

urements was 0.1 lower than the value found by several investigators from measurements in solution, although the solvent effect, which, in the case of chlorobenzene, lowers the solution value to such an extent that the gas value is 10% higher than that measured in solution, should lead to a similarly lower value for *o*-dichlorobenzene.⁶ Since addition of 10% to the solution value, 2.27, for *o*-dichlorobenzene gives a value, 2.50, practically identical with the newly determined gas value, 2.51, in Table II, it is evident that there is no anomaly in the solvent effect for this compound.

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Summary

The dielectric constants of the vapors of chloro-

bromo-, iodo-, *p*-fluorobromo-, *p*-fluoroiodo-, *p*-fluo-ronitro- and *o*-dichlorobenzene, and of *p*- and *o*-xylene have been measured and used to calculate the dipole moments of the molecules. The moment values found for chlorobenzene and bromobenzene agree closely with those in the literature, while that for iodobenzene is slightly higher than would be expected on the basis of previous measurements in solution. The moment value of *o*-dichlorobenzene is much higher than the one in the literature and in excellent agreement with that obtained by correcting the solution value for solvent effect. The data for the two xylenes give an accurate value, 0.36, for the group moment produced by the attachment of a methyl group to a benzene ring. The moments found for the *p*-disubstituted benzenes are larger than the differences between the corresponding mono-substituted compounds by amounts which may be accounted for by resonance.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Condensation Products of Ketene with Ketones¹

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The reactions of ketene have been studied rather extensively. It has been found to act as the anhydride of acetic acid. Although it is commonly prepared from acetone and therefore contaminated with it to some extent, no one appears to have noted a reaction between the two. Investigations have been reported in which the reactivity of ketene with ketones was studied without a catalyst² and in the presence of anhydrous sodium or potassium acetate.³ No reaction was noted. Acetone has been used as a solvent in the acid catalyzed acetylation of carbohydrates⁴ with ketene. A reaction undoubtedly took place in these cases but escaped notice. Similarly, in the acid catalyzed acetylation of butyl alcohol,⁵ the ketene was contaminated with acetone, and the two probably reacted to a limited extent.

(1) Abstract of a thesis by B. H. Gwynn, submitted to the faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, June, 1942. Present address, Westvaco Chlorine Products Corp., Carteret, New Jersey.

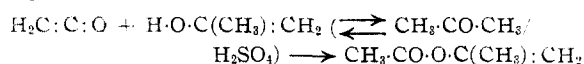
(2) Staudinger and Klever, *Ber.*, **41**, 594 (1908).

(3) Hurd and Williams, *THIS JOURNAL*, **58**, 962 (1936).

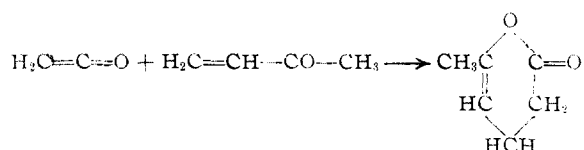
(4) Hurd, Cantor and Roe, *ibid.*, **61**, 426 (1939).

(5) Moresy, *Ind. Eng. Chem.*, **31**, 1129 (1939).

This investigation has shown that ketene does react with ketones. In the presence of a small amount of sulfuric acid the product is the acetate of the enol form of the ketone, as indicated by the equation



Since the completion of this work, ketene has been reported to react with vinyl ketones to yield cyclic esters of the enol form of *delta* keto acids,⁶ an entirely different type of reaction from that observed in this study, as indicated



Experimental Part

Apparatus.—Ketene was generated in a lamp which was constructed in the same manner as one described by Hurd.⁷ In order to separate acetone from the ketene, the

(6) U. S. Patent 2,265,165, Dec. 9, 1941; *C. A.*, **36**, 1614 (1942).

(7) Hurd, *J. Org. Chem.*, **5**, 122 (1940).

pyrolysis gases were passed through two water-cooled spiral condensers, then through two cold traps. The first of these cold traps was kept at 0°, the second at -35 to -40°. The resultant gas was practically acetone-free and was passed into the material with which it was desired to have it react. The inlet tube was placed in such a manner as to direct the entering gas into a rapidly revolving stirrer. The temperature of the reaction tube was maintained at the desired point by means of an oil-bath. An expansion chamber surrounded by an ice-bath was placed so as to return volatile liquids to the reactor. The output of the generator, determined by absorption in caustic,⁷ was approximately 0.25 mole (hr). All fractionations were made with a modified Podbielniak column.

Materials Used.—The ketones used in this work were either purchased or prepared by standard methods. In either case they were distilled or fractionated before use except for the acetone, which was Mallinckrodt analytical reagent grade, and the acetophenone, which was Eastman Kodak Company white label grade. The 2,4-dinitrophenylhydrazones were prepared from each of the ketones except 2,6-dimethyl-4-heptanone and 2,4-dimethyl-3-pentanone and found to melt properly. The semicarbazides were prepared from 2,6-dimethyl-4-heptanone and 2,4-dimethyl-3-pentanone and the melting points checked with those in the literature.

