to the taste or to litmus. The boiling rod should be put in the solution when it reaches the boiling point, not before. GREGORY TOROSSIAN.

CLEVELAND, OHIO.

CORRECTION.

Page 228, line 4, should read "... $\gamma = 1.530-1.535$; .....".

Page 228, line 26–7, should read "...parallel to the α-γ plane".

GEORGE W. MOREY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY. No. 230.]

THE PREPARATION AND PROPERTIES OF CERTAIN METHOXYLATED CARBINOLS, OLEFINS AND KETONES, DERIVED FROM TRIMETHYLGALLIC ACID.

BY MARSTON TAYLOR BOGERT AND ROBERT MELYNE ISHAM.

Received December 29, 1913.

1. Introductory.

In secondary and tertiary carbinols of types I and II, the introduction of methoxyl groups in place of one or more of the hydrogens of their

I. $C_6H_5.CH(OH)R$. II. $C_6H_5.C(OH)R_2$.

phenyl nuclei causes interesting alterations in their properties.

As compared with triphenyl carbinol itself, von Baeyer and Villiger,[1] Kauffmann,[2] and others have shown that methoxylated triphenyl carbinols exhibit increased halochromism and increased basicity, and are more easily reduced to the corresponding methoxylated triphenyl methane.

Hell[3] attempted to prepare carbinols of type III by the action of the Barbier-Grignard reagent upon anisic aldehyde and upon *p*-methoxybenzophenone, but found that the expected carbinols were so unstable, that when the magnesium compounds were hydrolyzed with dilute acid, the corresponding olefins (IV) were obtained, and not the carbinols at all.

III. $CH_3O.C_6H_4.CR(OH)CH_2R_1$ ($R = H$ or C_6H_5).

IV. $CH_3O.C_6H_4.CR : CH.R_1$ ($R = H$ or C_6H_5).

The instability of these secondary and tertiary carbinols, he attributed to the influence of the para methoxyl group. He noted also that anisyl phenyl propene and other methoxylated olefins of similar structure, do not give dibromo addition products when treated with bromine, but yield preferably monobromo substitution products (V), apparently by

V. $CH_3O.C_6H_4.C(C_6H_5) : CBr.CH_3$.

---

[1] *Ber.*, **35**, 3013 (1902).

[2] *Ibid.*, **38**, 2702 (1905); **41**, 4423 (1908); **45**, 766 (1912); **46**, 3779, 3788 (1913).

[3] *Ibid.*, **37**, 225, 457, 1429, 4188 (1904).

loss of HBr from an antecedent unstable dibromide. This instability of the dibromide cannot be referable, however, solely to the methoxyl group, since diphenyl propene shows an analogous behavior with bromine.

Having had occasion to carry out certain other syntheses with methyl trimethylgallate, a compound which is easily prepared in any desired amount, it was deemed worth while to study the carbinols and olefins obtainable therefrom, in the expectation that additional data bearing upon the influence of the methoxyl group would be secured, as the group is one of peculiar interest because of its frequent occurrence in natural products. Our results agree, in the main, with those obtained by previous workers in this field and, in addition, we have observed that the presence of the methoxyl groups in the phenyl nucleus of compounds of type VI materially heightens the reactivity of the halogen.

VI. $C_6H_5.C(R)(CH_2R)Cl$.

3,4,5-Trimethoxytriphenyl carbinol exhibits strong halochromism, and is very easily reduced to the trimethoxytriphenyl methane. It is more basic than triphenyl carbinol, but less basic than *p*-methoxytriphenyl carbinol. In other words, the *m*-methoxyl groups reduce the basicity of the *p*-methoxyl compound.

Experiments were carried out for the preparation of the following five carbinols of type VII by the Barbier-Grignard reaction, namely: (1)

VII. $(CH_3O)_3C_6H_2.C(OH)(CH_2R)_2$ (R = H or a radical).

trimethoxyphenyl dimethyl, (2) trimethoxyphenyl diethyl, (3) trimethoxyphenyl dipropyl, (4) trimethoxyphenyl diisoamyl, and (5) trimethoxyphenyl dibenzyl. When the magnesium compound was hydrolyzed with dilute acid, the following results were obtained: (1) gave chiefly olefin, although there was evidence of an unstable intermediate carbinol; (2) gave both carbinol and olefin, the former being very unstable; (3) and (4) gave olefin only and no carbinol; while (5) yielded a stable carbinol. The carbinol chlorides of (2) and (5) were quite unstable, readily losing HCl to give the olefin. By the action of dry hydrogen chloride upon an ether solution of either of these carbinols at 0°, the product was not the chloride, but the olefin. Klages[1] describes the chloride of phenyl diethyl carbinol as a colorless oil, which loses hydrochloric acid when heated alone or with pyridine, giving the corresponding olefin. Evidently the introduction of the methoxyl groups materially increases the instability of both the carbinol and the chloride. Klages[2] failed to obtain any reaction between phenyl dibenzyl carbinol and hydrogen chloride under conditions similar to those under which we obtained the chloride from the trimethoxyphenyl dibenzyl carbinol, so that the only conclusion to be drawn from the two

[1] *Ber.*, **36**, 3692 (1903).

