

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

**Ketene and Acetylketene**

BY CHARLES D. HURD AND JONATHAN W. WILLIAMS

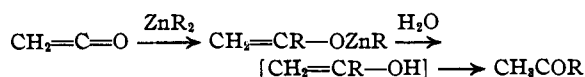
This paper extends the chemistry of ketene and its dimer, which is shown to be acetylketene. The new reactions of ketene will be mentioned first.

**Thioalcohols.**—To test Staudinger's prediction<sup>1</sup> that thioalcohols should react with ketene, we treated liquid ketene at  $-80^\circ$  with ethanethiol and obtained ethyl thioacetate

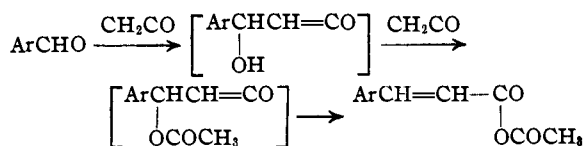


**Organo-metallic Compounds.**—It has been found in previous work<sup>2</sup> that the reaction between ketene and the Grignard reagent was too violent to be controllable. In the present work, the same vigorous behavior was noticed with diethylmagnesium. A brown resin was the only product formed.

Dialkylzinc compounds were next studied. They proved to be less reactive. Diethylzinc and dimethylzinc both reacted smoothly with ketene, giving methyl ethyl ketone and acetone, respectively, in about 40% yields

**The Reaction of Ketene and Aldehydes**

Recently it was shown<sup>3</sup> that ketene reacted with aromatic aldehydes in the presence of potassium acetate to produce mixed acid anhydrides by this sequence of steps



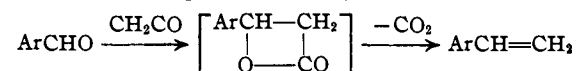
This reaction was extended to cinnamic aldehyde.  $\beta$ -Styrylacrylic acetic anhydride,  $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}=\text{CHCO}-\text{O}-\text{COCH}_3$ , was formed. The related  $\beta$ -styrylacrylic acid has been prepared from cinnamic aldehyde<sup>4</sup> by the Perkin reaction.

This reaction with ketene and potassium acetate is not applicable to aliphatic aldehydes (butyraldehyde) or to ketones (acetone or acetophenone) or to diphenylketene.

(1) Staudinger, "Die Ketene," 1912.

(2) Hurd, Sweet and Thomas, *THIS JOURNAL*, **55**, 336 (1933).(3) Hurd and Thomas, *ibid.*, **56**, 275 (1933).(4) Perkin, *J. Chem. Soc.*, **31**, 403 (1879).

A different mechanism is conceivable for the production of the mixed anhydride, namely, by the way of a  $\beta$ -lactone. As a matter of fact, styrene is formed in the benzaldehyde reaction. This may be explained through the lactone

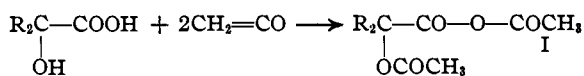


It might be imagined that the  $\beta$ -lactone would isomerize to an unsaturated acid,  $\text{ArCH}=\text{CHCOOH}$ , under the influence of ketene, and then react further to produce the mixed acid anhydride. That no such mechanism is allowable was demonstrated in the present work. There is no reaction between  $\beta$ -(*m*-nitrophenyl)- $\beta$ -propionolactone,  $\text{O}_2\text{NC}_6\text{H}_4\text{CH}-\text{CH}_2$ , and ketene.

In this connection also, experiments were conducted to determine the quantity of carbon dioxide (A) and styrene (B) formed during the Perkin reaction. In a run with 30 g. of benzaldehyde there was formed 18 g. of cinnamic acid, 0.9 g. of A and 0.5 g. of B. In a control experiment wherein cinnamic acid (18 g.) was substituted for the benzaldehyde (30 g.), other factors being unchanged, about the same yields of A (1.1 g.) and B (0.6 g.) were formed, which makes it appear that these are decomposition products from cinnamic acid, not products of a concurrent reaction.

**Ketene and  $\alpha$ -Hydroxy Acids**

Mandelic and benzoic acids were studied. When an excess of ketene was used, almost quantitative yields of the mixed acid anhydrides<sup>5</sup> were obtained



The simple acetic esters (II) were never obtained even when one mole each of ketene and the hydroxy acid were taken. Compound III is a structure which is both an acid anhydride and an alcohol. Therefore, it should not be stable but should change to II. From this, it is evident that

Compound III is a structure which is both an acid anhydride and an alcohol. Therefore, it should not be stable but should change to II. From this, it is evident that

(5) Compare Hurd and Dull, *THIS JOURNAL*, **54**, 3427 (1932).

I, not III, would result if the acidic hydroxyl is preferentially attacked. Since II represents a stable type, it should be isolable if the alcoholic hydroxyl were preferentially attacked. As stated above, type I is formed.

