Tubanol.—The procedure for the preparation of this compound was the same as that described by Takei.[12b] It is a thick viscous liquid: n^{20}_{D} 1.5623.

Rotenic Acid.—Rotenic acid was prepared from isorotenone by the same procedure employed in the preparation of tubaic acid. It melted at 186° with decomposition. In alcohol solution it gives an intensely blue color with ferric chloride.

Summary

An improved procedure for the preparation of tubaic and rotenic acids is given. Structural formulas are proposed for tubanol, "rotenol" and tubaic and rotenic acids.

WASHINGTON, D. C.

[A COMMUNCATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE ALCOHOLYSIS OF CERTAIN 1,3-DIKETONES IN THE PRESENCE OF HYDROGEN CHLORIDE

BY HOMER ADKINS, WALTER KUTZ AND DONALD D. COFFMAN

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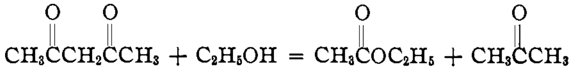
In the course of a study of the relationship of the constitution of the reactants to the point of equilibrium attained in the Claisen or acetoacetic ester condensation it seemed advisable to determine the rate of alcoholysis of a number of 1,3-diketones in the presence of hydrogen chloride. A typical reaction is as follows



$$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3 + C_2H_5OH = CH_3\overset{O}{\overset{\|}{C}}OC_2H_5 + CH_3\overset{O}{\overset{\|}{C}}CH_3 \qquad (1)$$

The alcoholysis of the diketones and analysis of the resultant solution for ethyl acetate were carried out as follows. Approximately 1×10^{-2} mole of the diketone was dissolved in dry ethanol, and a normal alcoholic solution of hydrogen chloride added so that the volume of the reaction mixture was 40 ml. and the desired amount of catalyst was present. If the amount of ethyl acetate expected in a reaction mixture was less than about 2×10^{-3} moles, the amounts of the reactants were increased so that at least that much ester would be present in the solution to be analyzed.

The reaction mixture contained in a 50-ml. tightly stoppered flask was placed in a thermostat and held at 60° for the desired length of time. The reaction was stopped by adding 2 ml. of phenylhydrazine. The mixture was then thoroughly shaken and cooled. The reaction flask, which bore on its side a Vigreux fractionating column 15 cm. in length, was then placed in an oil-bath whose temperature was slowly raised to 120° during the course of an hour or until the flask was dry. Three successive 10-ml. portions of dry ethanol were added to the residue in the flask and distilled out. The total time for the distillation was from two to three hours. An excess of an aqueous sodium hydroxide solution and a few drops of a phenolphthalein solution were added to the distillate and saponification allowed to proceed at 60° for three hours in a stoppered flask. The excess of alkali was then titrated and the amount of ester calculated. Determinations on samples containing from 1×10^{-3} to 1×10^{-2} mole of ethyl acetate showed that 1.5×10^{-4} mole of ethyl acetate was unaccounted for by the saponification value. This was presumably due to mechanical losses and saponification of the ester in the reaction flask before distillation. This correction was added to the amount of ester calculated from the saponification value. It was demonstrated that the recovery of ethyl acetate was the same irrespective of whether or not the mixture analyzed contained a monoketone, a diketone, other reaction products with phenylhydrazine, or an excess of phenylhydrazine. The above procedure was modified in those cases in which ethyl benzoate was to be determined. The distillation was then carried out at 16 mm. and three 10-ml. portions of tetrahydronaphthalene were used for boiling out the ester.

The rate of alcoholysis is, of course, a function of the temperature of the reaction mixture. In this investigation a temperature of 60° was selected as one at which alcoholysis proceeded at a reasonable rate, and one at which the vapor pressure of the alcoholic solution of hydrogen chloride was not large enough to complicate the experimentation. Another reason for avoiding higher temperatures is the probability of the reaction under such conditions of the ethanol and the hydrogen chloride.

