

mixture has been reduced to 1.5 liters. It is then poured into an open vessel to cool. The resulting tar is worked up in 200 g. lots, each lot being treated thoroughly with 300 cc. of 6 *N* sodium hydroxide solution. The brown oil which separates is extracted with ether and the ethereal extract fractionated at 17 mm. The oil coming over above 210° forms a yellow solid, crystallizable from alcohol, forming bright yellow crystals melting at 106°. A yield of 327 g. or 22% was obtained.

Preparation of acetophenone-*p*-arsonic acid, $\text{CH}_3\text{COC}_6\text{H}_4\text{AsO}_3\text{H}_2$.—Twenty-five g. of *p*-amino-acetophenone is diazotized in the usual manner and treated with a solution of sodium arsenite according to the method of Bart already described. The compound is insoluble in water but soluble in alkalies and glacial acetic acid.

Analyses. Subs., 0.2830, 0.3299: 49.3, 58.00 cc. of 0.0471 *N* iodine soln. Calc. for $\text{C}_8\text{H}_9\text{O}_4\text{As}$: As, 30.73. Found: 30.76, 31.03.

Summary

The application of the Friedel and Crafts reaction has been further extended to the preparation of new arsenated ketones and their derivatives. Dichloro-*o*-arsinobenzoyl chloride has been condensed with aromatic hydrocarbons, and various aromatic ethers and the arseno and halogen derivatives of these compounds have been studied. An arsenated mixed ketone, namely, acetophenone-*p*-arsonic acid has been prepared.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

A STUDY OF THE FORMATION OF HYDROXAMIC ACIDS FROM KETENE

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Received November 11, 1922

Much has been written concerning the structure of hydroxylamine. Although a unity of thought is still to be desired, the following facts stand out prominently in all such discussions. Towards alkylating agents, the 3 hydrogens in hydroxylamine are replaced successively by alkyl groups which are all joined directly to the nitrogen; towards acylating agents the process is different but equally characteristic. In this case, the first and the third acyl groups to enter the molecule are joined directly to the nitrogen, whereas the second is attached to the oxygen.

Several different kinds of acylating agents have been used successfully in the preparation of hydroxamic acids. For example, in standard methods for preparing hydroxamic acids from hydroxylamine, the use of acid chlorides, of acid anhydrides, of esters, and of amides are all advocated. Ketenes, which have been shown to be ideal acylating agents, are the newest addition to this list. A year ago it was demonstrated that diphenyl-acethydroxamic acid may be prepared from diphenyl ketene.¹

In the work described in this paper, the simplest ketene, $\text{CH}_2 : \text{C} : \text{O}$,

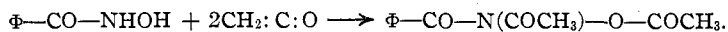
¹ Jones and Hurd, *THIS JOURNAL*, **43**, 2433 (1921).

was chosen to react not only with hydroxylamine, but also with certain hydroxamic acids. There was little doubt but that the following reaction would take place with free hydroxylamine: $\text{CH}_2:\text{C}:\text{O} + \text{H}-\text{NHOH} \longrightarrow \text{CH}_3-\text{CO}-\text{NHOH}$. There was no precedent, however, to determine the course of reaction between ketene and a monohydroxamic acid, $\text{R}-\text{CO}-\text{NHOH}$. If the addition was at the β -hydrogen, a compound would result which would be similar in structure to the dialkyl hydroxylamines, $\text{R}_2\text{N}-\text{OH}$. This type of compound, $\text{R}-\text{CO}-\text{N}(\text{OH})-\text{CO}-\text{CH}_3$, was not expected, neither was it formed. Ketene behaved in the normal manner, like other acylating agents, and added to the α -hydrogen. A dihydroxamic acid, $\text{R}-\text{CO}-\text{NH}-\text{O}-\text{CO}-\text{CH}_3$, was formed. The procedure was simple, and the yields were excellent.

