A mixture of equal portions of 1,4-piperazonium di-propionate and 1,4-piperazonium di-butyrate melts at 100–110°; a mixture of equal portions of 1,4-piperazonium di-valerate and 1,4-piperazonium di-caproate melts at 100–106°. Thus these derivatives are highly satisfactory for utilization in identification of the aforementioned acids.

Summary

1. Additional derivatives of piperazine have been prepared.

2. The procedure for the preparation and use of piperazine salts for identification of fatty acids has been described.

GAINESVILLE, FLORIDA RECEIVED MAY 1, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Ketene. I. Preparation and Reactions

BY F. O. RICE, JOSEPH GREENBERG, CHARLES E. WATERS AND R. E. VOLLRATH

Since the discovery of this interesting substance in 1907 by Wilsmore, a considerable number of studies of its preparation and properties have been made, particularly in the last few years.[1] However, both in respect to its method of preparation and to its reactions, the literature is somewhat contradictory. In the original method of Wilsmore, liquid acetone or acetic anhydride was decomposed by a platinum wire immersed in the liquid and heated electrically. We have made some experiments using this method in this Laboratory, but met with considerable difficulty because of the ease with which the platinum wire broke; we found the method much less convenient[2] than that first developed by Schmidlin and Bergmann,[1b] and later studied by Hurd and his co-workers,[1c,d,k,l] of decomposing gaseous acetone. In this method acetone vapor is passed through a hard glass tube, which may be filled with pieces of baked clay, and which is heated in the range 500–700°. The yields from this method were good but far from quantitative. Hinshelwood and Hutchinson[1e] studied the decomposition of acetone in a quartz static system and concluded that under these conditions the acetone decomposed according to the equation $CH_3COCH_3 \longrightarrow CO + CH_3 + CH_3$, and that the two methyl groups then reacted to give methane, ethylene and hydrogen. The reaction was homogeneous, since partly filling the reaction bulb with broken quartz had no effect on the rate of decomposition; it followed a unimolecular law and had an activation energy of 68,000 cal. Later, Rice and Vollrath[1f] showed that the decomposition in a quartz tube is the same as in hard glass and that quite high yields of ketene can be obtained in either case. We have since confirmed these experiments and have shown that the decomposition of acetone is homogeneous when either a quartz or a Pyrex reaction vessel is used.

Various claims have been made for solid catalysts that promote the decomposition of acetone into ketene and methane, but Hurd[3] in a review of this in 1929 states that up to that time no effective catalyst for the production of ketene from acetone had been developed. Subsequent to this, further claims[1h,i] have been made for catalysts, especially in a paper by Berl and Kullmann.[1i] Hurd, Sweet and Thomas[1k] have criticized the results of Berl and Kullmann and concluded that any catalytic effect was very small. Berl and Kullmann's conclusion as to the effect of catalysts and temperature must have been based on experiments in which less than 15% of the acetone was decomposed because all their other experiments (except two) show a yield of ketene of 55 ± 12%; we have found that their method of analysis does not give reliable results for small percentage decompositions.

The literature on the chemistry of this compound is also somewhat contradictory; van Alphen[4] concluded from a study of its reactivity with various substances that it is a somewhat weak acetylating agent; on the other hand,

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(1) (a) Wilsmore, *J. Chem. Soc*, **91**, 1938 (1907); (b) Schmidlin and Bergmann, *Ber.*, **43**, 2821 (1910); (c) Hurd and Cochran, THIS JOURNAL, **45**, 515 (1923); (d) Hurd and Tallyn, *ibid.*, **47**, 1427 (1925); (e) Hinshelwood and Hutchinson, *Proc. Roy. Soc.* (London), **A111**, 245 (1926; (f) Rice and Vollrath, *Proc. Nat. Acad. Sci.*, **15**, 702 (1929); (g) Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929; (h) Al, *Z. angew. Chem.*, **45**, 545 (1932); (i) Berl and Kullmann, *Ber.*, **65**, 1114 (1932); (k) Hurd, Sweet and Thomas, THIS JOURNAL, **55**, 335 (1933); (l) Hurd and Dull, *ibid.*, **54**, 3428 (1932).

