it is evident that the quantity of the latter (11.46 to 17.23%) which can be recovered from the germ or embryo is a function of the former. Furthermore, this observation holds true also of the degree of pigmentation of the oil, its physical and chemical constants, and the content of unsaponifiable matter and phosphorus. It appears also that the yields of oil which may be expected assume the following order: petroleum ether < ethyl ether < carbon tetrachloride < ethylene dichloride < carbon disulfide < benzene < chloroform < acetone.

The following minima and maxima were noted: d^{25} 0.9220 and 0.9483; n^{20} 1.4732 and 1.4789; iodine number 133.8 and 139.5; percentage of unsaponifiable matter 8.09 and 10.00; percentage of phosphorus (tentatively recorded as lecithin equivalent) 1.03 and 7.26.

MADISON, WIS. RECEIVED SEPTEMBER 14, 1933

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Tautomerism of Alpha Diketones. I. Benzyl Phenyl Diketone

BY E. P. KOHLER AND R. P. BARNES

At the time this investigation was planned little was known about the enolization of alpha diketones and still less concerning the manner in which they are alkylated and acylated. The work was hardly under way when Dufraisse and Moureu[1] published the first of a series of papers dealing with the preparation and properties of alpha diketones. Their work was continued by Moureu and finally presented as an admirable study of benzyl methyl diketone, benzyl phenyl diketone and a few other related substances.[2] Moureu supplied the answer to many of the questions we were asking, but since he emphasized the great similarity of alpha and beta diketones while we were interested especially in the differences between these closely related types, he also left a number unanswered.

Our interest in the physical properties of the tautomeric modifications of the diketone centered in chelation. The only plausible explanation for the relatively high volatility of the enolic modification of acetoacetic ester, its great solubility in non-polar solvents and the physical properties of many of its metallic derivatives has been offered by Sidgwick,[3] who accounted for these peculiarities by means of the cyclic formula proposed by Hantzsch.[4] In view of the work of Mills and Gotts[5] it can scarcely be doubted that the enolic modifications of beta ketonic esters and beta diketones are chelated at the ordinary temperature but it is surprising that these rings should persist at the high temperatures at which these substances boil. It was desirable, therefore, to compare the physical properties of a pair of tautomers in which chelation is less probable. Benzyl phenyl diketone served this purpose.

Since 5-rings with but one double bond are relatively unstable it is improbable that the enolic modification of an alpha diketone could form a chelate ring involving a hydrogen bond; alpha diketones should, therefore, lack the peculiar physical properties of acetoacetic ester. We found, in agreement with Moureu, that the enol of benzyl phenyl diketone is far less volatile than the ketone. And we also found that while the solubility of the two forms is almost the same in alcohol and chloroform, the enol is almost completely insoluble in petroleum ether. In contrast with acetoacetic ester, the physical properties of the two modifications are those which would be expected if one were a hydroxyl and the other a carbonyl compound.

With respect to the chemical properties, we were interested first of all in the autoxidation. Many years ago it was found that the enolic modifications of certain mono ketones combine rapidly with oxygen to form crystalline peroxides.[6] Despite many attempts it has not been possible to find any other type of enol capable of combining with oxygen or any other ethylenic compound that would form a monomeric crystalline peroxide. When we discovered the avidity with which alkaline solutions of alpha oxido ketones combine with oxygen we attributed it to the enolic forms and hoped to secure the peroxides. We found that a peroxide of some kind is formed when oxygen is passed into solutions of benzyl

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[1] Dufraisse and Moureu, *Bull. soc. chim.*, [4] **41**, 1613 (1912).

[2] Moureu, *Ann. chim.*, [10] **14**, 303 (1930).

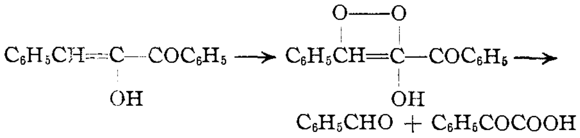
[3] Sidgwick, *J. Chem. Soc.*, **127**, 907 (1925).

