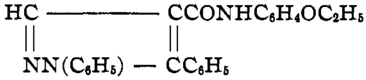
is eliminated and there is formed the *o*-ethoxyanilide of 1,5-diphenyl-4-pyrazol-carboxylic acid.



This separated from dilute alcohol in fine needles melting at 118°.

Calc. for $C_{24}H_{21}O_2N_3$: N, 10.97%. Found: 10.54%.

In the course of this investigation several compounds have been prepared, which will be briefly described, as they are not mentioned in the literature.

Di-*o*-phenetidyl formamidine and malonic ester at water-bath temperature gave a good yield of *o*-ethoxyanilido-methylene-diethyl-malonate, $C_2H_5OC_6H_4NHCH.C = (COOC_2H_5)_2$, long needles from 60% alcohol with a melting point of 66–7°.

Calc. for $C_{16}H_{21}O_5N$: N, 4.54%. Found: 4.63%.

1-*o*-Tolyl-3-methyl-4-monobromo-5-pyrazolone is formed when bromine (one mol) is added to a solution of the pyrazolone in glacial acetic acid. The yellow crystals from alcohol melt at 116°.

Calc. for $C_{11}H_{11}ON_2Br$: Br, 29.81%. Found: 30.13%, 29.99%.

1-*o*-Tolyl-3-phenyl-4-monobromo-5-pyrazolone, made in a like manner, crystallizes from alcohol in brownish yellow needles with a melting point of 110°.

Calc. for $C_{16}H_{13}ON_2Br$: Br, 24.29%. Found: 24.44%, 24.54%.

LAWRENCE, KANSAS.

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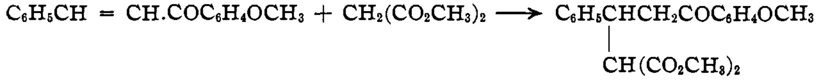
# THE REACTIONS OF SOME CARBOXYL DERIVATIVES OF TRIMETHYLENE.[1]

BY DOROTHY A. HAHN.

Received June 3, 1916.

The principal object of this investigation was the study of the products obtained by eliminating hydrobromic acid from bromine substitution products of the esters of anisoyl-phenyl-ethyl-malonic acid. These esters are easily obtained by adding the corresponding malonic esters to phenyl-anisyl-propenone:



$$C_6H_5CH = CH.COC_6H_4OCH_3 + CH_2(CO_2CH_3)_2 \longrightarrow \underset{\displaystyle CH(CO_2CH_3)_2}{C_6H_5CHCH_2COC_6H_4OCH_3}$$

They contain one hydrogen atom that is very readily replaced by bromine; the resulting bromine substitution product may be either

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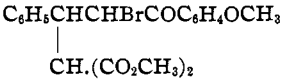
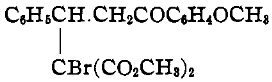
[1] Part of a dissertation presented to the Faculty of the Graduate School of Yale University, 1916, in candidacy for the degree of Doctor of Philosophy. The work, suggested by Prof. Elmer P. Kohler of Harvard, was done at Mount Holyoke College, and was accepted at Yale upon recommendation of Prof. Treat B. Johnson.



$$\begin{array}{l} C_6H_5CHCHBrCOC_6H_4OCH_3 \\ \;| \\ CH.(CO_2CH_3)_2 \end{array}$$

(I).

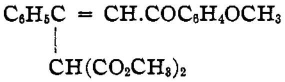
or



$$\begin{array}{l} C_6H_5CH.CH_2COC_6H_4OCH_3 \\ \qquad| \\ \quad CBr(CO_2CH_3)_2 \end{array}$$

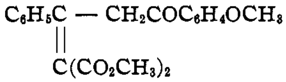
(II).

By cautious treatment with bases it is possible to remove hydrobromic acid from the bromine compound without hydrolyzing much of the ester, the yield being 80 to 87% of bromine-free ester. The main product of this process was always a substance melting at 86°, although an isomeric substance melting at 82° was sometimes obtained in sufficient quantity for separation. For products obtained in this way three formulas are possible.



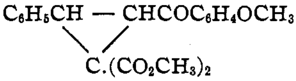
$$\begin{array}{l} C_6H_5C = CH.COC_6H_4OCH_3 \\ \;| \\ CH(CO_2CH_3)_2 \end{array}$$

(I).



$$\begin{array}{l} C_6H_5C - CH_2COC_6H_4OCH_3 \\ \quad\;\| \\ \;C(CO_2CH_3)_2 \end{array}$$

(II).

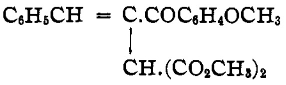


$$\begin{array}{c} C_6H_5CH - CHCOC_6H_4OCH_3 \\ \diagdown\;\diagup \\ C.(CO_2CH_3)_2 \end{array}$$

(III).

Between these formulas it is possible to decide by means of the following transformations:

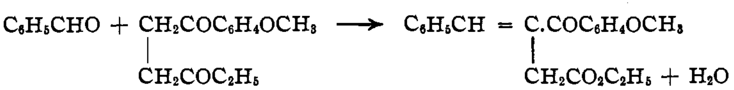
When the ester melting at 86° is treated with alcoholates it forms a metallic derivative that on acidification gives an isomeric ester melting at 82°. This on further action of the same reagent passes into another metallic derivative that yields a third isomer melting at 112°. The structure of this third ester must be represented by the formula



$$\begin{array}{l} C_6H_5CH = C.COC_6H_4OCH_3 \\ \qquad\qquad\;| \\ \qquad\qquad CH.(CO_2CH_3)_2 \end{array}$$

(IV).

This follows from the fact that on hydrolysis and loss of carbon dioxide, it passes into an acid that can be made synthetically by condensing benzaldehyde with ethyl-$\beta$-anisoyl-propionate, and hydrolyzing the product.



$$\begin{array}{l} C_6H_5CHO + CH_2COC_6H_4OCH_3 \longrightarrow C_6H_5CH = C.COC_6H_4OCH_3 \\ \qquad\qquad\quad| \qquad\qquad\qquad\qquad\qquad\qquad\quad| \\ \qquad\qquad CH_2COC_2H_5 \qquad\qquad\qquad\qquad\quad CH_2CO_2C_2H_5 + H_2O \end{array}$$

The structure of substances obtained by this reaction was established by Borsche.[1]

From this transformation of the ester melting at 86° into a substance with the formula represented by IV, it follows that the former must be a trimethylene compound, and that the relations between the three isomers is represented by the formulas

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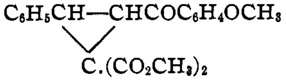
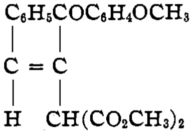
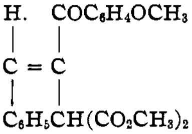
[1] *Ber.*, 47, 1112 (1914).



