

value 107 for the atomic mass of palladium. This value does not influence the position of palladium in the periodic system.

In conclusion I desire to express my obligations to Professor Edgar F. Smith for suggesting this line of work, and for many valuable suggestions during its prosecution.

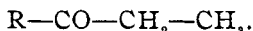
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

THE ACTION OF SODIUM METHYLATE UPON DIBROMIDES OF PROPENYL-COMPOUNDS AND OF UNSATURATED KETONES.

BY F. J. POND, O. P. MAXWELL, AND G. M. NORMAN.

Received July 28, 1899.

It was stated in a previous paper¹ that certain phenol ethers, which contain a C_3H_5 group having the propenyl structure, give bromine addition products which, on treatment with sodium alcoholate, yield ketones of the general formula,



Thus, the dibromides of anethol,² methyl-,³ ethyl-,² and benzyl-¹ isoeugenol and isosafrol³ form ketones when they are treated with sodium alcoholate. As the bromine derivatives of the corresponding isomeric compounds containing the allyl group are not converted into ketones by a similar treatment, this reaction is characteristic for those compounds containing the propenyl group. Therefore, the structure of the unsaturated group, C_3H_5 , in these two classes of compounds may be readily determined by means of this reaction.

The study of this reaction is here extended to isoapiol and propyl isoeugenol, both of which contain the propenyl group, $R-CH=CH-CH_3$, and form dibromides which are readily converted into ketones; the corresponding bromine derivatives of apiol and propyl eugenol do not yield ketones when subjected to an analogous treatment.

It is also shown that the dibromides of certain unsaturated ketones represented by the formula, $R-CH=CH-CO-C_6H_5$, may be readily changed into 1,3-diketones, $R-CO-CH_2-CO-C_6H_5$. The reaction by which these diketones are formed

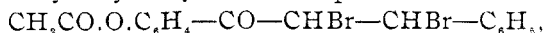
¹ Pond and Beers: This Journal, 19, 825.

² Wallach and Pond: *Ber. d. chem. Ges.*, 28, 2714.

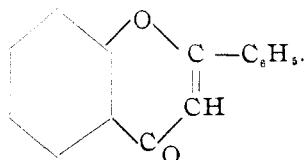
³ Hell and Portmann: *Ibid.*, 28, 2088; Hell and Hollenberg: *Ibid.*, 29, 682.

seems to proceed in much the same manner as in the formation of ketones from propenyl compounds; and there appears to be reasonable ground for the belief that this method of preparing the aromatic β -diketones will prove of certain interest, and perhaps of some value in the study of this interesting class of compounds.

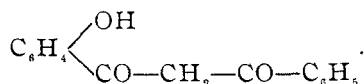
It should be noted in this connection that St. v. Kostanecki in his extended work on the unsaturated ketones obtained flavone and derivatives of flavone by the action of alcoholic potash on the dibromides of certain unsaturated *o*-oxyketones. Thus Feuerstein and St. v. Kostanecki¹ found that alcoholic potash converted 2'-acetyl oxybenzylidene acetophenone dibromide,



into *flavone*,

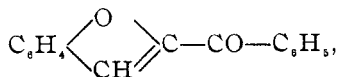


On boiling flavone with a concentrated solution of potassium hydroxide or with sodium alcoholate, it was decomposed into acetophenone, *o*-oxyacetophenone, salicylic acid and benzoic acid, indicating that the first intermediary product of decomposition was the 1,3-diketone, *o*-oxybenzoylacetophenone,



This diketone, however, could not be separated, nor was its presence noted in the formation of flavone from the dibromide of the unsaturated ketone.

Kostanecki and Tambor² obtained α -cumarylphenyl ketone,



by the action of warm, concentrated alcoholic potash on acetyl-2-oxybenzylidene acetophenone dibromide,

¹ Feuerstein and St. v. Kostanecki: *Ber. d. chem. Ges.*, **31**, 1760.

² Kostanecki and Tambor: *Ibid.*, **29**, 237.