The extent of alcoholysis of acetylbenzoylmethane at the end of seventy hours was found to be 32% at 50°, 56% at 60° and 67% at 70° using a reaction mixture containing 9.88×10^{-3} moles of the diketone, 3.29×10^{-3} mole of hydrogen chloride and 40 ml. of ethanol.

It is necessary to have a rather high concentration of hydrogen chloride in order to secure a reasonably rapid rate of alcoholysis. In most of the experiments (see Figs. 2 and 3) described in this paper one mole of hydrogen chloride was used for three moles of the diketone. Even with this high concentration of catalyst more than four days were required for complete alcoholysis at 60° of diacetylmethane, the most reactive of the diketones studied. In Fig. 1 is shown the variation in the amount of alcoholysis of three diketones determined at the end of forty-eight hours, the ratio of diketone to hydrogen chloride being varied from 0.6:1 to 28:1. It may be seen that the reaction is practically complete within forty-eight hours in the presence of a molecular excess of hydrogen chloride, while with decreasing amounts of catalyst the amount of alcoholysis falls off rapidly to 10 or 20% of its former value.

A discussion of the role of the catalyst in the alcoholysis of 1,3-diketones will be reserved for a later paper, which will consider the alcoholysis in both acid and alkaline media. It should be pointed out at this time, however, that although the hydrogen chloride in all probability forms an addition compound with one or more of the reactants and is thus lost as a catalyst, it is still titratable as an acid and as a chloride, and in fact becomes active as a catalyst for alcoholysis if transferred to a fresh reaction mixture.

The condensation of an ester with a ketone does not occur to a detectable extent in the presence of hydrogen chloride, although this well-known Claisen or acetoacetic ester condensation does occur if sodium, sodamide or sodium ethoxide is present. The non-reversibility of the alcoholysis of five diketones was demonstrated for the reaction of ethyl acetate with acetone, methyl isopropyl ketone, methyl isobutyl ketone, methyl phenyl ketone and *n*-propyl phenyl ketone. This was done by making up mixtures of ethyl acetate, the monoketone, ethanol and hydrogen chloride and allowing them to stand at 60° for some days. The amount of ester determined by the method of analysis described above was always equivalent to that used in making up the mixtures.

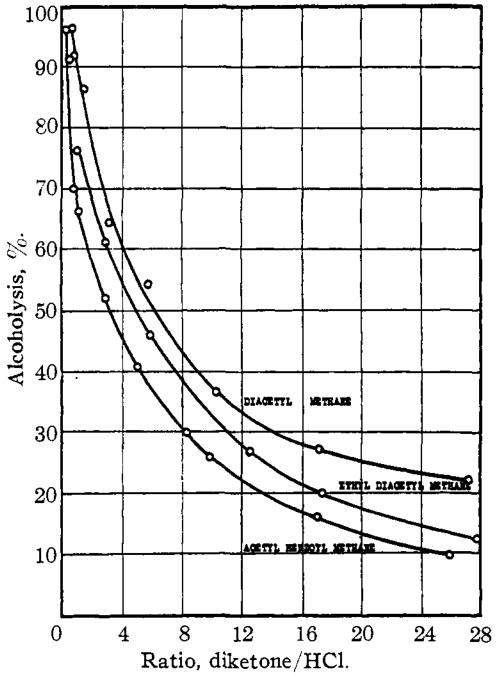
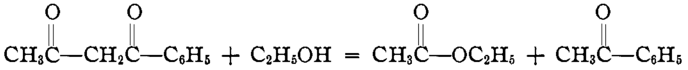


Fig. 1.—The percentage of alcoholysis of 9.8 × 10^{-3} moles of diacetylmethane, diacetylethylmethane and acetylbenzoylmethane in forty-eight hours at 60° in 40 ml. of ethanol is plotted against the moles of diketone per mole of hydrogen chloride in the reaction mixture.