[4] Hantzsch, *Ber.*, **43**, 3053 (1910).

[5] Mills and Gotts, *J. Chem. Soc.*, 3121 (1926).

[6] Kohler, *Am. Chem. J.*, **36**, 177 (1906).

phenyl diketone, but possibly owing to unfavorable solubility relations we were unable to isolate it. The oxidation products which were isolated, however, are those which would be formed by the decomposition of an enol peroxide



$$C_6H_5CH{=}\underset{OH}{C}{-}COC_6H_5 \longrightarrow C_6H_5\overset{O-O}{CH{=}C}{-}COC_6H_5 \longrightarrow C_6H_5CHO + C_6H_5COCOOH$$

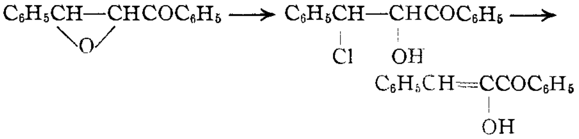
Another subject of interest was the behavior of the diketone in acylation and alkylation. Vorländer[7] reported that in the presence of alkali benzoyl chloride converts the enol into a benzoyl derivative. Moureu obtained the same product in pyridine—proving that it is a benzoate. We found that the alpha diketone differs from its isomer, dibenzoylmethane, in that it forms O-acyl derivatives exclusively not only in pyridine but by every other method of acylation—the direct action of acetyl chloride or acetic anhydride, the Schotten–Baumann reaction, and the reaction between the sodium derivative and benzoyl chloride. The product never contains enough of a C-acyl derivative to give a color reaction with ferric chloride.

In alkylation the difference in the behavior of alpha and beta diketones is equally marked, for while it seems probable that small quantities of O-alkylates are formed much more frequently than is suspected by the action of dimethyl sulfate on the sodium derivatives of beta diketones,[8] the alpha diketone forms both C and O alkyl derivatives by every method of alkylation. The relative amounts of these derivatives vary with the alkylating agents and the solvents, the largest amount of methoxyl compound being formed by the interaction of the sodium salt and dimethyl sulfate in acetone in which the yield is more than 80%.

The properties of these alkylation products lend no support to the hypothesis recently advanced by Hantzsch[9] that alkylation results in O-alkylates which subsequently undergo rearrangement to C-isomers. The O-methylate of benzyl phenyl diketone is completely stable even in the most concentrated alkali and it can be distilled without alteration.

Experimental Part

Since the methods by which benzyl phenyl diketone had been obtained seem ill adapted for the preparation of the quantity necessary for a study of its chemical properties, we undertook to prepare it by the rearrangement of benzalacetophenone oxide with acids in accordance with the equation



$$C_6H_5\underset{\diagdown O \diagup}{CH{-}CH}COC_6H_5 \longrightarrow C_6H_5\underset{Cl}{CH}{-}\underset{OH}{CH}COC_6H_5 \longrightarrow C_6H_5CH{=}\underset{OH}{C}COC_6H_5$$

We found that this rearrangement could be accomplished very simply and in any desired quantity in the following manner.

Dry hydrogen chloride was passed into a suspension of 200 g. of the oxido ketone in an equal weight of glacial acetic acid until the temperature rose to 45° and most of the oxide dissolved. The temperature was then gradually lowered and the solution was finally saturated with hydrogen chloride at 0°. The dark red solution was left in an ice-chest for fifteen to eighteen hours in a securely stoppered flask. The flask was then partially evacuated with a water pump—about 30 mm.—and freed from hydrogen chloride and acetic acid by distillation at this pressure in a current of dry oxygen-free nitrogen.[10] The residue, fractionated at a lower pressure, yielded 144 g. of a pale yellow liquid which boiled at about 175° (8 mm.) and which was almost pure diketone. From this liquid both the pure ketonic modification and the pure enol could be obtained at will.

