, 59.3%. *Mol. wt.* Subs. 0.3883. Solvent (benzene), 21.9. Freezing point lowering, 0.505°. *Mol. wt.* calcd. for $C_9H_8O_4$, 180; found, 175.

Conversion into Furylethylene

(a) **Direct Heating.**—Some of the tarry reaction product was heated in a small distillation flask. The liquid distillate was collected in a test-tube which contained a trace of pyrogallol to prevent polymerization. This distillate possessed the properties of furylethylene.³ It was a liquid insoluble in water. It boiled at 100°. It polymerized and turned dark colored on standing and it decolorized potassium permanganate solution instantly.

(b) **Steam Distillation.**—Steam was passed into the reaction mixture of a new run starting again with 50 cc. of furfural. The non-aqueous layer of the distillate was the top layer. Its volume was 32 cc. It was separated and dried over calcium chloride. In these and in subsequent manipulations, a trace of pyrogallol was always present. When dry, 16.5 cc. was collected by distillation to 110°. The remaining 10.5 cc. was largely furfural. After washing the 16.5 cc. to remove acetone, about 9.5 cc. of liquid

(17) Compare Autenrieth, *Ber.*, **34**, 186 (1901).

remained which was very unsaturated toward permanganate solution and bromine water. After drying and distilling all boiled at 97° or below showing it to be chiefly furylethylene.

The residue from which the furfural and furylethylene had been steam distilled was made alkaline with aqueous sodium hydroxide. Four grams of a black tar remained undissolved. The yield of furylacrylic acid (m. p. 139°) which separated by adding acid to the alkaline solution was 36 g. This 36 g., coming from 58 g. of furfural, is a 43.5% yield. From the furylacrylic acetic anhydride content (59.3%) of the crude reaction product which weighed 85 g., it would have been possible to obtain 38.6 g. of furylacrylic acid. The value of 36 g., therefore, is confirmatory evidence that the mixed anhydride was present in the amount indicated.

Ketene-Benzaldehyde Reaction Product.—Fifty cc. (53 g. or 0.5 mole) of benzaldehyde which had been freshly distilled and 3 g. of fused potassium acetate were treated with ketene until there was no further action as evidenced by a heating effect (tested by feeling with the hand). During most of the time the ketene was being added the reaction mass maintained itself at a temperature of about 60°. The gain in weight of the reaction flask was 26 g. which, if caused entirely by addition of ketene, represents 0.62 mole. The product was a thick, brown liquid having the odor of benzaldehyde as well as a slight ester odor. Actually, its benzaldehyde content was at least 14% since from one gram of the crude substance there was produced 0.25 g. of benzaldehyde phenylhydrazone. The crude material was analyzed for its acetic cinnamic anhydride content with anhydrous oxalic acid and pyridine. Also, its apparent molecular weight was determined.

Anal. Subs., 1.0437, 1.0712; cc. of gas (corr.), 75.4, 76.4. Anhydride content calcd. as $C_6H_5CH=CHCOOCOCH_3$, 30.6, 30.2. *Mol. wt.* Subs. 0.7847; g. of solvent (benzene), 30.7; depression of freezing point, 0.745°. Calcd. for $C_{11}H_{10}O_3$, mol. wt., 190; found, 172.

By steam distilling the ketene-benzaldehyde product from one run as above the excess of benzaldehyde was removed. The residue was extracted with alkali and the extract acidified to precipitate the cinnamic acid, m. p. 126°. Sixteen grams of it was isolated, which is a 21.8% yield based on the original benzaldehyde. Since the cinnamic acetic anhydride content of the crude reaction mixture which weighed 79 g. was 30.6%, the weight of cinnamic acid which this should create is 18.8 g. The 16 g. which was isolated is satisfactory agreement.

The product from another identical run was vacuum distilled at 6 mm. Between 40–55°, 25 cc. of benzaldehyde which was admixed with a little styrene distilled. From 55–170°, there was collected 5 cc. of styrene which contained a little benzaldehyde. From 170–174°, a light yellow solid distilled (5 g.) which was colorless when purified. It melted at 129° and was shown to be cinnamic anhydride. The styrene was identified by converting it into the dibromide which melted at 61°.

Five grams of the ketene-benzaldehyde product was distilled with 5 g. of phosphorus trichloride and the liquid boiling up to 85° was collected. On redistillation, 0.5 cc. of liquid was collected up to 65°. Assuming a quantitative reaction, this yield of acetyl chloride would require 2.4 g. of acetic cinnamic anhydride. When treated with aniline, this acetyl chloride gave acetanilide, m. p. 114°.

***m*-Nitrobenzaldehyde and Ketene.**—Fifty grams of *m*-nitrobenzaldehyde was suspended in 100 cc. of benzene and a little fused potassium acetate added. Ketene was then passed in till there was no longer a heating effect. This aldehyde gradually went into solution and the solution turned dark brown. Toward the end of the reaction an almost black oil separated on the bottom of the flask. After standing for several days, this black oil changed into a light yellow solid. This solid was filtered off and

washed with benzene; yield, 15.5 g. or 25%. It melted at 206°. Its insolubility in 5% potassium hydroxide combined with the fact that a mixed melting point value of 180° was obtained with known *m*-nitrocinnamic acid demonstrated that it was not *m*-nitrocinnamic acid. When some of the solid was boiled with 5% potassium hydroxide solution it slowly dissolved. Acidification of this solution gave *m*-nitrocinnamic acid melting at 196°. The melting point of known *m*-nitrocinnamic acid was not lowered by mixing with this acid. Thus, the original substance was a hydrolyzable derivative of *m*-nitrocinnamic acid.