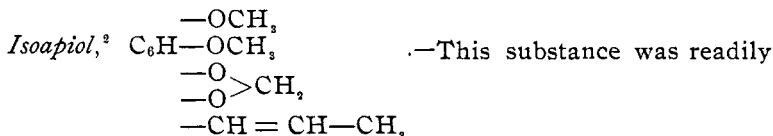


α -Cumarylphenyl ketone decomposes into benzoic acid and cumarone when fused with potash.

These results are therefore quite distinct from those described in this paper.

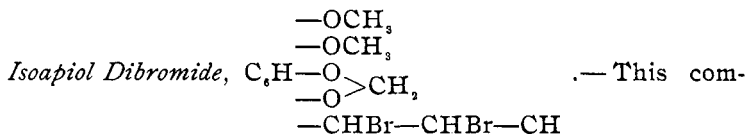
EXPERIMENTAL.

The apiol,¹ $\text{C}_{12}\text{H}_{14}\text{O}_4$, used in our experiments was a very pure specimen, obtained from Schimmel & Co., of Leipzig. It was in the form of fine, white needles, which melted sharply at 30° to 31° and boiled at 294° to 295° .



prepared from apiol according to the method of Eykman,³ and Ciamician and Silber² by heating apiol with an alcoholic potash solution.

Twenty-four grams of apiol were heated with a solution of fifty grams of potassium hydroxide in 250 cc. of alcohol, on a water-bath, for twenty-four hours. The resulting isoapiol was precipitated with a large quantity of water and recrystallized from alcohol. It was obtained in large, white crystals, which melted at 55° to 56° .



pound was prepared by Ciamician and Silber⁴ by adding the theoretical quantity of bromine to a solution of isoapiol in ether, which was cooled to -18° .

Twenty-nine grams (one molecule) of bromine were added

¹ Blanchet and Sell : *Ann. Chem.* (Liebig), **6**, 301 ; Ciamician and Silber : *Ber. d. chem. Ges.*, **21**, 913 ; Gerichten : *Ibid.*, **9**, 1477.

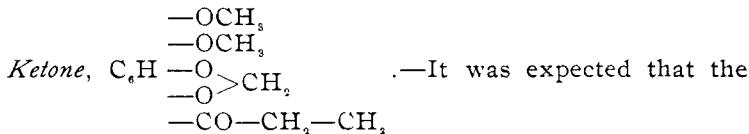
² Ciamician and Silber : *Ber. d. chem. Ges.*, **21**, 1621 ; Ginsberg : *Ibid.*, **21**, 1192 ; Gerichten : *Ibid.*, **9**, 1479.

³ Eykman : *Ibid.*, **23**, 855.

⁴ Ciamician and Silber : *Ibid.*, **23**, 2287.

carefully to a solution of forty grams of isoapiol in 200 cc. of dry ether, well cooled by a mixture of ice and salt. The very slight excess of bromine was at once removed by shaking with sulphurous acid, and, after evaporation of the ether, the resultant oil was dried over sulphuric acid. After standing for about twelve hours the oil solidified to a mass of small, white crystals, which were pressed on a porous plate and crystallized from petroleum ether. It melted at 70° to 72° . It is impossible to obtain this dibromide in a solid form unless the bromine be added very slowly to the ethereal solution of isoapiol, and the resulting, thick oil be carefully dried over sulphuric acid or calcium chloride in a desiccator. It decomposes at once on warming with alcohol, and tends to decompose when crystallized from ordinary solvents, petroleum ether being best adapted for its purification.

Treatment of Isoapiol Dibromide with Sodium Methylate.—Forty-three grams of isoapiol dibromide were added to a solution of ten grams of sodium in 150 cc. of methyl alcohol. A vigorous reaction took place at once with separation of sodium bromide. The reaction was completed by heating the mixture in a flask with a reflux condenser, on a water-bath, for five hours. Water was added to dissolve the sodium bromide, and the solution was acidified with hydrochloric acid, and boiled for two hours to insure the hydrolysis of the unsaturated ether, $R-C(OCH_3)=CH-CH_3$, which is formed by the action of sodium methylate on the dibromide.¹ The dark-red oil which had separated was non-volatile with steam; it was separated by a funnel and allowed to stand for twenty-four hours. At the end of this time, the oil had for the most part solidified; the crystals were filtered by the aid of the pump, and washed with cold ether in which the red oil was very easily soluble, while the crystals were only sparingly soluble. The compound was recrystallized from alcohol, and obtained in white prisms, melting at 95° .