It was found possible to convert acetylbenzic acetic anhydride (I) into acetylbenzic acid (II) by water or by aniline, providing acetone was present as solvent. Curiously, none of II could be isolated by interaction of I with benzilic acid.

Similarly, water (but not mandelic acid) brought about the transformation of acetylmandelic acetic anhydride to acetylmandelic acid. Both acetanilide and acetylmandelanilide were formed as a result of the reaction of the anhydride with aniline. Heating of the anhydride brought about its pyrolysis into acetic anhydride, benzaldehyde and an unidentified residue.

**Acetylsalicylic Acid.**—Van Alphen<sup>6</sup> obtained acetylsalicylic acid from ketene and salicylic acid. Its melting point was brought up to 133.5° by crystallization from dilute alcohol. Rice<sup>7</sup> suspected the presence of a mixed acid anhydride in this reaction since the product, if recrystallized from dry ether instead of dilute alcohol, smelled of acetic anhydride and melted at 125–130°.

The method outlined above for the preparation of acetylbenzic acid was found to be well suited for the preparation of acetylsalicylic acid, namely, treatment of acetylsalicylic acetic anhydride in acetone solution with water. The acetylsalicylic acid which separated was of high purity.

***t*-Butyl Alcohol.**—This alcohol was submitted to the action of gaseous and liquid ketene under varying conditions. No pure *t*-butyl acetate was isolable. The material which was considered to be *t*-butyl acetate in earlier work<sup>2</sup> was shown to be a mixture of *t*-butyl alcohol and ketene dimer, thus confirming the findings of Rice<sup>7</sup> and co-workers.

**Triphenylmethyl.**—No evident reaction occurred when ketene gas was passed into a solution of triphenylmethyl in benzene.

#### Structure of Ketene Dimer

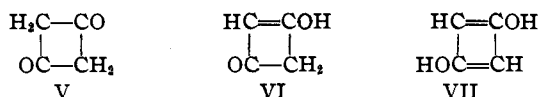
A recent paper by Angus and others<sup>8</sup> takes up the matter of the constitution of dimeric ketene. Unfortunately the chemical evidence regarding the dimer was disregarded and it was assumed that

(6) Van Alphen, *Rec. trav. chim.*, **43**, 823 (1924).

(7) Rice, Greenberg, Walters and Vollrath, *This Journal*, **56**, 1764 (1934).

(8) Angus, Leckie, LeFèvre, LeFèvre and Wassermann, *J. Chem. Soc.*, 1751 (1935).

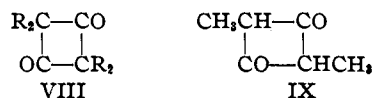
the dimer must possess one of the three structures related to cyclobutanedione (V, VI, VII). To



distinguish between them, physical methods were used. The observed dipole moment, the molecular refraction and the observed heat of formation were incompatible with V and VII but were satisfactory for VI. For example, the observed heat of formation was 1081 kcal. The calculated value for VI was 1075 kcal., whereas the values for V and VII were 1101 and 1049 kcal., respectively.

It will be shown below that the structure of the dimer is either acetylketene (X) or its resonance isomer (XIV). The calculated heat of formation for X is 1086 kcal., which is in close agreement with the observed value. Obviously this method could not be used to decide between VI and X. The calculated heat of formation for XIV (1068 kcal.) is fairly close also.

The cyclobutanedione structure (V or VI) seemingly has two points in its favor. First, it is analogous to VIII, the structure for dimers of disubstituted ketenes. Second, it yields  $\gamma$ -bromoacetoacetyl bromide with bromine, but



since rearrangement of  $\alpha$ - to  $\gamma$ -bromoacetoacetyl bromide may occur<sup>2</sup> spontaneously, this argument is valueless. Even less forceful is the first argument, because of the great difference in properties of ketene dimer and actual cyclobutanedione types. For example, dimethylcyclobutanedione, IX, is an odorless solid<sup>9</sup> which gives no esters of the acetoacetic type with alcohols. In contrast, dimeric ketene is a liquid with a sharp, insufferable odor. It reacts with water to produce acetoacetic acid, and with alcohols<sup>10</sup> (if catalyzed by R<sub>2</sub>ONa or HCl) to yield acetoacetic esters.

Compound VIII, which is the dimer of R<sub>2</sub>C=C=O, is quite unrelated in properties to the dimer of H<sub>2</sub>C=C=O. Depolymerization of VIII into its ketene occurs on heating,<sup>11</sup> but no such depolymerization occurs in the case of ketene dimer. As a matter of fact, VIII appears to depolymerize during reaction with aniline or phenylmagnesium

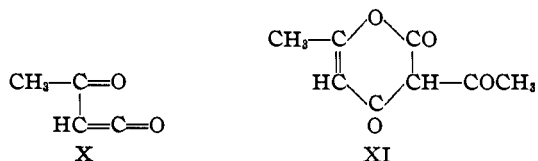
(9) Schroeter, *Ber.*, **49**, 2697 (1916).