When a solution of the liquid in an equal volume of alcohol was cooled in a refrigerator it soon deposited the ketonic modification in pale yellow needles melting at 36°. In contact with the mother liquors these needles gradually redissolved and in the course of a week the concentration of the enol had increased sufficiently to permit its crystallization, either spontaneously or upon inoculation. By successive concentrations of the mother liquors it was possible to obtain 140 g. of pure enol melting at 89–90°—a yield of 70%.

Tautomerism.—We determined the amount of enol by titration with bromine by the indirect method, using only Pyrex apparatus for sampling and for titration. To test the accuracy of the method in this particular case we first applied it to the pure solid enol and the solid ketone; for the former we found 98.3% and for the latter 0.03% enol. The enol content of equilibrium mixtures was obtained by heating the pure enol for an hour or more at constant temperature in soft glass or in the presence of a trace of sodium methylate, then chilling it and titrating it in the usual manner. The values were: 28.5% at 100°; 25.5% at 125°; 23.5% at 145°; 21% at 165°; 9.1% in the distillate and 27.0% in the residue after one distillation from soft glass into a Pyrex condenser and receiver. The value of 28.5% at 100° agrees well with the value 29.6% found by Moureu from the index of refraction. The low enol content of the distillate shows that the keto form has a considerably higher vapor pressure than the

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[7] Vorländer, *Ber.*, **50**, 416 (1917).

[8] Auwers, *ibid.*, **45**, 996 (1912).

[9] Hantzsch, *Z. anorg. allgem. Chem.*, **209**, 213 (1932).

[10] All operations described in this paper were carried out either in a current of nitrogen or in closed vessels filled with nitrogen.

enol. The enol content of solutions was obtained by dissolving the pure enol, equilibrating by adding a trace of sodium methylate and titrating aliquot portions at intervals. The values show solvent effects which at present are difficult to interpret; for decinormal solutions they are as follows: 43% in methyl alcohol; 38% in ethyl alcohol; 53% in chloroform; 39% in benzene.

Autoxidation.—The solid enol liquefies in the air and soon emits the vapor of benzaldehyde. In order to determine the course of the oxidation a solution of the enol in ether was shaken with oxygen until it had absorbed slightly more than one mole, then freed from ether by distillation. It left an oily residue which was distilled with steam. The distillate contained benzaldehyde and the residue in the flask contained phenylglyoxylic acid which was identified and weighed as the phenyl hydrazone.

Two flasks, the one containing only ether, the other an ethereal solution of the enol, were connected with the same oxygen supply and shaken. Samples removed at intervals and tested with acidified iodide showed that an oxidizing agent was formed in the solution containing the diketone, but that the concentration at no stage exceeded 8% of the concentration of the diketone. The peroxide evidently is unstable in solution at the ordinary temperature. All attempts to precipitate it by operating at lower temperatures and in other solvents have been unsuccessful.

The Sodium Salt.—Alkaline solutions of the diketone are rapidly oxidized by atmospheric oxygen and in these solutions the diketone readily undergoes the benzilic acid rearrangement, but the pure sodium salt can be obtained by operating at low temperatures with a large excess of alcoholate. Thus a solution of 6.2 g. of sodium in 62 g. of absolute alcohol was chilled until most of the alcoholate solidified. To this solution was added slowly and with constant stirring a solution of 34.7 g. of the diketone in 62 g. of absolute alcohol and 20 g. of dry ether. The solid alcoholate gradually dissolved and when all of the diketone had been added, the dark red solution began to deposit a sodium salt in lustrous yellow plates. The salt was washed with absolute alcohol and analyzed. The analyses indicated half a molecule of alcohol and the presence of alcohol was established by means of the iodoform reaction.

Anal. Calcd. for $C_{15}H_{11}O_2Na \cdot {}^1/_2C_2H_5OH$: C, 71.3; H, 5.2; Na, 8.5. Found: C, 70.9; H, 5.1; Na, 8.4.

The yield of sodium salt was 39.5 g. It is readily soluble in ether and even in methyl iodide but the solutions in these solvents almost immediately deposit a new sodium salt which is lighter in color and free from alcohol.