I (86°).



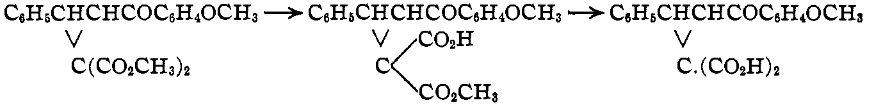
II (82°).



III (112°).

All the properties of these three isomers support this conclusion. The substances melting at 82 and 112° readily reduce permanganate while the ester melting at 86° does not. They also, as would be expected, form highly colored metallic derivatives from which they are regenerated by acids, a process that is impossible with the trimethylene compound. That the esters melting at 82 and 112° are stereoisomers is shown also by the fact that the former passes into the latter under the influence of sunlight.

By using aqueous alkalies or alcoholates under special conditions it is possible to hydrolyze the trimethylene compound to the corresponding ester-acid, and then to the dibasic acid.



This was established by esterifying the resulting acids with methyl alcohol and hydrochloric acid—the product in each case being the ester melting at 86°. The trimethylene ring in these acids is not sensitive to bases as it is in the ester, but it opens readily on heating. Thus when the dibasic acid was heated at about 200° it lost carbon dioxide and gave a mixture of products from which four substances, two neutral and two acid, were readily separated. The neutral substances were found to be a green and a yellow unsaturated lactone, so closely related as to suggest geometrical isomerism. The green lactone is the labile form and in recrystallizing from all solvents about one-third passes over into the yellow modification. Both substances dissolve in chloroform and ethyl acetate to give deep red solutions; and in acetone, alcohol and ether to give pale yellow or greenish yellow solutions. The green lactone in solution in acetone reduces permanganate instantly, the yellow lactone does not. Both substances, when dissolved in methyl alcoholic potassium hydroxide and acidified, yield a monobasic unsaturated acid, melting at 165°. This acid, when dissolved in methyl alcohol saturated with hydrogen chloride, passes quantitatively into the yellow lactone.

Both the green and yellow lactones have been obtained by heating a mixture of β-anisoyl-propionic acid, benzaldehyde, and acetic anhydride. As this reaction according to Borsche[1] should give a lactone with the structure

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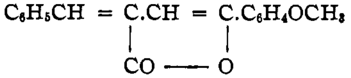
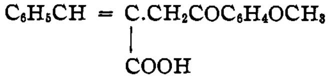
[1] *Ber.*, 47, 1114 (1914).



$$\begin{array}{l}C_6H_5CH = \underset{|}{C}.CH = \underset{|}{C}.C_6H_4OCH_3 \\ \quad\quad\quad\quad\; CO \text{———} O\end{array}$$

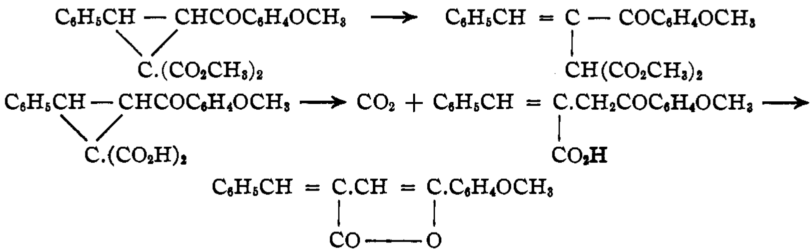
this formula must represent the isomeric green and yellow lactones; and the corresponding acid must be $\alpha$-benzal-$\beta$-anisoyl-propionic acid,



$$C_6H_5CH = \underset{\substack{|\\COOH}}{C}.CH_2COC_6H_4OCH_3$$

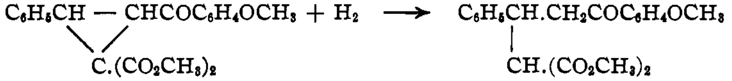
It is noteworthy that when the dibasic acid is heated, the ring opens to some extent in a different place from that in which it opens when the corresponding ester is treated with an alcoholate:

(I). (II).

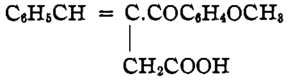


The ring may be opened in still another way. When the ester melting at 86°, in solution in acetic acid, was reduced with zinc dust, the corresponding ester of anisoyl, phenyl-ethylmalonic acid was obtained:

(III).

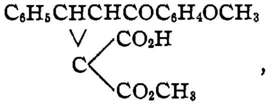


The acid products obtained as a result of heating the dibasic acid were monobasic acids, melting, respectively, at 124 and 198°. The acid melting at 124° was identified as $\beta$-benzal-$\beta$-anisoyl-propionic acid,



$$C_6H_5CH = \underset{\substack{|\\CH_2COOH}}{C}.COC_6H_4OCH_3$$

It was obtained both as free acid, and as the sodium salt, and was synthesized by the method mentioned in an earlier part of this paper.[1] Both acid and salt reduce potassium permanganate in aqueous solution. The oxidation was attended by the formation of benzaldehyde, and the products of the reaction were identified as benzoic and anisic acids. The acid melting at 198° was obtained only in small quantity. When esterified with methyl alcohol and hydrochloric acid, it gives a solid ester which is identical with one of the products obtained by heating the ester acid,



, at 200°.

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[1] *Ber.*, 47, 1112 (1914).

## Experimental.

When dimethyl β-anisoyl-α-phenyl ethylmalonate was dissolved in chloroform and treated with a molecular equivalent of bromine, a reaction took place with the evolution of hydrobromic acid, the bromine disappearing as rapidly as added. The chloroform was distilled under diminished pressure and the oily residue dissolved in alcohol. This on evaporation deposited an oil; and all efforts to obtain a solid bromine substitution product failed. The oil, when treated with reagents such as potassium methylate, alcoholic potassium hydroxide, and magnesium methylate, yielded a number of solid isomeric products, which crystallized readily. Three substances melting at 86, 82 and 112° were separated.