(10) Chick and Wilsmore, *J. Chem. Soc.*, **93**, 946 (1907); **97**, 1978 (1910).

(11) Staudinger and Bereza, *Ber.*, **42**, 4908 (1909).

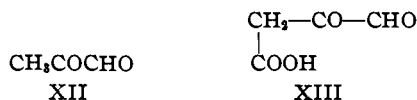
bromide<sup>12</sup> giving, respectively,  $R_2CHCONHC_6H_5$  and  $R_2CHCOC_6H_5$ . Analogously, V should react with aniline to produce acetanilide, but actually acetoacetanilide is formed from ketene dimer.

A more adequate structure for ketene dimer is X, acetylketene. It accounts not only for the



reactions cited above, but also for the non-reaction with sodium and for the further polymerization to the tetramer, which is dehydroacetic acid, XI.

To decide between structures VI and X, the dimer was subjected to ozonization. Pyruvic aldehyde (XII) would be anticipated from X, whereas carboxypyruvic aldehyde (XIII) should result from VI. Actually, XII was formed, not XIII. Added confirmation was the production

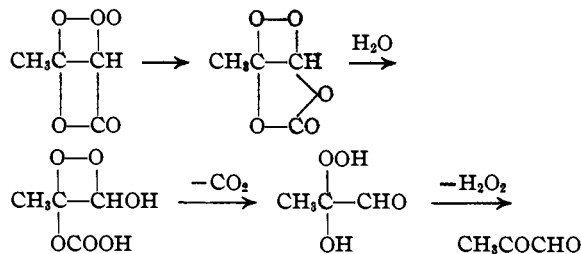


of acetic acid (from XII +  $\text{H}_2\text{O}_2$ ) but not malonic acid (from XIII +  $\text{H}_2\text{O}_2$ ) in experiments wherein no precautions were taken to destroy the hydrogen peroxide formed in the reaction.

The above evidence eliminates structures V or VI for ketene dimer but it leaves unsolved one important question, namely, that of resonance isomers.  $\beta$ -Crotonolactone (XIV) is an important modification to consider in this connection. Since it is a resonance isomer of X, it is justifiable to speak of both X and XIV as acetylketene. The cyclic structure would explain the relative inertness of acetylketene toward alcohols. On the basis of the usual Harries mechanism, ozonolysis of a mixture of X and XIV would give rise to pyruvic aldehyde and acetic acid. However,



with the Staudinger mechanism<sup>13</sup> pyruvic aldehyde would be anticipated from either X or XIV. The sequence of steps from the ozonide of XIV on this basis would be



**Parachor.**—The parachor of acetylketene was determined as a matter of record but not with the thought of using it in defense of any structure since it is the first such compound to be tested in this manner. The observed parachor was 182. That part of the calculated<sup>14</sup> parachor contributed by the atoms alone (C, 4.8; H, 17.1; O, 20.0) is 127.6, which leaves a structural correction factor of 54.4. Sugden lists these correction factors as applicable to most compounds: double bond 23.2, 4-membered carbon ring 11.6,  $\text{O}_2$  of esters 60.0.

**Pyrolysis of Acetylketene and its Bearing on the Pyrolysis of Ketene.**—In a paper dealing with the kinetics of the pyrolysis of ketene, Williamson<sup>15</sup> found that at temperatures between 400 and 500° ketene polymerized readily to the dimer. The extent of polymerization decreased rapidly with increasing temperature, as measured by pressure changes. Above 530°, ketene was found to decompose chiefly into carbon monoxide, methane and carbon, although a little ethylene was always formed. Between 530 and 550° the ratio of CO to  $\text{CH}_4$  was approximately 2:1.

Williamson regarded the transformation of ketene into its dimer as being strictly reversible and endeavored unsuccessfully to determine the equilibrium constants. In his words: "Even when the equilibrium was approached from the diketene side the interference of the decomposition process obscured the polymerization."

Williamson was impressed by the high proportion of methane in the reaction products from his 530–550° experiments. To quote: "The most striking result is the high proportion of methane. Assuming that the initial process is  $\text{CH}_2=\text{CO} \rightarrow \text{CH}_2= + \text{CO}$  we should obtain a mixture containing 66.7% CO and 33.3%  $\text{C}_2\text{H}_4$  after the methylene radicals had polymerized. The experiments show, however, that such a process is secondary in importance to one such as  $\text{CH}_2= + \text{CH}_2= \rightarrow \text{CH}_4 + \text{C}$  or some similar process in

(14) Sugden, "The Parachor and Valency," Routledge and Sons, London, 1930, p. 38.

(15) Williamson, THIS JOURNAL, 56, 2216 (1934).

(12) Hurd, Jones and Blunck, THIS JOURNAL, 57, 2034 (1935).

(13) Staudinger, Ber., 58, 1088 (1925).

which carbon or a highly unsaturated hydrocarbon is deposited. A black deposit was always formed during these runs." Thus, Williamson regarded ketene as capable of reversible polymerization and of direct splitting into carbon monoxide and a methylene fragment.