Anal. Calcd. for $C_{15}H_{11}O_2Na$: Na, 9.3. Found: Na, 9.3.

Acetylation, $C_6H_5CH{=}C(OCOCH_3)COC_6H_5$.—A solution of 5 g. of the enol in 20 g. of acetic anhydride and a drop of concd. sulfuric acid was boiled for nine hours, then freed from anhydride by distillation under diminished pressure and from acid by washing its solution in ether with bicarbonate. Removal of the ether and distillation of the residue gave 5.5 g. of a very pale yellow liquid which boiled at 195–200° (5 mm.).

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.6; H, 5.3. Found: C, 76.3; H, 5.3.

Although the product is yellow in color it cannot contain any of the triketone that would be formed by C acylation because when it is freshly distilled it gives no color reaction with ferric chloride. It is slowly hydrolyzed in contact with moist air and alcoholic hydrochloric acid converts it quantitatively into ethyl acetate and the diketone. It must therefore be the enol acetate. Since a certain amount of oxidation is unavoidable, the yield was not quite quantitative but we failed to find any evidence of C-acylation. The same substance is formed when the sodium salt is stirred into excess of acetyl chloride. The solution does not at any stage give a color reaction with ferric chloride.

Methylation, $C_6H_5CH(CH_3)COCOC_6H_5$ and $C_6H_5CH{=}C(OCH_3)COC_6H_5$.—The enol was methylated: (1) by adding, drop by drop and with vigorous shaking, 20% aqueous potassium hydroxide to an aqueous suspension of the enol and twice the calculated quantity of dimethyl sulfate until permanent alkalinity was established; (2) by adding excess of dimethyl sulfate to a solution of the alcohol-free sodium salt in acetone and leaving the mixture to itself until it became colorless; (3) by adding excess of dimethyl sulfate to a suspension of the alcohol-free sodium salt in absolute ether; (4) by adding a 10% solution of sodium methylate, drop by drop, to a boiling solution of the enol and excess of methyl iodide in methyl alcohol; (5) by adding methyl iodide to a solution of the alcohol-free sodium salt in acetone. An attempt to methylate by boiling a suspension of the sodium salt in absolute ether with methyl iodide was unsuccessful, the salt being recovered after boiling for forty-eight hours.

All methods of methylation gave mixtures. By appropriate manipulations the product in each case was a pale yellow oil boiling at 156–158° (3 mm.).

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.6; H, 5.9. Found: C, 80.3; H, 5.9.

The composition of the oils proves that they contain only mono methyl derivatives. Methoxyl determinations showed that all products contained methoxyl, that the methoxyl content of the products obtained by the various methods was not the same and that the mixtures could not be separated completely by distillation. It became necessary, therefore, to identify the components of the mixtures by chemical methods.

The O-methylate was readily identified because Malkin and Robinson,[11] who had obtained it in a different manner, reported a dibromide melting at 103°. This same dibromide was formed when bromine was added to a well-cooled solution of our product in ether.

The presence of the C-methylate was established by subjecting the mixture to a benzilic acid rearrangement whereby the C-methylate was converted into a hydroxylic acid, $(C_6H_5)(CH_3)CH(C_6H_5)C(OH)COOH$. When an excess of 40% aqueous potassium hydroxide was added to a methyl alcoholic solution of the oil it immediately turned from a yellow to a deep red color, and then in the course of a few days during which it was kept in an ice-chest, deposited a potassium salt from which the corresponding acid was obtained in the usual manner. The hydroxylic acid is readily soluble in ether and moderately soluble even in petroleum ether, from which it crystallizes in needles melting at 179–180°.

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[11] Malkin and Robinson, *J. Chem. Soc.*, **127**, 369 (1925).

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 75.0; H, 6.3. Found: C, 75.2; H, 6.2.