(2) See however Ott, Schröter and Packendorff, *J. prakt. Chem.*, **130**, 177 (1931), who used a tungsten filament instead of platinum.

(3) See Ref. 1g, p. 251.

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

Partridge[5] states that the chief difficulty in the use of ketene for acetylating cellulose is the difficulty of controlling the extremely vigorous reaction. Our own experiments prove that ketene is a powerful acetylating agent; substances such as cetyl alcohol and phenol which van Alphen reported as not reacting can be converted quantitatively into the acetyl derivatives. Under proper conditions it will acetylate most organic substances containing an active hydrogen atom, provided they can be liquefied or dissolved in a solvent not attacked by the ketene. Even at temperatures as low as −80° it reacts violently with some substances, such as aniline or methyl alcohol. On the other hand, water dropped into liquid ketene freezes, and the ketene can be distilled off and both the water and the ketene recovered unchanged. Furthermore, our experiments indicate that, under various conditions, ketene does not appear to have any action on such polysaccharides as cane sugar or cellulose. The reaction that occurs when an acetic anhydride solution of ketene is employed is probably to be ascribed to acetylation by the acetic anhydride followed by conversion of the acetic acid back into its anhydride by the ketene.

The chief difficulty connected with the use of ketene for acetylation arises from the ease with which it polymerizes and the conditions for its successful use should be those least favorable to the polymerization process. These conditions are that the ketene shall be kept in a very dilute state and the substance to be acetylated in a relatively very concentrated state; in this way we favor the reaction of the ketene with the substrate instead of with itself.

Mechanism.—The mechanism of the decomposition of acetone is of considerable interest in connection with the question as to the conditions for optimum yield of ketene. The decomposition may occur in a single step through the migration of a hydrogen atom to give methane and ketene or it may occur through the intermediate formation of free radicals. Since the thermal decomposition of acetone has been shown[6] to result in the production of methyl radicals and since the reaction producing the methyl groups has an activation energy about the same as the over-all decomposition into methane and ketene[7] we may assume a mechanism similar to that which has successfully predicted the products formed in the thermal decomposition of hydrocarbons;[8] this consists of a primary rupture of a C–C bond, resulting in the production of two free radicals, followed by a chain reaction. In the case of acetone it would be represented as follows

$$CH_3COCH_3 \longrightarrow CH_3 + CH_3CO;\ CH_3CO \longrightarrow CH_3 + CO;\ CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_3COCH_2 \longrightarrow CH_4 + CH_2{=}CO + CH_3$$

The primary rupture gives a methyl group and an acetyl group. The latter is probably very unstable and presumably decomposes rapidly to carbon monoxide and a second methyl group; when a methyl group reacts with an acetone molecule it takes off a hydrogen atom to form CH_4 and leave the radical CH_3COCH_2; this radical decomposes forming a molecule of ketene and regenerating the methyl group; in this way we have a chain reaction producing methane and ketene in equal proportions. The chain probably consists of at least 100 cycles[9] so that for small fractional decompositions no products other than methane and ketene should be formed in significant amounts.

On the basis of this mechanism, an essential condition for good yields of ketene must be a small fractional decomposition of the acetone;[10] as the concentration of the ketene rises it not only decomposes on its own account but is open to attack by the free radicals produced in the chain mechanism; if one plots the yield of ketene (based on the decomposed acetone) against the percentage of acetone decomposed a curve is obtained (Fig. 2) which approaches a 100% yield of ketene for a very small percentage decomposition of acetone and which indicates a very low yield of ketene for large percentage decompositions of acetone. Factors, therefore, such as temperature of decomposition, time in the furnace, and presence of inert gases should not have any great effect on the yield of ketene (except in so far as they affect the fraction of acetone decomposed) and would be expected to be only second or third order effects. However, for small laboratory scale experiments it is probably more convenient to decompose a considerable fraction

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(5) Partridge, *Ind. Eng. Chem.*, **23**, 496 (1931).

