mercial Chloramine Yellow in fastness, although somewhat lighter in shade.

The direct dyeing on cotton was carried out as already described for the direct azo dyes.

A Chloramine Yellow from 2-*p*-Aminophenyl-5-phenylbenzoxazole Disulfonic Acid.—A solution of 5 g. of the disulfonic acid in 500 cc. of an aqueous solution of excess of sodium carbonate was boiled for thirty minutes, cooled and filtered. The filtrate was subjected to the action of a freshly prepared sodium hypochlorite solution, at 0–10°, for twelve hours, maintaining a slight excess of hypochlorite (as indicated by potassium iodide paper), or until the solution became yellowish-orange, after passing through an intermediate red stage. The dye was then salted out, washed with a 15% salt solution, dissolved in dilute sodium hydroxide and the sodium salt precipitated by the addition of alcohol. The final product resembled closely the dye described in the immediately preceding paragraph, except that the shade produced on cotton was a very pale greenish-yellow. Chemically it differed from the latter in being a tetra- instead of a di-sulfonic acid.

A Chloramine Yellow from 2-*p*-aminophenyl-5-methylbenzoxazole was also prepared by the customary procedure of sulfonation and hypochlorite oxidation and was found to resemble closely the above dye, in its direct dyeings on cotton, both as to shade and fastness.

A Chloramine Yellow from 2,7-diphenyl-5-aminobenzoxazole sulfonic acid, prepared similarly, dyed both wool and silk good deep shades. Its direct dyeings on cotton, however, were much paler and weaker than those obtained with the Chloramine Yellows from the 2-*p*-aminophenyl-5-phenyl- or 5-methylbenzoxazole sulfo acids.

Summary

1. From 2-*p*-aminophenyl-5-phenylbenzoxazole, 2,7-diphenyl-5-aminobenzoxazole, and their sulfo acids, azo dyes have been prepared, of mono- or bis-azo type, as well as some of Chloramine Yellow structure.

2. The tinctorial properties of these new dyes have been studied and it has been shown that those in which the azo grouping is in the *p*-position on the 2-phenyl nucleus are far better substantive cotton dyes than those having this grouping in position 5 on the benzoxazole portion of the molecule.

3. Azo dyes of Ingrain Red type, in the thiazole and oxazole series, were examined spectroanalytically. The curves plotted from these observations paralleled each other closely.

4. In general, these benzoxazole dyes resemble the analogously constituted benzothiazoles but, as expected, give lighter shades.

NEW YORK, N. Y. RECEIVED AUGUST 21, 1935

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Structure of the Metallic Derivatives Which Are Formed by Adding Grignard Reagents to Unsaturated Ketones

BY E. P. KOHLER, M. TISHLER AND H. POTTER

It is known that when a Grignard reagent is added to an α,β-unsaturated ketone which has a hydrocarbon residue in the α position, the product is an enolate in which a magnesium halide group is joined to oxygen. In all other addition products obtained in this manner the location of the halide residue is uncertain. Magnesium compounds of the type of these addition products can now be obtained in other ways. Thus the magnesium bromide derivative of β,β-diphenylpropionylmesitylene may be prepared by any of the three reactions which are represented by the equations

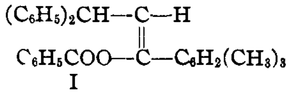
$$(1)\quad C_6H_5CH{=}CHCOC_6H_2(CH_3)_3 + C_6H_5MgBr \longrightarrow [(C_6H_5)_2CHCHCOC_6H_2(CH_3)_3]MgBr$$

$$(2)\quad (C_6H_5)_2CHCH_2COC_6H_2(CH_3)_3 + C_2H_5MgBr \longrightarrow [(C_6H_5)_2CHCHCOC_6H_2(CH_3)_3]MgBr + C_2H_6$$

$$3)\quad (C_6H_5)_2CHCHBrCOC_6H_2(CH_3)_3 + C_2H_5MgBr \longrightarrow [(C_6H_5)_2CHCHCOC_6H_2(CH_3)_3]MgBr + C_2H_5Br$$