The primary product obtained from the bromine derivative of methyl β-anisoyl-α-phenyl-ethylmalonate was a bromine-free ester melting at 86°. Difficulties were experienced in getting good percentage yields of this substance, because of the ease with which it is isomerized in solution. In the first experiments potassium hydroxide was used as the reagent for eliminating hydrobromic acid. An alcoholic solution of the oil obtained in the reaction between methyl anisoyl-phenyl-ethylmalonate and bromine was treated with a 10% solution of potassium hydroxide in equal parts of methyl alcohol and water, the base was added slowly, and the reaction was complete when a yellow color and an alkaline solution remained for a moment after vigorous shaking. The methyl alcohol was then removed by distillation, the residue taken up with ether, and washed with water until free from alcohol. The addition of a few crystals of ester to the dried ethereal solution caused the precipitation of a large part of the ester in almost pure form. In the absence of seed, the separation of a solid product may take place immediately, or it may be necessary to wait weeks for spontaneous crystallization in the resulting oil. The yield of pure solid varied between 30 and 60%. A better average yield was obtained by substituting magnesium methylate for potassium hydroxide. The magnesium compound was added directly to an alcoholic solution of the oil obtained by the action of bromine on methyl anisoyl-phenyl-ethylmalonate. The addition of the base was attended by a change in color varying from salmon to red. Part of the alcohol was removed immediately by distillation and the residue was decomposed with aqueous hydrochloric acid and extracted with ether. The ethereal solution, when washed and dried over calcium chloride, yielded an average of 60 to 70% pure crystalline ester. In all experiments the separation of a solid product was greatly interfered with by the presence of a thick, yellow oil. Residues consisting of this oil deposited additional small quantities of crystals very slowly. The method finally used was a modification of the second and eliminated extraction with ether. 100 g. of methyl anisoyl-phenyl-ethylmalonate were dissolved in chloroform and treated with 45 g. of bromine. The chloroform was immediately distilled from a water bath under diminished pressure, and the residue, while still hot, was dissolved in a solution of magnesium methylate, prepared by adding 8 g. of magnesium to 200 cc. of alcohol. The magnesium compound was added slowly, with constant shaking, and its addition was attended by an evolution of heat, and by marked changes in color to green, yellow, orange, and finally deep red. A series of parallel experiments showed that the ultimate color of the solution did not influence in any apparent way the quantity nor the quality of the product. The separation of a solid crystalline substance began almost immediately, and was complete within 4 to 12 hrs.; and the yield varied between 82 and 87% of almost pure ester, melting at 82–84°. It was purified by recrystallization from ether.

0.1540 g. subs. and 0.1452 g. subs. gave 0.3866 and 0.3646 g. $CO_2$ and 0.0718 and 0.0641 g. $H_2O$.

Calc. for $C_{21}H_{20}O_6$: C, 68.4%; H, 5.4%. Found: C, 68.4, 68.4; H, 5.1, 4.9.

The substance is very soluble in ether acetone, and hot alcohol, slightly soluble in cold alcohol and ligroin. The ester melting at 86° does not reduce permanganate. In solution in carbon tetrachloride it slowly decolorizes bromine with the evolution of hydrobromic acid. Ten grams of substance reacted readily with an equivalent of bromine, but the resulting oil showed no tendency to crystallize even after standing for months. Dissolved in glacial acetic acid and treated with zinc dust and a small quantity of water, the substance passed quantitatively into methyl-$\gamma$-anisoyl-$\beta$-phenyl-ethylmalonate.

Under the proper conditions the ester may be hydrolyzed to an ester acid and then to a dibasic acid.

**Methyl Potassium 1-Phenyl-2 Anisoyl Trimethylene Dicarbonate (3-3).**—The pure ester melting at 86° may be hydrolyzed to a neutral monopotassium salt by adding exactly one equivalent of potassium hydroxide to a solution of the ester in five times its weight of methyl alcohol. The base was added slowly as a 25% solution in equal parts of methyl alcohol and water; and the mixture became neutral upon standing from 10 to 12 hrs. in an ice-chest. Since there was no separation of solid product upon standing, the solution was concentrated by evaporation on a water bath. Addition of a small quantity of ether to the cooled solution caused the immediate precipitation of a white crystalline solid.

0.1054, 0.1023 and 0.1025 g. subs. gave 0.0221, 0.0218 and 0.0217 g. $K_2SO_4$.

Calc. for $C_{20}H_{17}O_6.K$: K, 9.94%. Found: K, 9.39, 9.55, 9.49.

The salt is readily soluble in water and in alcohol, insoluble in ether.

It was recrystallized from alcohol-ether mixtures, from which it separates in glistening plates that melt at 152°. At about 170° the substance changes color to a reddish brown and a little above this temperature decomposition with the rapid evolution of $CO_2$ takes place. When acidified in aqueous solution it gives an oily precipitate which slowly solidifies. When purified this was found to consist of a monobasic acid melting at 162°.

**Methyl-1-phenyl-2-anisoyl-trimethylene Dicarbonic Acid.**—The ester-acid may be prepared by acidifying an aqueous solution of the pure potassium salt; or by hydrolyzing the ester melting at 86° with one equivalent of potassium hydroxide and, after allowing the mixture to stand overnight in a cool place, acidifying with hydrochloric acid. The oil precipitating from acid solution was taken up by chloroform, washed and dried over calcium chloride. The acid crystallizes from chloroform on evaporation, or on the addition of a small quantity of ligroin.

0.1484 and 0.1572 g. subs. gave 0.3674 and 0.3903 g. $CO_2$; and 0.0690 and 0.0680 g. $H_2O$.

Calc. for $C_{20}H_{18}O_6$: C, 67.7%; H, 5.08%. Found: C, 67.5, 67.7; H, 5.1, 4.8.

