variety of the common phosphatic materials of the fertilizer industry, the determination of phosphoric acid as phosphomolybdic anhydride was found to give satisfactory results even without a reprecipitation of the ammonium phosphomolybdate.

The presence in considerable quantity of some of the common acids and bases was found to be without appreciable effect.

With either modification of the method the average result obtained on all the samples analyzed was practically the same as that yielded by the official method which would seem to indicate that such variations as occur are due mainly to manipulation.

By the method described a determination may be completed in much less time than by any other gravimetric method with which we are familiar but in handling several samples simultaneously, the saving of time is less apparent.

COLUMBIA UNIVERSITY, NEW YORK CITY, July, 1900.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

THE ACTION OF SODIUM ALCOHOLATE UPON ANISYLIDENE ACETOPHENONE DIBROMIDE.

BY F. J. POND AND ARTHUR S. SHOFFSTALL.

Received August 1, 1900.

IN a preceding communication[1] on this subject it was mentioned that sodium methylate reacts with the dibromides of certain unsaturated ketones of the general formula,

$$R-CH=CH-CO-C_6H_5,$$

yielding 1,3-diketones of the formula,

$$R-CO-CH_2-CO-C_6H_5.$$

Thus benzylidene acetophenone dibromide was readily converted into *dibenzoyl methane*, and anisylidene acetophenone dibromide was found to give a 1,3-diketone analogous to dibenzoyl methane, and called *anisoyl benzoyl methane*. It was suggested that the formation of these diketones from the dibromides of unsaturated ketones was accomplished by the production of unsaturated ethers,

$$R-C(OCH_3)=CH-CO-C_6H_5,$$

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[1] Pond, Maxwell, and Norman: This Journal, **21**, 955.

which were converted by hydrolysis with dilute acids into the unsaturated ketone alcohols,

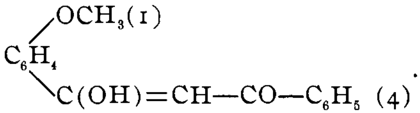
$$R—C(OH)=CH—CO—C_6H_5,$$

and these, in turn, by an intramolecular change into the saturated 1,3-diketones,

$$R—CO—CH_2—CO—C_6H_5.$$

Such a reaction would be somewhat analogous with the formation of ketones from the dibromides of anethol, isosafrol, and other propenyl compounds.

Closer investigation of the compound obtained from anisylidene acetophenone dibromide and of its derivatives leads us to believe that the last-mentioned change of the unsaturated ketone alcohol into the saturated diketone does not take place, and that the compound is a keto-enolic modification of anisoyl benzoyl methane and may be called *α-oxyanisylidene acetophenone*,



$$C_6H_4\begin{cases}OCH_3(1)\\C(OH)=CH—CO—C_6H_5\ (4)\end{cases}.$$

Its solution in alcohol is colored an intense brownish red by the addition of ferric chloride; aqueous ferric acetate, made by mixing the solutions of one part of ferric chloride and three parts of sodium acetate, throws out the ferric salt of α-oxyanisylidene acetophenone as a brick-red, crystalline precipitate, which is insoluble in water and alcohol, but soluble in dilute hydrochloric acid. W. Wislicenus[1] has suggested that the formation of such colored iron compounds on the addition of ferric chloride to the alcoholic solutions is a property of compounds containing the group,

$$C(OH)=C—,$$

such as phenols and the enolic modifications of β-keto-compounds; also, that in these colored iron compounds the metal is joined to the oxygen atom, a view which Claisen[2] also holds regarding the constitution of the iron salts of the β- or 1,3-diketones.

This compound is soluble in dilute alkalies, and is reprecipitated by acids. A green, crystalline copper salt is precipitated from its alcoholic solution by an alcoholic solution of copper ace-

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[1] W. Wislicenus: *Ann. Chem.* (Liebig), 291, 174.

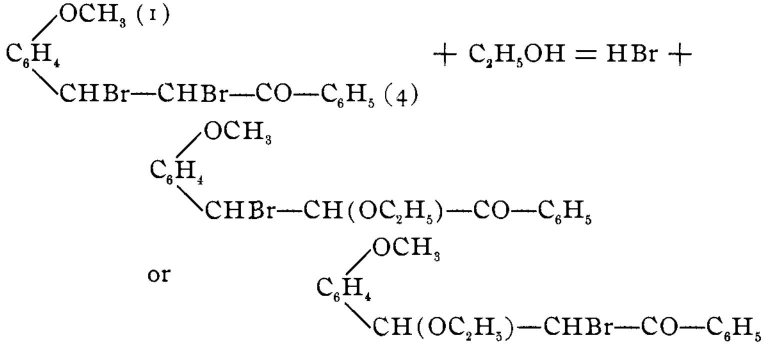
[2] L. Claisen: *Ibid.*, 281, 344.

tate. It decolorizes immediately a solution of potassium permanganate in the cold, but it does not yield an additive product with bromine. It is indifferent towards acetic anhydride and benzoyl chloride.

The experimental part of our work is preceded by the following brief review of the contents of this paper.

The method of preparation of anisylidene acetophenone, the starting-point of our investigation, is slightly modified, by means of which a larger yield of the compound, melting at 78°, is obtained. This substance unites readily with two atoms of bromine, forming an additive product. The dibromide can not be recrystallized unchanged from alcohol, but it separates without change from acetic ether in large crystals, melting at 139° to 140°.

When anisylidene acetophenone dibromide is dissolved in alcohol and the solution is boiled for a short time, hydrogen bromide is eliminated and an alcohol addition-product of monobromoanisylidene acetophenone is produced :



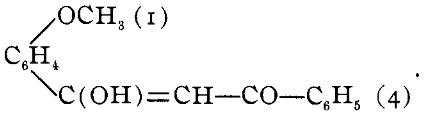
$$C_6H_4\begin{array}{l}\diagup OCH_3\ (1)\\ \diagdown CHBr—CHBr—CO—C_6H_5\ (4)\end{array} + C_2H_5OH = HBr + C_6H_4\begin{array}{l}\diagup OCH_3\\ \diagdown CHBr—CH(OC_2H_5)—CO—C_6H_5\end{array}$$

$$\text{or}\quad C_6H_4\begin{array}{l}\diagup OCH_3\\ \diagdown CH(OC_2H_5)—CHBr—CO—C_6H_5.\end{array}$$

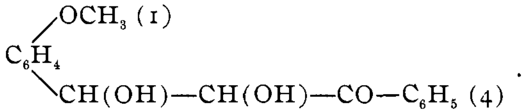
This is a saturated compound, which melts at 73.5° to 74.5°. When heated carefully in a distilling flask, no change is to be noted until the temperature reaches about 155° to 160° ; a clear liquid then comes over having the odor and boiling-point of ethyl alcohol, and yielding the iodoform reaction. If the distillation be interrupted as soon as alcohol ceases to be given off, the liquid remaining in the flask solidifies and crystallizes from alcohol or ethyl acetate in large plates, melting at 94.5° ; these are shown to be monobromoanisylidene acetophenone.

The analogous methyl alcohol addition-product was prepared, and crystallized from methyl alcohol in fine crystals, which melt at 102°. The propyl alcohol addition-product is an oil, and is not further examined.

In a previous paper[1] it was shown that when anisylidene acetophenone dibromide was heated with two molecules of sodium methylate or ethylate and the resultant product hydrolyzed with hydrochloric acid, a compound was formed which melted at 131° to 132°; this compound was called anisoyl·benzoyl methane. Further investigation has shown that it consists of α-oxyanisylidene acetophenone, *i. e.*, it is the α- or acid-modification of the diketone, $C_{16}H_{14}O_3$, and is to be represented by the formula,

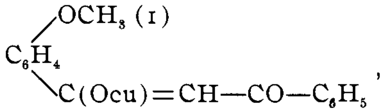


The filtrate obtained in the preparation of this compound yields an exceedingly small quantity of a silky, crystalline substance, which melts at 90° and is exceptionally soluble in alcohol; the analysis of this compound indicates that it has the composition represented by the formula, $C_{16}H_{16}O_4$. It may possibly prove to be the keto-glycol,



Until a method of preparation is found by which a suitable quantity of this substance can be obtained and further experimental evidence is secured, we do not care to commit ourselves regarding its structure. Should further investigation prove it to be the keto-glycol suggested above, its study will lead to very interesting results.