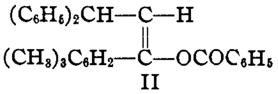
In appearance, in solubility and in many of their chemical properties the magnesium derivatives which are obtained in these various ways seem to be identical but their reactions with benzoyl chloride show that they are not. When the derivative that is formed in the first reaction is treated with benzoyl chloride at least 96% of the product is a benzoyl derivative which melts at 161°, while similar treatment of the magnesium derivative obtained by either of the other two methods leads to an equally high yield of an isomeric benzoyl derivative melting at 148°. These results are not affected by the solvents used or the temperature at which the successive operations are conducted. And in the case of the second and third reactions the nature of the Grignard reagent is likewise of no moment. These reactions—the one addition and the other substitution—therefore give rise to two isomeric magnesium compounds.

The two benzoyl derivatives that are formed from these magnesium derivatives must both be benzoates because both are much more easily hydrolyzed than the isomeric diketone which can be synthesized by a different method. These benzoates are evidently the geometrical isomers represented by formulas I and II and the magnesium halides from which they are formed must be the corresponding enolates. In the case of benzal acetomesitylene, therefore, addition of a Grignard reagent to the conjugated system C=C—C=O gives rise to an -OMgX compound even though there is no hydrocarbon residue in the α position.



$$\begin{array}{l}(C_6H_5)_2CH\text{—}C\text{—}H\\ \qquad\qquad\ \ \|\\ C_6H_5COO\text{—}C\text{—}C_6H_2(CH_3)_3\end{array}$$

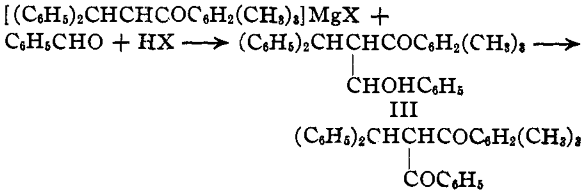
I



$$\begin{array}{l}(C_6H_5)_2CH\text{—}C\text{—}H\\ \qquad\qquad\qquad\ \ \|\\ (CH_3)_3C_6H_2\text{—}C\text{—}OCOC_6H_5\end{array}$$

II

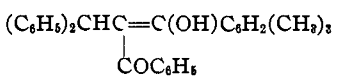
The isolation of these stereomeric magnesium derivatives supports the views of Michael and Ross[1] who obtained stereomeric O-carbmethoxy keto esters by treating the sodium compounds of benzoyl acetone with chlorocarbonic ester and concluded that solutions of the sodium derivatives contain the corresponding stereomeric enolates. The magnesium enolates, even though they give almost exclusively O-benzoyl derivatives, can nevertheless be added to benzaldehyde in the same manner as simple Grignard reagents. Ability to combine with aldehydes, therefore, is no criterion for the structure of a magnesium halide derivative. This reaction with aldehydes provides an excellent method for securing the β-diketone corresponding to the benzoates



$$\begin{array}{l}[(C_6H_5)_2CHCHCOC_6H_2(CH_3)_3]MgX +\\ C_6H_5CHO + HX \longrightarrow (C_6H_5)_2CH\underset{\displaystyle CHOHC_6H_5}{\underset{|}{C}}HCOC_6H_2(CH_3)_3 \longrightarrow\\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \text{III}\\ \qquad\qquad\qquad\qquad (C_6H_5)_2CH\underset{\displaystyle COC_6H_5}{\underset{|}{C}}HCOC_6H_2(CH_3)_3\end{array}$$

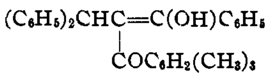
IV

This diketone, like most other alkylated di-aryl β-diketones does not enolize to a detectable extent in solution but as it is not easily cleaved it can be converted without difficulty into one of two possible enolic modifications



$$(C_6H_5)_2CH\underset{\displaystyle COC_6H_5}{\underset{|}{C}}{=}C(OH)C_6H_2(CH_3)_3$$