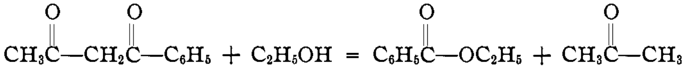
The extent of alcoholysis for a given length of time was not a function of the ratio of diketone to alcohol when the ratio was varied from approximately 1:1 to 1:40. For example 1 × 10^{-2} mole of diacetylmethane was allowed to undergo alcoholysis for forty-eight hours at 60° in the presence of 3.6 × 10^{-3} mole of hydrogen chloride. The extent of alcoholysis was 19.0 to 19.2% for 4 × 10^{-1} mole of ethanol, 17.7 to 18.2% for 5 × 10^{-2} mole and 17.4 to 18.1% for 8.6 × 10^{-3} mole. In a similar fashion 1 × 10^{-2} mole of acetylbenzoylmethane with 1.4 × 10^{-3} mole of hydrogen chloride showed 31.8% alcoholysis with 4 × 10^{-1} mole of ethanol and 30.4% with 8.6 × 10^{-3} mole of alcohol. Thiophene-free benzene was added so that all reaction mixtures had a volume of 40 ml. An attempt was made to determine whether the extent of alcoholysis varied with different alcohols. It was found that under comparable conditions the extent of alcoholysis after forty-eight hours at 60° using 9.9×10^{-3} mole of diacetylmethane, 3.9×10^{-1} mole of ethanol and 3.6×10^{-4} mole of hydrogen chloride was 21.7%, while with butanol it was 20.8%. Tertiary butyl and isopropyl alcohols showed 11.1 and 18.3% alcoholysis, respectively, but this decrease in alcoholysis was no doubt due to the fact that 89% of the hydrogen chloride had reacted to form an alkyl chloride in the case of the tertiary alcohol, only 7% in the case of the secondary alcohol and to no measurable extent with the primary alcohols.

The rate of alcoholysis of the following list of diketones was investigated: diacetylmethane, ethyldiacetylmethane, *n*-propyldiacetylmethane, isopropyldiacetylmethane, *n*-butyldiacetylmethane, benzyldiacetylmethane, diethyldiacetylmethane, dibenzyldiacetylmethane, acetylbenzoylmethane, ethylacetylbenzoylmethane, isopropylacetylbenzoylmethane, benzylacetylbenzoylmethane and dibenzoylmethane.

Nine of these thirteen diketones contain two identical acyl groups in the same molecule, so that only one set of alcoholysis products are possible. On the other hand, such a diketone as acetylbenzoylmethane might give rise upon alcoholysis to two sets of products as shown in Equations 2 and 3, but fortunately the experimental work shows that only one pair of products is produced, Reaction 3 not taking place.



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}-CH_2\overset{\overset{O}{\|}}{C}-C_6H_5 + C_2H_5OH = CH_3\overset{\overset{O}{\|}}{C}-OC_2H_5 + CH_3\overset{\overset{O}{\|}}{C}-C_6H_5} \qquad (2)$$



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}-CH_2\overset{\overset{O}{\|}}{C}-C_6H_5 + C_2H_5OH = C_6H_5\overset{\overset{O}{\|}}{C}-OC_2H_5 + CH_3\overset{\overset{O}{\|}}{C}-CH_3} \qquad (3)$$

The fact that benzoylacetylmethane suffers decomposition according to Equation 2 and not at all according to Equation 3 was established by Dr. A. E. Broderick in the following manner. A mixture of 25 ml. of ethyl alcohol containing 1.6×10^{-2} mole of hydrogen chloride and 3.3 g. of acetylbenzoylmethane was placed in a pressure bottle and heated at 80° for thirteen hours. The mixture was then distilled and the alcoholic distillate saponified. The distillate showed a saponification number corresponding to 1.3×10^{-2} mole of ethyl acetate. The alcohol was removed by distillation, the residue of sodium salts was taken up in water, treated with sulfuric acid and a little potassium permanganate to oxidize the hydrogen chloride. This was distilled and a Duclaux determination made upon the distillate showed acetic acid to be present. Acetophenone was isolated and identified and the absence of acetone shown.