[2] *Ibid.*, **37**, 1456 (1904).

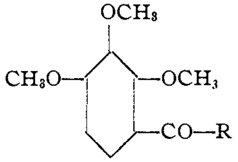
cases is that the methoxyl groups appear to increase the mobility of the carbinol hydroxyl.

In harmony with the observations of Hell, alluded to above, it was found that every one of the five olefins obtained by these reactions formed an unstable dibromo addition product, which lost hydrobromic acid with production of a monobromo substitution product.

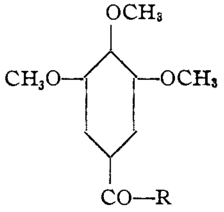
In an attempt to prepare the β-trimethoxyphenyl β-lactic acid by reduction of trimethylgalloyl acetic ester with activated aluminum, we obtained instead the corresponding trimethoxy cinnamic acid, showing that the intermediate secondary carbinol must have been unstable under the conditions of the experiment, losing a molecule of water to form the unsaturated acid, in the same way that the above tertiary carbinols lose water to form the olefins; and here, too, the methoxyl groups appear largely responsible for the instability of the carbinol.

Nencki,[1] Mannich and Hahn,[2] and others, have obtained ketones of type VIII by the application of the Friedel-Crafts reaction to trimethyl pyrogallol; but of the isomeric type IX, the only one we found in the literature at the time this work was undertaken was the 3,4,5-trimethoxy acetophenone prepared by Mauthner[3] from trimethylgallic aldehyde by the action of diazo methane, and from trimethylgalloyl acetic ester by hydrolysis with dilute sulfuric acid. We have succeeded in obtaining Mauthner's compound, and a number of others of this type (IX), by taking the olefins secured in our Grignard reactions and treating them with ozone, according to the Harries method:

VIII.



IX.



$$(CH_3O)_3C_6H_2.CR_1 : CHR + O_3 + H_2O = (CH_3O)_3C_6H_2.CR_1O + OCH.R + H_2O_2$$

The action of the ozone on the olefins with the longer chains was quite slow, in some cases 20 hours' treatment being insufficient to complete the reaction.

From the trimethoxy acetophenone, the corresponding chalkone (X) was prepared by condensation with benzaldehyde; and from the trimethylgalloyl acetic ester and resorcinol, the trimethoxyphenyl umbelliferone (XI).

---

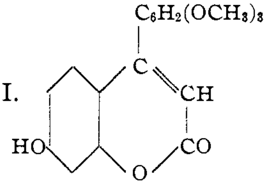
[1] *Ber.*, **27**, 2738 (1894).

[2] *Ibid.*, **44**, 1542 (1911).

[3] *J. prakt. Chem.*, [2] **82**, 275 (1910).

X. $C(H_3O)_3C_6H_2.CO.CH:CH.C_6H_5$.

XI.



By the oxidation of syringin, a glucoside of *Syringa vulgaris*, Koerner[1] obtained syringic acid and subsequently showed it to be probably the 3,5-dimethylgallic acid (XII).

XII. $(3.5)(CH_3O)_2.C_6H_2(OH)(4)COOH(1)$.

Gadamer[2] demonstrated the correctness of this formula by preparing syringic acid from sinapinic acid (XIII).

XIII. $(3,5)(CH_3O)_2.C_6H_2(OH)(4)CH : CH.COOH(1)$.

Attempts to synthesize the acid by the partial methylation of gallic acid[3] all failed, for the reason that the hydroxyl group in position 4 is the one first methylated. Graebe and Martz[4] did, however, succeed in obtaining it by the partial hydrolysis of trimethylgallic acid, by heating in sealed tubes with concentrated hydrochloric acid and by heating for two hours at 100° with 48% hydrobromic acid.

Gallic acid itself is sulfonated by 20% fuming sulfuric acid. A similar treatment of trimethylgallic acid, we found resulted in no sulfonation, but in a quantitative hydrolysis of the para methoxyl group and production of syringic acid. The reaction is a very convenient one for the preparation of the latter acid in any desired amount. The identity of the acid was further established by the preparation of its methyl ester and by oxidation to 3,5-dimethoxyquinone.