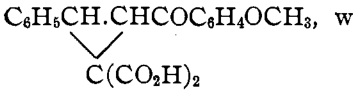
The substance crystallizes in large, white prisms, that melt at 162°, and that decompose with the evolution of $CO_2$ at about 200°. It is very soluble in chloroform, ethyl acetate, and acetone, soluble in ether, and insoluble in ligroin. It may be most readily separated from small quantities of the dibasic acid, occurring as impurities, by recrystallization from chloroform-ligroin mixtures. The basicity of the substance was determined by titration. When dissolved in alcohol and hydrolyzed in the presence of an excess of potassium hydroxide, the acid ester passes into a dipotassium salt, which on acidification gives a dibasic acid, melting at 192°. In alcoholic solutions saturated with hydrogen chloride, it passes quantitatively into the dimethyl ester, melting at 86°. When heated at about 200° the ester-acid loses $CO_2$. The reddish brown mass obtained as the result of this action was poured into ether and the ethereal solution was extracted with sodium carbonate. The product was found to be neutral in character. When a small quantity of ligroin was added to the washed and dried ethereal solution, a substance separated slowly, in the form of fine needles or plates. This on recrystallization from ether-ligroin mixtures and finally from methyl alcohol melted at 121°. It was identified as the ester of an acid melting at 198°. The filtrates from which this solid separated were evaporated to dryness on a water bath and were treated with a solution of potassium hydroxide in methyl alcohol. The alkaline solution on dilution with a large quantity of water remained clear, and on acidification with hydrochloric acid, precipitated an oil which slowly solidified. This was found to consist almost entirely of an acid melting at 147° and identified as $\beta$-anisoyl-propionic acid.

**Dipotassium 1-Phenyl-2-Anisoyl-trimethylene Dicarbonate** (3-3).—This substance was obtained by hydrolyzing the ester melting at 86° in alcoholic solution with an excess of concentrated aqueous potassium hydroxide. The base was added slowly with constant shaking to the cooled solution of the ester and the salt separated almost immediately in the form of white, glistening plates. It was filtered and washed first with a small quantity of alcohol and then with acetone.

0.1320 g. subs. and 0.1140 g. subs. gave 0.0551 g. and 0.0477 g. of $K_2SO_4$.
Calc. for $C_{19}H_{14}O_6K_2$: K, 18.7%. Found: K, 18.7, 18.6.

The substance is very soluble in water, sparingly soluble in alcohol and almost insoluble in acetone. Its aqueous solution gave, on acidification, a white, oily precipitate, which slowly solidified, and which consisted of a dibasic acid, melting at 192°.

**1-Phenyl-2-anisoyl-trimethylene Dicarbonic Acid** (3-3).—



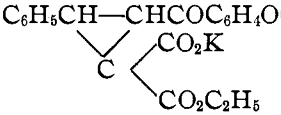
$C_6H_5CH.CHCOC_6H_4OCH_3$ / $C(CO_2H)_2$

was obtained by hydrolyzing the dimethyl ester melting at 86° and the ester acid melting at 162°, in the presence of excess of concentrated aqueous potassium hydroxide, and acidifying the product. It was also obtained, along with other substances, when the two dimethyl esters, isomeric with the ester melting at 86°, were hydrolyzed with potassium hydroxide. Finally it was obtained by the hydrolysis of the corresponding ethyl esters. The oil which separated on acidifying the aqueous solution of the dipotassium salt of this acid, was allowed to solidify, and then washed and dried. It was extracted repeatedly with small quantities of chloroform to remove any acid ester present as impurity, washed once with a very small quantity of ether, and recrystallized from ethyl acetate, or from acetic acid. The pure substance melted at 192°, changed in color to a golden brown at about this temperature and at about 200° decomposed with the rapid evolution of $CO_2$.

0.1497 g. and 0.1226 g. subs. gave 0.3680, 0.3008 g. $CO_2$; and 0.0623, 0.0519 g. $H_2O$.
Calc. for $C_{19}H_{16}O_6$: C, 67.0; H, 4.7. Found: C, 67.0, 66.9; H, 4.6, 4.7.

The substance is sparingly soluble in water from which it separates slowly in crystalline form. It is very soluble in acetic acid, acetone and ethyl acetate, 1 pt. by weight of substance dissolving in 4, 4, and 14 pts., by weight of these respective solvents. It is slightly soluble in ether, almost insoluble in chloroform, and insoluble in ligroin. It is most readily recrystallized from ethyl acetate-ligroin mixtures from which about 90% of the dissolved substance separates upon cooling. The basicity of the acid was determined by titration with standard alkali. In solution in carbon-bisulfide the substance reacts readily with a molecular equivalent of bromine with the evolution of hydrobromic acid, but no solid was separated from the resultant oil. In solution in methyl alcohol saturated with hydrogen chloride, the acid passes readily into the methyl ester melting at 86°. Heated above 200° the acid decomposes with the evolution of carbon dioxide. Two neutral and two acid products were obtained as a result of this decomposition, which will be considered later on in this paper.

**1-Phenyl-2-anisoyl-trimethylene Dicarbonic Acid (3–3)** was also obtained by hydrolyzing the corresponding monoethyl ester. The diethyl ester was never isolated, so that a description of this ester-acid and its salt may be considered at this point.

**Ethyl Potassium 1-Phenyl-2-anisoyl Trimethylene Dicarbonate (3–3),**  $\underset{C(CO_2K)(CO_2C_2H_5)}{C_6H_5CH{-}CHCOC_6H_4OCH_3}$, was obtained by treating diethyl (β-bromo-β-anisoyl-α-phenyl-ethyl) malonate[1] in alcoholic solution with two equivalents of potassium hydroxide. The alkali was added as a 25% solution in equal parts of alcohol and water, and the mixture was allowed to stand overnight. The solution was then concentrated and allowed to cool when a small quantity of ether was added. The salt separated slowly in the form of large colorless hexagonal prisms.

0.0987, 0.1207 g. subs. gave 0.0204 and 0.0250 g. $K_2SO_4$.
Calc. for $C_{21}H_{19}O_6K$: K, 9.60%. Found: K, 9.26, 9.28.

The substance is very soluble in water and in alcohol. Its aqueous solution is neutral to litmus.

**Ethyl-1-phenyl-2-anisoyl Trimethylene Dicarbonate Acid (3–3)** may be prepared by acidifying an aqueous solution of the corresponding potassium salt. The reaction is quantitative. The substance separates in the form of an oil which solidifies on standing, but which is most conveniently extracted with ether. The ester-acid separates from the dry ethereal solution on evaporation, or on the addition of a small quantity of ligroin in the form of large, colorless hexagonal prisms.

0.1449 and 0.1556 g. subs. gave 0.3622 and 0.3882 g. $CO_2$; and 0.0737, 0.0786 g. $H_2O$.
Calc. for $C_{21}H_{20}O_6$: C, 68.4%; H, 5.4%. Found: C, 68.1, 68.0; H, 5.6, 5.6.