Benzylacetylbenzoylmethane in the presence of hydrogen chloride undergoes alcoholysis in a similar fashion, *i. e.*, the products of the reaction are ethyl acetate and benzylbenzoylmethane (benzylacetophenone). The diketone (2×10^{-2} mole) was refluxed with 1×10^{-2} mole of hydrogen chloride in 75 ml. of ethanol for fifty hours. The reaction mixture was then distilled on an oil-bath (120°) and 2 ml. of phenylhydrazine added to the distillate. This was then redistilled and yielded 6×10^{-3} mole of an ester. A Duclaux determination upon a solution of the acid from the ester gave values of 5.9, 6.4 and 6.0°; these indicate acetic acid. The residue from the first distillation was dissolved in 200 ml. of dry ether and treated with 2×10^{-2} mole of sodium ethoxide at 0°. The salt of the unchanged diketone precipitated out and was filtered off. After evaporating off the ether, the residue was refluxed for two hours with 5×10^{-2} mole of sodium hydroxide in a solution containing equal parts of water and alcohol. The alcohol was distilled off and the water solution extracted with ether. The ether extract yielded 1.3 g. of a ketone melting at 71–72° and its oxime melted at 80–81°. The ketone $C_6H_5CH_2CH_2COC_6H_5$ is reported to melt at 73° and its oxime at 82°.[1] Tests for the presence of benzoic acid gave negative results. Similar determinations upon the splitting of ethylacetylbenzoylmethane and of isopropylacetylbenzoylmethane were not made.

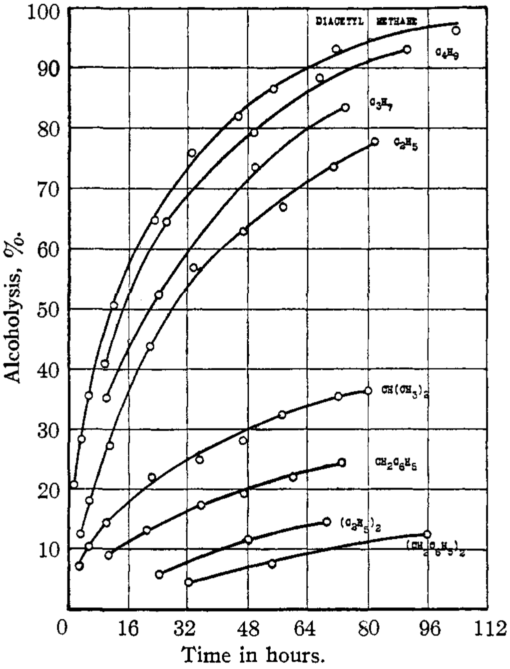


Fig. 2.—The percentage of alcoholysis of 1×10^{-2} mole of diacetylmethane and seven alkyl derivatives determined in the presence of 40 ml. of ethanol, and 3.33×10^{-3} moles of hydrogen chloride at 60° is plotted against the time in hours.

The relative rates of alcoholysis of diacetylmethane and seven of its derivatives in which substitution has been made on the methane carbon atom are shown in Fig. 2. These reactions were carried out at 60° in a reaction mixture containing the reactants in the ratio of 1×10^{-2} mole of the diketone, 3.3×10^{-3} mole of hydrogen chloride and 40 ml. of ethanol. A consideration of these data shows that substitution in the diketone decreases the rate of alcoholysis. Among the three purely aliphatic primary radicals the retarding effect decreases with the weight of the radical. The secondary propyl group is much more

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[1] "International Critical Tables," McGraw-Hill Book Co., New York City, **1926**, Vol. I, p. 256; Perkin, *J. Chem. Soc.*, **59**, 1007 (1891).

effective in retarding alcoholysis than is the normal group. The benzyl group is very effective and disubstitution even more so.