α-Oxyanisylidene acetophenone yields quantitatively a copper salt,[2]



which melts with decomposition at 247° to 249°. α-Oxyanisyli-

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[1] *Loc. cit.*

[2] cu = ½ atom Cu.

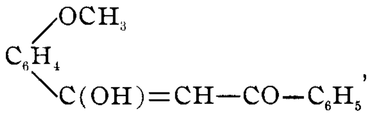
dene acetophenone is easily regenerated in a pure condition by warming this copper salt with dilute hydrochloric acid.

The action of hydroxylamine hydrochloride upon an alcoholic solution of α-oxyanisylidene acetophenone gives α,γ-methoxy-phenyl-phenyl-isoxazole, melting at 120°; it crystallizes from alcohol in small flakes, which possess a brilliant mother-of-pearl luster. Claisen[1] has shown that monoximes of the β- or 1,3-diketones are not generally known. In attempts to prepare them, water usually splits off and an intramolecular anhydride formation takes place, giving the isoxazoles. J. Wislicenus[2] succeeded in preparing a monoxime from α-benzylidene acetophenone by the action of free hydroxylamine; but it showed a great tendency to lose water with the formation of α,γ-diphenyl-isoxazole.

An isomeric methoxyphenyl-phenyl-isoxazole is formed by the action of an excess of potassium hydroxide upon the mixed alcoholic solutions of anisylidene acetophenone dibromide and hydroxylamine hydrochloride. It crystallizes from alcohol in small, silky needles, which melt at 128°.

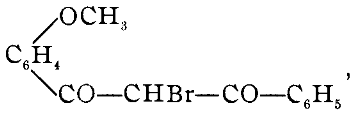
Acetic anhydride and benzoyl chloride do not react with the hydroxyl group of α-oxyanisylidene acetophenone.

Bromine seems to convert α-oxyanisylidene acetophenone into a bromine derivative of the β-modification of the diketone. Instead of absorbing two atoms of bromine and yielding an additive product as would naturally be anticipated by the formula,



$$C_6H_4\begin{matrix}\diagup OCH_3\\ \diagdown C(OH)=CH-CO-C_6H_5\end{matrix},$$

an atom of bromine is substituted for one hydrogen atom, and the compound,



$$C_6H_4\begin{matrix}\diagup OCH_3\\ \diagdown CO-CHBr-CO-C_6H_5\end{matrix},$$

anisoyl benzoyl monobromomethane, is formed. It crystallizes well, and melts at 127.5° to 128.5°. It gives no coloration with ferric chloride and alcohol, and does not form a copper salt by

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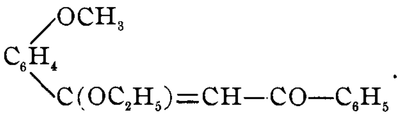
[1] L. Claisen: *Ber. d. chem. Ges.*, **24**, 3906; **21**, 2178; **24**, 390; **25**, 1787.

[2] J. Wislicenus: *Ann. Chem.* (Liebig), **308**, 250.

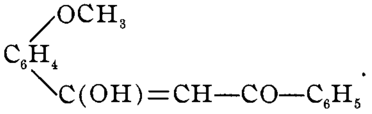
the addition of an alcoholic solution of copper acetate. It apparently contains no hydroxyl group.

An important part of our work is to determine, if possible, the exact course of the reaction by which the enolic-ketone is formed from anisylidene acetophenone dibromide by the action of sodium alcoholate. When one molecule of the dibromide is boiled with two molecules of sodium ethylate, the resulting product consists of an unsaturated ether,



$$C_6H_4\begin{matrix}\diagup OCH_3\\ \diagdown C(OC_2H_5)=CH-CO-C_6H_5\end{matrix}.$$

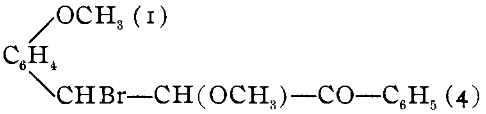
Dilute acids hydrolyze this compound with the formation of ethyl alcohol and the keto-enole,



$$C_6H_4\begin{matrix}\diagup OCH_3\\ \diagdown C(OH)=CH-CO-C_6H_5\end{matrix}.$$

When sodium methylate is employed, the unsaturated methyl ether is produced, which also yields α-oxyanisylidene acetophenone on hydrolysis. The sodium alcoholate seemed to have a double action in that it split off one bromine atom as hydrogen bromide and then replaced the second bromine atom with the methoxyl or ethoxyl group. It therefore remained to determine whether the sodium alcoholate could react under certain conditions so that the two phases of the reaction could be separated, and the intermediate products isolated.

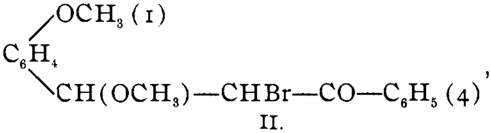
For this purpose we treated one molecule of the dibromide with a dilute solution of one molecule of sodium methylate in methyl alcohol. The product consists of two compounds: the one crystallizing in small needles and melting at 101.5° to 102.5° is the methyl alcohol addition-product of monobromoanisylidene acetophenone, and is formed in small quantity; the other is monobromoanisylidene acetophenone, which crystallizes in beautiful plates and melts at 94°. On heating the methyl alcohol additive compound it loses methyl alcohol and yields monobromoanisylidene acetophenone. This alcohol addition-product should probably be represented by one of the two following structural formulas,



$$C_6H_4\begin{array}{l}\diagup OCH_3\ (1)\\ \diagdown CHBr-CH(OCH_3)-CO-C_6H_5\ (4)\end{array}$$

I.

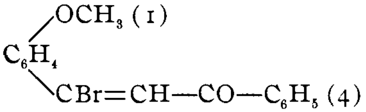
or



$$C_6H_4\begin{array}{l}\diagup OCH_3\ (1)\\ \diagdown CH(OCH_3)-CHBr-CO-C_6H_5\ (4)\end{array},$$

II.

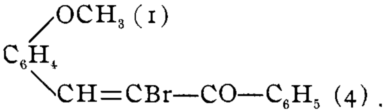
and monobromoanisylidene acetophenone by the formula,



$$C_6H_4\begin{array}{l}\diagup OCH_3\ (1)\\ \diagdown CBr=CH-CO-C_6H_5\ (4)\end{array}$$

I.

or

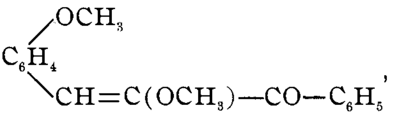


$$C_6H_4\begin{array}{l}\diagup OCH_3\ (1)\\ \diagdown CH=CBr-CO-C_6H_5\ (4)\end{array}.$$

II.

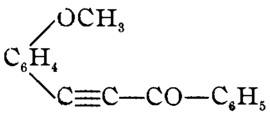
For the present we prefer the formula I for each compound for the following reasons:

If the alcohol addition-product has the structure as represented by formula II, the unsaturated monobromide resulting from it by the elimination of methyl alcohol must have the formula II, thus containing the bromine atom in the β-position to the methoxyphenyl group. It would be expected that by the action of another molecule of sodium methylate upon this compound, a new ether,



$$C_6H_4\begin{array}{l}\diagup OCH_3\\ \diagdown CH=C(OCH_3)-CO-C_6H_5\end{array},$$

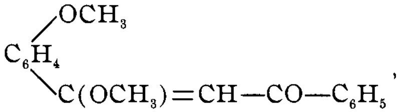
would be formed by the replacement of the bromine atom by methoxyl, or the monobromide might loose hydrogen bromide and yield a compound containing a triple linkage, benzoyl methoxyphenyl acetylene,



$$C_6H_4\begin{array}{l}\diagup OCH_3\\ \diagdown C\equiv C-CO-C_6H_5\end{array}$$

Neither of these compounds, however, have been obtained.