The substance is very soluble in chloroform, quite soluble in ether and insoluble in ligroin. Its basicity was determined by titration. When hydrolyzed in the presence of an excess of potassium hydroxide it passes into a dipotassium salt, which on acidification gives a dibasic acid melting at 192° and identified as 1-phenyl-2-anisoyl-trimethylene dicarbonic acid (3–3).

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[1] *Am. Chem. J.*, 49, 178 (1913).

When the ester melting at 86° was treated with alcoholates it formed a metallic derivative which on acidification gave an isomeric ester melting at 82°. This on further action of the same reagents gave a third isomer melting at 112°.

**Methyl β-Benzal-β-Anisoyl-methylmalonate** (II and III, p. 1520), M. p. 82° and 112°.—The labile form of this ester, melting at 82°, was prepared by adding a few drops of sodium methylate to a well cooled ethereal solution of the ester melting at 86°. The separation of a solid metallic derivative took place slowly. This consisted of fine, yellow needles which were filtered and washed with ether. It was decomposed by shaking with ether and cooled hydrochloric acid; and the colorless ethereal solution, after being washed free from acid and dried over calcium chloride, gave an almost pure product melting at 82°. The yield varied between 30 and 50%. This was improved by modifying the method, magnesium methylate being substituted for sodium methylate, when a yield varying between 70 and 90% was obtained. The procedure in this case was as follows: 1.3 grams of magnesium were dissolved in 27 cc. of methyl alcohol to which a small quantity of mercuric chloride had been added. At the conclusion of this reaction, 10 g. of the ester melting at 86° were added to the mixture in small quantities, and in the form of a fine powder; and its solution took place immediately. The solution was heated on the water bath for about an hour, part of the alcohol was then distilled off, and the residue shaken with ether and cooled hydrochloric acid. The ethereal solution after being washed free from acid and dried over calcium chloride, deposited a crystalline solid melting at 82°. This substance was finally purified by recrystallization from ether and alcohol.

0.1373 and 0.1671 g. subs. gave 0.3486 and 0.4249 g. $CO_2$; and 0.0629, 0.0755 g. $H_2O$.
Calc. for $C_{21}H_{20}O_6$: C, 68.4; H, 5.4. Found: C, 69.2, 69.3; H, 5.0, 5.0.

The substance is extremely soluble in ether and in hot methyl alcohol. It crystallizes from both solvents in the form of long, fine needles, which appear soft and felt-like while moist, but which dry in hard lumps. It readily reduces potassium permanganate in solution in acetone. In solution in chloroform or carbon tetrachloride, the substance reacts readily with a molecular equivalent of bromine. The reaction was attended by the evolution of hydrobromic acid, but the resulting oil showed no tendency to form a solid product. When the ester in solution in methyl alcohol was treated with an equivalent of potassium hydroxide dissolved in the same solvent, the separation of a deeply colored metallic derivative took place at once. The substance crystallized in the form of coarse, orange-colored needles, which were filtered, washed with alcohol, and analyzed.

0.0730, 0.0831 and 0.0904 g. subs. gave 0.0149, 0.0170 and 0.0185 g. $K_2SO_4$.
Calc. for $C_{21}H_{19}O_6K$: K, 9.6%. Found: K, 9.15, 9.17, 9.17.

The substance is insoluble in water and ether, but dissolves readily in alcohol forming deep red solutions. The solution in alcohol is very unstable, and the color was completely discharged upon standing, or upon boiling the solutions. When the dry metallic derivative was shaken with ether and hydrochloric acid, it passed back quantitatively into the ester, melting at 82°.

The stable form of β-benzal-β-anisoyl-methylmalonate, m. p. 112°, was formed by the action of sunlight on an ethereal solution of the low melting ester, in the presence of a small quantity of iodine. The transformation was quantitative. The same substance was obtained by treating the ester, m. p. 82°, with sodium and magnesium methylates and decomposing the product with hydrochloric acid. Since the yield was better in the case of the latter reagent, the procedure in this case will be described. Magnesium methylate was prepared by dissolving 1.3 g. magnesium in 27 cc. methyl alcohol. As soon as the reaction was complete, 10 g. of ester were added to the solution in the form of a fine powder. Either of the isomeric substances, melting at 86 and 82° could be used for this reaction. The substance dissolved on warming, and the resulting mixture was evaporated to dryness on a water bath. If the dried residue appeared greenish or yellow, a small quantity of alcohol was added and the mass was again evaporated to dryness. This process was repeated until the product appeared white. The mass was then decomposed by shaking with ether and cooled hydrochloric acid, when the final product, which is sparingly soluble in ether, separated in crystalline form. It was filtered, washed with ether and dried. It was further purified by recrystallizing from chloroform-ether mixtures. The yield varied between 80 and 90%.

0.1628, 0.1701 and 0.1547 g. subs. gave 0.4100, 0.4293, 0.3913 g. $CO_2$, and 0.0743, 0.0747, 0.0683 g. $H_2O$.

Calc. for $C_{21}H_2O_6$: C, 68.4%; H, 5.4%. Found: C, 68.7, 68.8, 68.9; H, 5.1, 4.9, 4.9.

The substance is very soluble in chloroform, soluble in hot alcohol, sparingly soluble in cold alcohol, and almost insoluble in ether. It separates from chloroform-ether mixtures, or from solutions in hot alcohol, in the form of large, well-defined prisms. Dissolved in chloroform or carbon tetrachloride, it readily reacts with an equivalent of bromine. The reaction was attended by an evolution of hydrobromic acid, but the resulting oil gave no solid product. A solution of the substance in acetone immediately reduced permanganate in solution in the same solvent. Subjected to prolonged heating with magnesium methylate, it suffered no change and was regenerated quantitatively when shaken with ether and hydrochloric acid. When the ester in solution in methyl alcohol was treated with potassium hydroxide dissolved in the same solvent, a highly colored metallic derivative was formed. This substance separated immediately in the form of long, fine, yellow needles, which were soft and felt-like while moist. It was filtered, washed with ether, and analyzed.

0.0991, 0.1173, 0.1420 g. subs. gave 0.0196, 0.0232 and 0.0280 g. $K_2SO_4$.
Calc. for $C_{21}H_{19}O_6K$: K, 9.6%. Found: K, 8.87, 8.87, 8.84.