***m*-Nitrocinnamic Anhydride.**—This compound has not been described in the literature. Elemental analyses cannot be used to identify it since the percentages are so nearly identical to the values with the free acid. A molecular weight determination and an equivalent weight titration were used to prove that the 206° compound was *m*-nitrocinnamic anhydride. The former was determined by Pastak's method¹⁸ using trinitrotoluene as solvent.

Mol. wt. Subs. 0.2443, 0.5269; g. of solvent (TNT), 12,569, 12,790. Depression of freezing point, 0.65°, 1.3°. Calcd. for $C_{18}H_{12}O_7N_2$, mol. wt., 368; found, 344, 364. ($K = 11.5^\circ/\text{mole}/1000 \text{ g. of solvent.}$) *Equiv. wt.* Subs. 0.1123 g. dissolved in 5.00 cc. of alc. KOH (5 cc. \approx 25.88 cc. of 0.2016 *N* HCl); cc. 0.2016 *N* HCl, 22.95. Calcd. for $C_{18}H_{12}O_7N_2$, equiv. wt., 184; found, 190.

The benzene filtrate from which the 15.5 g. of *m*-nitrocinnamic anhydride precipitated was evaporated. The residue was a thick brown liquid. It reacted with concd. alcoholic potash so vigorously as to make the alcohol boil. However, the reaction was quite slow when 20 g. of it was treated at 0° with a solution of 10 g. of potassium hydroxide in 250 cc. of alcohol. After standing overnight the solution was evaporated on the steam-bath. No success attended efforts to extract the tar with ether or benzene. On adding water a brown solution formed but most of the tar remained behind. The solution was decolorized with charcoal and acidified. Three grams of *m*-nitrocinnamic acid separated; m. p. 193° and mixed m. p. 195°. This is a 15% yield.

The original *m*-nitrobenzaldehyde-ketene product does not contain acid since on standing for one week with sodium carbonate solution there was no brown color in the aqueous layer and there was no evidence of gas being evolved at any time.

Twenty grams of the *m*-nitrobenzaldehyde-ketene product was heated by an open, moving flame in an evacuated apparatus. Before there was any profound decomposition, 3.5 g. of a liquid was collected as a distillate. This liquid was thought to contain *m*-nitrostyrene for it decolorized potassium permanganate solution readily, it absorbed bromine instantly and its odor was similar to that of styrene. It froze at a temperature below -20°, whereas *m*-nitrostyrene is stated to freeze at -15° and to melt at -5°. Although the liquid absorbed bromine it was not possible to isolate any *m*-nitrostyrene dibromide from the reaction mixture. Hence, it cannot be stated definitely whether or not *m*-nitrostyrene was formed, but its presence is strongly indicated.

Synthesis of *m*-Nitrocinnamic Anhydride.—One gram of *m*-nitrocinnamic acid was refluxed with 3 cc. of acetic anhydride for five minutes. White crystals separated on cooling. These were washed with benzene and then with ether; yield, 0.3 g.; m. p. 206°. A mixed melting point with the product obtained by the action of ketene gave 204°. *m*-Nitrocinnamic anhydride did not react with a mixture of dry oxalic acid and pyridine.

The anhydride was further identified by converting it into the methyl ester. One gram of the anhydride was refluxed for four hours with 10 cc. of methanol, the insoluble part filtered off, and the filtrate diluted with water. Methyl *m*-nitrocinnamate separated as small, slightly colored crystals. With no further purification, it melted at 118° as compared with the literature value¹⁹ of 124°.

(18) Pastak, *Bull. soc. chim.*, **39**, 82 (1926).

(19) Sudborough and Lloyd, *J. Chem. Soc.*, **73**, 85 (1898).

By warming 7 g. of *m*-nitrocinnamic anhydride with 5 cc. of aniline, *m*-nitrocinnam-anilide was prepared. The solid was washed with dilute alkali and then with dilute acid. After recrystallization from benzene the needle crystals melted at 194–195°.

Summary

In the presence of a little potassium acetate, ketene reacts exothermically with aromatic aldehydes (benzaldehyde, furfural, *m*-nitrobenzaldehyde). The primary product was considered to be a non-isolable hydroxyketene, $\text{Ar}-\text{CHOH}-\text{CH}=\text{C}=\text{O}$, but the chief product isolated was a mixed acetic anhydride, $\text{ArCH}=\text{CH}-\text{CO}-\text{O}-\text{COCH}_3$. The presence of a β -lactone was indicated in lesser amounts inasmuch as moderate heating of the reaction product gave rise to arylethylenes, $\text{ArCH}=\text{CH}_2$. The mechanism for the production of these substances is given. The similarity of this reaction to the Perkin reaction is pointed out and the mechanism for the latter reaction discussed. In this connection, some serious objections to Kalnin's mechanism are raised.

Acetic cinnamic anhydride and acetic furylacrylic anhydride were synthesized by the reaction of ketene and cinnamic acid or furylacrylic acid. These mixed anhydrides undergo pyrolysis into the symmetrical anhydrides. Also, they give good yields of acetyl chloride with phosphorus trichloride and they react quantitatively with dry oxalic acid and pyridine, each mole of mixed anhydride giving rise to a mole each of carbon monoxide and carbon dioxide. Cinnamic anhydride reacts with oxalic acid and pyridine, but not quantitatively.

m-Nitrocinnamic anhydride was synthesized and studied.

EVANSTON, ILLINOIS

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