above-mentioned solid, melting at 95° , would prove to be a ketone, since the method of its preparation was analogous to that

¹ Pond and Beers: This Journal, 19, 827.

employed in the preparation of ketones from anethol, isosafrol, etc. The substance was, indeed, readily converted into an oxime, and the latter, in turn, reverted into the ketone by warming with dilute sulphuric acid. This process gave a very pure product which crystallized from alcohol in large, white prisms, melting at 95.5° .

It was found rather difficult to remove a slight red color from the crude ketone unless the oxime was first prepared. This red color is due to a slight admixture of the red oil which is formed together with the ketone.

The pure crystals gave the following results on combustion :

I. 0.1366 gram gave 0.3045 gram carbon dioxide and 0.0692 gram water.

II. 0.1242 gram gave 0.2760 gram carbon dioxide and 0.0664 gram water.

	Calculated for		I. Found.	II.
	$\begin{array}{l} -\text{OCH}_3 \\ -\text{OCH}_3 \\ \text{C}_6\text{H}-\text{O} > \text{CH}_2 \\ -\text{O} > \text{CH}_2 \\ -\text{CO}-\text{CH}_2-\text{CH}_3 \end{array}$			
Carbon.....	60.79		60.50	60.60
Hydrogen.....	5.88		5.66	5.94

$\begin{array}{l} -\text{OCH}_3 \\ -\text{OCH}_3 \\ \text{Oxime, C}_6\text{H}-\text{O} > \text{CH}_2 \\ -\text{O} > \text{CH}_2 \\ -\text{C}(\text{NOH})-\text{CH}_2-\text{CH}_3 \end{array}$

—This compound was

very easily prepared by treating six grams of the ketone with an alcoholic solution of hydroxylamine in the usual manner. It crystallizes from methyl alcohol in white needles, which melt at 124° . It is readily changed into the ketone by heating with dilute sulphuric acid on the water-bath for twenty minutes.

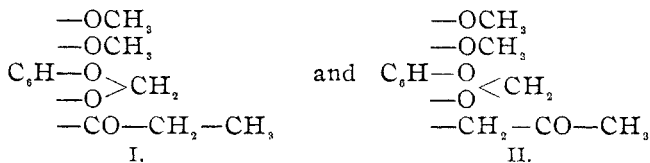
An analysis gave the following results :

I. 0.1513 gram gave 0.3142 gram carbon dioxide and 0.0786 gram water.

II. 0.1420 gram gave 0.2945 gram carbon dioxide and 0.0725 gram water.

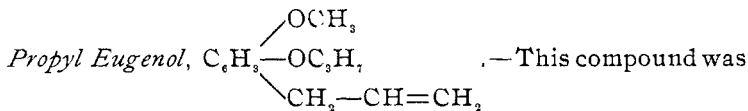
	Calculated for		I. Found.	II.
	$\begin{array}{l} -\text{OCH}_3 \\ -\text{OCH}_3 \\ \text{C}_6\text{H}-\text{O} > \text{CH}_2 \\ -\text{O} > \text{CH}_2 \\ -\text{C}(\text{NOH})-\text{CH}_2-\text{CH}_3 \end{array}$			
Carbon.....	56.91		56.63	56.56
Hydrogen.....	5.93		5.77	5.67

Only two formulas are possible for the ketone obtained from isoapiol; *viz.*,



In order to determine between these two formulas, five grams of the oxime were dissolved in ten cc. of concentrated sulphuric acid and cautiously heated to 250°. The reaction product was diluted with water and distilled with steam. An acid having the odor of a lower fatty acid was obtained in the distillate, separated by the usual method and characterized as propionic acid. This indicates that the ketone has the structure represented by formula I, since a ketone having the formula II could not yield propionic acid by this treatment.