2. Experimental.

Trimethylgallic acid, $(3,4,5)(CH_3O)_3C_6H_2.COOH$, was prepared by the methylation of gallic acid with dimethyl sulfate and sodium hydroxide in aqueous solution, essentially as described by Graebe and Martz,[5] and by Perkin and Weizmann,[6] purifying the crude acid by recrystallization from very dilute acetic acid, in presence of boneblack. As thus prepared, it formed colorless needles, melting at 168°,[7] in agreement with the results recorded by other investigators. Yield of pure acid, 65%.

---

[1] *Gazz. chim. ital.*, 18, 215 (1888).

[2] *Ber.*, 30, 2330 (1897).

[3] Hertzig and Pollack, *Monatsh.*, 23, 700 (1902); Graebe and Martz, *Ber.*, 36, 215 (1903).

[4] *Ber., Loc. cit.; Ann.*, 340, 221 (1905).

[5] *Ann.*, 340, 219 (1905).

[6] *J. Chem. Soc.*, 89, 1655 (1906).

[7] The melting points recorded in this paper were all taken with Anschütz standard short-scale thermometers unless otherwise stated.

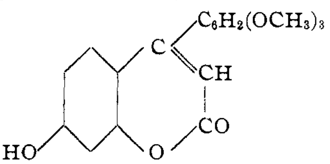
This acid was esterified by suspending it in methyl alcohol and passing in dry hydrogen chloride until solution was complete and the alcohol saturated with the hydrogen chloride. On cooling the solution, the ester separated almost completely, in glistening colorless plates, which were filtered out, washed with methyl alcohol and dried. Yield of practically pure ester, 90–95%. On concentrating the mother liquor and adding water, a further small amount was recovered. Recrystallized from dilute methyl alcohol, it melted at 84°. Powers and Moore,[1] by whom it was first prepared, give its melting point as 84°.

Trimethylgalloyl chloride, $(CH_3O)_3.C_6H_2.COCl$, was prepared from the trimethylgallic acid and phosphorus pentachloride, as described by Perkin and Weizmann.[2] The reaction is a vigorous one. At its close, the phosphorus oxychloride was distilled off under diminished pressure and the residue, which solidified on cooling, was crystallized from ligroin, giving colorless needles, melting at 77–8°. Yield, nearly theoretical.

Ethyl trimethylgalloyl acetoacetate, $(CH_3O)_3C_6H_2.CO.CH(COCH_3).COOC_2H_5$, was obtained by condensing galloyl chloride with acetoacetic ester, in the presence of sodium alcoholate.[3] Eighteen grams of the chloride yielded 15 grams of the product sought. Recrystallized from methyl alcohol, it melted at 86°.

Following the work of the authors cited, it was hydrolyzed with dilute ammonium hydroxide solution, giving ethyl trimethylgalloyl acetate, $(CH_3O)_3C_6H_2.CO.CH_2.COOC_2H_5$. Fifteen grams of the acetoacetic ester gave 9 grams of the acetic ester. Recrystallized from methyl alcohol, it melted at 95°.

β-(3,4,5-Trimethoxyphenyl) Umbelliferone,



—Two grams of ethyl trimethylgalloyl acetate and 0.77 gram resorcinol were dissolved in 15 cc. 73% sulfuric acid at 0°.[4] The solution rapidly turned a deep orange, and on standing over night deposited a mass of yellowish crystals. Ice was added in considerable quantity, the mixture left at 0° for an hour, the crystals were filtered out, washed with water, and recrystallized from alcohol. The umbelliferone was thus obtained as a

---

[1] *J. Chem. Soc.*, **95**, 254 (1909).

[2] *Loc. cit.*

[3] Perkin and Weizmann, *loc. cit.*

[4] Compare Von Pechmann and Duisberg, *Ber.*, **16**, 2126 (1883); Von Pechmann and Hanke, *Ibid.*, **34**, 356 (1901); Von Kostanecki and Weber, *Ibid.*, **26**, 2907 (1893).

colorless micro-crystalline solid, sintering at about 245°, and melting with decomposition at about 253°.

0.2144 g. substance: 0.5162 g. CO_2, 0.0959 g. H_2O. Calcd. for $C_{18}H_{16}O_6$: C, 65.83%; H, 4.94%. Found: C, 65.53%; H, 5.00%.