Nearly a quantitative yield of trihydroxamic acid resulted when an excess of ketene was used with monohydroxamic acids. When the ease with which the second ketene molecule adds is contrasted with the difficulty which is encountered when one attempts to introduce 2 acetyl groups by such an agent as acetic anhydride, the difference is striking. For example, an excess of acetic anhydride even in the absence of solvents will introduce but one acetyl group² into pyromucyl-hydroxamic acid,



$\text{CO}-\text{NHOH}$. Ketene will form a diacetyl ester readily in spite of the fact that ethyl acetate is used as a solvent. A general equation is



There is recorded in the literature what would seem to be a precedent for the addition of 1 molecule of ketene to the β -hydrogen of a monohydroxamic acid, $\text{R}-\text{CO}-\text{NHOH}$. Kjellin³ described a compound formed by the addition of 1 mole of phenyl isocyanate to phenyl-hydroxyurea; the structure which he assigned to it was $\text{C}_6\text{H}_5\text{NH}-\text{CO}-\text{N}(\text{OH})-\text{CO}-\text{NHC}_6\text{H}_5$, diphenyl-hydroxybiuret. This compound was also formed by the action of 2 moles of phenyl isocyanate upon hydroxylamine. Inasmuch as there is an intimate relationship between the reactions of ketenes and of isocyanates, this work seems especially interesting. One of us has recently shown⁴ that Kjellin's formula is not based upon sound reasoning, and that a formula suggested by Kall⁵ is much to be preferred. This formula is that of carbanilido-phenyl-hydroxyurea, $\text{C}_6\text{H}_5\text{NH}-\text{CO}-\text{NH}-\text{O}-\text{CO}-\text{NHC}_6\text{H}_5$. It is a structure of the normal dihydroxamic acid type. This brings the behavior of phenyl isocyanate and of ketene into harmony.

The method which we used to prepare ketene was a modification of the

² Ref. 1, p. 2443.

³ Kjellin, *Ber.*, **26**, 2384 (1893).

⁴ Hurd, unpublished data.

⁵ Kall, *Ann.*, **263**, 264 (1891).

method described by Schmidlin and Bergman.⁶ In their method, acetone was passed through a combustion tube, filled with pieces of clay, which was heated to 600°. $\text{CH}_3\text{-CO-CH}_3 \longrightarrow \text{CH}_2\text{:C:O} + \text{CH}_4$.

It is interesting and profitable to consider the results of other investigators who have heated acetone with other objects in view. Several years ago, Barbier and Roux⁷ passed acetone vapor through a copper tube 1 m. long, and reported an almost quantitative reaction at 1000°, in accordance with the equation, $2\text{CH}_3\text{-CO-CH}_3 \longrightarrow 2\text{CH}_4 + 2\text{CO} + \text{C}_2\text{H}_4$. Some of the ethylene had decomposed at the high temperature with the resultant formation of acetylene and of hydrogen. More recently, Maihle and Godon⁸ passed acetone vapors over a thoria catalyst at 410–420° and reported the formation of mesityl oxide. Alumina and zirconia replaced thoria with similar results. $2\text{CH}_3\text{-CO-CH}_3 \longrightarrow (\text{CH}_3)_2\text{C:CH-CO-CH}_3 + \text{H}_2\text{O}$. These catalysts are known as "dehydrating catalysts," so that a condensation to mesityl oxide could be expected. It would also be expected that phorone or even mesitylene would be formed by further dehydration. This would serve to explain, in part, the higher boiling portions obtained in the fractionation of the mesityl oxide. There was no mention of ketene in the article. If it was formed it must have been in such small quantities as not to be noticeable. These results indicate that no one of these 3 "catalysts" will catalyze the ketene reaction.

Mlle. E. Peytral⁹ studied the decomposition of acetone vapor at 1150° in a platinum tube 11 cm. long. She noticed a pronounced odor of ketene when the acetone was forced through the tube rapidly. An analysis of the gases given off when the vapor was passed at a slower rate was made, and the following gases were identified: ethylene, carbon monoxide, methane, and traces of acetylene and hydrogen. Her conclusions were that there is but one primary reaction when acetone is decomposed at high temperatures, namely, to form ketene and methane. Ketene, in turn, is then broken further into ethylene and carbon monoxide.

Quite recently also, Adkins and Krause¹⁰ have passed acetone over an alumina catalyst at 455°. They reported the recovery of 62 to 65% of acetone, and the formation of a negligible amount of gas. In spite of the fact that the gases were collected over a solution of salt in water,¹¹ there is ample proof that ketene was not formed at this temperature. Methane would have been present as a by-product together with any ketene, but it too was absent. Neither ketene nor methane was mentioned in the article.

The chief purpose of the paper of Adkins and Krause, and also of the later paper of Adkins,¹² was to discuss the catalytic decomposition of ethyl acetate at moderately high temperatures, usually at 455°. Inasmuch as acetone was one of the important decomposition products, it would have been interesting from our standpoint to have known whether ketene and methane were formed from this "nascent" acetone. Unfortunately, the conditions of the experiment were not favorable for the isolation of ketene or of its reaction products. The presence of methane in the gaseous mixture was not determined, although ethane and total hydrocarbons were measured in some of the runs.