(6) Rice, Johnston and Evering, THIS JOURNAL, **54**, 3529 (1932).

(7) Rice and Johnston, *ibid.*, **56**, 214 (1934).

(8) Rice, *ibid.*, **53**, 1959 (1931); *ibid.*, **55**, 3035 (1933).

(9) Rice and Herzfeld, *ibid.*, **56**, 284 (1934).

(10) This conclusion holds also if the thermal decomposition consists simply of a migration of a hydrogen atom. It is now generally recognized that secondary reactions can only be avoided by decomposing organic compounds to a small extent. See Schneider and Per K. Frolich, *Ind. Eng. Chem.*, **23**, 1405 (1931); Frey and Hepp, *ibid.*, **25**, 441 (1933).

(50–60%) of the acetone, with a resulting smaller yield on the basis of acetone decomposed.

Analytical Procedure.—It seems probable that the analytical procedure, in estimating both the acetone decomposed and the ketene produced, is responsible to some extent for the conflicting claims regarding yields of ketene. Owing to the highly reactive character of this compound, a special technique must be developed if the results are to have more than a qualitative value, especially at low percentage decompositions. In our earlier experiments we passed acetone either alone or mixed with nitrogen through a quartz tube maintained at a definite temperature in an electric furnace. A known quantity of acetone was run through and the undecomposed acetone and ketene were absorbed in a series of three wash bottles containing water. A fourth wash bottle was kept in the line and was examined separately as a check on the complete absorption of both the acetone and the ketene. The acetone was estimated by Messinger's method[11] and the ketene was estimated by titrating the acetic acid present after boiling the solution to expel traces of carbon dioxide. Separate experiments showed that this boiling caused no loss of acetic acid. In some of the experiments the acetone was recovered and estimated directly by distilling it from the aqueous solution in a special fractionating column.[12] In still another series of experiments the gases were passed from the furnace into wash bottles containing aniline and afterward the acetone and acetanilide were separated and estimated by distillation. Finally some experiments were performed in which the gases from the furnace were passed directly into a trap immersed in liquid air; the contents of the trap were distilled through a vacuum jacketed still and the ketene was estimated by titration and the residual acetone by weighing. All these methods gave fairly concordant results, although naturally the error is fairly large in those experiments in which only a small fraction of the acetone is decomposed.

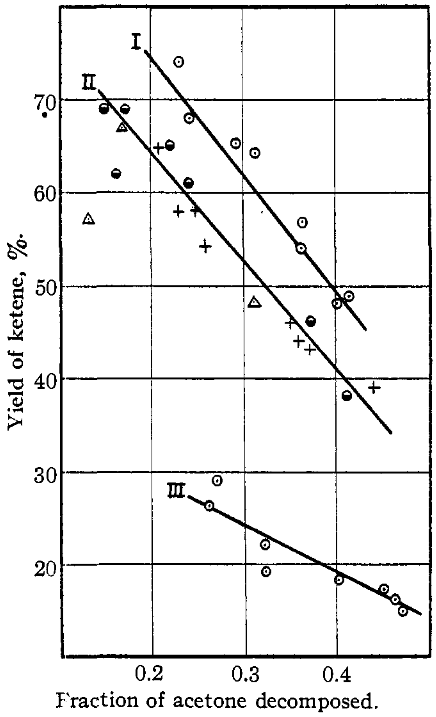

Fig. 1.—Effect of different factors on the yield of ketene, temperature 600° in all experiments: Curve I, empty quartz tube, N_2 as carrier gas, acetone pressure 70 mm.; Curve II, quartz tube, N_2 as carrier gas, acetone pressure 280 mm. (+ tube empty, ● tube packed with broken quartz, △ tube packed with broken Pyrex); Curve III, empty quartz tube, H_2 as carrier gas, acetone pressure 280 mm.