V

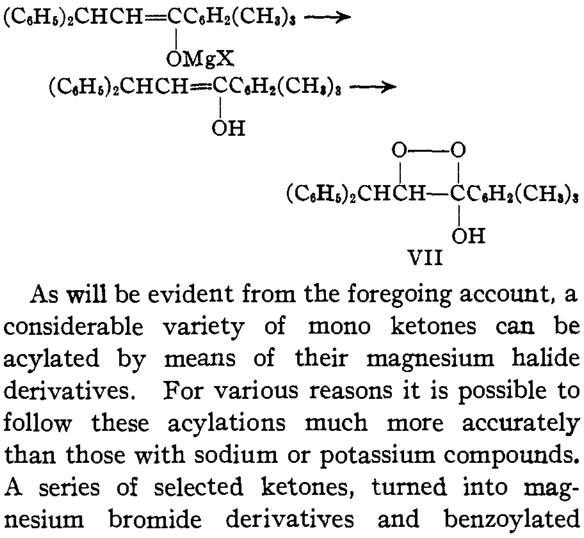


$$(C_6H_5)_2CH\underset{\displaystyle COC_6H_2(CH_3)_3}{\underset{|}{C}}{=}C(OH)C_6H_5$$

VI

The enol has remarkable vitality; in solid form it appears to be completely permanent and it can be crystallized from all common solvents without recognizable change. Even in glacial acetic acid it retains for weeks its power of giving a color reaction with ferric chloride. It however reverts rapidly to the diketone in solutions containing traces of alkalies or piperidine. The unusual lack of mobility in this enol, doubtless, is due largely to the mesityl group, because one of the phenyls of the benzhydryl groups can be replaced with methyl without materially affecting the mobility but when the mesityl group is replaced with phenyl the mobility becomes normal, the enol of benzhydryl dibenzoylmethane ketonizing as rapidly as the corresponding methyl and ethyl compounds.

If the relative stability of the enolic form of the diketone is really due to the influence of the mesityl group, then this group should exercise a similar influence upon the enol of the mono ketone. It does. Its effect is sufficiently great to permit the formation of the type of peroxides which, heretofore, could be obtained only from the enols of mono ketones that have hydrocarbon residues in the α-position.



$$\begin{array}{l}(C_6H_5)_2CHCH{=}\underset{\displaystyle OMgX}{\underset{|}{C}}C_6H_2(CH_3)_3 \longrightarrow\\ \quad (C_6H_5)_2CHCH{=}\underset{\displaystyle OH}{\underset{|}{C}}C_6H_2(CH_3)_3 \longrightarrow\\ \qquad\qquad\qquad (C_6H_5)_2CH\overset{\displaystyle O\text{——}O}{\overset{|\qquad\ \ |}{CH\text{—}\underset{\displaystyle OH}{\underset{|}{C}}}}C_6H_2(CH_3)_3\end{array}$$

VII

As will be evident from the foregoing account, a considerable variety of mono ketones can be acylated by means of their magnesium halide derivatives. For various reasons it is possible to follow these acylations much more accurately than those with sodium or potassium compounds. A series of selected ketones, turned into magnesium bromide derivatives and benzoylated under similar conditions, gave the following percentages of diketones, the remainder of the product being composed mainly of benzoates representing O-acylation.

$(C_6H_5)_2CHCH_2COC_6H_5$	100
$(C_6H_5)_2CHCH(C_6H_5)COC_6H_5$	0
$CH_3COC_6H_2(CH_3)_3$	100
$C_6H_5CH_2CH_2COC_6H_2(CH_3)_3$	12
$C_6H_5CH(CH_3)CH_2COC_6H_2(CH_3)_3$	8
$(C_6H_5)_2CHCH_2COC_6H_2(CH_3)_3$	1.5

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[1] Michael and Ross, This Journal, 53, 2394 (1931).

To judge from this limited number of cases there is a certain degree of correlation between the complexity of the hydrocarbon residues surrounding the carbonyl group, the stability of the enol and the mode of acylation. The results therefore lend some support to the view that C-acylation is preceded by ketonization of the metallic derivative or its ion.