The substance is insoluble in water and in ether, but is very soluble in alcohol. Like its isomer it is very unstable in solution, the deep red color of its alcoholic solutions being quickly discharged even upon standing in the cold. The dried substance, when shaken with ether and hydrochloric acid, passed back quantitatively into the ester, melting at 112°.

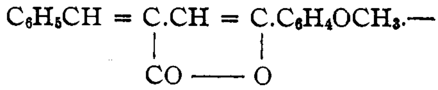
When the esters melting at 82 and 112°, in solution in alcohol, are hydrolyzed by concentrated aqueous potassium hydroxide, the metallic derivative which at first forms, dissolves on standing or upon boiling. The resulting straw-colored liquid was poured into water in a separatory funnel, and extracted repeatedly with ether. The ether when washed, dried and evaporated, left no residue, showing the absence of any neutral product, and showing also that the original ester had been completely hydrolyzed. The alkaline solution when acidified precipitated a yellow oil. This was found to consist of a mixture of acids, three of which were finally separated and identified. They were 1-phenyl-2-anisoyl-trimethylene dicarbonic acid (3-3), m. p. 192°; $\beta$-anisoyl-propionic acid, m. p. 147°; and $\beta$-benzal-$\beta$-anisoyl-propionic acid, m. p. 124°. The first was found to be identical with the dibasic acid obtained by the hydrolysis of the ester melting at 86°. The second and third were acids whose identity was established by syntheses to be described later in this paper.

Both the dibasic acid and the ester-acid, obtained by hydrolyzing the ester, m. p. 86°, lose carbon dioxide when heated at about 200°. The result of the decomposition of the first named substance was a mixture from which four solid products were isolated.

When the acid, melting at 192°, was heated at about 210°, it was decomposed with an evolution of carbon dioxide. At the same time it changed color first to amber and then to greenish brown. When gas was no longer evolved, the product was poured at once into a small quantity of alcohol-free ether. The mixture dissolved at once in the ether, but in the course of a few moments the separation of a greenish brown precipitate took place. The precipitate consisted of a mixture of three substances, all of which are very sparingly soluble in ether. The precipitate was filtered, washed with ether and the products separated by fractional crystallization from ethyl acetate. They consisted of a yellow and a green unsaturated lactone, melting at about 173 and 176°, respectively; and of a monobasic acid melting at 198°. After the separation of these substances, the filtrates contained in ethyl acetate and ether were combined, and the mixture was then extracted repeatedly with dilute sodium carbonate in order to remove the acid products. The ethereal solution containing neutral substances was then washed, dried and allowed to evaporate. It gave an oil from which small quantities of the yellow lactone slowly crystallized. No other solid product was separated. Since this oil represented at least 80% of the original dibasic acid, the attempt was made to study it by dissolving it in sodium methylate and then acidifying. The oil was readily soluble in this reagent, and the solution on dilution with water remained clear. The addition of hydrochloric acid to the aqueous solution caused the precipitation of a yellow oil which was found to consist in large part of $\beta$-anisoyl-propionic acid. The identification was made by comparison with a specimen of this acid obtained by synthesis.

The sodium carbonate extracts were combined and extracted once with ether. Either of two subsequent methods of procedure were employed—favoring, respectively, the separation of one or the other of two monobasic acids whose sodium salts were present in the alkaline solution. (*a*) The aqueous solution containing sodium carbonate was acidified with hydrochloric acid. A yellow oil was precipitated which partially solidified on standing. The acid solution was decanted, the oil was washed with water and allowed to stand until it seemed quite dry. The addition of a small quantity of alcohol-free ether caused the immediate separation in crystalline form of additional small quantities of the acid melting at 198°. It was necessary to handle the material very quickly at this point, and to filter the acid at once; since, upon standing, it passed into solution in ether, the ethereal solution on evaporation giving an oil which showed no tendency to crystallize. (*b*) The aqueous solution containing sodium carbonate was evaporated to dryness on a water bath, and the residue was extracted repeatedly with small quantities of alcohol in order to remove any soluble salts of organic acids. The alcoholic extracts were then combined, concentrated by evaporation on a water bath, and, when cool, treated with a small quantity of ether. The addition of ether caused the immediate precipitation of a white crystalline substance, and further small additions of ether increased the quantity of this substance. It was filtered, washed with a small amount of acetone, and recrystallized from alcohol or from alcohol-ether mixtures. It was found to consist of a salt, melting at 212°, and its aqueous solution, on addition of hydrochloric acid, gave an unsaturated monobasic acid melting at 124°. The filtrates from this salt were combined, concentrated on a water bath, diluted with water and acidified. The precipitated oil was taken up with ether, the ether washed, dried, and evaporated. It deposited an oil which showed no tendency to crystallize.

**α-Benzal-γ-anisyl-crotonlactone,**



$$\begin{array}{cccc} C_6H_5CH = & C.CH & = & C.C_6H_4OCH_3.— \\ & | & & | \\ & CO & — & O \end{array}$$

Two substances corresponding to this formula were formed when 1-phenyl-2-anisoyl-trimethylene-dicarbonic acid (3–3) was heated above 200°. In a series of five parallel experiments, using 20 g. portions of the same specimen of dibasic acid, and varying the temperature between 210 and 250°, it was found that the quantity of colored lactone obtained remained almost constant and corresponded to about 4% of the acid used in the experiment. Quick heating at 230° gave the best yield of solid product when poured into ether, and, therefore, the best yield of the acid melting at 198°. The lactones were readily separated from the acid product by recrystallizing from ethyl acetate. Both substances were prepared by synthesis by methods analogous to those used by Borsche in preparing 1-benzal-3-phenyl-croton-lactone.[1] 18.6 g. of pure sodium β-anisoyl-propionate and 12 g. of benzaldehyde were heated with 24 g. of acetic anhydride in a metal bath at a temperature between 110 and 115° for 24 hrs. The mixture while still hot was treated with 200 cc. of alcohol, allowed to cool, and then filtered, and washed with alcohol. After crystallization from ethyl acetate it gave 5.2 g. of green lactone, m. p. 168–170°. In recrystallizing this, the filtrates yielded the yellow modification. Other products separated from the mother liquors were sodium β-anisoyl-propionate, 7.8 g., and free β-anisoyl-propionic acid, 3.8 g. The reaction thus took place entirely in one sense, although only about one-third of the original salt reacted with benzaldehyde. The lactones obtained in this way were identical in every respect with those obtained by heating the dibasic acid. The relation existing between the green and yellow lactone is very interesting, the results of analysis showing them to be isomeric substances.