In Fig. 3 are shown the relative rates of alcoholysis of acetylbenzoylmethane and three of its derivatives. It is evident that the replacement of a methyl group in diacetylmethane by a phenyl group greatly reduces the rate of alcoholysis. However, the effects of substituting an ethyl, benzyl or isopropyl group in this unsymmetrical diketone are quite similar to their effects when substituted in diacetylmethane.

The alcoholysis of dibenzoylmethane was also studied but even when a molecular excess of hydrogen chloride was used the extent of alcoholysis was not greater than 7%. In view of the difficulties attendant upon the determination of such small quantities of ethyl benzoate as are here involved it is questionable whether the diketone undergoes an appreciable alcoholysis in the presence of hydrogen chloride at 60°. The stabilizing influence of one benzoyl group as in benzoylacetylmethane is very marked so that it is not surprising that a diketone containing two benzoyl groups should be quite stable to alcoholysis in the presence of hydrogen chloride.

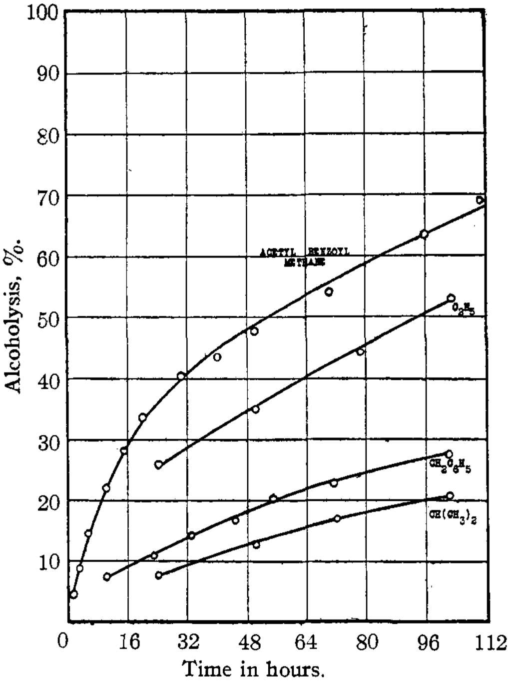

Fig. 3.—The percentage of alcoholysis of 1 × 10^{-2} mole of acetylbenzoylmethane and three alkyl derivatives determined in the presence of 40 ml. of ethanol and 3.33 × 10^{-3} mole of hydrogen chloride at 60° is plotted against the time in hours.

The significance of these facts in connection with the mechanism of alcoholysis of the diketones will be considered further in a forthcoming paper describing the result of an experimental study, already completed, upon alcoholysis of these same diketones in the presence of sodium ethoxide. It will suffice for the present to point out that the relative rates of alcoholysis in the presence of hydrogen chloride are roughly proportional to the extent of enolization of the diketones in an alcoholic solution.[2] Isopropyldiacetyl-

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[2] K. V. Auwers, *Ann.*, **415**, 169 (1918); K. H. Meyer, *Ber.*, **45**, 2843 (1912); W. H. Perkin, *J. Chem. Soc.*, **61**, 800 (1892); Ida Smedley, *ibid.*, **97**, 1493 (1910).

methane forms no copper salt,[3] gives no coloration with ferric chloride and shows a very slow rate of alcoholysis.

It is obvious from an inspection of the curves given in Figs. 2 and 3 that the reaction velocity "constant" is a steadily decreasing value. For example, in the case of diacetylmethane the constant calculated on the basis of a monomolecular reaction (since there is a great excess of alcohol) is at one hour 0.24, three hours 0.11, five hours 0.09, twelve hours 0.06 and at twenty-three hours 0.04. This is not suprising in view of the fact that the rate of alcoholysis had previously been shown to be independent of the concentration of alcohol and also in view of the high concentration of "catalyst" required.