Experimental Part

The general methods employed for preparing the isomeric magnesium derivatives have been described in earlier papers.[2] In order to ensure comparable conditions, all reactions were conducted in an atmosphere of nitrogen and the resulting solutions or suspensions were boiled until most of the magnesium compound had separated in solid form. After the addition of the acid chloride the mixture was boiled again until the benzoylation was manifestly complete. The magnesium derivatives were then treated with iced acid in the usual manner.

In the quantitative experiments the entire product was dissolved in cold dilute methyl alcoholic sodium hydroxide, separate experiments with the pure substances having shown that in these conditions the diketones are not affected while the benzoates are hydrolyzed with great rapidity. The separation of the resulting mixtures presented no great difficulty. After acidification all the organic components were collected in ether, and from this ethereal solution the benzoic acid was removed with bicarbonate and the diketone or its enol by successive extractions with methyl alcoholic sodium hydroxide or sodium methylate—leaving only the mono ketone and other indifferent materials to be separated by physical methods.

The Isomeric Benzoates of Benzhydryl Benzoyl Acetomesitylene.—The higher melting benzoate crystallizes from acetone in large transparent prisms melting at 162°, the lower melting isomer, which is much more soluble, in needles melting at 142°.

Anal. Calcd. for $C_{31}H_{28}O_2$: C, 86.3; H, 6.5. Found (162°): C, 86.2; H, 6.5. (142°): C, 86.0; H, 6.7.

Alcoholic solutions of sodium hydroxide rapidly hydrolyzed both benzoates to diphenylpropionyl mesitylene and sodium benzoate. Toward acid they are much more stable but they can be hydrolyzed by prolonged heating in sealed tubes with methyl alcoholic hydrochloric acid, the lower melting being destroyed much more rapidly than its isomer. They are not interconvertible by protracted heating above the melting point or by exposure to sunlight. It has not been possible thus far to devise any method for determining the configuration of these benzoates.

The Magnesium Halide Derivatives.—The stereometric magnesium compounds are of special interest because they show that both addition to the conjugated system and the enolization of the mono ketone are controlled by mechanisms that lead to products which have definite configurations. Benzoylation of the derivative which is obtained by addition (equation 1) usually gave along with the lower melting benzoate and from one to two per cent. of diketone, a very small quantity of the higher melting benzoate. Neither the amount of diketone nor that of the isomeric benzoate were increased by prolonged boiling in ether–benzene before benzoylation. By treatment with bromine both magnesium derivatives were converted into α-bromo-β,β-diphenylpropionyl mesitylene.

Acetylation with Trimethylbenzoyl Chloride, $(C_6H_5)_2CH—CH=C(C_6H_5)OCOC_6H_2(CH_3)_3$.—When the magnesium compound of diphenylpropiophenone obtained by the third reaction was acylated in the usual manner with trimethylbenzoyl chloride it gave a mixture which was separated by crystallization from methyl alcohol and petroleum ether. One of the products was the same β-diketone (IV) which had been obtained by benzoylating the mesitylenic ketone. The second product was an isomer which was readily hydrolyzed by bases to diphenylpropiophenone and mesitylene carbonic acid—therefore a trimethyl benzoate due to O-acylation. It crystallizes in flattened needles and melts at 93°. As nearly as can be estimated from the results of a separation that was not very accurate 40% of the product was diketone and at least 95% of the remainder was the trimethylbenzoate.

α-Benzhydryl-β-phenyl-β-hydroxy Propionyl Mesitylene, III.—To a magnesium compound obtained by boiling 20 g. of α-bromo-β,β-diphenyl propionyl mesitylene with a solution of ethylmagnesium bromide containing 1.5 g. of magnesium was added 5.5 g. of benzaldehyde. The mixture was boiled for two hours, then decomposed in the usual manner. After the removal of excess of benzaldehyde there remained a yellow solution which yielded 18 g. of condensation product—the balance being a yellow oil and a small quantity of diphenyl propionyl mesitylene. The hydroxyl compound crystallizes well from ether–petroleum ether in colorless plates and it melts at 132°.