It seemed desirable therefore to devise a method which would enable us to measure with greater certainty the yield of ketene obtained when only a relatively small fraction of the acetone was decomposed. This was done by decomposing a known amount of acetone to a small extent in a circulating system, recovering the undecomposed acetone by distillation and repeating the experiment using the recovered acetone. After several repetitions the total ketene formed was estimated by titration and the acetone decomposed was found by difference. In one such experiment[13] performed at 762°, 2.72 moles of acetone was circulated three times through the furnace at a rate such that approximately 20% of the acetone decomposed at each passage; 1.35 moles of acetone was finally recovered and 0.92 mole of ketene was formed and estimated as acetic acid. This represents 70% of the theoretical yield of ketene.

We also made frequent analyses of the composition of the gases leaving the furnace after absorption of the acetone and ketene. We found these to consist mainly of methane accompanied by smaller amounts of ethylene and carbon monoxide and traces of hydrogen. A typical analysis is: CH_4, 82.2%; CO, 11.2%; C_2H_4, 5.1%; H_2, 0.9%. This experiment was performed at 667° and the rate of flow of the acetone was such that 11% was decomposed.

Yields of Ketene.—In Fig. 1, Curves I and II, we have summarized the results of a series of experiments which show the effect on the yield of ketene of (1) fraction of acetone decomposed, (2) the initial partial pressure of the acetone, (3) packing the tube with broken quartz, (4) packing the tube with broken Pyrex. We performed this series of experiments very carefully and it seems certain that dilution of the acetone vapor with nitrogen has a small beneficial effect on the yield of ketene. One or two experiments using methane or carbon monoxide showed the same effect, whereas substitution of hydrogen as carrier gas (Curve III) diminished the yield of ketene very considerably. The presence of broken quartz had no effect, while broken Pyrex very slightly diminished the yield of ketene.

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[11] Goodwin, THIS JOURNAL, **42**, 39 (1920).

[12] Cooper and Fasce, *Ind. Eng. Chem.*, **20**, 420 (1928).

[13] This experiment was performed by Dr. R. N. Washbourne.

It is evident that the effect of an inert gas such as nitrogen or carbon monoxide, or of a quartz or Pyrex packing in the tube, is a very secondary factor compared with the effect of the fraction of acetone decomposed.

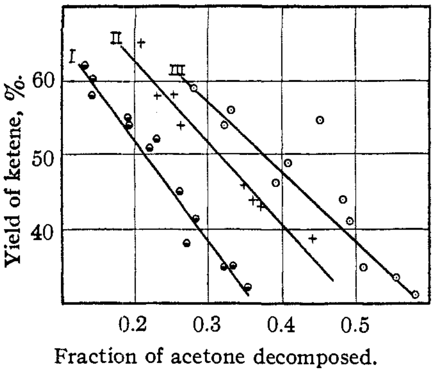

Fig. 2.—Effect of temperature on the yield of ketene. In all the experiments an empty quartz tube was used, with N_2 as carrier gas and the acetone pressure 280 mm. Curve I, 588°; Curve II, 600°; Curve III, 617°.

In Fig. 2 we have summarized the results of a series of experiments which show the effect of (1) fraction of acetone decomposed, (2) the temperature. Below 600°, the yield of ketene shows a measurable diminution but above 600° the effect of changing the temperature is not much greater than our experimental error; we have verified this up to temperatures of about 900°. We also find that the temperature of the decomposition, provided it is above 600°, is only at best a second order effect compared with the effect of the extent of the decomposition of the acetone.

In Fig. 3 we have plotted the results of a large number of experiments made in the range 650–900°, in some of which pure acetone vapor was used both at atmospheric and lower pressures, and in others of which nitrogen was used as carrier gas. Owing to the difficulty of obtaining accurate measurements of the amount of acetone decomposed, especially with smaller fractional decompositions, there is considerable scattering of the points; however, the trend of the curve is unmistakable and shows clearly that the amount of acetone decomposed is definitely the predominant factor in securing good yields of ketene.