The ketone was reduced in an absolute alcohol solution with sodium, yielding a solid substance; this separated from ether in crystals, which melted sharply at 88° to 89°. It is probably the *alcohol*, C₁₂H₁₆O₅, but owing to lack of material no further work could be done with the compound.



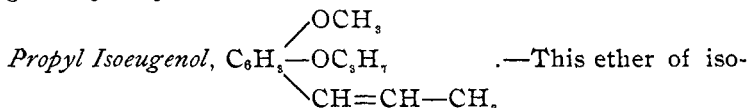
prepared according to the method of Cahours¹ and Wassermann² by heating an alcoholic solution of the potassium salt of eugenol with propyl bromide.

Fifty-seven grams of propyl bromide were added slowly to a hot solution of seventy-five grams of freshly distilled eugenol and twenty-seven grams of potassium hydroxide in 100 cc. of alcohol, and the mixture was heated for two hours on the water-bath. The reaction product was diluted with water and the resultant oil, being non-volatile with steam, was extracted with ether. The ethereal solution was dried with calcium chloride, the ether distilled off, and the propyl eugenol rectified under atmospheric pressure. On redistillation a colorless oil was

¹ Cahours: *Jsb. d. Chem.* (1877), 580; *Ber. d. chem. Ges.*, 10, 237.

² Wassermann: *Ann. Chem.* (Liebig), 179, 375.

obtained, which boiled at 270.5° ; its specific gravity at 15° was 1.0032. Cahours¹ described this substance as a yellow oil, boiling at 263° - 265° .



eugenol containing the propenyl group was produced by heating an alcoholic solution of propyl eugenol with potassium hydroxide. Fifty grams of propyl eugenol, 125 grams of potassium hydroxide, and 250 cc. of alcohol, were heated in the water-bath for twenty-four hours. The reaction-mixture was poured into a large quantity of water, and the resulting solid was filtered, dried, and distilled at the ordinary pressure. It boiled without decomposition at 280° - 281° . The distillate was crystallized from alcohol, and obtained in very large, beautiful, white prisms, which melted at 53° - 54° .

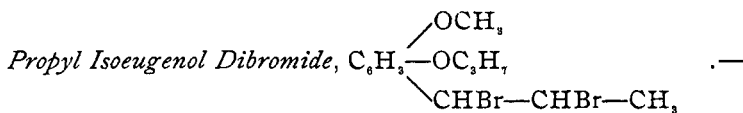
This compound was also readily formed from isoeugenol by heating the potassium salt of the latter in an alcoholic solution with propyl bromide.

Analysis gave the following :

I. 0.1498 gram gave 0.4145 gram carbon dioxide and 0.1170 gram water.

II. 0.1422 gram gave 0.3896 gram carbon dioxide and 0.1098 gram water.

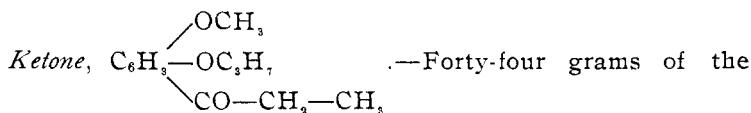
	Calculated for $C_{13}H_{18}O_2$.	I.	Found. II.
Carbon.....	75.72	75.46	75.48
Hydrogen.....	8.73	8.67	8.57



The dibromide was quantitatively formed by adding the theoretical quantity of bromine to the well-cooled, ethereal solution of propyl isoeugenol. A very slight excess of bromine was removed by agitation with a sulphurous acid solution and the ether allowed to evaporate. No evolution of hydrobromic acid was noticed either during the addition of bromine or on evaporation of the ether. The compound at first formed an oil which

¹ Cahours: *Ber. d. chem. Ges.*, 10, 237.

gradually solidified to a mass of fine, white crystals, melting at 53° – 54° . It is very soluble in alcohol and ether, but cannot be recrystallized without decomposing.