If the alcohol addition-product be represented by formula I, then by the splitting off of alcohol an unsaturated bromide having the above formula I with the bromine atom in the *α*-position would result. Such a compound might react with one molecule of sodium methylate giving rise to the same unsaturated methyl ether,



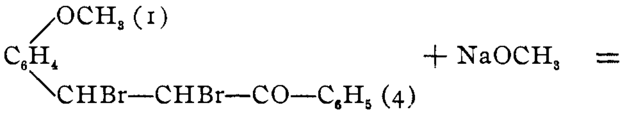
$$C_6H_4\begin{matrix}\diagup OCH_3\\ \diagdown C(OCH_3)=CH-CO-C_6H_5\end{matrix},$$

which is produced by the treatment of the dibromide with two molecules of sodium methylate, and by the hydrolysis of this ether the same keto-enole must result. Our experiments show that the reaction takes place in this manner, since the monobromide does react with sodium methylate, yielding the same ether which results by the action of an excess of methylate upon the dibromide, and from which *α*-oxyanisylidene acetophenone is formed by hydrolysis.

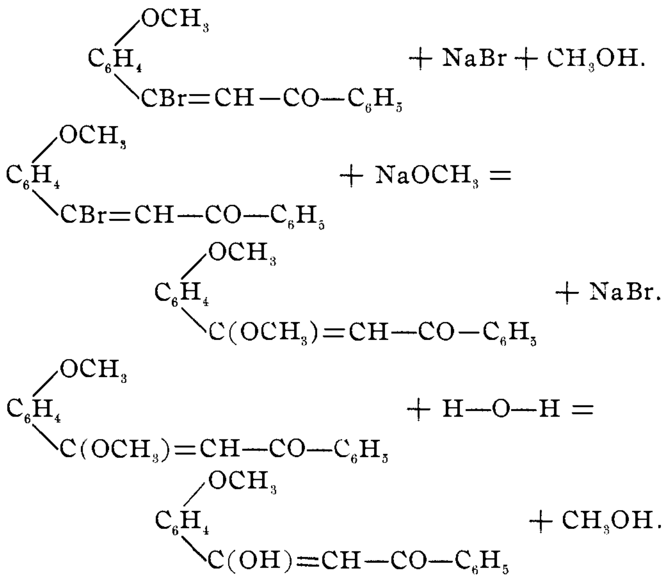
The formation of *α*-monobromoanisylidene acetophenone and of its alcohol addition-product in the same reaction would seem to indicate that one molecule of sodium alcoholate eliminates hydrogen bromide from a large part of the dibromide, yielding the unsaturated monobromide, and at the same time it replaces one atom of bromine in another smaller portion of the dibromide with the methoxyl group. It is also possible that, under the conditions of the experiment in which great care must be taken to avoid any excess over one molecule of sodium methylate, in order to prevent the elimination of both bromine atoms, that all of the sodium methylate is employed to remove hydrobromic acid, and that the small quantity of the methyl alcohol addition-product is due simply to the action of the methyl alcohol on some unchanged dibromide.

α-Oxyanisylidene acetophenone is probably formed by the action of sodium alcoholate upon anisylidene acetophenone dibromide in accordance with the following equations:

1.



$$C_6H_4\begin{matrix}\diagup OCH_3\ (1)\\ \diagdown CHBr-CHBr-CO-C_6H_5\ (4)\end{matrix} + NaOCH_3 =$$



$$C_6H_4\begin{array}{l}\diagup OCH_3\\ \diagdown CBr=CH-CO-C_6H_5\end{array} + NaBr + CH_3OH.$$

2. $$C_6H_4\begin{array}{l}\diagup OCH_3\\ \diagdown CBr=CH-CO-C_6H_5\end{array} + NaOCH_3 =$$

$$C_6H_4\begin{array}{l}\diagup OCH_3\\ \diagdown C(OCH_3)=CH-CO-C_6H_5\end{array} + NaBr.$$

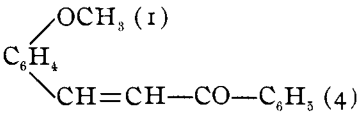
3. $$C_6H_4\begin{array}{l}\diagup OCH_3\\ \diagdown C(OCH_3)=CH-CO-C_6H_5\end{array} + H-O-H =$$

$$C_6H_4\begin{array}{l}\diagup OCH_3\\ \diagdown C(OH)=CH-CO-C_6H_5\end{array} + CH_3OH.$$

In the first phase of the reaction, the bromine atom in the β-position to the methoxyphenyl group is eliminated as hydrogen bromide with the formation of an unsaturated monobromide, while in the second stage, the bromine atom in the α-position is replaced by the methoxyl group, giving an unsaturated ether, which is readily hydrolyzed into the enolic ketone.

EXPERIMENTAL.

Anisylidene Acetophenone,



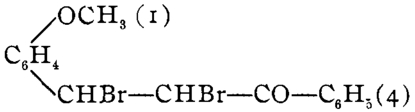
$$C_6H_4\begin{array}{l}\diagup OCH_3\ (1)\\ \diagdown CH=CH-CO-C_6H_5\ (4)\end{array}$$

This substance is very readily prepared by the following method: Twelve grams of acetophenone and 13.6 grams of anisaldehyde (molecular proportions) are dissolved in 50 cc. of alcohol and treated with 5 cc. of a 20 per cent. solution of sodium methylate. After standing for about fifteen minutes, the solution is shaken vigorously for a few minutes, when the product separates as a yellow, crystalline solid; this is filtered by the pump, washed sparingly with cold alcohol, dried, and recrystallized from alcohol. It crystallizes from alcohol in long, light yellow needles, and melts at 77° to 78°. It is easily soluble in hot ethyl and methyl alcohols, ether, and chloroform. Upon analysis it gave the following results:

I. 0.1582 gram gave 0.4674 gram carbon dioxide and 0.0822 gram water.
II. 0.1603 gram gave 0.4733 gram carbon dioxide and 0.0846 gram water.

	Calculated for $C_{16}H_{14}O_2$.	Found. I.	Found. II.
Carbon	80.65	80.58	80.53
Hydrogen	5.88	5.77	5.86

Anisylidene Acetophenone Dibromide,



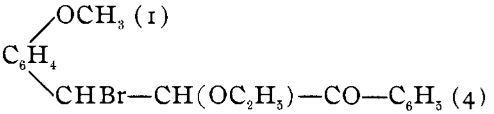
$$C_6H_4\left\langle\begin{array}{l}OCH_3\ (1)\\ CHBr{-}CHBr{-}CO{-}C_6H_5\,(4)\end{array}\right.$$

Twenty-five grams of anisylidene acetophenone were dissolved in 125 cc. of ether and the solution was cooled; 16.8 grams (one molecule) of bromine were added slowly and with constant shaking. After two-thirds of the bromine had been introduced, the product began to separate in fine, white crystals. The crystalline precipitate was filtered, washed well with cold ether to remove any slight excess of bromine, and dried on a porous plate. It was crystallized from ethyl acetate and obtained in thick prisms, melting with decomposition at 139° to 140°. It can not be recrystallized unchanged from ethyl or methyl alcohol; when dissolved in either of these solvents, hydrogen bromide is given off and crystalline compounds are formed, which will be subsequently described. It is readily soluble in acetic ether and crystallizes from it without evolution of hydrobromic acid; it is only sparingly soluble in ether.

It was analyzed with the following results:

I. 0.1807 gram gave 0.3228 gram carbon dioxide and 0.0567 gram water.
II. 0.1708 gram gave 0.3024 gram carbon dioxide and 0.0543 gram water.
III. 0.1669 gram gave 0.1566 gram silver bromide.
IV. 0.1825 gram gave 0.1738 gram silver bromide.