A more rational picture for the pyrolysis of ketene is to regard it as a summation process of two competing reactions: (1) the polymerization reaction (to acetylketene, dehydroacetic acid, etc.); (2) the high temperature decomposition of acetylketene formed in the first reaction. The polymerization reaction has a noticeable velocity even at very low temperatures whereas the second reaction requires a temperature high enough to sever the C-C bond. This temperature, as would be imagined, is in the same 500-600° zone which is required for the cracking of paraffin hydrocarbons.

To test this idea, acetylketene was subjected to pyrolysis at 550°. If ketene was formed it was in quantities too small to identify. Carbon monoxide, methane and ethylene were obtained and in practically the same ratio as Williamson found from ketene. Also, dehydroacetic acid, resinous matter and considerable carbon were formed.

The unsaturated nature of the acetylketene accounts for the polymerization processes. High temperature splitting of the C-C bonds gives rise to a transient methyl radical which, in turn, accounts for the methane, carbon monoxide and carbon. The latter may be summarized in the equation  $\text{CH}_3\text{COCHCO} \rightarrow \text{CH}_4 + \text{C} + 2\text{CO}$ .

### Experimental Part

Ketene was prepared in quantities of 0.5 mole per hour by passing acetone vapors through a tube<sup>2</sup> maintained at 700°. Ketene was prepared also in a modification of Ott's<sup>16</sup> ketene lamp. The filament was platinum, not tungsten. The reaction chamber was about twice as long as Ott's. Also, it was constructed with a ground glass joint at the top so that the filament could be withdrawn at will. The output was about 0.1 mole per hour when the filament was heated to a dull red.

#### Liquid Ketene and Acetylketene

The gases from a three-hour run with the ketene lamp were passed through two traps at -80°. About 50 cc. of liquid was in the first trap and 2 or 3 cc. in the second. The first trap was warmed to room temperature and the gases allowed to distil into the second trap. About 15 cc. of liquid distilled in this manner. This was then distilled through a Davis column with solid carbon dioxide and acetone at the top. Between -42 and -40°, as recorded on a pentane thermometer, 10-11 cc. was collected.

(16) Ott, Schroeter and Packendorff, *J. prakt. Chem.*, **130**, 177 (1931).

The residue (39-40 cc.) from these two distillations was distilled. It gave 6.5 cc. of acetylketene, b. p. 125-128°. The rest was acetone.

Liquid ketene, even when purified by two distillations, cannot be kept at -80° for more than twenty-four hours without polymerization occurring. Hence ketene must be freshly distilled before using. When acetylketene is prepared by the polymerization of pure liquid ketene standing at -80° for three or four days, it is accompanied by considerable dehydroacetic acid. This further polymerization of ketene dimer is retarded in an acetone solution.

**Ketene and Ethanethiol.**—Four grams of liquid ketene and 3.5 g. of ethanethiol were mixed and kept at -80° for three days, then warmed to room temperature. On distillation, 5.1 g. (6.3 cc.) of ethyl thioacetate was collected at 109-115°. This represents a 92.6% yield of crude ester.

In contrast, a negligible amount was realized when a stream of ketene gas (equivalent to 5 g. of ketene) was bubbled through 5 cc. of ethanethiol at -80°. The mixture was kept at -80° for twelve hours, then distilled. Since 3.5 cc. was collected at 36-40° and 2 cc. at 40-65°, this is chiefly unchanged mercaptan.

**Ketene and Diethylzinc.**—To 5 cc. of redistilled liquid ketene (b. p. -42 to -41°) kept at -80° was added dropwise 30 cc. of a solution of diethylzinc (10 g.) in toluene. Considerable heat was evolved. The mixture was kept at -80° overnight, after which it was slowly (during twelve hours) brought to room temperature. It was poured into 50 cc. of 25% sulfuric acid. The toluene and water layers were separated, the former dried, and both were distilled through a Davis column. The 75-90° fractions from both were combined and redistilled. In this way 3.2 cc. (43% yield) of methyl ethyl ketone was collected at 77-82°; semicarbazone, m. p. 137-138°.

**Ketene and Dimethylzinc.**—Six cc. of pure liquid ketene and 15 g. of dimethylzinc (in toluene to make 40 cc.) reacted as above. The acetone which was isolated boiled at 52-56°; yield, 4.0 cc. (39%); oxime, m. p. 59°.

**Ketene and Diethylmagnesium.**—To the ether solution of the Grignard reagent (Mg, 5 g.; C<sub>2</sub>H<sub>5</sub>Br, 20 g.) was added about 13 cc. of dry dioxane<sup>17</sup> until precipitation of the magnesium bromide complex was complete. It was filtered in a nitrogen atmosphere and added dropwise into 10 cc. of pure liquid ketene at -80°. Considerable heat was evolved. A white precipitate formed which turned to a brown resin (insoluble in ether, water or dilute acid) on warming to room temperature. After treating the ether layer with cold hydrochloric acid, it was distilled. No methyl ethyl ketone was found, but 3.5 cc. of dioxane was recovered.