Reaction of Ketene with Acetone.—Ketene was passed into a well-stirred solution of one mole of acetone and a trace of sulfuric acid at the rate of 0.25 mole per hour. Forty-one runs were made to determine optimum conditions. The best reaction temperature at atmospheric pressure was found to be about 55°, and the optimum yield of the enol acetate was obtained with 0.007 mole of sulfuric acid and 0.81 mole of ketene per mole of acetone.

In a run which approximated optimum conditions, 0.87 mole of ketene was passed into a solution of 0.007 mole of sulfuric acid in one mole of acetone at 55°. The product was then fractionated to give 39.5 ml. of product boiling in the range 90–96.5°, leaving 8.5 ml. of residue; conversion, 45%. The residue was shown to be principally diketene with some higher polymers and acetic anhydride.

Identification of Product.—Several 90–96.5°-fractions were refractionated and a material obtained which boiled at 96° (750 mm.). This had a sharp, ester-like odor. It reacted quite vigorously with bromine and reduced alkaline permanganate readily. Metallic sodium appeared to induce polymerization. These qualitative observations suggested that the product might be 1-propen-2-ol acetate. This compound was previously prepared by Nieuwland⁸ from acetic acid and methylacetylene. He reported a b. p. of 92–94° (736 mm.). The saponification equivalent, as determined, was 106.0, 105.3. Calculated value for 1-propen-2-ol acetate is 100.07. The method is reported to give high values for esters of tertiary alcohols.⁹ The 2,4-dinitrophenylhydrazone was prepared by the standard method¹⁰ and a derivative, m. p. 125°, obtained. The derivative prepared from pure acetone melted at 126°, and a mixture of the two melted at 125.5°, thereby indicating the identity of the two. The formation of this

derivative occurs in acid solution so that 1-propen-2-ol acetate should revert to acetic acid and acetone.

Anal. Calculated for C₅H₈O₂: C, 59.96; H, 8.06. Found: C, 60.03; H, 8.18.

Reaction of Ketene with 2-Butanone.—Several runs were made in which catalyst concentration, temperature and amount of ketene introduced were varied. Optimum conditions, however, were not determined. Best results were obtained by passing ketene, at the rate of 0.25 mole per hour, into a solution of 70 ml. of 2-butanone and 0.007 mole of sulfuric acid for two and one-half hours at 75°. The product was fractionated and 40 ml. of a fraction, b. p. 112–122°, obtained, leaving 5.5 ml. of residue. Refractionation of the 112–122°-fraction gave principally material with a b. p. of 118–120° (751.5 mm.), which could not be further purified by this method. The 2,4-dinitrophenylhydrazone was prepared and found to melt at 110°. A similar derivative prepared from the starting ketone melted at 112°, and a mixture of the two melted at 111.25°. The saponification equivalent was determined.⁹ Calculated value for 1-buten-2-ol acetate or 2-buten-2-ol acetate is 114.08. Found: fraction boiling 118–19°, 118.4, 116.4; fraction boiling 119–20°, 113.9, 114.8. The product is, therefore, the acetate of the enol form of 2-butanone but, probably, is a mixture of both possible forms; conversion, 47%.

Phosphoric Acid and *p*-Toluenesulfonic Acid as Catalysts.—Ketene was passed into a solution of 70 ml. of 2-butanone and 3 drops of 85% phosphoric acid for five hours at 55°. The product was fractionated and found to yield only 2 ml. of material, b. p. 112–122°. A similar run using 3 drops of sulfuric acid gave 20 ml. of material boiling in this range. Another run was made in which ketene was passed into 70 ml. of 2-butanone for three and one-half hours at 55° and a small amount of *p*-toluenesulfonic acid. The product was fractionated and it was found to yield no distillate in the range 112–122°.

Reaction of Ketene with Acetophenone.—Ketene was passed through a solution of 3 drops of sulfuric acid in 70 ml. of acetophenone for three and one-half hours at 64°. This product was fractionated and 25 ml. of product obtained, b. p. 85° (2 mm.). The saponification equivalent was determined.⁹ Calculated for 1-phenylethenol acetate, 162.08. Found: 160.4. The 2,4-dinitrophenylhydrazone was prepared¹⁰ and found to melt at 243°; derivative from acetophenone, m. p. 244°, mixed m. p. 243.5°, conversion, 19%.