	Calculated for $C_{16}H_{14}O_2Br_2$.	Found. I.	II.	III.	IV.
Carbon	48.24	48.72	48.28	....	....
Hydrogen	3.52	3.49	3.53	....	....
Bromine	40.20	....	....	39.93	40.52

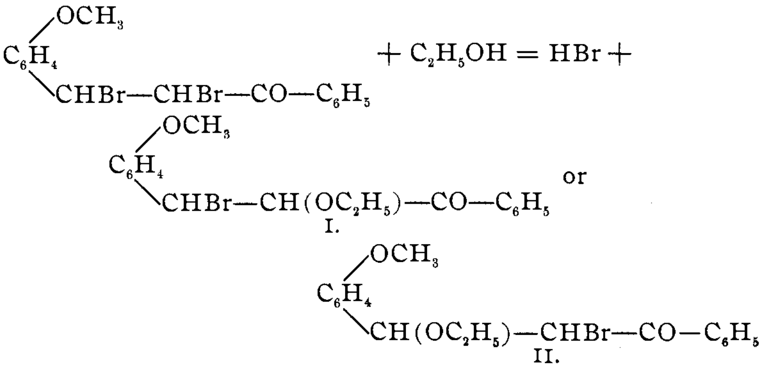


The Ethyl Alcohol Addition-product of α-Monobromoanisylidene Acetophenone, $C_6H_4<^{OCH_3\ (1)}_{CHBr—CH(OC_2H_5)—CO—C_6H_5\ (4)}$ —It was noticed that when the preceding compound was crystallized from alcohol, considerable hydrogen bromide was given off and the resultant compound was quite different from the original dibromide. Fifty grams of anisylidene acetophenone dibromide were crystallized from ethyl alcohol and the resulting crystals were repeatedly recrystallized until they showed the constant melting-point, 74° to 75°. It is deposited from alcohol in long, white needles. It is unaltered by crystallization from methyl alcohol and by boiling its solution in methyl alcohol for several hours. It was dried *in vacuo*, and analyzed with the following results:

I. 0.1832 gram gave 0.4017 gram carbon dioxide and 0.0877 gram water.
II. 0.1822 gram gave 0.3969 gram carbon dioxide and 0.0872 gram water.
III. 0.1871 gram gave 0.0970 gram silver bromide.
IV. 0.1671 gram gave 0.0870 gram silver bromide.

	Calculated for $C_{16}H_{13}O_2Br$.	Calculated for $C_{18}H_{19}O_3Br$.	Found. I.	II.	III.	IV.
Carbon	60.56	59.50	59.80	59.41	....	....
Hydrogen	4.10	5.23	5.32	5.32	....	....
Bromine	25.23	22.04	....	....	22.06	22.15

The analysis indicated that the compound was not the monobromoanisylidene acetophenone, $C_{16}H_{13}O_2Br$, at first anticipated, but that it was the ethyl alcohol addition-product of this bromide. It probably results from anisylidene acetophenone dibromide according to the following equation:



$$C_6H_4<^{OCH_3}_{CHBr—CHBr—CO—C_6H_5} + C_2H_5OH = HBr + C_6H_4<^{OCH_3}_{CHBr—CH(OC_2H_5)—CO—C_6H_5}\ \text{I.}\quad \text{or}\quad C_6H_4<^{OCH_3}_{CH(OC_2H_5)—CHBr—CO—C_6H_5}\ \text{II.}$$

For the reasons suggested in the introduction we prefer formula I.

The substance behaves like a saturated compound. When it is dissolved in carbon tetrachloride it absorbs no bromine; the first drop of bromine added gives it a permanent red color, hydrogen bromide being evolved, and when one molecular proportion of bromine is added and the solvent evaporated, a crystalline substitution-product results.

The following experiment also indicates that it is an alcohol addition-product of α-monobromoanisylidene acetophenone.

Twenty-five grams of the substance (m. p. 74°) were heated in a distilling flask. It melted to a clear liquid which gradually assumed a yellowish color. At about 161° bubbles began to form and rise from the bottom of the flask, and a clear liquid distilled over. The temperature was further increased very slowly to 175°, when the distillation was interrupted. Two and one-half grams of liquid distillate were obtained having the odor of ethyl alcohol, and boiling at 77° to 78°; it yielded iodoform on treatment with iodine and potassium hydroxide, and was thus identified as alcohol. The yellow oil remaining in the flask was poured into a beaker, when it solidified at once, and was recrystallized from acetic ether; it separated in large plates, melting at 94.5°, and was proved to be α-bromoanisylidene acetophenone.

The same addition-product results on boiling the dibromide with alcohol in a reflux apparatus for several hours. Thus, 25 grams of anisylidene acetophenone dibromide were boiled with 200 cc. of alcohol on the water-bath for several hours, and the contents then allowed to crystallize. On recrystallization from alcohol, the product separated in long, white needles, which melted at 73.5° to 74.5°, and gave the following on analysis:

I. 0.1963 gram gave 0.1004 gram silver bromide.
II. 0.1230 gram gave 0.1187 gram silver bromide.

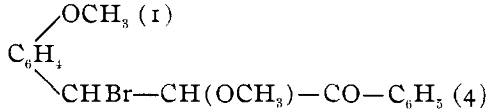
	Calculated for $C_{18}H_{19}O_3Br$.	Found. I.	II.
Bromine	22.04	21.76	21.95

An attempt to prepare monobromoanisylidene acetophenone by boiling an alcoholic solution of the dibromide with a molecular proportion of potassium acetate resulted in the formation of the alcohol addition-product. Twenty-five grams of anisylidene acetophenone dibromide were dissolved in 200 cc. of alcohol and treated with an alcoholic solution of 6.2 grams of potassium acetate; after boiling for three hours, the resulting potassium bromide was filtered off at once. On cooling, a compound separated from the clear filtrate in long, white needles; these were recrystallized from alcohol, and melted at 73.5° to 74.5°. Analysis showed it to be the ethyl alcohol addition-product:

I. 0.2055 gram gave 0.1076 gram silver bromide.
II. 0.2008 gram gave 0.1044 gram silver bromide.

	Calculated for $C_{18}H_{19}O_3Br$.	Found. I.	II.
Bromine	22.04	22.23	22,12

The Methyl Alcohol Addition-product of α-Monobromoanisylidene Acetophenone, C_6H_4



$$C_6H_4\begin{cases} OCH_3\ (1) \\ CHBr{-}CH(OCH_3){-}CO{-}C_6H_5\ (4) \end{cases}$$

It was to be expected that a compound analogous to the preceding one would result on crystallizing the dibromide from methyl alcohol. Accordingly, 20 grams of anisylidene acetophenone dibromide were dissolved in hot methyl alcohol, the solution boiled for a few minutes and then allowed to crystallize. Hydrobromic acid fumes were given off during the boiling of the solution and continuously during the cooling. The resulting crystalline compound was repeatedly crystallized from methyl alcohol and obtained in the form of small, white needles, melting sharply at 102°. The compound is fairly soluble in methyl alcohol, and very soluble in acetic ether; it is also readily soluble in ethyl alcohol, and crystallizes from it, without change, in small needles, melting at 102°.

Analyses of the product recrystallized from methyl alcohol and dried *in vacuo* gave the following:

I. 0.1819 gram gave 0.3905 gram carbon dioxide and 0.0800 gram water.
II. 0.1818 gram gave 0.3887 gram carbon dioxide and 0.0800 gram water.
III. 0.2022 gram gave 0.1073 gram silver bromide.
IV. 0.1961 gram gave 0.1048 gram silver bromide.

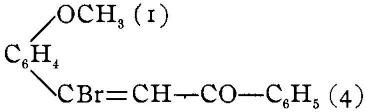
	Calculated for $C_{17}H_{17}O_3Br$.	Found. I.	II.	III.	IV.
Carbon	58.45	58.55	58.31	....	....
Hydrogen	4.87	4.89	4.89	....	....
Bromine	22.92	....	....	22.58	22.74

This compound is the methyl alcohol addition-product expected. In attempting to distil it under diminished pressure, it suffered complete decomposition. When 25 grams were heated at the ordinary pressure, the substance melted to a clear liquid and, on raising the temperature to 160°, bubbles began to rise; from 167° to 180° a small quantity of a clear distillate was obtained, while the liquid in the flask had assumed a yellowish color. At 180° the heat was removed, and, on cooling, the contents of the flask solidified at once; this solid was crystallized from ethyl acetate and obtained in large, slightly yellow-colored plates, melting at 94°, thus showing it to be α-monobromoanisylidene acetophenone.