**Ketene and Cinnamic Aldehyde.**—Two grams of fused potassium acetate was added to 10 g. of cinnamic aldehyde (b. p. 125-130° (20 mm.)). Then about 0.25 mole of ketene gas was passed into the mixture. That a mixed acid anhydride was formed was evidenced by the reaction with aniline to give a mixture of anilides (m. p. 76-78°).

The reaction mixture was taken up in ether and extracted with 10% sodium hydroxide solution. The alkaline extract was acidified with sulfuric acid. The  $\beta$ -styrylacrylic acid which separated was collected and crys-

(17) Schlenk and Schlenk, *Ber.*, **62**, 920 (1929).

tallized from alcohol. The pure product weighed 2.9 g. (22% yield) and melted at 165°.

**Ketene and *n*-Butyraldehyde or Acetophenone.**—The above procedure was followed. Two grams of fused potassium acetate was placed with 20 cc. of the aldehyde or ketone. A rapid stream of ketene gas (0.3 to 0.5 mole) was passed through. A considerable heating effect was noticed with acetophenone, and the color of the solution changed from light yellow to an opaque red-black. No such effect was noticed with butyraldehyde. The reaction mixtures had no effect on anhydrous oxalic acid in the presence of pyridine. Hence, no mixed acid anhydride was formed. Furthermore, the product did not react with aniline. The liquid was taken up in ether, extracted with alkali and distilled. These quantities of recovered materials were found: butyraldehyde, 15.5 cc. from 22 cc. (experiment performed at room temp.), 5 cc. from 12 cc. (refluxing temp.); acetophenone, 18 cc. from 20 cc. (room temp.). As would be expected, part of the butyraldehyde was swept away by the gas stream. No significant products were isolable from butyraldehyde, but the non-volatile residue from acetophenone yielded 0.8 g. of impure dehydroacetic acid, m. p. 104–106°, and 0.2 g. of unidentified material which melted at 146–150°.

**Ketene and Acetone.**—In this case (50 cc. acetone, 10 g. potassium acetate, 0.35 mole ketene) the reaction vessel was kept at 0°. Even so, much of the acetone was swept away. The mixture was distilled directly. In addition to the 18.3 cc. of recovered acetone (b. p. 56–60°) there was 2 cc. of acetylketene (b. p. 61–131°). The latter was converted to acetoacetanilide, m. p. 84°, yield 1.5 g.

**Ketene and  $\beta$ -Lactone.**—To 0.4 g. of  $\beta$ -(*m*-nitrophenyl)- $\beta$ -propionolactone<sup>18</sup> (m. p. 98°), dissolved in 25 cc. of dry acetone, was added 0.2 g. of fused potassium acetate. Then 0.05 mole of ketene gas was introduced. The acetone solution was decanted and evaporated under reduced pressure. The residue of the unchanged lactone was crystallized from a mixture of benzene and ligroin; m. p. 96–97°, weight 0.33 g. It was identified by its insolubility in sodium carbonate solution and by its conversion to  $\beta$ -(*m*-nitrophenyl)- $\beta$ -hydroxypropionic acid, m. p. 105° (with hot 10% alkali, then acidification).

**Ketene and Diphenylketene.**—Diphenylketene was prepared by Staudinger's method,<sup>1</sup> b. p. 160–170° (23 mm.). About 0.1 mole of ketene gas was passed into a mixture of 2.3 g. of the diphenylketene, 50 cc. of dry acetone and 2 g. of fused potassium acetate. The reaction mixture changed in color from pale yellow to deep red. On working up the products, nothing significant was found.

#### Carbon Dioxide and Styrene in the Perkin Reaction

**First Run.**—The Perkin reaction was run in the ordinary manner starting with these materials: 30 g. of freshly distilled benzaldehyde, 40 g. of acetic anhydride and 18 g. of fused potassium acetate. A gas-tight apparatus was used which allowed the gases evolved at the top of the reflux condenser to be passed through one liter of a saturated solution of barium hydroxide. The mixture was refluxed in a bath kept at 160–170° for five hours. Barium carbonate was precipitated, especially during the first hour of refluxing. This precipitate, after being filtered off and

dried at 110° in an oven for one hour, weighed 4.2 g. This represented 0.94 g. of carbon dioxide.

The refluxed mixture was distilled at atmospheric pressure and the fraction below 180° (6.8 cc.) was dissolved in carbon tetrachloride. A dilute solution of bromine in carbon tetrachloride was added to this distillate until the bromine color remained after shaking. This required about 10 cc. of solution which contained 1 g. of bromine. The solution was evaporated to obtain styrene dibromide; yield 1.3 g., m. p. 72–73°. This represented 0.51 g. of styrene.

The residue from the distillation was worked up in the customary manner for cinnamic acid: yield 18.1 g., m. p. 130–131°.