0.1012 and 0.1392 g. subs. (yellow) gave 0.2865, 0.3944 g. $CO_2$; and 0.0459, 0.0621 g. $H_2O$.

0.1261 g. subs. (green) gave 0.3583 g. $CO_2$ and 0.0589 g. $H_2O$.

Calc. for $C_{18}H_{14}O_3$: C, 77.6%; H, 5.0%. Found: C, 77.2, 77.2, 77.4; H, 5.0, 4.9, 5.1.

Both substances melt to a deep red liquid, both dissolve in chloroform and ethyl acetate to give deep red solutions, in acetone alcohol and ether to give yellow or pale greenish yellow solutions. One gram of substance dissolves in 38 g. of ethyl acetate, 66 g. acetone, 14 g. chloroform, and 500

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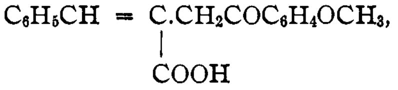
[1] *Ber.*, 47, 1114 (1914).

g. ether, respectively. In recrystallizing from all solvents about one-third of the green lactone passes over into the yellow modification. Both substances crystallize from all solvents in the form of long, glistening plates. In the matter of chemical properties the only point of difference observed was that the green modification instantly reduced permanganate in solution in acetone, while the yellow form did not. Both dissolve in alcoholic potassium hydroxide, and sodium methylate; and these solutions, when diluted with water and acidified, gave the same acid. This acid, when recrystallized from chloroform-ligroin mixtures, melted at 165°. It corresponds to α phenylacyl-cinnamic acid, obtained in an analogous manner by Borsche.

**α-Benzal-β-anisoyl-propionic Acid,**



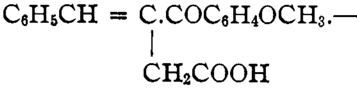
$C_6H_5CH = \underset{\displaystyle COOH}{\underset{|}{C}}.CH_2COC_6H_4OCH_3,$

was obtained from the corresponding crotonlactone in the manner described. It separated from aqueous alkaline solutions as a fine, white flocculent precipitate on the addition of acid. This was filtered, washed with water and dried. It was recrystallized first from chloroform-ligroin mixtures, and then from acetone from which it separated in long, hexagonal prisms.

0.1099 g. subs. gave 0.2938 g. $CO_2$ and 0.0523 g. $H_2O$.
Calc. for $C_{18}H_{16}O_4$: C, 72.9; H, 5.4. Found: C, 72.9; H, 5.3.

The substance is sparingly soluble in water. Its aqueous solution reacts acid toward litmus and reduces permanganate instantly in the cold. The acid dissolves readily in chloroform, ethyl acetate, acetone, and ether, but is almost insoluble in ligroin. In solution in carbon bisulfide it readily decolorizes bromine with the evolution of hydrobromic acid. Its solution in methyl alcohol, when saturated with hydrogen chloride, gives an immediate precipitation of the corresponding yellow crotonlactone, m. p. 173°.

**β-Benzal-β-anisoyl-propionic Acid,**



$C_6H_5CH = \underset{\displaystyle CH_2COOH}{\underset{|}{C}}.COC_6H_4OCH_3.$

—This acid, m. p. 124°, was formed together with an isomeric acid, m. p. 198°, when 1-phenyl-2-anisoyl-trimethylene dicarbonic acid (3–3) was heated at above 200°. It was separated from the other substances formed as a result of this reaction by means of its sodium salt and in the manner already described. The substance was also prepared by synthesis. The method used was analogous to that employed by Borsche in the preparation of benzoyl-phenyl-isocrotonic acid[1] (β-benzal-β-benzoyl-propionic acid). 1.47 g. of sodium in 30 cc. absolute alcohol were cooled with ice-water, and added drop by drop, with constant shaking, to a mixture of

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[1] *Ber.*, 47, 1112 (1914).

15 g. of ethyl β-anisoyl-propionate and benzaldehyde. There was no heat evolved during this reaction so far as could be observed. The mixture was allowed to stand overnight and in the morning showed the separation of a solid substance in the form of a white, flaky precipitate. This was filtered and washed, first with alcohol, and then with acetone. When dry it dissolved in water to give a clear solution and this on addition of hydrochloric acid gave an oily precipitate. This, when washed, dried, and recrystallized, gave an acid melting at 124°. This acid was the only substance that was separated in pure form as a result of this condensation. This yield was, however, very unsatisfactory, since only about 25% of solid product was obtained, the remaining 75% being accounted for as an oil which showed no tendency to crystallize. The acid was purified by crystallization from chloroform-ligroin mixtures and then from acetone from which it separated in long, hexagonal prisms.

0.1496 and 0.1694 g. subs. gave 0.3951, 0.4475 g. $CO_2$; and 0.0704, 0.0803 g. $H_2O$.
Calc. for $C_{18}H_{16}O_4$: C, 72.9%; H, 5.4%. Found: C, 72.0, 72.0; H, 5.2, 5.2.

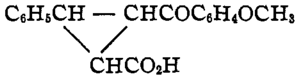
The substance is soluble in ether, chloroform, ethyl acetate and acetone, 1 g. of substance dissolving in 15, 8, 6 and 2.4 g. of these solvents, respectively. It is insoluble in ligroin and only slightly soluble in hot water, from which it crystallizes on cooling. Its aqueous solution gives an acid reaction with litmus and reduces permanganate instantly in the cold. When dissolved in methyl alcohol saturated with hydrogen chloride, it passes into an oil. This oil showed no tendency to crystallize after standing for months.

**Sodium β-Benzal-β-anisoyl-propionate** was obtained when phenyl-anisoyl-trimethylene dicarbonic acid was decomposed and the product treated in the manner described. It was purified by repeated recrystallizations from alcohol, and from alcohol-ether mixtures, from which it separated in the form of soft, white needles melting at 212°.

0.1805 and 0.1515 g. subs. gave 0.0368 and 0.0307 g. $Na_2SO_4$.
Calc. for $C_{18}H_{15}O_4Na$: Na, 7.32%. Found: Na, 6.60, 6.56.