Preparation of the Diketones

The substituted diacetylmethanes were prepared through the reaction in a glass or steel bomb of the monosodium salt of diacetylmethane with the proper alkyl halide. The sodium salt was prepared by adding diacetylmethane to the calculated amount of powdered sodium suspended in benzene or ether. The solid was filtered and used without purification.[4] The substituted acetylbenzoylmethanes were made in a similar manner. There is given in Table I for the preparation of each of the substituted diketones the following information: the amounts of reactants, the time and temperature for reaction, the yield, boiling range (or melting point) and density of the product, and the names of the authors who have reported the preparation of the compound under consideration. The analysis of the diketone not previously reported is given at the bottom of Table I.

Diacetylmethane was prepared by Claisen and Erhardt[5] through the condensation of ethyl acetate (3 moles) and acetone (1 mole) with sodium (1 mole) or with sodium ethoxide (1 mole). They reported a yield of 50% in the first case and 30 to 40% in the latter. Several runs were made in this Laboratory in which both catalysts were used in varying amounts. The result of this study indicated that the maximum yields for the two catalysts were the same and were obtained by using 2 moles of sodium or 1 mole of sodium ethoxide per mole of acetone. In this connection it is of interest to note that Claisen[6] reports the use of two moles of sodamide per mole of ketone and then compares the yield with that obtained when one mole of sodium and one mole of ketone were used.

A typical preparation was made as follows. A 5-liter, three-necked flask was fitted with a stirrer, a dropping funnel and an efficient condenser. Into the flask was poured 4 moles (92 g.) of sodium along with two or three hundred ml. of xylene. Twelve to fifteen hundred ml. of dry, alcohol-free ethyl acetate was now added and the flask immediately surrounded by a plentiful supply of ice. The stirrer was started and after ten or fifteen minutes dry acetone was added through the dropping funnel. Seventy ml. was added at once but no more added until it was certain that the reaction was under way. This was evidenced by the evolution of a large amount of heat and the separation

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[3] Morgan and Thomason, *J. Chem. Soc.*, **125**, 755 (1924).

[4] *Cf.* Combes, *Ann. chim. phys.*, [6] **12**, 207 (1887).

[5] Claisen and Erhardt, *Ber.*, **22**, 1011 (1889).

[6] Claisen, *ibid.*, **38**, 696 (1905).

TABLE I

PREPARATION AND PROPERTIES OF VARIOUS ALKYLATED DIKETONES

Alkyl halide	Preparational reagents Moles	Sodium-( )-methane	Mole	Time, hours	Temp., °C.
Ethyl iodide	2.5	Diacetyl-	0.5	3	150
n-Propyl iodide	0.75	Diacetyl-	.25	12	150
Isopropyl iodide	2.0	Diacetyl-	.5	3	160
n-Butyl iodide	2.0	Diacetyl-	.5	3	180
Benzyl chloride	2.0	Diacetyl-	.5	12	180
Ethyl iodide	0.75	Ethyldiacetyl-	.2	10	150
Benzyl chloride	0.5	Benzyldiacetyl-	.1	10	250
Ethyl iodide	1.25	Acetylbenzoyl-	.3	6	145
Isopropyl iodide	0.75	Acetylbenzoyl-	.2	10	150
Benzyl chloride	2.0	Acetylbenzoyl-	.25	6	180