**Second Run.**—This was identical to the preceding except that the heating period was shortened to one hour; yields: barium carbonate 1.57 g.; styrene dibromide 0.49 g. These are equivalent to 0.35 g. of carbon dioxide and 0.19 g. of styrene.

**Control Runs.**—A mixture of 20 g. of cinnamic acid, 30 cc. of acetic anhydride and 18 g. of fused potassium acetate was refluxed in a bath kept at 160–170° for three hours. Another similar run with 19 g. of cinnamic acid and a five-hour heating period was performed. The products, worked up as before, were as follows (in grams): barium carbonate 1.34, 5.1; styrene dibromide 0.52, 1.62; equivalent carbon dioxide 0.30, 1.14; equivalent styrene 0.19, 0.62; recovered cinnamic acid 19, 17.2.

#### Ketene and Hydroxy Acids

**Acetylbenzilic Acetic Anhydride.**—Ten grams (0.044 mole) of benzilic acid, dissolved in 150 cc. of acetone, was treated with 0.1 mole (or more) of ketene gas. After removing the acetone on a steam-bath under reduced pressure there remained 11.8 g. of the mixed anhydride. It was a viscous, dark red liquid. It was analyzed by the method of Whitford.<sup>3,5,19</sup>

*Anal.* Calcd. cc. of gas for  $\text{CH}_3\text{COOC}(\text{C}_6\text{H}_5)_2\text{—CO—O—COCH}_3$ , 42.0; found, 41.7. Percentage purity, 99.3.

**Reaction with Water.**—Water was added in 2-cc. portions to the reaction mixture from benzilic acid (5 g., 0.022 mole), acetone (20 cc.), ketene (0.05 mole). About 20 cc. was required until a faint permanent turbidity resulted. The solution yielded beautiful orthorhombic crystals on standing overnight. Then more water was again stirred in until turbidity. After several hours the process was repeated. After about 40 cc. of water had been added thus during three days the crystals were collected on a filter and air-dried; m. p. 96°, yield, 6.1 g. These crystals of acetylbenzilic acid monohydrate,<sup>20</sup> when left in a desiccator over concentrated sulfuric acid for one month, changed to acetylbenzilic acid (5.55 g.); m. p. 101–102°.

**Behavior toward Benzilic Acid.**—Benzilic acid (10 g.) was added to the acetone solution of acetylbenzilic acetic anhydride (from 10 g. benzilic acid in 250 cc. acetone) to see if acetylbenzilic acid could be isolated by this method. After fifteen hours the acetone was removed. The residue was a glassy mass from which no crystals separated.

**Reaction with Aniline.**—Aniline (2.6 g.) was added to the mixed anhydride, prepared from 6.4 g. of benzilic acid (in 50 cc. of acetone), and the mixture was left for six hours.

(19) Whitford, *THIS JOURNAL*, **47**, 2939 (1925).

(20) La Mer and Greenspan, *ibid.*, **56**, 956 (1934).

(18) Prausnitz, *Ber.*, **17**, 595 (1884).

Then water was added (100 cc.) to the point of permanent turbidity. Crystals of acetylbenzilic acid monohydrate, m. p. 95–96°, formed overnight; yield, 7.1 g. Acetanilide was in the filtrate.

**Acetylbenzyl Chloride and Acetylbenzilanilide**,  $\text{CH}_3\text{COOC}(\text{C}_6\text{H}_5)_2\text{CO—NHC}_6\text{H}_5$ .—To 6 g. of anhydrous acetylbenzilic acid, m. p. 101°, was added 10 g. of thionyl chloride. The mixture generated considerable heat but it was refluxed for two hours to carry the reaction to completion. The excess thionyl chloride was then removed by distillation and the acid chloride distilled under reduced pressure. A 48% yield, or 3.1 g., boiled at 193–195° (27 mm.). There was considerable tar formation and no other volatile fraction. The material reacted vigorously with water to give acetylbenzilic acid hydrate, m. p. 95–96°.

Acetylbenzyl chloride (3.0 g.) was allowed to react with an excess of aniline (2.5 g.). The organic reaction product was taken up in hot benzene. It crystallized out on cooling. The acetylbenzilanilide weighed 2.8 g. (78% yield) and melted at 176°.

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{19}\text{O}_3$ : N, 4.06. Found: N, 4.2.

#### Acetylmandelic Acetic Anhydride

Five grams of mandelic acid (0.033 mole) was dissolved in 20 cc. of acetone and ketene gas (0.08 mole) was passed into the solution. The acetone was removed under reduced pressure with the aid of a steam-bath. The residue of acetylmandelic acetic anhydride was a viscous, light red liquid. This material, the residue from a 5-g. run, will be referred to below as (R). Analysis was by Whitford's method.

*Anal.* Calcd. cc. of gas for  $\text{CH}_3\text{COOCH}(\text{C}_6\text{H}_5)\text{—CO—O—COCH}_3$ , 40.8; found, 39.7. Percentage purity, 97.3.