Anisylidene acetophenone dibromide dissolves in propyl alcohol with evolution of hydrogen bromide; on evaporation of the solvent, a colorless oil results, but it was not examined.

THE ACTION OF ONE MOLECULE OF SODIUM METHYLATE UPON ANISYLIDENE ACETOPHENONE DIBROMIDE.

α-Monobromoanisylidene Acetophenone,



$$C_6H_4\begin{cases} OCH_3 \ (1) \\ CBr{=}CH{-}CO{-}C_6H_5 \ (4) \end{cases}$$

To a solution of sodium methylate, made by dissolving 1.5 grams of sodium in 125 cc. of methyl alcohol, was added 25 grams of the dibromide. The dibromide dissolved at once, forming a light yellow colored solution. After boiling for one hour, a small quantity of sodium bromide had separated and the solution was no longer alkaline to litmus. The sodium bromide was separated by filtration and the filtrate allowed to evaporate slowly. A product began to separate in large, yellow plates, and, after standing for some time, it was removed and the mother-liquor allowed to evaporate to dryness, when a second product, more soluble in alcohol than the plates, was obtained. The yellow plates were washed with water, pressed on a porous plate, and crystallized from acetic ether. The resulting crystals were again rubbed on a plate to remove oily impurities, and recrystallized first from alcohol and then acetic ether. The pure product separates from acetic ether in large, beautiful plates, which are nearly colorless and melt at 94.5°. Its composition is shown by the analysis:

I. 0.1816 gram gave 0.4001 gram carbon dioxide and 0.0676 gram water.
II. 0.1873 gram gave 0.4125 gram carbon dioxide and 0.0680 gram water.
III. 0.1938 gram gave 0.1161 gram silver bromide.
IV. 0.1898 gram gave 0.1130 gram silver bromide.

	Calculated for $C_{16}H_{13}O_2Br$.	Found. I.	II.	III.	IV.
Carbon	60.56	60.09	60.06	....	....
Hydrogen	4.10	4.13	4.03	....	....
Bromine	25.23	....	....	25.49	25.33

This compound is, therefore, monobromoanisylidene acetophenone, and apparently constitutes the chief product of this reaction.

The second product, which is obtained by the evaporation to dryness of the methyl alcoholic filtrate as above mentioned, was pressed on a plate, since it contained some oil. It was then dissolved in acetic ether; plates of monobromoanisylidene acetophenone separated at first, and when the ether had nearly all evaporated, the second product was deposited in fine, white needles. A complete separation of the two compounds was made by fractional crystallization from acetic ether and then alcohol. The second product was purified by crystallization from alcohol, from which it was deposited in small, white needles, melting at 101.5° to 102.5°.

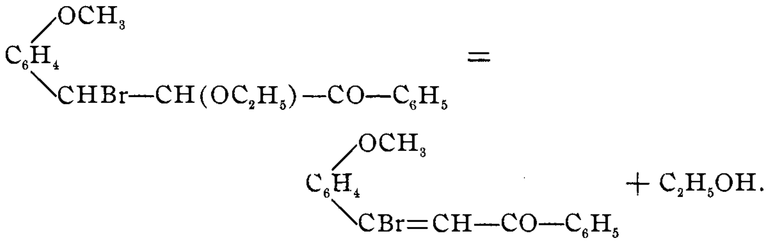
Analysis gave the following:

I. 0.1805 gram gave 0.3859 gram carbon dioxide and 0.0800 gram water.
II. 0.1808 gram gave 0.3874 gram carbon dioxide and 0.0825 gram water.
III. 0.2096 gram gave 0.1114 gram silver bromide.
IV. 0.2068 gram gave 0.1110 gram silver bromide.

	Calculated for $C_{17}H_{17}O_3Br$.	Found. I.	II.	III.	IV.
Carbon	58.45	58.31	58.44	....	....
Hydrogen	4.87	4.92	5.07	....	....
Bromine	22.92	....	....	22.62	22.84

This substance is, therefore, the methyl alcohol addition-product of α-monobromoanisylidene acetophenone.

The α-monobromide is also readily formed by the action of one molecule of sodium ethylate on the dibromide. It is, however, best prepared by carefully heating the ethyl or methyl alcohol addition-products until the alcohol is removed, as was mentioned in the consideration of these compounds. It is purified by crystallizing from alcohol and then ethyl acetate, and forms large, well-defined plates, which melt at 94°. Its formation by the decomposition of the alcohol addition-products on heating may be represented as follows:



$$C_6H_4\left\langle\begin{matrix}OCH_3\\ CHBr{-}CH(OC_2H_5){-}CO{-}C_6H_5\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}OCH_3\\ CBr{=}CH{-}CO{-}C_6H_5\end{matrix}\right. + C_2H_5OH.$$

THE ACTION OF TWO MOLECULES OF SODIUM METHYLATE UPON ANISYLIDENE ACETOPHENONE DIBROMIDE.

Fifty grams of the dibromide were added to a solution of sodium methylate, made by the action of 7.5 grams of metallic sodium on 150 cc. of methyl alcohol. After heating the mixture for a short time on the water-bath, a reaction took place, the liquid became dark colored, and sodium bromide was deposited; the mixture was boiled for about one hour. On completion of the reaction, the sodium bromide was dissolved by adding 200 cc. of water, a dark colored oil, heavier than water, being thrown out. Twenty cc. of concentrated hydrochloric acid[1] were introduced, rendering the liquid acid and changing its color from brown to light yellow; it was then boiled for one-half hour, or until the oil was completely converted into a light yellow solid. After cooling, this was filtered off and the filtrate allowed to stand for several days, when another compound separated in very fine, white needles; this will be described in a subsequent part of this paper. The solid was washed well with water, dried, and crystallized from alcohol, in which it is spar-

[1] In other experiments it was determined that dilute sulphuric acid and even acetic acid also affect the conversion of the oil into the solid, giving identically the same product as concentrated hydrochloric acid. Carbon dioxide, however, does not affect this transformation.

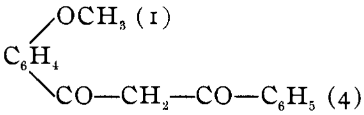
ingly soluble; it separated in fine, white crystals, melting at 130° to 131°.

The analysis gave the following:

I. 0.2003 gram gave 0.5498 gram carbon dioxide and 0.1018 gram water.
II. 0.1981 gram gave 0.5424 gram carbon dioxide and 0.1001 gram water.

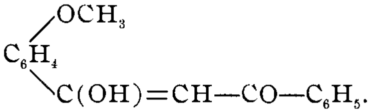
	Calculated for $C_{16}H_{14}O_3$.	Found. I.	Found. II.
Carbon	75.59	74.86	74.67
Hydrogen	5.51	5.65	5.61

This compound was first obtained by G. M. Norman and was previously described[1] as the 1,3-diketone, anisoyl benzoyl methane,



$$C_6H_4\begin{cases} OCH_3 \ (1) \\ CO-CH_2-CO-C_6H_5 \ (4) \end{cases}$$

Its alcoholic solution is colored a deep violet-red with ferric chloride, and it is soluble in the hydroxides of potassium and sodium. Closer investigation, however, leads us to believe that this compound consists wholly, or at least for the most part, of the unsaturated ketone alcohol, α-oxyanisylidene acetophenone,



$$C_6H_4\begin{cases} OCH_3 \\ C(OH)=CH-CO-C_6H_5. \end{cases}$$

J. Wislicenus[2] obtained a mixture of α-oxybenzylidene acetophenone and dibenzoyl methane by the treatment of benzylidene acetophenone dibromide with an alcoholic solution of potassium hydroxide, and he found that the two substances could be readily and completely separated by the action of an alcoholic solution of copper acetate; the keto-enolic modification gave an insoluble copper salt, while the other remained unchanged in the alcoholic solution. This method of treatment with alcoholic copper acetate was applied to the above-mentioned substance (m. p. 130° to 131°) with the result that it was completely converted into a copper salt.