We have also made some experiments on the effect of the purity of the acetone on the yield of ketene. In most of the work we used acetone purified through the bisulfite compound; results using this acetone checked very well with one or two experiments in which acetone was purified by sodium iodide[14] and by shaking with permanganate and distilling. We also tried the effect of adding various substances to the acetone to the extent of 0.1 molar per cent. Methyl iodide, dimethyl sulfide, dimethyl sulfate, isoamyl nitrite and tetraethyllead diminished the yield of ketene considerably, whereas acetaldehyde, azoisopropane, ammonia and triphenylmethane at most diminished the yield only to a slight extent. In preparing ketene from acetone it seems well therefore to free the acetone from traces of iodine or sulfur compounds.

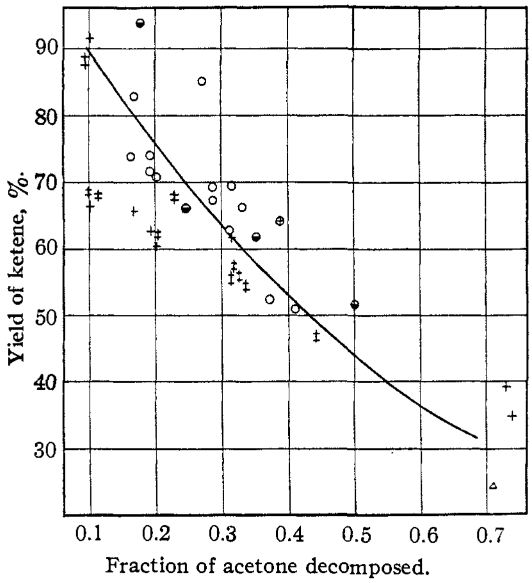

Fig. 3.—Effect of different factors on the yield of ketene, using an empty quartz tube:

○ acetone pressure 760 mm. (in some experiments 280 mm. with N_2 as carrier gas), temperature 650°;

⊖⊕ acetone pressure 280 mm. with N_2 as carrier gas, temperature 700 and 750°, respectively;

+‡△ acetone pressure 5–20 mm., no carrier gas, temperature 800, 850 and 900°, respectively.

Laboratory Preparation.—Ketene can be prepared conveniently by dropping acetone directly from a separatory funnel into a quartz reaction tube heated in the range 650–750°.[11] The rate of introduction of the acetone is adjusted so that from 10–40% of the acetone is decomposed. The exit gases from the reaction tube are led into a Pyrex tube immersed in dry ice in order to condense the undecomposed acetone and the ketene, incidentally also dissolving out part of the ethylene. Ketene is completely miscible with acetone; at −80° the vapor pressure of ketene over a 5–10% solution in acetone is sufficiently low that a large volume of inert gas can be passed through it without appreciable loss of the ketene; on the other hand,

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(14) Shipsey and Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

ethylene, on account of its much higher vapor pressure, escapes to some degree along with methane and carbon monoxide. At the end of half an hour the receiver is changed and the ketene immediately distilled off into a second receiver at −80° by warming the solution rapidly to the boiling-point of acetone. A reflux condenser cooled by water prevents the acetone from distilling into the second receiver. In order to prevent solution of the ethylene as far as possible the delivery tube into this second receiver is not allowed to dip into the condensed ketene. The ketene is then distilled a second time by allowing the vessel to warm up to 0° and is again condensed in a receiver at −80°. After a third distillation, the ketene is substantially free from acetone but still contains from 5–10% of ethylene. The ketene–acetone mixture condensed out from the gases leaving the furnace contains particles of carbon and resinous material and these appear to catalyze the polymerization even at −80°. We have also observed the same effect if ketene is allowed to come in contact with fragments of rubber from tubing or stoppers. For this reason the entire distillation apparatus must be so arranged that neither the ketene vapor nor the liquid can come in contact with rubber; ketene prepared in the manner just described is quite stable at −80°. In one experiment 15 g. of ketene prepared as described was distilled into a weighed Pyrex trap which was kept at −80° for one week. The ketene was then distilled off and the trap was again weighed to determine the amount of polymer which had been formed. It was found that slightly less than 1% of the ketene had polymerized, and several similar experiments confirmed this result.