**Pyrolysis.**—Ten cc. (12 g.) of acetylmandelic acetic anhydride was heated by a free flame in a 25-cc. distilling flask. These fractions were obtained: (°C., cc.) 110–140, 5; 140–210, 2; 210–212, 0.1; tar-like residue. The 5-cc. portion was chiefly acetic anhydride. The 2-cc. fraction contained much benzaldehyde, since it was readily converted into the phenylhydrazone, m. p. 153–154°. The 0.1-g. portion solidified and melted at 55° but was otherwise unidentified.

**Reaction with Water.**—Two cc. of water was added to (R). The acetic acid was removed in a vacuum desiccator over sulfuric acid. After two weeks, the crystals of acetylmandelic acid<sup>21</sup> weighed 6.1 g.; m. p. 80°.

In another experiment, the acetone was not removed from (R). It was necessary to add 25 cc. of water to bring the mixture to permanent turbidity. An oil separated overnight which did not crystallize in one month.

**Reaction with Aniline.**—Aniline (3.1 g., 0.033 mole) was added to (R). The resulting product required two days to crystallize. It was warmed with 50 cc. of 5% sodium carbonate solution, cooled, filtered off, washed with water and recrystallized twice from 50% alcohol. The acetylmandelanilide thus formed weighed 2.8 g.; m. p. 116–117°.

In another experiment, the acetone was not removed from (R). Aniline (2.8 g.) was added and the solution was left for twelve hours. Water (20 cc.) caused the separation of a brown oil which refused to crystallize.

(21) Anschütz and Böcker, *Ann.*, **368**, 57 (1909).

#### Salicylic Acid and Ketene

Salicylic acid (9.6 g., 0.07 mole) was dissolved in 50 cc. of acetone and 0.15 mole of ketene passed into the solution. To the solution of acetylsalicylic acetic anhydride was added water (100 cc.) in small portions to the point of permanent turbidity. The cloudy solution was allowed to stand overnight and the slightly yellow crystals (A) which weighed 5.7 g. were removed by filtration; m. p. 132–133°. Most of the acetone was removed at room temperature with a water pump. This caused precipitation of a crop of pure white crystals (B) which weighed 3.7 g.; m. p. 134°. Fractions A and B were fairly pure acetylsalicylic acid but further concentration gave less pure material.

#### Ketene and *t*-Butyl Alcohol

Gaseous ketene (0.33 mole) was bubbled through 20 cc. of *t*-butyl alcohol after which the mixture was distilled through a Davis column. The material boiling below 85° was unused *t*-butyl alcohol. The material coming over at 96° (the b. p. of *t*-butyl acetate) was negligible, but there was a 2-g. fraction of acetylketene at 105–135° and 4 g. of residue which contained considerable dehydroacetic acid, m. p. 105–106°. The acetylketene, when treated with aniline, gave rise to 3.5 g. of acetoacetanilide, m. p. 83–84°.

Two cc. of *t*-butyl alcohol was added to 3 cc. of liquid ketene at –80°. The alcohol formed a solid layer. Twenty cc. of dry ether was added to effect solution. It was left for three days and evaporated. At 79–85°, 1.4 cc. of the alcohol was recovered. There was 0.7 cc. of higher boiling material and a small solid residue, presumably dehydroacetic acid. The 0.7-cc. portion contained at least 0.52 g. of acetylketene for it gave rise to 1.1 g. of acetoacetanilide, m. p. 84°.

Essentially the same results were obtained by sealing 7 cc. of pure liquid ketene (b. p. –42 to –40°) and 10 cc. of *t*-butyl alcohol in a tube at –80°, then warming the tube to room temperature. The tube was opened in three days. The pressure was somewhat greater than atmospheric. Some ketene was still present. Two fractionations of the liquid through a Davis column gave these data: 8.9 cc. of recovered alcohol at 75–85°, 0.6 cc. at 85–105°, 1.4 cc. of acetylketene (which yielded the anilide, m. p. 84°) at 105–131°, and 2.5 g. of solid residue, chiefly dehydroacetic acid, m. p. 106–107°.

#### Ketene and Triphenylmethyl

About 0.3 mole of ketene gas was passed into a filtered benzene solution of triphenylmethyl, prepared from 20 g. of triphenylchloromethane.<sup>22</sup> The ketene apparatus was swept out with nitrogen prior to the run and the solution was surrounded by ice while the ketene was being introduced. No change of the brilliant red color was noticed. On working up the mixture in air, only triphenylmethyl peroxide and triphenylcarbinol were found.

#### Ozonization of Ketene Dimer

**First Run.**—Ten cc. of the dimer, b. p. 125–128°, was dissolved in 100 cc. of carbon tetrachloride. An 8% ozone stream was passed through this solution for three hours.

(22) Gomberg, *Ber.*, **33**, 3150 (1900).