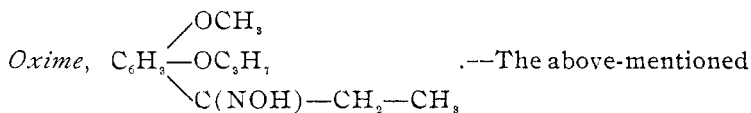
dibromide were added to a solution of eight grams of sodium in 150 cc. of methyl alcohol, and heated on the water-bath for four hours. Water was added, an oil being thrown out, and the mixture was rendered acid with hydrochloric acid and boiled for two hours. On cooling, the oil completely solidified, and was separated, dried, and crystallized from alcohol. It is best obtained in a pure condition by distillation in a vacuum and recrystallization from methyl alcohol. It forms large, splendid prisms, which melt at 63° – 64° and boil with slight decomposition at 284° – 287° under atmospheric pressure. The yield of the ketone from propyl isoeugenol dibromide is quantitative.

The following are the results of the analysis :

I. 0.1316 gram gave 0.3400 gram carbon dioxide and 0.0998 gram water.

II. 0.1303 gram gave 0.3362 gram carbon dioxide and 0.0990 gram water.

	Calculated for $C_{13}H_{18}O_3$.	I.	Found.	II.
Carbon.....	70.27	70.46		70.37
Hydrogen.....	8.10	8.42		8.44



ketone was readily converted into an oxime by treating in the usual manner with hydroxylamine. The oxime separates from alcohol in large crystals, melting at 114° . It is easily reverted into the ketone by warming with dilute sulphuric acid, while concentrated sulphuric acid decomposes it with the formation of propionic acid.

Analysis gave the following results :

I. 0.1380 gram gave 0.3323 gram carbon dioxide and 0.1000 gram water.

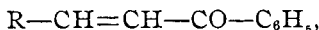
II. 0.1386 gram gave 0.3334 gram carbon dioxide and 0.1016 gram water.

	Calculated for $C_{12}H_{19}O_3N$.	I.	Found.	II.
Carbon.....	65.82	65.67		65.60
Hydrogen.....	8.01	8.05		8.14

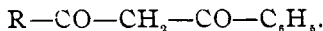
The formation of ketones from isoapiol- and propylisoeugenol-dibromide may be represented by formulas similar to those given in a previous publication.¹ Two molecules of sodium methylate act upon one molecule of the dibromide with elimination of one molecule of hydrobromic acid and production of an unsaturated ether, $R-C(OCH_3)=CH-CH_3$; this ether yields an unsaturated alcohol by hydrolysis with dilute acids, and this in turn suffers a molecular transformation into the isomeric, saturated ketone.

In connection with the study of the action of sodium alcoholate on the dibromides of compounds containing the propenyl group, we thought it of interest to extend our observations to the behavior of the same reagent towards the dibromides of some unsaturated ketones.

Since propenyl compounds, $R-CH=CH-CH_3$, are so readily converted into ketones, $R-CO-CH_2-CH_3$, it seemed probable that unsaturated ketones,



could, by a similar treatment, be changed into diketones of the formula



The results of our experiments on benzylidene acetophenone have fully substantiated this conclusion. Indeed, the reaction takes place so readily, and the yield of the diketone is so large, that this method seems to be especially well adapted to the preparation of this class of compounds.

Benzylidene Acetophenone, $C_6H_5-CH=CH-CO-C_6H_5$.—The benzylidene acetophenone which served as the starting-point of this work was prepared by the method of Claisen and Claparède.¹ Molecular quantities of benzaldehyde and acetophenone were allowed to stand in an alcoholic solution with a small quantity of ten per cent. sodium hydroxide solution. The resulting con-

¹ This Journal, 19, 827.

densation-product separated from ligroin in large crystals, melting at 57° .

Benzylidene Acetophenone Dibromide,¹ $C_6H_5-CHBr-CHBr-CO-C_6H_5$.—This addition-product was obtained by adding one molecular proportion of bromine to the cold ethereal solution of benzylidene acetophenone. It crystallized in small, white prisms, and melted sharply at 156° .