The facts seem to indicate that the reaction, $\text{CH}_3\text{-CO-CH}_3 \longrightarrow \text{CH}_2\text{:CO} + \text{CH}_4$, is an endothermic one, and that the optimum temperature is the maximum temperature

⁶ Schmidlin and Bergman, *Ber.*, **43**, 2821 (1910).

⁷ Barbier and Roux, *Bull. soc. chim.*, [2] **46**, 268 (1886).

⁸ Maihle and Godon, *Bull. soc. chim.*, [4] **21**, 61 (1917).

⁹ Peytral, *Bull. soc. chim.*, [4] **31**, 122 (1922).

¹⁰ Adkins and Krause, *THIS JOURNAL*, **44**, 389 (1922).

¹¹ Ketene reacts with water to form acetic acid.

¹² Adkins, *THIS JOURNAL*, **44**, 2175 (1922).

which is compatible with the decomposition of ketene itself by heat. It would seem, then, that a comparatively rapid flow of the acetone vapor is desirable, in order to push the ketene out of the hot reaction chamber once it is formed. By this method more of the acetone escapes from the furnace undecomposed, but with the apparatus described below, this acetone is readily condensed and recovered.

A few details of Schmidlin and Bergman's results⁶ will be given for reference. Two thirds of the acetone which passed through the combustion tube reacted to form ketene; the remainder was condensed in a series of 6 bottles filled with glass wool and cooled by an ice-salt mixture. About 23% of the total yield of ketene was dissolved in this distillate. The yield of "available ketene" which was not absorbed by the acetone in these bottles was slightly less than 11%. This is based not upon the total acetone which was used, but upon that part of it which was not recovered. Schmidlin and Bergman estimated the ketene by titration of the acetic acid which was formed when ketene reacted with water, with 2 *N* sodium hydroxide solution.

In our experiments, about 50% of the acetone which was passed through the combustion tube could be recovered. As a result, we designed an apparatus which would remove most of this distillate so as to minimize the loss of ketene by solution in it. In addition to acetone, the distillate may have contained condensation products; it also unavoidably contained small quantities of ketene. The yield of ketene, also based upon the acetone which was not recovered in the process, was 17.5%.

A permanent apparatus, similar to that which is described below, cannot be recommended too highly for those who have to do acetylations constantly. There are no by-products, and the method is very simple once the apparatus is assembled. The cost of acetone, for a 17.5% yield of ketene, is somewhat less than the cost for an equivalent amount of acetic anhydride, or of acetyl chloride, even if we assume a 100% yield from these 2 reagents.

Experimental Part

Preparation of Ketene

Ketene was prepared by the pyrogenic decomposition of acetone at 600°. The principle of this method was originally described by Schmidlin and Bergman.⁶

The details of our modification of their method are represented in the illustration. Drops of acetone were vaporized as they fell into the 500cc. flask. This flask was maintained at the temperature of boiling water. The combustion tube, into which the vapors passed, was filled with pieces of porcelain, broken from an evaporating dish, as a contact agent. Corks were used at the ends of the combustion tube. Water glass, which was painted over the possible points of leakage, served as an efficient medium to make these joints gas-tight. Most of the acetone which escaped decomposition was condensed as a distillate by means of the vertical condenser. This distillate was withdrawn at frequent intervals, by opening the pinchcock. In this manner, there was prevented the possibility of prolonged contact between ketene and an organic solvent in which the ketene would be dissolved and lost. The gaseous portion, which contained ketene, passed from the upper end of the condenser into 2 empty,¹³ dry U-tubes, which were cooled by a

¹³ We avoided the use of glass wool in the U-tubes since it is reported to cause the condensation of ketene to a brown liquid. See Wilshire, *J. Chem. Soc.*, **91**, 1941 (1907).

mixture of ice and salt.¹⁴ From there, the gases passed directly into the reaction flask, which was also surrounded by an ice-bath.

The combustion tube was heated in an ordinary gas furnace, with the burners giving their full blast. This temperature was about 600°, indicated by a quartz thermometer placed alongside of the combustion tube. The customary clay covers were placed over the tube during the process. It was found that the yield of ketene diminished considerably when a lower temperature than this was maintained.