Anal. Calcd. for $C_{32}H_{30}O_2$: C, 85.7; H, 6.9. Found: C, 85.7; H, 7.1.

Benzhydryl Benzoylacetomesitylene, IV.—The oxidation of the hydroxyl compound to the diketone presents considerable difficulty. The best results were obtained by the following procedure. To a solution of 5 g. of the hydroxyl compound in 40 cc. of glacial acetic acid was added 1 cc. of a solution of 2.5 g. of chromic acid in 2.5 g. of water and 7.5 g. of glacial acetic acid. The mixture was warmed until oxidation was rapid, then the remainder of the oxidizer was added and the mixture was kept at the oxidizing temperature for five minutes before it was poured on ice. The result was a mixture of diketone and some complex yellow polymer from which the diketone was most easily isolated by repeated extraction with cold petroleum ether.

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[2] Kohler and Tishler, This Journal, **54**, 1594 (1931); Kohler and Baltzly, *ibid.*, **54**, 4015 (1931).

Anal. Calcd. for $C_{31}H_{28}O_2$: C, 86.3; H, 6.5. Found: C, 86.3; H, 6.5.

The diketone crystallizes well from petroleum ether in small colorless prisms or tables and it melts at 107°. It was subsequently obtained in small quantities in the benzoylation of the magnesium derivatives of diphenyl propionyl mesitylene and in much larger quantities by treating the magnesium derivative of diphenyl propiophenone with trimethylbenzoyl chloride. The diketone is unusually insensitive to alkalies; practically all of it was recovered after it had been boiled for six hours with 40% methyl alcoholic potassium hydroxide but by boiling it for ten hours with 50% aqueous sodium hydroxide most of it was hydrolyzed to diphenyl propiophenone and sodium trimethyl benzoate.

Enolization, V or VI.—The diketone dissolves freely in methyl alcoholic sodium hydroxide but unlike the corresponding dibenzoylmethane derivative it is not reprecipitated by diluting the solution with water. When the cold aqueous alcoholic solution is acidified with a mineral acid it precipitates an isomeric compound which crystallizes in minute colorless prisms and which melts at 137°.

Anal. Calcd. for $C_{31}H_{28}O_2$: C, 86.3; H, 6.5. Found: C, 86.3; H, 6.6.

This isomer is evidently one of the enolic forms of the diketone; it reacts instantaneously with bromine, gives with ferric chloride the blue-purple color reaction which is characteristic of mono-alkylated β-diketones, and forms a green copper compound when its ethereal solution is shaken with aqueous copper acetate. In small quantities the enol is most easily recrystallized from ether–petroleum ether, in larger quantities from methyl alcohol. It can also be recrystallized from glacial acetic acid–water but in the presence of piperidine or other organic bases it reverts quantitatively to the diketone. As it could neither be reduced catalytically nor ozonized in such a manner as to secure significant products it could not be definitely related to either of the possible formulas.

α-Benzoyl-β-phenylbutyro Mesitylene, $CH_3CH(C_6H_5)$-$CH(COC_6H_5)COC_6H_2(CH_3)_3$.—An ethereal solution of benzalacetomesitylene was added to excess of methylmagnesium iodide and the resulting magnesium compound was benzoylated in the usual manner. The product was an oil which could not be induced to crystallize. It was therefore treated with cold methyl alcoholic methyl hydroxide and thus converted into benzoic acid and one of the enolic modifications of the diketone. The yield of enol was only 8%, all the rest of the product being benzoate.

Anal. Calcd. for $C_{26}H_{26}O_2$: C, 84.4; H, 7.0. Found: C, 84.5; H, 6.9.

The enol is readily soluble in all common organic solvents including petroleum ether from which it crystallizes in small prisms melting at 128°. Its chemical properties are the same as those of the corresponding benzhydryl compound.

The Diketone.—When the foregoing enol is recrystallized from methyl alcohol containing piperidine it is converted into the diketone which crystallizes in thin needles and melts at 130°. Solutions of the diketone do not contain enough enol, if any, to give a color reaction with ferric chloride.