Since the methoxyl compound is not affected by strong alkali it was possible to determine the relative amounts of C and O alkylates with sufficient accuracy by dissolving the entire product of the reaction in ether, extracting the ethereal solutions with successive portions of 40% aqueous potassium hydroxide until the extracts remained colorless, removing the ether and then distilling the methoxyl compound in a high vacuum. It boiled at 180–185° (0.05 mm.) and melted at 32°. The relative amounts of methoxyl compound obtained by various methods of alkylation were as follows: the reaction between the sodium salt and dimethyl sulfate in acetone gave 80.9% and in ether 64.2%. The reaction between the same salt and methyl iodide gave in acetone 64.6% and in methyl alcohol 50.9%. The potassium salt treated with dimethyl sulfate in water gave 57.1% but owing to experimental difficulties this value is not as accurate as the others.

Coupling, C_6H $COCOCH(C_6H_5)CH(C_6H_5)COCOC_6H_5$.—A suspension of the sodium salt in ether was treated with the calculated quantity of iodine and left to itself until all the yellow salt had disappeared. The mixture was then washed with thiosulfate and water, and the ethereal layer was dried and concentrated. It deposited a yellow solid which after recrystallization from ether, in which it is sparingly soluble, melted at 198°. The yield was small.

Anal. Calcd. for $C_{30}H_{22}O_4$: C, 80.7; H, 5.0. Found: C, 80.8; H, 5.1.

In order to prove the structure of the tetraketone 0.2 g. of the substance was suspended in an alkaline solution of hydrogen peroxide. The solid gradually dissolved and the solution became colorless. On acidification it deposited a mixture of acids that could be separated by distillation with steam. The distillate contained benzoic acid and the residue deposited a solid acid which crystallized from ether in needles and which melted at 229°—the melting point of diphenylsuccinic acid. The identification was completed by converting the acid into the silver salt and this in turn into the ethyl ester. The ester melted at 135°.

Reaction with Phenylmagnesium Bromide, $C_6H_5CH_2COC(C_6H_5)_2OH$.—An ethereal solution of 10 g. of the diketone was added to phenylmagnesium bromide prepared from 5.5 g. of magnesium. The product of the reaction, isolated in the usual manner, crystallized from ether–petroleum ether in colorless needles and melted at 60°. The yield was 89%.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 82.0; H, 6.0. Found: C, 81.8; H, 6.0.

The position of the entering phenyl group was established by oxidation with chromic acid in glacial acetic acid; the products were benzophenone, phenyl acetic acid and a trace of benzoic acid. When added to a standard solution of methylmagnesium iodide the substance rapidly liberated one mole of gas in the cold and a second mole slowly on heating. Two moles of reagent were consumed; the substance therefore enolizes more readily than it combines with a second mole of the reagent.

Summary

This paper contains a description of the most conspicuous properties of benzyl phenyl diketone—the extent to which it is enolized under various conditions, its autoxidation and the manner in which it is alkylated and acylated.

Cambridge, Mass. Received September 21, 1933

[Contribution from the Chemical Laboratory of the Johns Hopkins University]

The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. V. The Strength of Bonds in Organic Molecules

By F. O. Rice and William R. Johnston[1]

In order to develop a theory of the thermal decomposition of organic compounds through a free radical mechanism[2] it is necessary to know the activation energies of the various processes occurring during the different stages of the decomposition. In general, according to the theory, these elementary processes may be divided into three classes: (1) the primary unimolecular dissociation of the original compound into two free radicals through rupture of a bond; (2) the decomposition of a large free radical which may be thus formed into one or more unsaturated compounds and a smaller free radical or a hydrogen atom; (3) the reactions of the free radicals with the surrounding molecules of the original substance. In this paper we will report some measurements which we believe give the activation energy of the primary process for a number of different compounds.

Since most compounds appear to decompose homogeneously and according to a unimolecular law, and since this decomposition seems to involve a primary splitting of the molecule into two fragments, we can approximate the strength of the bond which breaks by ascertaining the activation energy involved in this decomposition proc-

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(1) Fleischmann Company Fellow, 1930–1933.

(2) Rice, This Journal, **53**, 1959 (1931); **55**, 3035 (1933).