Treatment of the Dibromide with Sodium Methylate.—Twenty grams of benzylidene acetophenone dibromide were heated with a solution of sodium methylate, formed by dissolving three grams of sodium in fifty cc. of methyl alcohol, for three hours, on the water-bath. On completion of the reaction, the sodium bromide was dissolved by the addition of water; a dark-colored oil separated, and the mixture was then acidulated with hydrochloric acid, and boiled for two hours. The oil, which had now assumed a dark red color, was separated from the clear liquid, and after standing for a few hours it solidified to a crystalline mass. This was pressed on a porous plate and crystallized from methyl alcohol, yielding red crystals. These crystals melted at 79° – 80° , but did not appear quite pure. The red color of the crystals could not be removed by repeated crystallization or by boiling with animal charcoal, but when the compound was distilled at ten mm. pressure the distillate solidified at once to a pure, white, crystalline mass. This was crystallized from methyl alcohol and obtained in large, colorless crystals, melting at 80.5° . It is readily soluble in alcohol and ether, and also in sodium and potassium hydroxides; it is precipitated from alkaline solutions by acids. It is insoluble in sodium carbonate. Ferric chloride imparts a dark-violet color to its alcoholic solution. In all its properties the compound agrees with those of dibenzoyl methane, $C_6H_5-CO-CH_2-CO-C_6H_5$, which was first obtained by Baeyer and Perkin,² and has subsequently been investigated by Claisen.³

Analysis gave the following:

I. 0.1257 gram gave 0.3720 gram carbon dioxide and 0.0629 gram water.

¹ Claisen and Claparède: *Ber. d. chem. Ges.*, **14**, 2463; see also Kostanecki and Rossbach: *Ibid.*, **29**, 1492.

² Baeyer and Perkin: *Ber. d. chem. Ges.*, **16**, 2134; Perkin: *J. Chem. Soc.*, **47**, 250.

³ Claisen: *Ber. d. chem. Ges.*, **20**, 655; *Ann. Chem. (Liebig)*, **291**, 83.

II. 0.1278 gram gave 0.3773 gram carbon dioxide and 0.0665 gram water.

	Calculated for (C ₈ H ₈ CO) ₂ CH ₂ .	I.	Found. II.
Carbon.....	80.35	80.49	80.51
Hydrogen.....	5.35	5.56	5.78

Eight grams of dibenzoyl methane were obtained from twenty grams of benzylidene acetophenone dibromide.

The diketone was further characterized by its conversion into *dibenzoyl-dibromomethane*, C₁₅H₁₀Br₂O₂. This separated from methyl alcohol in white crystals, melting at 95°, and agreed in all respects with the compound obtained by Neufville and Pechmann.¹

The formation of dibenzoyl methane from the dibromide, C₁₅H₁₀O.Br₂, is probably accomplished by the production of the unsaturated ether, C₈H₅—C(OCH₃)=CH—CO—C₆H₅, which, on hydrolysis with dilute hydrochloric acid, is converted into the unsaturated ketone-alcohol, and then into the diketone.

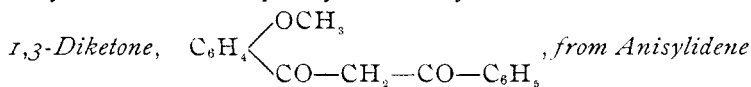
In order to isolate the unsaturated ether, twenty grams of the dibromide were treated as usual with sodium methylate. On the addition of water to the reaction-mixture, a dark oil heavier than water was thrown out; this was separated and dried over calcium chloride. It showed no trace of bromine, and did not solidify after standing for forty-eight hours, or when placed in a freezing-mixture. When a little of the oil was shaken with dilute hydrochloric acid, it immediately became solid, and after crystallization it gave the melting-point of dibenzoyl methane, 80° to 81°. The oil was distilled under 20 mm. pressure, but it came over without a constant boiling-point and suffered considerable decomposition. The distillate did not solidify on standing or after cooling, and was only partially changed into a solid by agitation with dilute acids. Although this oil could not be obtained in a pure condition for analysis, the readiness with which it is converted into the diketone by the action of dilute acids indicates that it contains the unsaturated ether.