Presumably, Hurd, Sweet and Thomas,[1k] in their report that polymerization of ketene occurs even at −80° but is retarded by a trace of hydroquinone, refer to the impure ketene. We did not investigate their method of stabilizing the ketene because distillation seemed quite satisfactory. We may, however, remark here that we found that hydroquinone, in contrast to phenol, is acetylated with great readiness by ketene at room temperature in acetone solution.

Preparation of Pure Ketene.—The ketene prepared in the foregoing manner was finally purified from ethylene by distillation in a vacuum-jacketed column packed with pieces of Pyrex tubing. After one distillation the ketene seemed to be quite pure and a sample of the vapor examined in a gas analysis apparatus showed complete absorption in the potash bulb. The b. p. (−41.0°) and m. p. (−134°) of the pure ketene were determined using a copper–constantan thermocouple which we compared with one checked by the Bureau of Standards. Wilsmore's figures[1a] are b. p. −56° and m. p. −151° but his analysis indicates that his sample of ketene contained about 8% ethylene.

Method of Acetylation.—Most organic substances having an active hydrogen atom, which are liquids or which melt without decomposition, can be acetylated by ketene very simply. The method used was to place 10 g. of the substance in a large Pyrex reaction tube provided with a stopper fitted with inlet and outlet tubes; the inlet tube was connected with a reservoir containing ketene at −80°; by allowing the reservoir to warm up, ketene could be passed through the reaction tube at a convenient rate. The outlet from the reaction vessel was connected to a third Pyrex test-tube kept at −80°, in which the unreacted ketene was condensed. The reaction vessel could be heated in an oil-bath above the melting point of the compound to be acetylated (usually to some temperature in the range 100–200° depending on the ease of acetylation of the compound). The rate of reaction varied considerably: with some substances the ketene reacted as fast as it could be passed in, whereas with other compounds only a small fraction of the ketene reacted and most of it was recovered in the receiver tube at −80°; however, even in such cases fairly complete acetylation could be obtained in the course of thirty minutes passage of the ketene vapor. The following are the results of some of our acetylation experiments.

Acetylation of Alcohols.—The lower primary and secondary alcohols react very readily with ketene even at room temperature[4] and pure esters can be prepared in this way very conveniently.

Van Alphen has reported[4] that cetyl alcohol may be recovered unchanged after standing in ethereal solution at room temperature for one day with ketene. We found, however, that if cetyl alcohol is treated with ketene at 180° according to the foregoing method, acetylation occurs instantaneously; the cetyl acetate melted at 19° without purification.

Of the tertiary alcohols, we have examined only tertiary butyl alcohol[15] and have found that it does not react readily with ketene. In one experiment we mixed 12 cc. of liquid ketene free from acetone with 6 cc. of pure tertiary butyl alcohol (m. p. 25°) and allowed the mixture to stand overnight at −80°. The next morning the tertiary butyl alcohol had not dissolved and there was no perceptible change. The vessel containing the mixture was then placed in a bath at −10° and the ketene was evaporated off and condensed in a vessel at −80°. Practically all of the ketene was recovered and although the tertiary butyl alcohol had a slight odor of the ester, 5.5 cc. distilled over at 82°. A repetition of this experiment using ketene containing a little acetone gave substantially the same result except that the tertiary butyl alcohol dissolved slowly in the ketene–acetone mixture at −80°. From these experiments it seems certain that the reaction between ketene and tertiary butyl alcohol is extremely slow at −80°.

When gaseous ketene is passed into tertiary butyl alcohol just below its boiling point, the substances react slowly but the reaction is accompanied by considerable polymerization of the ketene. The reaction is slow and incomplete even when small bubbles are used to give as much contact as possible between the reactants; less than half of the ketene consumed is converted into ester, the remainder being polymerized.