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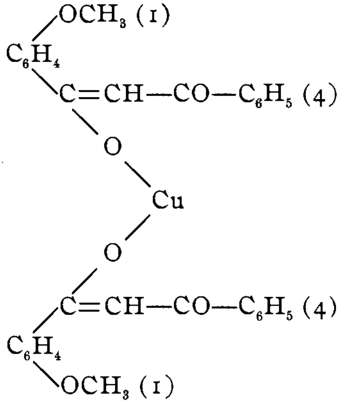
[1] Pond, Maxwell, and Norman: This Journal, 21, 966.

[2] J. Wislicenus: *Ann. Chem.* (Liebig), 308, 241.

Copper Salt of α-Oxyanisylidene Acetophenone,



The substance is formed when an alcoholic solution of the preceding compound is treated with alcoholic copper acetate. An alcoholic solution of 3 grams of copper acetate is added slowly and with vigorous agitation to the hot, alcoholic solution of 5 grams of the above compound (m. p. 130° to 131°). A fine, green precipitate of the copper salt separates almost immediately. The liquid above the precipitate remains colorless or slightly yellow until an excess of copper acetate is added, when it becomes green. It is essential that the liquid be kept near the boiling-point during the operation, otherwise the original compound separates. The precipitate is filtered and washed with alcohol until no trace of copper acetate is observed; it is further washed with water, then alcohol, and finally ether. It is insoluble in water, alcohol, ether, and carbon disulphide; very sparingly soluble in chloroform and benzene, and separates from the latter solvent in exceedingly small needles.

When the precipitated substance is purified by repeated washing with water, alcohol, and ether, it melts with decomposition at 247° to 249°. The analysis of such a preparation yielded the following figures:

I. 0.1984 gram gave 0.4868 gram carbon dioxide, 0.0832 gram water, and 0.0282 gram copper oxide.

II. 0.2386 gram gave 0.5850 gram carbon dioxide, 0.0955 gram water, and 0.0334 gram copper oxide.

III. 0.1825 gram gave 0.0257 gram copper oxide.

	Calculated for $C_{32}H_{26}O_6Cu$.	Found. I.	II.	III.
Carbon	67.41	66.92	66.86	....
Hydrogen	4.56	4.66	4.45	....
Copper	11.16	11.36	11.18	11.25

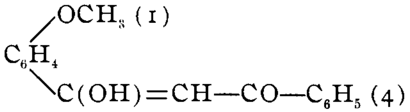
The formation of this copper salt is, therefore, represented by the following equation:

$$Cu(C_2H_3O_2)_2 + 2C_{36}H_{14}O_3 = Cu(C_{16}H_{13}O_3)_2 + 2CH_3COOH.$$

It consists of small, light green needles. It burns with a very smoky flame, leaving a residue of cupric oxide. Hot, dilute sulphuric acid decomposes it only very slowly, while hot, dilute hydrochloric acid readily converts it into cupric chloride and α-oxyanisylidene acetophenone; this reaction forms an excellent method of obtaining the latter compound in a pure condition.

The alcohol was distilled off from the combined green filtrate of the copper salt and the wash alcohol, and the residue extracted with ether. The excess of copper acetate was filtered, the ethereal solution dried, and the ether evaporated in a vacuum over calcium chloride. The residue consisted of a small amount of a dark, thick oil, which did not solidify after standing for two months, and decomposed on distillation under diminished pressure. No definite compound could be obtained from it.

α-Oxyanisylidene Acetophenone,



$$C_6H_4\begin{cases}OCH_3 & (1)\\ C(OH){=}CH{-}CO{-}C_6H_5 & (4)\end{cases}$$

This compound was easily regenerated by boiling the copper salt for a short time with hydrochloric acid (1 : 3), and crystallizing the product from alcohol. It separates in small, yellowish white needles, melting at 130° to 131°, and boils at 284° to 286° under 44 mm. pressure, the distillate solidifying at once to an almost white, crystalline mass. The substance, purified by distillation and subsequent crystallization from alcohol, gave the following results on analysis:

I. 0.3009 gram gave 0.8309 gram carbon dioxide and 0.1501 gram water.
II. 0.2516 gram gave 0.6959 gram carbon dioxide and 0.1268 gram water.

	Calculated for $C_{16}H_{14}O_3$.	Found. I.	II.
Carbon	75.59	75.31	75.43
Hydrogen	5.51	5.54	5.60

It decomposes on distillation under atmospheric pressure. It is almost insoluble in cold alcohol, soluble in hot alcohol. It is easily soluble in chloroform, benzene, ethyl acetate, and carbon disulphide. Its alcoholic solution is colored a deep violet-red by ferric chloride, while ferric acetate precipitates the neutral iron salt of the keto-enole as a brick-red, crystalline substance, insoluble in alcohol and water. It readily forms the copper salt when treated with copper acetate and alcohol. Dilute nitric acid oxidizes it, forming a mixture of acids, probably benzoic and anisic. It dissolves in sodium and potassium hydroxide solutions and is reprecipitated with acids, melting at 129° to 130°. When the solution of the alkali is fairly concentrated and hot, the compound suffers decomposition into anisic acid, melting at 182° to 183°, and a ketone having an odor similar to that of acetophenone.

The Compound, $C_{16}H_{16}O_4$.—The filtrate obtained in the preparation of the crude α-oxyanisylidene acetophenone by the action of two molecules of sodium methylate upon anisylidene acetophenone dibromide was allowed to stand; after twenty-four hours, a white, silky, crystalline substance separated. After two weeks, when no further separation of crystals was observed, it was filtered, pressed carefully on a plate to remove oily impurities and repeatedly crystallized from alcohol. It is exceedingly soluble in alcohol, and it was found best in crystallizing to make a concentrated solution and then to place the dish in a freezing-mixture, when the compound is deposited in very fine, silky needles, melting at 90°. Its alcoholic solution is neither colored by ferric chloride nor precipitated by copper acetate. Its solution in benzene removes the color of a permanganate solution very slowly.

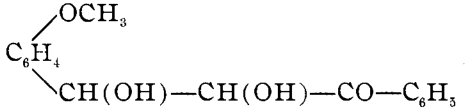
This substance is formed in an extremely small quantity. The analysis gave values required for $C_{16}H_{16}O_4$.

I. 0.1573 gram gave 0.4082 gram carbon dioxide and 0.0865 gram water.
II. 0.1441 gram gave 0.3736 gram carbon dioxide and 0.0794 gram water.

	Calculated for $C_{16}H_{16}O_4$.	Found.	
		I.	II.
Carbon	70.59	70.77	70.70
Hydrogen	5.88	6.11	6.12

When one gram of the compound was boiled with an excess of acetic anhydride for two hours, and the product poured into cold water, a thick, yellow oil separated. We were unable to isolate a definite compound from the oil.

Until a method of preparation is discovered by which a larger yield of this compound may be obtained, no satisfactory conclusions can be arrived at regarding its constitution. The analysis indicates the formula, $C_{16}H_{16}O_4$, and from its method of formation it is possible that the compound may prove to be the ketone glycol,



$$C_6H_4\begin{matrix}\diagup OCH_3\\ \diagdown CH(OH)-CH(OH)-CO-C_6H_5\end{matrix}$$

Owing to the want of material and limited time, the investigation of this substance was interrupted; the study of it will, however, be continued during the year.

THE ACTION OF SODIUM ETHYLATE UPON ANISYLIDENE ACETOPHENONE DIBROMIDE.

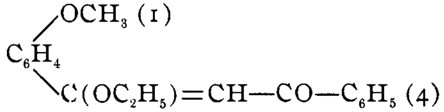
The following experiments indicate that the product of the action of two molecules of sodium ethylate or methylate on the dibromide consists of the ethyl or methyl ether of α-oxyanisylidene acetophenone, which, on the addition of hydrochloric, sulphuric, or acetic acid, is converted into the corresponding alcohol and α-oxyanisylidene acetophenone.

Twenty-five grams of the dibromide were added to a slight excess over two molecules of sodium ethylate (4 grams of sodium in 100 cc. of ethyl alcohol), and heated for about two hours on the water-bath. All of the alcohol was then distilled off, water was added, and the solution rendered neutral to litmus by a few drops of acetic acid; the heavy oil, which separated, was taken up with ether, the ethereal solution washed repeatedly with water, dried with anhydrous sodium sulphate, and the ether distilled off. The residue consisted of a light red colored oil.