Anal. Calcd. for $C_{26}H_{26}O_2$: C, 84.4; H, 7.0. Found: C, 84.5; H, 7.2.

Benzyl Acetomesitylene, $C_6H_5CH_2CH_2COC_6H_2(CH_3)_3$.—The saturated ketone was prepared by shaking benzal acetomesitylene with hydrogen and Adams catalyst until the calculated quantity of hydrogen was absorbed. It was obtained as a very pale yellow, viscous oil which boiled at 191–2° under a pressure of about 5 mm.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 85.6; H, 7.9. Found: C, 85.5; H, 7.8.

Benzyl Benzoylaceto Mesitylene $C_6H_5CH_2CH(COC_6H_5)$-$COC_6H_2(CH_3)_3$.—Benzyl aceto mesitylene was converted into the magnesium bromide derivative with ethylmagnesium bromide and the solid magnesium compound was boiled with excess of benzoyl chloride. The product—a colorless viscous oil—was hydrolyzed in the usual manner with methyl alcoholic sodium hydroxide. It was thus converted into sodium benzoate and a solid which crystallized from petroleum ether in flat colorless needles and which melted at 118°.

Anal. Calcd. for $C_{25}H_{24}O_2$: C, 8.43; H, 6.8. Found: C, 84.2; H, 7.2.

The product has the composition of an enol and it both gave the characteristic color reaction of these enols with ferric chloride and formed a copper derivative but it could not be converted into an isomeric diketone by the usual treatment with piperidine. A titration with bromine by the method of Kurt Meyer showed that fresh solutions in methyl alcohol contain relatively small quantities of enol (4–6%), that the proportion of enol increases gradually with time and that 4% solutions in methyl alcohol which have been equilibrated with piperidine contain nearly equal quantities of enol (49.3%) and diketone.

As the mobility of this keto–enol system was quite unexpected we prepared the benzyl compound by benzylating the sodium derivative of benzoyl acetomesitylene with benzyl chloride. The product was identical in every respect with the substance obtained by acylation. Finally we decided to prepare the benzyl derivative by a third method which was devised to give as pure a product as it is possible to make. To this end we first prepared benzal benzoylaceto mesitylene by condensing benzaldehyde with benzoylacetomesitylene by the general method of Knoevenagel.[3]

Benzal Benzoylaceto Mesitylene, $C_6H_5CH{=}C(COC_6H_5)$-$COC_6H_2(CH_3)_3$.—The unsaturated diketone crystallized well from methyl alcohol in large yellow crystals. The yield was poor.

Anal. Calcd. for $C_{25}H_{22}O_2$: C, 84.6; H, 6.2. Found: C, 84.6; H, 6.3.

The unsaturated ketone was easily reduced, catalytically, and the benzyl compound which was prepared in this manner was likewise identical with the substance that was obtained by acylation.

Benzoylation of Mesityl Phenyl Propiophenone, $(CH_3)_3$-$C_6H_2CH(C_6H_5)CH = C(C_6H_5)OCOC_6H_5$.—Trimethylbenzal acetophenone was added to phenylmagnesium bromide and the resulting magnesium compound was benzoylated in the usual manner. The product was separated into a solid and an oil which has not been identified. The

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[3] Knoevenagel. *Ber.*, **36**, 2131 (1903).

solid crystallized from methyl alcohol in small prisms and melted at 110°.

Anal. Calcd. for $C_{31}H_{28}O_2$: C, 86.3; H, 6.5. Found: C, 86.3; H, 6.6.

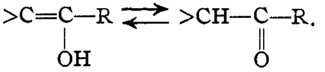
This solid is evidently a benzoate because cold methyl alcoholic sodium hydroxide hydrolyzes it rapidly to mesityl phenyl propiophenone. The yield was about 50%.