Reaction of Ketene with Mesityl Oxide.—Ketene was passed into a solution of 3 drops of sulfuric acid in 70 ml. of mesityl oxide for three and one-half hours at 75°. The product was fractionated to give 62 ml. of material with a b. p. of 57.5–58° (10 mm.). Calculated saponification equivalent⁹ for 4-methyl-1,3-pentadiene-2-ol acetate 140.10. Found: 146.4, 147.0. The 2,4-dinitrophenylhydrazone¹⁰ melted at 200°; derivative from mesityl oxide, m. p. 199°, mixed m. p. 199°. Since this is close to the melting point of the reagent, a mixed melting point was determined for a mixture of reagent and derivative prepared from the ester (m. p. 177–180°). Whereas the derivative formed immediately when the ketone was used, a period of several minutes was necessary when the ester was used. This was the behavior noted with all of these

(8) Nieuwland, *This Journal*, **56**, 1802 (1934).

(9) Redeman and Lucas, *Ind. Eng. Chem., Anal. Ed.*, **9**, 521 (1937).

(10) Shriner and Fuson, "Identification of Organic Compounds," J. Wiley and Sons, Inc., New York, N. Y., 1940.

esters. Conversion, 46.8%. This ester showed some tendency to polymerize to a tar when heated at too high a temperature.

Reaction of Ketene with 2,4-Dimethyl-3-pentanone.—A total of three runs was made with 2,4-dimethyl-3-pentanone at temperatures up to 117°. In one of these runs ketene was passed through a solution of 5 drops of sulfuric acid in 70 ml. of the ketone for four and one-quarter hours at 117°. Upon fractionating only the ketone and a small amount (1.4 ml.) of diketene were obtained. The conditions employed in the other runs were less severe and likewise yielded no ester.

Reaction of Ketene with Pinacolone.—Ketene was passed into a solution of 15 drops (0.007 mole) of sulfuric acid in 70 ml. of pinacolone for two and two-thirds hours (0.66 mole) at 110°. Upon fractionation, 3.5 ml. of a fraction was obtained, b. p. 134–135° (752 mm.). The saponification equivalent⁹ of this was only 88.3 as compared with a calculated value of 142 for 3,3-dimethyl-1-buten-2-ol acetate. This probably indicates contamination with diketene, boiling only a few degrees lower. The 2,4-dinitrophenylhydrazone was prepared¹⁰ and separated into two fractions, one of which melted high, the other at 123.5°. The derivative prepared from the ketone melted at 125° and a mixture of the two at 124.5°.

Determination of Physical Properties.—The boiling points, densities and refractive indices for the compounds (or mixtures of isomers) were determined and are shown in Table I.

TABLE I
PHYSICAL PROPERTIES OF ENOL ACETATES

Acetate of	B. p. °C.	Mm.	n_{20}^D	d_{25}^{25}
Acetone	96	750	1.4001	0.9308
2-Butanone	118–120	751.5	1.4111	.9043
Mesityl oxide	57.5–58	10	1.4611	.9250
Acetophenone	85	2	1.5329	1.0715
4-Methyl-2-pentanone	143–145	741.5	1.4164	0.8695
2-Heptanone	112–114	93	1.4262	.7488
2-Octanone	108	42.5	1.4283	.8692
2,6-Dimethyl-4-heptanone	74	12	1.4281	.8541
Cyclohexanone	99	48	1.4573	.9952

Discussion

In nearly all of the cases investigated, ketene reacted with ketones to form the acetate of the

enol form. The exceptions are worthy of mention since they are those which would be expected to react with most difficulty. Diisopropyl ketone, with only two *alpha* (or 4-position) H-atoms to the carbonyl group, did not react at all, whereas pinacolone with three *alpha* (or 4-position) H-atoms, reacted only slightly. In every case where four or more *alpha* (or 4-position) H-atoms were present, reaction occurred to an appreciable extent. Acetophenone, with only three such groupings, reacted quite readily but an additional factor is present in this case—namely, the formation of a conjugated system upon enolization. Although the evidence is not complete, the results strongly indicate that ease of reaction with ketene parallels the ease of enolization of the ketone. This is well illustrated by the much greater ease of reaction of mesityl oxide than of 4-methyl-2-pentanone. Mesityl oxide, in one form at least, is a substituted vinyl ketone and in this investigation it did not show any differences in behavior from the saturated ketones. Although both types of derivative would give the same saponification equivalent, the lactone would not be expected to give a 2,4-dinitrophenylhydrazone identical with that of the starting material.

Summary

Ketene has been found to react with ketones possessing three or more *alpha* (or 4-position) H-atoms to yield the enol acetates. The tendency to react appears to be dependent upon the ease of enolization. The presence of a catalyst is necessary, sulfuric acid being the best of those investigated. Optimum conditions were determined for the reaction with acetone. It was found that higher temperatures favor the acetylation reaction whereas at lower temperatures considerable polymerization of the ketene occurs. The amount of catalyst present is also critical.

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