On standing, this oil is changed, crystals being gradually deposited, and, in the course of two or three weeks, a large part of the oil is converted into a crystalline mass. This change is accelerated by the addition of acids, and, indeed, strong hydrochloric acid causes the conversion to take place in a few seconds, dilute sulphuric and acetic acids reacting more slowly. The solid is identified in each case as α-oxyanisylidene acetophenone.

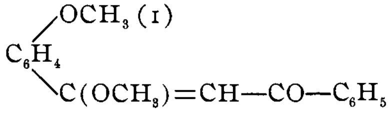
This transformation of the oil into a solid is caused by the oil being readily hydrolyzed by the acids with the splitting off of alcohol and the formation of α-oxyanisylidene acetophenone, as is shown by the following: About 15 grams of freshly prepared oil were treated in the cold with 10 cc. of dilute hydrochloric acid (1 part acid to 1 of water); the oil solidified almost immediately, with a great evolution of heat. Twenty-five cc. of water were added, the solid was filtered, and the presence of ethyl alcohol in the filtrate was easily and distinctly recognized by the iodoform test. The solid crystallized from alcohol and melted at 128.5°; it gave the reaction with ferric chloride and copper acetate, and was identified as α-oxyanisylidene acetophenone.

The elimination of alcohol and the production of this solid indicates, without doubt, that the substance obtained by the action of two molecules of sodium ethylate on the dibromide contains an ethoxyl group, and we regard it as the *ethyl ether of α-oxyanisylidene acetophenone*,



$$C_6H_4\begin{matrix}\diagup OCH_3\ (1)\\ \diagdown C(OC_2H_5)=CH—CO—C_6H_5\ (4)\end{matrix}.$$

When the dibromide is treated with 2 molecules of sodium methylate, in the same manner as above, an oil is obtained which remains unchanged for several weeks when kept in a tightly closed flask. On standing in an open flask, it is very gradually converted into a crystalline solid. When the oil is acted upon by dilute hydrochloric acid in the cold, it is quickly changed into a solid, with considerable elevation of the temperature. The solid is brittle and slightly yellow in color; it crystallizes from alcohol in small needles, melting at 129°, and is α-oxyanisylidene acetophenone. Although the oil could not be secured in a suitable condition for the analysis, it is exceedingly probable that the substance is to be regarded as the *methyl ether of α-oxyanisylidene acetophenone*,



$$C_6H_4\begin{matrix}\diagup OCH_3\ (1)\\ \diagdown C(OCH_3)=CH—CO—C_6H_5\end{matrix}.$$

The reaction of 2 molecules of sodium alcoholate upon anisylidene acetophenone dibromide appears to consist in first splitting off 1 molecule of hydrobromic acid with the formation of the unsaturated compound, α-bromoanisylidene acetophenone, and then in replacing the bromine atom in this compound with methoxyl or ethoxyl. The resulting unsaturated ether is readily hydrolyzed by acids with the production of α-oxyanisylidene acetophenone.

THE ACTION OF SODIUM METHYLATE ON THE ADDITION-PRODUCT OF α-MONOBROMOANISYLIDENE ACETOPHENONE AND ETHYL ALCOHOL.

Twenty-five grams of the addition-product were treated in the usual manner with 1 molecule of sodium methylate (2 grams of sodium in 100 cc. of methyl alcohol). On the completion of the reaction, 150 cc. of water were introduced, a dark colored oil being thrown out; hydrochloric acid was added until the liquid gave an acid reaction, and the mixture heated on the water-bath for a short time. The oil was rapidly converted into a solid, which was filtered and crystallized from alcohol; it melted at 129°, gave the color reaction with ferric chloride and alcohol, and a green precipitate with alcoholic copper acetate. It is α-oxyanisylidene acetophenone.

After standing during twenty-four hours, a small quantity of the compound, $C_{16}H_{16}O_4$, was deposited in long, slender needles from the filtrate obtained above; it melted at 89°.

THE ACTION OF SODIUM METHYLATE ON α-MONOBROMOANISYLIDENE ACETOPHENONE.

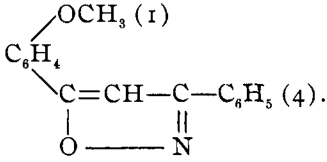
Fifteen grams of the monobromide were added to a solution of 1 molecule of methylate in methyl alcohol (1 gram of sodium in 75 cc. of methyl alcohol). After boiling for half an hour, the resultant sodium bromide was dissolved by the addition of water, the solution rendered strongly acid with acetic acid and heated for thirty minutes. On cooling, a crystalline substance separated, was filtered, and recrystallized from alcohol. It melts at 129.5°, reacts with ferric chloride and copper acetate, and is α-oxyanisylidene acetophenone. The yield of the enolic ketone was very good. A small quantity of the compound, $C_{16}H_{16}O_4$, melting at 89°, was deposited from the filtrate.

α-Oxyanisylidene Acetophenone and Acetic Anhydride.—Ten grams of α-oxyanisylidene acetophenone were boiled with 25 grams of acetic anhydride for eight hours, and the mixture then allowed to stand for forty-eight hours. On pouring the product into ice-water, a red oil, heavier than water, was produced; this was separated, washed with water, and allowed to stand. Since it did not become solid, it was taken up in alcohol, from which a substance crystallized in yellowish white needles similar to the original compound. It melted at 130° to 131°, reacted with ferric chloride and copper acetate, and appeared to be unchanged α-oxyanisylidene acetophenone. The acetate could not be isolated.

No better success was attained on treatment with benzoyl chloride, as in every case the unchanged material was obtained.

ACTION OF HYDROXYLAMINE HYDROCHLORIDE UPON α-OXYANISYLIDENE ACETOPHENONE.

αγ-Methoxyphenyl-phenyl-isoxazole,



$$\mathrm{C_6H_4}\begin{array}{l}\diagup \mathrm{OCH_3}\ (1)\\ \diagdown \mathrm{C{=}CH{-}C{-}C_6H_5}\ (4).\\ \ \ |\qquad\quad\ \ \| \\ \ \ \mathrm{O{-\!-\!-\!-}N}\end{array}$$

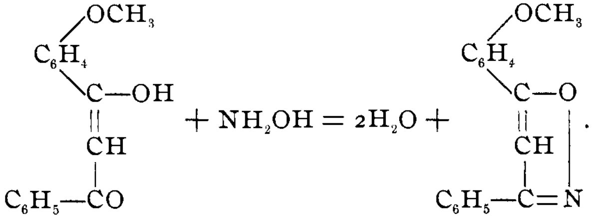
Five grams of α-oxyanisylidene acetophenone were dissolved in just enough hot alcohol to effect a solution in a small flask with reflux apparatus; 4 grams (3 molecules) of hydroxylamine hydrochloride were added, and the mixture was boiled gently during four hours. On cooling, a substance crystallized in beautiful, white crystals, resembling somewhat those of sulphocarbanilide. It was filtered, washed with water, dried, and crystallized from alcohol; it separated from this solvent in colorless, shining leaflets, which melted sharply at 119° to 120°. The following numbers were obtained upon analysis:

I. 0.1502 gram gave 0.4199 gram carbon dioxide and 0.0722 gram water.
II. 0.1935 gram gave 0.5422 gram carbon dioxide and 0.0914 gram water.
III. 0.7050 gram gave 39.2 cc. nitrogen at 23° and 726 mm.
IV. 0.6945 gram gave 39.4 cc. nitrogen at 24° and 726 mm.

	Calculated for $C_{16}H_{13}O_2N$.	Found. I.	II.	III.	IV.
Carbon	76.49	76.24	76.42	....	....
Hydrogen	5.18	5.34	5.25	....	....
Nitrogen	5.57	....	....	5.97	6.06

This compound is insoluble in water, alkali solutions, and dilute acids, difficultly soluble in cold alcohol, more readily soluble in hot alcohol and carbon disulphide, and very easily soluble in chloroform, ether, benzene, and ethyl acetate. Ferric chloride and copper acetate do not react with its alcoholic solution. It appears to be a very stable substance. It remains unaltered by boiling with a solution of potassium hydroxide. Concentrated hydrochloric acid dissolves it very sparingly, but is without further action upon it.