In order to determine the yield of ketene, 55 g. of acetone was heated as described. Only 27 g. of this acetone reacted to form ketene, since 28 g. of distillate, chiefly acetone, was collected by the vertical condenser. Ketene was removed from the gaseous de-

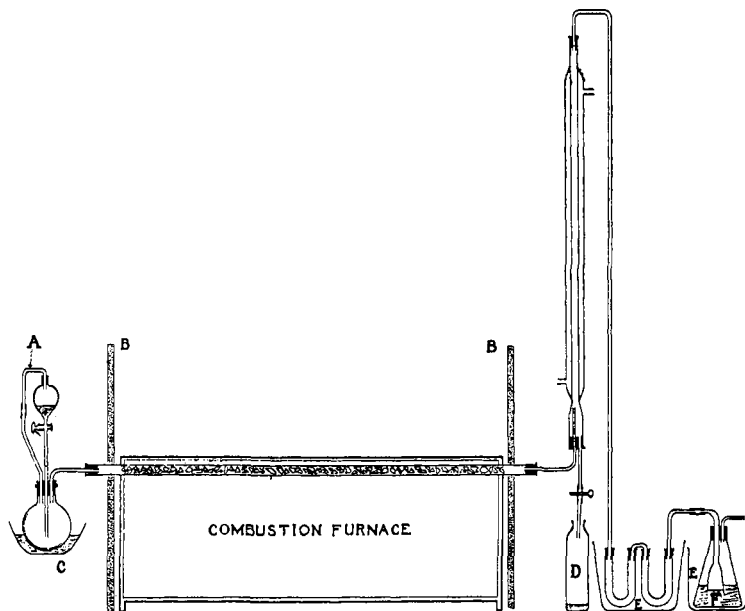


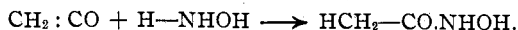
Fig. 1.—A, pressure equalizer; B, asbestos board; C, boiling water-bath; D, receiver for distillate; E, ice-bath; F, reaction flask.

composition products in the reaction flask, where it was passed through absolute ether in which was dissolved 15 g. of aniline. At the conclusion of the experiment, the ether and most of the excess of aniline were removed by distillation. The residue of acetanilide, after purification with ether, melted at 113°; weight, 11 g. This is a yield of 17.5% of ketene, based upon the acetanilide formed, and upon the acetone which was decomposed into gaseous products. It will be recalled that Schmidin and Bergman's yield, calculated similarly, was slightly less than 11%.

By means of such a "calibration" of our apparatus, we knew how much acetone we were to start with in order to obtain a definite weight of ketene in the reaction flask. This assumed, of course, that the system was in operation, and that the same quantity of ketene remained in the apparatus at the end of the operation as was present at the start.

¹⁴ It was necessary to remove even small amounts of acetone, inasmuch as it would react with the free hydroxylamine in the reaction flask to form acetone oxime. Our experience was that the U-tubes collected but a very small amount of liquid.

Ketene and Hydroxylamine

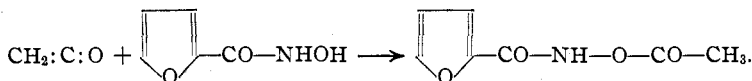


The hydroxylamine was prepared by treating a solution of hydroxylamine hydrochloride in methanol with an equivalent portion of sodium methylate, also dissolved in methanol.

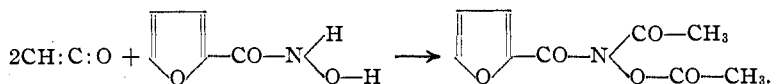
This mixture was filtered from sodium chloride and was partially evaporated in a vacuum. It was then filtered again, and the filtrate was distilled in a vacuum. Three cc. of free hydroxylamine was obtained, which distilled at 55–60° at 20 mm. pressure. It was suspended in dry ether and treated with a slight excess of ketene. The reaction flask was then stoppered and was shaken at frequent intervals in order to mix the 2 liquid phases. After a few hours, the ether was distilled and the oily residue which remained was placed in a vacuum desiccator over sulfuric acid. After a week, transparent crystals formed. These were pressed upon a porous plate and, with no further purification, melted at 86–88°, the melting point of acethydroxamic acid. The crystals gave an intense ferric chloride reaction in water solution, which indicated that the product was not di-acet-hydroxamic acid, which melts at 89°.