A reaction very similar to the above is found in the action of sodium ethylate upon cinnamic ester dibromide. Leighton² found that sodium ethylate acts upon α , β -dibromohydrocinnamic

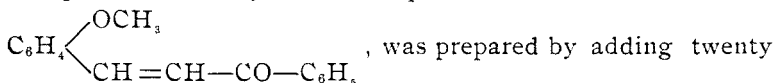
¹ Neufville and Pechmann: *Ber. d. chem. Ges.*, 23, 3377.

² V. L. Leighton: *Am. Chem. J.*, 20, 133.

ester to form β -ethoxycinnamic ester, and the latter yields benzoylacetic acid on hydrolysis with hydrochloric acid.

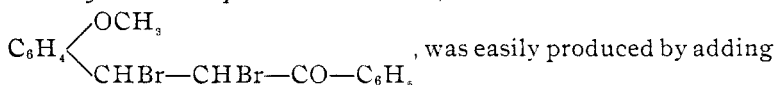


Acetophenone.—Anisylidene acetophenone,



cc. of a ten per cent. solution of sodium hydroxide to a solution of twenty-five grams of anisaldehyde and twenty-two grams of acetophenone in 200 cc. of alcohol. After standing for about eight hours, with an occasional shaking, the condensation-product separated in yellow crystals. It was recrystallized from alcohol and obtained in fine, yellow needles, melting at 77° to 78° .

Anisylidene acetophenone dibromide,



two atoms of bromine to the cold, ethereal solution of the unsaturated ketone. It crystallized from methyl alcohol in small white prisms, and melted at 140° to 141° .

Thirty grams of the dibromide were heated with a solution of five and one-half grams (two atoms) of sodium in 125 cc. of methyl alcohol for three hours. The reaction product was diluted with water, acidified with hydrochloric acid and boiled for two hours. At the end of this time, the dark oil, which had been thrown out on the addition of water, had completely solidified, and was filtered and dried. The substance had a reddish color, and was purified by distillation under diminished pressure, and crystallization from alcohol. It crystallized in white leaflets, which melted at 131° to 132° . It is only sparingly soluble in methyl and ethyl alcohol and ether, but dissolves readily in chloroform and may be precipitated from its solution in this solvent by methyl alcohol. It is very difficultly soluble in sodium hydroxide. Its alcoholic solution is colored an intense reddish violet by ferric chloride.

Analysis gave the following :

I. 0.1410 gram gave 0.3877 gram carbon dioxide and 0.0718 gram water.

	Calculated for $C_{10}H_{14}O_3$.	Found. I.
Carbon.....	75.58	74.99
Hydrogen.....	5.51	5.65

This compound, anisoyl benzoyl methane, was also readily formed when sodium ethylate was used instead of methylate. There appeared to be no difference in the yield, but the product was darker colored when ethylate was employed.

Bromine acts upon this diketone with formation of substitution products. When six and one-half grams (two molecules) of bromine were added to a solution of ten grams (one molecule) of the diketone in 150cc. of ether, a vigorous reaction took place with evolution of considerable hydrogen bromide. On evaporation of the ether, a white, crystalline product resulted; this crystallized from methyl alcohol in well-defined white prisms, and melted at 127° to 128° . This compound is probably anisoyl benzoyl dibromomethane, $C_{10}H_{12}O_3Br_2$, and will be further examined.

When piperonal acetophenone dibromide¹ is treated with sodium methylate according to the above-described process, a compound is obtained which crystallizes in small yellow needles, and melts at 86.5° . This substance is at present under investigation.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.
No. 48.]

THE ELECTROLYTIC OXIDATION OF SUCCINIC ACID.

By CHARLES H. CLARKE AND EDGAR F. SMITH.

Received July 21, 1899.

THE oxidizing action of the current on organic bodies is sure to yield most interesting results. Indeed, the whole organic field remains practically open to investigation along this line. Turn in any direction and ample material will be found for such study. We selected succinic acid as the subject of our investigation. It is, indeed, true that in the past this acid and its salts have engaged the attention of chemists in the electrolytic way, but unfortunately their results are contradictory. No attention was given to the important conditions of current density, voltage, temperature, etc., with the consequence that

¹ St. v. Kostanecki and Schneider: *Ber. d. chem Ges.*, 29, 1892.