It is, without doubt, an isoxazole derivative, and results from the reaction of hydroxylamine upon α-oxyanisylidene acetophenone according to the equation,



It is probably analogous to the isoxazoles obtained by Claisen[1] by the action of hydroxylamine on the 1,3-diketones. J. Wislicenus[2] also obtained $\alpha\gamma$-diphenyl-isoxazole, melting at 140.5° to 141°, by the action of hydroxylamine hydrochloride on α-oxybenzylidene acetophenone. Goldschmidt[3] had previously produced a diphenyl-isoxazole, melting at 141°, by the reaction of an excess of sodium hydroxide on the mixed, warm, alcoholic solutions of benzylidene acetophenone dichloride and hydroxylamine hydrochloride.

It was, therefore, of interest to determinew hether the isoxazole above described or an isomeric compound would be formed by the treatment of anisylidene acetophenone dibromide with

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[1] L. Claisen: *Ber. d. chem. Ges.*, **24**, 3906.

[2] J. Wislicenus: *Ann. Chem.* (Liebig), 308, 249.

[3] Goldschmidt: *Ber. d. chem. Ges.*, **28**, 2540.

hydroxylamine hydrochloride and an excess of potassium hydroxide.

Isomeric Methoxyphenyl-phenyl-isoxazole, $C_{16}H_{13}O_2N$.—Twenty grams of anisylidene acetophenone dibromide are dissolved in 200 cc. of alcohol; to this is added a solution of 7 grams (2 molecules) of hydroxylamine hydrochloride in 10 cc. of water, and the mixture is heated to the boiling-point; 17 grams of potassium hydroxide in 20 cc. of water are then added very gradually, and with constant shaking, to the hot solution. A very vigorous reaction takes place with elimination of potassium salts, the solution assuming a yellowish red color. After standing for about ten minutes, the inorganic salts are filtered off, and on cooling the filtrate, a product separates in very fine, white needles. These are filtered, washed well with water, dried, and recrystallized from alcohol. It is deposited in very slender, silky needles, which melt at 127° to 128°.

The yield is further increased by precipitating the first alcoholic filtrate with water.

The analysis gave the following results:

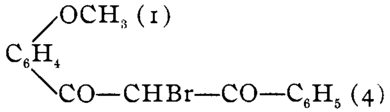
I. 0.1887 gram gave 0.5282 gram carbon dioxide and 0.0894 gram water.
II. 0.1693 gram gave 0.4737 gram carbon dioxide and 0.0837 gram water.
III. 0.6972 gram gave 39.2 cc. nitrogen at 25° and 728 mm.

	Calculated for $C_{16}H_{13}O_2N$.	Found. I.	II.	III.
Carbon	76.49	76.34	76.31	....
Hydrogen	5.18	5.26	5.49	....
Nitrogen	5.57	....	....	6.00

This compound is soluble in alcohol, ether, carbon disulphide, and readily soluble in chloroform, benzene, and acetic ether. It dissolves, to a slight extent, in hot, concentrated hydrochloric acid, and is reprecipitated on the addition of water; cold, concentrated sulphuric acid dissolves it quite easily with almost no development of color, and when the solution is poured into water, the substance is thrown out apparently unaltered. Boiling potassium hydroxide solution is without action on the substance, and ferric chloride gives no coloration with its alcoholic solution, and copper acetate no precipitate.

This compound, melting at 127° to 128°, is probably isomeric with the preceding isoxazole, melting at 119° to 120°, although its constitution is not yet definitely determined.[1]

Anisoyl Benzoyl Monobromomethane,



$$C_6H_4\begin{cases}OCH_3\ (1)\\ CO{-}CHBr{-}CO{-}C_6H_5\ (4)\end{cases}$$

When α-oxyanisylidene acetophenone is dissolved in ether or chloroform and treated with one molecular proportion of bromine, hydrobromic acid is given off with gradual decoloration. On the evaporation of the solvent, a crystalline residue is obtained, which separates from alcohol in brilliant, white crystals, melting at 128°.

The analysis gave results corresponding to the formula, $C_{16}H_{13}O_3Br$.

I. 0.1784 gram gave 0.3790 gram carbon dioxide and 0.0655 gram water.
II. 0.1792 gram gave 0.3787 gram carbon dioxide and 0.0643 gram water.
III. 0.2062 gram gave 0.1158 gram silver bromide.
IV. 0.2060 gram gave 0.1166 gram silver bromide.

	Calculated for $C_{16}H_{13}O_3Br$.	Found.			
		I.	II.	III.	IV.
Carbon	57.66	57.94	57.64	....	....
Hydrogen	3.90	4.08	3.99	....	....
Bromine	24.02	....	....	23.89	24.08

It is soluble in alcohol, carbon disulphide, and ether; readily soluble in chloroform, benzene, and acetic ether.

Its alcoholic solution is not colored by ferric chloride, and gives no precipitate with copper acetate. It is probable, therefore, that the compound contains no hydroxyl group, and it may

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[1] In an investigation which is being carried on in this laboratory, Mr. H. J. York has obtained the $\alpha\gamma$-diphenyl-isoxazole described by J. Wislicenus (*Ann. Chem.* (Liebig), 308, 249) by the treatment of α-oxybenzylidene acetophenone (resulting by the action of two molecules of sodium alcoholate upon benzylidene acetophenone dibromide and subsequent hydrolysis of the unsaturated ether with hydrochloric or acetic acid) with hydroxylamine hydrochloride. It crystallizes from hot alcohol in thick, colorless tablets, and melts at 141° to 142°. On treating benzylidene acetophenone dibromide in alcoholic solution with hydroxylamine hydrochloride and an excess of potassium hydroxide in a manner similar to the above, a compound resulted which was deposited from alcohol in thin, lustrous leaflets; these melted sharply at 140°. This compound contains nitrogen and is apparently identical with the substance described by Goldschmidt (*Ber. d. chem. Ges.*, **28**, 2540) as diphenyl-isoxazole. Although at the present time it is not proved that these two isoxazoles are different, the indications are that they are isomeric and not identical, and that they are analogous to the isoxazoles obtained from α-oxyanisylidene acetophenone and from anisylidene acetophenone dibromide.

be regarded as a bromine derivative of the neutral or β-modification of the diketone, anisoyl benzoyl methane.

We expect to continue this work in various directions, and to extend the investigations to other analogously constituted compounds.

A NEW VOLUMETRIC METHOD FOR THE ESTIMATION OF COPPER.

BY S. W. PARR.

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EXPERIMENTS looking to the use of the thiocyanates in volumetric processes have been carried on in this laboratory for over two years past. While the results obtained are in many ways very satisfactory, it is intended here to make note of one application, which gives results of great practical value.

The iodine and cyanide methods for the estimation of copper are far from satisfactory. Two methods, recently proposed in this Journal,[1] making use of the precipitation of copper as cuprous thiocyanate, mark a decided advance in methods. It is believed that the process here outlined has further points of advantage. It involves the precipitation of the copper as cuprous thiocyanate, the oxidation of the copper without decomposition of the alkali thiocyanate and the titration of the acidified thiocyanate with standard permanganate. In practice the two latter steps are one operation, but one filtration is necessary and for most ores thirty to forty minutes are ample for a determination from the time of weighing the sample to the time of the final titration.

Some attention must be given to the condition of the solution before precipitating the copper as cuprous thiocyanate. If the solution contains free sulphuric acid it should not exceed 1 or 2 per cent. in amount. Stronger solutions on heating with thiocyanate have a tendency to liberate free sulphur which remains with the precipitate and in the final reading gives variable results. The same thing is true regarding hydrochloric acid. With nitric acid no free sulphur is liberated. Here, however, an excess of acid prevents the reduction and complete pre-

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[1] This Journal, 19, 940 (1899) and 20, 610 (1900).