Ketene and Hydroxamic Acids

A. Ketene and Pyromucyl-hydroxamic Acid.—1. One g. of pyromucyl-hydroxamic acid was dissolved in ethyl acetate and the solution was treated with ketene until no discoloration resulted when a drop was mixed with ferric chloride solution. The solvent was then distilled and the residue was dried over sulfuric acid in a vacuum desiccator. The solid was washed with ether and pressed upon a porous plate. It melted at 94–96°. Jones and Hurd² reported that the acetyl ester of pyromucyl hydroxamic acid melted at 95–96°. The reaction, therefore, was



2. A new sample (1 g.) of pyromucyl-hydroxamic acid was dissolved in ethyl acetate as before. It was treated with an excess of ketene, the desired product being the diacetyl ester of pyromucyl-hydroxamic acid. About 10–12 cc. of acetone was used.



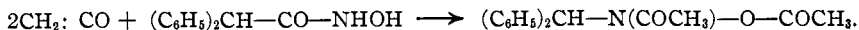
An oil remained after distillation of the solvent. This oil was dried over sulfuric acid in a vacuum for 4 days without solidification, but crystals formed readily when it was cooled to 0°. The white mass was dissolved in hot alcohol and twice the volume of water was added. Crystallization did not start until the side walls were scratched. The precipitate, which was rather abundant, was filtered, washed with water and dried. The melting point was distinct at 54–55°.

This diacetyl ester is soluble in ethyl acetate, in acetone, in hot alcohol, and in benzene. It is insoluble in water, in ether, and in petroleum ether. There is no color reaction when ferric chloride is added to it in alcoholic solution.

Analysis. Subs., 0.2579: N, 15.60 cc. (over 40% KOH at 25.5° and 743 mm.). Calc. for C₉H₉O₅N: N, 6.63. Found: 6.62.

B. Ketene and Diphenyl-acethydroxamic Acid.—Slightly more than 2 equivalents of ketene were passed into a solution of diphenyl-acethydroxamic acid in ethyl acetate.

The solvent was then distilled, and the residue was dried over sulfuric acid in a vacuum. The resulting ester was the diacetyl derivative;¹⁵ it melted at 95.5–97°.



C. Ketene and Benzhydroxamic Acid.—An excess of ketene was allowed to react with a solution of benzhydroxamic acid in ethyl acetate. The oil which remained after the solvent was removed resisted the ordinary means to induce crystallization. The oil could be hydrolyzed to benzhydroxamic acid by contact with a warm solution of sodium hydroxide. This was shown by a recurrence of the ferric chloride reaction. The oil was probably the diacetyl ester of benzhydroxamic acid, but it was not purified and analyzed.

Neither with benzhydroxamic acid nor with diphenyl-acethydroxamic acid did we attempt to isolate the mono-acetyl ester by this method. There is no doubt but that they could have been prepared simply, however, had equivalent quantities of the ketene and of the acid been employed.

In the reactions between ketene and the several hydroxamic acids, the yields in each case approached the theoretical.

Summary

The mechanism of the addition of ketene to hydroxylamine, and of ketene to hydroxamic acids is discussed. The similarity of the behavior of ketene and of phenyl-isocyanate in this respect is pointed out.

Ketene will form not only a mono-acetyl ester, but also a diacetyl ester of a mono-hydroxamic acid with great ease.

An improved apparatus for the preparation of ketene from acetone is described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND THE UNIVERSITY OF ILLINOIS]

CONTRIBUTION TO THE STRUCTURE OF BENZIDINE

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Received November 13, 1922

Shortly after the discovery of benzidine, unexpected reactions of this compound and its derivatives were shown to take place. In particular it was found that the two amino groups acted in many instances as they do in *o*-phenylenediamine; it was possible, for example, with anhydrous oxalic acid, to obtain oxalyl benzidine;¹ with phosgene, carbonyl benzidine;² with carbon disulfide, thiocarbonyl benzidine;³ with phthalic anhydride, phthalyl-benzidine.⁴ Whether these compounds consist of 1 molecule of benzidine and 1 molecule of the other reacting substance was not determined until the molecular weight of phthalyl-benzidine⁵ in nitrobenzene

¹⁵ Ref. 1, p. 2436.

¹ Borodine, *Jahresber.*, **1860**, 356.

² Michles and Zimmerman, *Ber.*, **14**, 2178 (1881).

³ Strakosch, *ibid.*, **5**, 240 (1872).

⁴ Koller, *ibid.*, **37**, 2882 (1904). Schaff and Vanin, *Ann.*, **258**, 363 (1890).

⁵ Käufer, *Ann.*, **351**, 156 (1907); *Ber.*, **40**, 3250 (1907).