The salt is very soluble in water and in hot alcohol, less soluble in cold alcohol, and insoluble in ether. Its aqueous solution when acidified with hydrochloric acid deposited a white oil, which crystallized on standing and which consisted of pure β-benzal-β-anisoyl-propionic acid. An aqueous solution of the salt reduced permanganate as rapidly as added. The reaction was accompanied by the liberation of benzaldehyde which was recognized by its odor. The products of the reaction were readily separated and identified as benzoic and anisic acids.

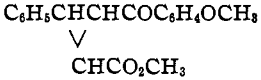
**1-Phenyl-2-anisoyl-trimethylene-3-monocarbonic Acid,**



This acid was obtained in very small quantities along with β-benzal-β-anisoyl-propionic acid as a result of heating the dibasic acid. It was separated as one of a number of substances formed when methyl γ-bromo-γ-anisoyl-β-phenyl-butyrate[1] was heated with dimethyl aniline. It was obtained in the form of its methyl ester when the ester acid, m. p. 162°, was heated above 200°. The acid was purified by recrystallizing from acetone and ethyl acetate and washing with ether. It crystallized from acetone in the form of prisms, m. p. 198°.

0.1207 and 0.1108 g. subs. gave 0.3230 and 0.2958 g. $CO_2$; and 0.0576, 0.0529 g. $H_2O$.
Calc. for $C_{18}H_{16}O_4$: C, 72.9%; H, 5.4%. Found: C, 72.9, 72.8; H, 5.3, 5.3.

The substance is sparingly soluble in ether, chloroform, ethyl acetate and acetone, 1 g. of substance dissolving in 514, 87, 35 and 15 g. of these solvents, respectively. It is slightly soluble in water, its aqueous solution giving an acid reaction with litmus. In solution in carbon tetrachloride it decolorized bromine with the evolution of hydrobromic acid. Its solution in methyl alcohol saturated with hydrogen chloride deposited a crystalline ester on standing.



$$\begin{array}{c} C_6H_5CHCHCOC_6H_4OCH_3 \\ \vee \\ CHCO_2CH_3 \end{array}$$

was formed from the corresponding acid in the method just described. It was also obtained as a result of heating the ester-acid, m. p. 162°, at about 200°. It was purified by ether-ligroin mixtures, and finally by recrystallizing from methyl alcohol.

0.1364 and 0.1260 g. subs. gave 0.3657, 0.3382 g. $CO_2$ and 0.0678, 0.0624 g. $H_2O$.
Calc. for $C_{19}H_{18}O_4$: C, 73.5%; H, 5.8%. Found: C, 73.1, 73.2; H, 5.5, 5.5.

The substance is very soluble in ether and in hot methyl alcohol, less soluble in cold alcohol, and sparingly soluble in ligroin. It crystallizes in the form of soft, white, glistening needles, melting at 121°. When dissolved in alcoholic potassium hydroxide and poured into water the solution remained clear, but on acidifying with hydrochloric acid, precipitated an oil which partially solidified upon standing. The solution was decanted, the oil was washed and allowed to stand until it appeared quite dry. The addition of a small quantity of ether caused the separation of a white crystalline solid, which was filtered at once and washed with ether. It consisted of the acid, m. p. 198°.

**β-Anisoyl-propionic Acid,** $CH_3OC_6H_4CO.CH_2CH_2CO_2H$, was obtained as one of the decomposition products formed when the unsaturated methyl esters melted at 82° and 112°, respectively, were hydrolyzed in the presence of an excess of aqueous potassium hydroxide It was also obtained from residues that had stood for some time after the separation of the main products formed by heating the dibasic acid. It was prepared

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[1] *Am. Chem. J.*, 49, 177 (1913).

synthetically by a method analogous to that used by Borsche in the preparation of $\beta$-benzoyl-propionic acid.[1] One part anisole was added to 1 part succinic anhydride and 1.5 parts $AlCl_3$ suspended in 4 parts carbon disulfide. The mixture was heated on a water bath until hydrogen chloride was no longer evolved. The dark red semisolid addition product was decomposed with ice, when a white, insoluble product was obtained. The crude product was dried, and was finally purified by preparing ethyl-$\beta$-anisoyl propionate, recrystallizing it, and from it, regenerating the acid. This was then further purified by recrystallizing from acetone, from which it separated in large hexagonal prisms, m. p. 147°.

0.1354 and 0.1318 g. subs. gave 0.3141, 0.3058 g. $CO_2$; and 0.0623, 0.0614 g. $H_2O$; (recrys.) 0.1344 g. gave 0.3136 g. $CO_2$ and 0.0663 g. $H_2O$.

Calc. for $C_{11}H_{12}O_4$: C, 63.4%; H, 5.7%. Found: C, 63.2, 63.2, 63.6; H, 5.1, 5.1, 5.4.

The acid is sparingly soluble in most organic solvents, one part dissolving in 54 parts acetone, 48 parts ether, 36 parts ethyl acetate and 30 parts methyl alcohol. It is soluble in hot water, 15 parts of substance dissolving in 800 parts of solvent, from which about 90% crystallizes on cooling. Its solutions in methyl and ethyl alcohol, when saturated with hydrogen chloride, gave the corresponding esters. These melted at 47° and 52°, respectively. Both are very soluble in alcohol and ether, but may be readily purified by recrystallization from their respective alcohols, from which they crystallize in large colorless crystals. The acid contains hydrogen that is exceedingly sensitive to oxidizing agents, and its sodium salt reduces permanganate solution instantly in the cold. The products of this oxidation were anisic acid, and another acid product which was not fully studied. It was very soluble in water, from which, however, it was readily extracted by ether. The dried ethereal solution on evaporation deposited the acid in the form of large, glistening, white plates, but the substance was so extremely sensitive that its solution in ligroin decomposed with the deposition of carbon when evaporated on the water bath.

MT. HOLYOKE COLLEGE LABORATORY.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF SOUTH DAKOTA.]

# THE MONONITRO PHENYL ETHERS.

BY HILTON IRA JONES AND ALFRED N. COOK.

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In 1873 Maikopar[2] made a dinitrophenyl ether by heating dinitrochlorobenzene, caustic potash and phenol in alcoholic solution. These substances react according to the following equation:

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[1] *Ber.*, **47**, 1110 (1914).

[2] *Ibid.*, **6**, 564 (1873).