Methane compound	Yield, %	Boiling point °C.	Mm.	d_{25}^{25}
Diacetylethyl-[7]	52	175–178	740	0.9365
Diacetylpropyl-[8]	30	192–194	740	.9328
Diacetylisopropyl-[8]	35	180–183	740	.9205
Diacetyl-*n*-butyl-[9]	38	90–94	10	.9312
Diacetylbenzyl[10]	48	155–160	5	1.0125
Diacetyldiethyl-[11]	32	95–100	10	0.9448
Diacetyldibenzyl-[10]	25	111–112 (melting point)		
Acetylbenzoylethyl-[12]	26	135–138	10	1.057
Acetylbenzoylisopropyl-[13]	12	146–149	10	1.043
Acetylbenzoylbenzyl-[14]	47	55–56 (melting point)		

of a light yellow solid in the reaction mixture. After the reaction had slowed down the remainder of the acetone (total amount, 116 g., 2 moles) was added at such a rate that only a gentle refluxing took place. After the addition of the acetone the reaction mixture was stirred for two hours and then allowed to stand in a refrigerator for at least ten hours. The reaction mixture was poured into ice water with vigorous stirring and sufficient water added to dissolve the sodium salt completely. The upper layer of ethyl acetate and xylene was removed and the water layer acidified with glacial acetic acid. To this acid solution was added a concentrated ammoniacal aqueous solution containing 200 g. of copper acetate. The copper salt of the diketone separated at once. After standing for an hour it was filtered off with suction, washed with water and the copper salt decomposed with 500 ml. of a cold 25% solution of sulfuric acid. A small portion of the solid was not decomposed by this treatment and was filtered off and discarded. The acid solution was extracted twice with ether, first with 500 ml. and then with 300 ml. The ether solution was dried over calcium chloride, the ether distilled and the residue fractionated. The fraction between 130 and 142° was saved, dried over calcium

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[7] Morgan and Rawson, *J. Soc. Chem. Ind.*, **44**, 462 (1925).

[8] Morgan and Thomason, *J. Chem. Soc.*, **125**, 754 (1924).

[9] Morgan and Holmes, *ibid.*, **125**, 760 (1924).

[10] Morgan and Taylor, *ibid.*, **127**, 797 (1925).

[11] Combes, *Ann. chim. phys.*, [6] **12**, 250 (1887).

[12] Claisen and Lowman, *Ber.*, **21**, 1151 (1888).

[13] Kutz: Acetylbenzoylisopropylmethane. *Anal.* Calcd. for $C_{13}H_{16}O_2$: C, 76.5; H, 8.0. Found: C, 76.4; H, 7.8.

[14] Trotman, *J. Chem. Soc.*, **127**, 94 (1925).

chloride, decanted and then allowed to stand for two or three days with 3–4 g. of anhydrous potassium or sodium carbonate. The treatment with carbonate gave a final product which after distillation has remained colorless for over a year. After filtering off the carbonate the crude acetylacetone was fractionated. The fraction from 136–139° (uncorr.) was 120 g. or 60% of the theoretical based on the acetone introduced.

Acetylbenzoylmethane was obtained in the best yields by using two moles of sodium or one mole of sodium ethoxide per mole of acetophenone.[15] The procedure for the preparation was similar to that described for diacetylmethane up to the point where the reaction mixture was poured into water. At this point the sodium salt of acetylbenzoylmethane was filtered with suction, washed with benzene, dried in air, ground in a mortar and dissolved in water. The crude diketone was precipitated by acidification of the solution with acetic acid, filtered, dried and distilled under reduced pressure, 120–122° at 3 mm. or 128–130° at 10 mm. The yield was 208 g. or 64% based on the acetophenone. After recrystallization in an ethanol–water mixture the melting point was 56–67° (uncorr.).

Dibenzoylmethane was prepared as described in "Organic Syntheses"[16] and had a melting point of 76–78° (uncorr.).

Summary

The rate of alcoholysis at 60° of thirteen 1,3-diketones in the presence of hydrogen chloride has been studied. It has been shown that the rate of alcoholysis was independent of the ratio of diketone to alcohol when the latter was varied from 1:1 to 1:40. It was also independent of whether ethanol or butanol was used but fell off markedly with secondary propyl or tertiary butyl alcohol, due no doubt to the reaction of the latter with hydrogen chloride at 60° The alcoholysis of the diketones was not a reversible reaction in the presence of hydrogen chloride.