α-Mesityl-γ,γ-diphenyl Propenol Peroxide, VII.—To a solution of phenylmagnesium bromide containing 1.9 g. of magnesium was added 10 g. of benzalaceto mesitylene. The mixture was boiled for fifteen minutes, then decomposed with iced hydrochloric acid. The ethereal layer was diluted with about five times its volume of petroleum ether and washed thrice with ice water. A rapid stream of oxygen was then passed through the moist solution. It gradually caused the precipitation of a solid which separated in microscopic needles. The solid was purified by solution in ether and reprecipitation with petroleum ether. The yield was 9 g.

Anal. Calcd. for $C_{24}H_{24}O_3$: C, 80.1; H, 6.7. Found: C, 80.6; H, 6.5.

In a capillary tube the peroxide melts quietly with decomposition at 116–117°. Heated in larger quantity on a spatula it decomposes with a flash, one of the decomposition products being mesitylene carbonic acid. Like other peroxides of this type it liberates iodine from alcoholic solutions of iodides.

Summary

A study of the magnesium halide derivatives of a series of related mesitylenic ketones showed that the mesityl group in some manner decreases the speed of the processes represented by  $>\mathrm{C}{=}\underset{\mathrm{OH}}{\underset{|}{\mathrm{C}}}{-}\mathrm{R} \rightleftarrows >\mathrm{CH}{-}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}{-}\mathrm{R}$. It also showed that there is a certain degree of correlation between the complexity of the hydrocarbon residues surrounding a carbonyl group, the stability of the enolic form and the mode of acylation.

CAMBRIDGE, MASS. RECEIVED SEPTEMBER 24, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

Some Derivatives of Beta-Sulfopropionic Acid[1]

BY LUCIUS A. BIGELOW, HUGH W. SIGMON AND DAVID H. WILCOX, JR.

The original point of interest which led to the choice of β-sulfopropionic acid as a subject for study, was the fact that it is the aliphatic analog of *o*-sulfobenzoic acid, the imide of which is the well-known sugar substitute, saccharin. While the latter acid has been the subject of intensive and detailed research, our knowledge concerning the former is very meager and incomplete. The purpose of this paper is to present the results of a study of a number of the simpler derivatives of this interesting aliphatic sulfonic acid.

β-Sulfopropionic acid was originally described by Rosenthal[2] in 1886. He also prepared a large number of the salts, the ethyl ester, and an impure acid chloride, to which he assigned the formula  $\begin{array}{l}\mathrm{CHCl{-}COCl}\\ |\\ \mathrm{CH_2SO_2Cl}\end{array}$ on the basis of rather unsatisfactory evidence. His work includes practically all that is known about the compound or its derivatives, although certain of them have been mentioned indirectly by Kohler[3] and others.

In the present work, barium β-sulfopropionate was prepared from β-iodopropionic acid, and subsequently converted into the silver salt, which, in turn, was treated with the appropriate alkyl halides to form the corresponding neutral methyl-, ethyl-, *n*-propyl- and *n*-butyl esters. These were colorless liquids at room temperature, crystallized from ether at low temperatures and melted at 17, 4, −7 and −25° (all ± 1°), respectively. The methyl ester boiled with slight decomposition at 132–3° at 1 mm., and the others could not be distilled.

In the hope of obtaining a solid ester, the silver salt was treated with benzyl bromide, benzyl iodide and phenacyl bromide, but without results. Phenylethyl iodide, however, reacted normally, yielding the neutral phenylethyl ester in white needles, melting at 59°. This ester, on saponification with barium hydroxide, yielded the barium salt of the acid, in 73% yield, apparently identical, under the microscope, with the corresponding salt obtained from β-iodopropionic acid.

When the dry potassium salt of the acid, in benzene suspension, was treated with phosphorus pentachloride, it yielded, ultimately, a light colored oil, thermally unstable even at 0°, which, when crystallized from ether at low temperatures

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[1] This paper has been abstracted from the Doctorate Thesis of Hugh W. Sigmon, and the Master's Thesis of David H. Wilcox, Jr., presented to the Graduate School of Arts and Sciences of Duke University in 1935 and 1932, respectively.

(2) Rosenthal, *Ann.*, **233**, 15 (1886).

(3) Kohler, *Am. Chem. J.*, **19**, 732 (1897).