Acetylation of Phenols.—Van Alphen reports[4] that phenol in ethereal solution at room temperature does not react with ketene. However, we found that on heating to just below its boiling point (183°) phenol acetylates almost instantaneously when ketene gas is passed into it. The phenyl acetate formed has a boiling point of 196° without further purification. On the other hand, *o*-nitrophenol

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(15) Our results do not agree with those of Davis and Murray, *Ind. Eng. Chem.*, **18**, 846 (1933), and Hurd, Sweet and Thomas, THIS JOURNAL, **55**, 335 (1933).

reacted much more slowly; even after gaseous ketene had been passed through the solution for thirty minutes, only a 60–70% yield of *o*-nitrophenyl acetate was obtained. The acetate was separated from the unchanged *o*-nitrophenol by extraction and crystallization from petroleum ether.

Van Alphen passed ketene vapor into an ethereal solution of salicylic acid at room temperature, evaporated off the ether and crystallized the product from dilute alcohol.[4] In this way he obtained acetylsalicylic acid (m. p. 133.5°). In repeating this experiment but crystallizing from anhydrous ether instead of aqueous alcohol, we obtained crystals which melted at 125–130°, and which gave off an odor of acetic anhydride on standing. They were further shown to contain more than one equivalent of the acetyl group by refluxing a weighed amount with standard alkali. It seems that a mixed acid anhydride, the formation of which we were not able to avoid under these or similar conditions, is also formed in the acetylation of *o*-hydroxybenzoic acid. An attempt was made to acetylate *m*-hydroxybenzoic acid (m. p. 200°) at 225°, but acetic anhydride distilled off and the residue solidified to a solid resinous mass from which no crystals could be obtained. Apparently some acetylation had taken place but the acetylated product was presumably unstable at 225°.

Acetylation of NH_2 Groups.—It is known[4] that ketene reacts with great readiness with basic amines but as the substance becomes less basic the difficulty of acetylation increases. Van Alphen reports[4] no action in ethereal solution at room temperature with *o*- or *p*-nitroaniline and only slow action with *m*-nitroaniline. We found that *o*-nitroaniline reacts very slowly; after half an hour's treatment at 140° only a 25% yield of *o*-nitroacetanilide was obtained by crystallization from alcohol. Acetanilide is also only slowly acetylated by ketene; after half an hour's passage of the gas at 140°, about a 50% yield of the diacetanilide was obtained by extraction and crystallization from petroleum ether. Attempts to acetylate benzamide by means of ketene (at 180°) resulted in the production of benzonitrile and acetic anhydride which distilled off. The probable course of the reaction is

$$CH_2{=}CO + C_6H_5CONH_2 \longrightarrow C_6H_5CONHCOCH_3$$
$$C_6H_5CONHCOCH_3 \longrightarrow C_6H_5CN + CH_3COOH$$
$$CH_3COOH + CH_2CO \longrightarrow (CH_3CO)_2O$$

About 70% of the benzamide was recovered as benzonitrile after five minutes' passage of the ketene. It seems probable that complete conversion could have been obtained by the use of larger amounts of ketene.

Summary

In order to obtain good yields of ketene from acetone it seems to be essential to decompose only a small fraction of the acetone. Factors such as the temperature of decomposition (provided it is not much below 600°), time in the furnace and the presence of inert gases do not appear to have any very appreciable effect on the yield of ketene except in so far as they affect the fraction of acetone decomposed.

Liquid ketene is stable at −80° when freed by distillation from accidental impurities such as carbon particles. As ordinarily prepared it contains from 5–10% of ethylene which can be removed by distillation in a vacuum-jacketed still. Pure ketene melts at −134.6° and boils at −41° at 760 mm.

Ketene is a powerful acetylating agent and under proper conditions acetylates most organic substances containing active hydrogen atoms, provided the substances can be liquefied or dissolved in a solvent inactive toward ketene. Polymerization may almost always be avoided by keeping the ketene very dilute and the substrate relatively very concentrated during the acetylation process, which is then carried out at as high a temperature as possible. *t*-Butyl alcohol and probably other *t*-alcohols are exceptional, in that the rate of acetylation is so slow that polymerization of the ketene occurs to a considerable extent.

BALTIMORE, MARYLAND

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