Acetylbenzoylmethane and benzylacetylbenzoylmethane which might split to give ethyl acetate or ethyl benzoate gave only the former ester.

The rate of alcoholysis and the apparent extent was a function of the amount of hydrogen chloride in the reaction mixture. A high ratio of catalyst to diketone (1:1) was necessary to secure practically complete alcoholysis of the most reactive of the diketones at 60° in forty-eight hours. The rate of alcoholysis of substituted diacetylmethanes fell off as the substituent was varied from *n*-butyl to *n*-propyl, ethyl, isopropyl, benzyl, diethyl and dibenzyl. Acetylbenzoylmethane underwent alcoholysis more slowly than did diacetylmethane. The introduction of a third substituent on the "methane carbon atom" still further inhibited alcoholysis.

Dibenzoylmethane underwent little or no alcoholysis under the conditions used for the alcoholysis of the other diketones investigated.

The maximum yields (60–65%) of diacetylmethane and acetylbenzoylmethane were obtained when the ratio of ketone to condensing agent was 1:1 for sodium ethoxide and 1:2 for sodium.

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[15] *Cf.* Claisen, *Ann.*, **291**, 51 (1896).

[16] "Organic Syntheses," John Wiley and Sons, New York City, **1928**, Vol. VIII, p. 60.

The preparation of isopropylacetylbenzoylmethane is reported for the first time.

Madison, Wisconsin

[Contribution from the Pittsburgh Experiment Station, U. S. Bureau of Mines]

THE MECHANISM OF THE FORMATION OF HIGHER HYDROCARBONS FROM WATER GAS[1]

By David F. Smith,[2] Charles O. Hawk[3] and Paul L. Golden[4]

Received March 12, 1930 Published August 5, 1930

Introduction

In April, 1926, Fischer and Tropsch[5] announced that higher homologs of methane are formed when mixtures of hydrogen and carbon monoxide are passed at atmospheric pressure over catalysts of iron or cobalt mixed with various supporting materials, at temperatures from 250 to 300°. The catalysts were stated to have been prepared by reduction from the oxides with hydrogen at 350°. It was said that no oxygen-containing organic compounds were found. The mechanism of the process was thought to be through formation of metallic carbides, although it was found impossible to obtain the higher paraffins by passing hydrogen alone over the supposed carbides. Upon further examination, Fischer and Tropsch[6] announced the product to consist of ethane, propane, butane and higher homologs up to solid paraffin, with only inappreciable amounts of olefins. It was said that a wide range of space velocities and $CO-H_2$ mixtures were used. Elvins and Nash[7] reported the formation of oily material on a cobalt–manganese oxide–copper catalyst at atmospheric pressure and temperatures from 245 to 284°. The yields were small, however. In July, 1926, Elvins and Nash[8] reported the presence of oxygen-containing compounds in addition to hydrocarbons in this product. Fischer and Tropsch[9] stated that oxygen-containing compounds were present in their product in only very small quantities compared to the amounts of hydrocarbons produced. At the September, 1927, Meeting of the American Chemical Society, Smith, Davis and Reynolds gave results of preliminary work in which olefin as well as paraffin hydrocarbons were obtained. Full details of this work

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[4] Assistant scientific aid, U. S. Bureau of Mines.

[5] Fischer and Tropsch, *Brennstoff-Chemie*, **7**, 97 (1926); *Ber.*, **59**, 830, 832 (1926).

[6] Fischer and Tropsch, *ibid.*, p. 923.

[7] Elvins and Nash, *Fuel*, **5**, 263 (1926).

[8] Elvins and Nash, *Nature*, **118**, 154 (1926).

[9] Fischer and Tropsch, *Brennstoff-Chemie*, **7**, 299 (1926).