Eleven cc. of viscous ozonide remained after evaporation of the solvent. This ozonide was in two layers for a time until a spontaneous exothermic decomposition, accompanied by gas evolution set in. Then the two layers mixed.

To 6 cc. of the ozonide was added 50 cc. of 3% hydrogen peroxide solution. After standing overnight the solution was neutralized with sodium hydroxide and evaporated. The salts were treated with dilute hydrochloric acid and the organic acid was extracted with three 25-cc. portions of ether. Evaporation of the ether left about 2 cc. of acetic acid which contained no malonic acid. The acetic acid was identified by converting a portion of it to acetanilide, m. p. 114°. Malonic acid was shown to be absent by heating 1 cc. of it in a bath at 180° in a vessel provided with a delivery tube leading into barium hydroxide solution. No carbon dioxide was formed as evidenced by the non-precipitation of barium carbonate.

The remaining 5 cc. of ozonide was hydrolyzed by water and zinc dust. Pyruvic aldehyde was formed and identified. This was confirmed in a second ozonization.

**Second Run.**—Seven cc. of ketene dimer (in 50 cc. of carbon tetrachloride was ozonized during twelve hours with a 3% ozone stream (until a blue coloration was imparted to the solvent). The oily ozonide floated on top. Twenty-five cc. of water was added and the mixture was shaken with 15 g. of zinc dust for ten minutes to destroy hydrogen peroxide. The liquids were decanted from the zinc, left overnight and then distilled on a steam-bath under reduced pressure. The 15 cc. of residue was added to a solution of 2 cc. of phenylhydrazine, 5 cc. of alcohol and 1 cc. of acetic acid. At the end of three days, the light yellow precipitate of pyruvic osazone was collected on a filter and dried. It weighed 1.38 g. and melted at 144–145°.

#### Surface Tension and Parachor

The surface tension of acetylketene was determined by the rise in a capillary tube which had been standardized against pure benzene. These data were obtained with acetylketene.

|  |        |        |
|--|--------|--------|
| Temperature, °C.                               | 24.0   | 20.4   |
| Average height of column, <i>h</i> , cm.       | 1.34   | 1.40   |
| Average radius of capillary, <i>r</i> , cm.    | 0.0424 | 0.0424 |
| Density <sup>23</sup> at 24°, <i>D</i>         | 1.0898 | 1.0923 |
| Vapor density, <i>d</i> (from gas law)         | 0.0034 | 0.0034 |
| Acceleration due to gravity, <i>g</i> .        | 981    | 981    |
| Surface tension, $\frac{1}{2}hrDg$ , dynes/cm. | 30.37  | 31.82  |
| Parachor ( $M\gamma^{1/4}/D - d$ )             | 181.5  | 183.2  |

#### Pyrolysis of Acetylketene

Six grams of acetylketene was introduced into the top of an electrically-heated, nitrogen-filled, vertical Pyrex tube during thirty-five minutes. The effluent vapor passed

through two traps, cooled by ice, to remove condensable material. Then the gas was passed through a bottle containing aniline, dissolved in acetone, to remove any ketene. Finally, the gas was collected over saturated salt solution.

The liquid condensate was a mixture of 1.4 g. of acetylketene and 0.7 g. of dehydroacetic acid, m. p. 104–106°. No acetanilide was found in the aniline trap, hence no ketene was present. On a nitrogen-free basis, there was formed 2.1 liters of gas with the following composition: CO, 56.8; CH<sub>4</sub>, 24.7; C<sub>2</sub>H<sub>4</sub>, 8.9; CO<sub>2</sub>, 9.6. There were no higher olefins and there was no hydrogen. Much carbon was formed, which remained on the walls of the reaction tube.

#### Summary

Several new reactions of ketene are described: namely, the reactions with ethanethiol, diethylzinc, dimethylzinc, diethylmagnesium, cinnamic aldehyde and potassium acetate, mandelic acid, benzilic acid, salicylic acid. No reaction was apparent between ketene and the following substances: triphenylmethyl, a  $\beta$ -lactone, *t*-butyl alcohol. Potassium acetate was not effective in bringing about a reaction between ketene and acetone, butyraldehyde, acetophenone or diphenylketene.

Small amounts of carbon dioxide and styrene are formed in the Perkin reaction with benzaldehyde, evidently by decomposition of the cinnamic acid.

Decomposition of acetylmandelic acetic anhydride occurs on distillation. Acetic anhydride and benzaldehyde were identified in the reaction products.

The dimer of ketene has been shown to be acetylketene or a resonance isomer of it. Ozonization gives rise to pyruvic aldehyde and acetic acid. The parachor for acetylketene was determined.

Products of the pyrolysis of acetylketene have been shown to be carbon monoxide, methane, carbon and dehydroacetic acid. Small quantities of ethylene and carbon dioxide were present, but ketene was absent. The significance of these results in explaining the behavior of ketene at high temperatures has been expounded.

(23) Chick and Wilsmore, *J. Chem. Soc.*, 97, 1985 (1910).