3,4,5-Trimethoxycinnamic Acid (Methyl Sinapinic Acid), $(CH_3O)_3C_6H_2.CH : CH.COOH$.—Ten grams trimethylgalloyl acetic ester were dissolved in 150 cc. 95% alcohol and 7 grams activated aluminum[1] added. A lively reaction ensued, with production of hydrogen, which was at first largely absorbed. After standing for two days, the mixture was filtered and the insoluble aluminum alcoholate washed with alcohol. Upon concentration of the alcoholic filtrate, a colorless oil of geranium-like odor remained which could not be brought to crystallization. It was therefore dissolved in dilute alcohol and saponified by warming for four hours with dilute sodium hydroxide solution. The alkaline solution was acidified with dilute hydrochloric acid, evaporated to dryness at 100°, the residue extracted with absolute alcohol, the alcoholic extract concentrated to crystals, and the crystals recrystallized from benzene. Colorless needles were obtained, melting at 126.8°. Yield, 5 grams.

0.2176 g. substance: 0.4796 g. CO_2, 0.1160 g. H_2O. Calcd. for $C_{12}H_{14}O_5$: C, 60.50%; H, 5.88%. Found: C, 60.11%; H, 5.93%.

Gadamer[2] obtained this acid by direct methylation of sinapinic acid, and called it, therefore, methylsinapinic acid. It was later prepared by Mauthner[3] from the trimethoxybenzaldehyde by the Perkin reaction. Although our product melts about 3° higher, it was found to be identical with the product of Gadamer and Mauthner. A solution of the acid in chloroform rapidly decolorized a similar solution of bromine.

Syringic Acid, $(3,5)(CH_3O)_2C_6H_2(OH)(4)COOH(1)$.—Thirty grams trimethylgallic acid were added slowly, with constant stirring, to 150 grams 20% fuming sulfuric acid, the temperature being kept below 40°. The gallic acid dissolved with production of a deep red solution and with evolution of heat, and at the same time the characteristic aromatic odor of syringic acid became apparent. The solution was kept at 40° for 30 minutes, and on cooling it set to a crystalline mass. An equal volume of water was added, the mixture let stand for eight hours, and the crystals were then filtered out, washed with cold water and dried. Yield, 25 grams. Recrystallized from water, it was obtained in colorless needles, melting at 204°. Graebe and Martz[4] give the melting point as 204° (corr.).

0.2010 g. substance: 0.4024 g. CO_2, 0.0949 g. H_2O. Calcd. for $C_9H_{10}O_5$: C, 54.54%; H, 5.05%. Found: C, 54.59%; H, 5.22%.

---

[1] Compare Wislicenus, *J. prakt. Chem.*, [2] **54**, 54 (1896).

[2] *Arch. Pharm.*, **235**, 109 (1897); *Ber.*, **30**, 2331 (1897).

[3] *Ibid.*, **41**, 2531 (1908).

[4] *Ann.*, **340**, 220 (1905).

Ten grams of the acid were suspended in 70 cc. methyl alcohol and dry hydrogen chloride passed in until all was dissolved and the solution thoroughly saturated with the hydrogen chloride. It was then allowed to to stand for 30 minutes, evaporated to dryness, and the residue freed from hydrogen chloride by repeated evaporation with methyl alcohol. The residual brownish crystalline mass, recrystallized from water, gave beautiful colorless needles of the hydrated ester, melting at 83–4°. Dehydrated at 110°, the anhydrous ester melted at 106–7°. Yield of anhydrous ester, 8 grams. These melting points agree with the observations of Graebe and Martz.[1]

Two grams of syringic acid and two and a half of sodium chromate were dissolved in 100 cc. of water by warming, and dilute sulfuric acid was added slowly to slight excess. An immediate evolution of carbon dioxide resulted. When cold, the solution was extracted with chloroform, the chloroform evaporated, and the residue recrystallized from acetic acid. The characteristic yellow needles of 3,5-dimethoxyquinone were obtained, melting sharply at 255°, this melting point being unaltered when the substance was mixed with an equal amount of 3,5-dimethoxyquinone prepared in a different synthesis.

3,4,5-Trimethoxytriphenyl Carbinol, $(CH_3O)_3C_6H_2.C(C_6H_5)_2.OH$.—5.2 grams magnesium turnings were placed in a flask connected by means of a brominating tube with a return condenser. Dry ether was added to cover these turnings, then 40 grams of brombenzene, and finally a small crystal of iodine. In a few minutes, a vigorous reaction began, which was moderated from time to time by external cooling, and was completed by warming for an hour at 100°. After cooling, a suspension of 18 grams of finely powdered methyl trimethylgallate in 100 cc. of dry ether was run in slowly. The mixture was let stand for several hours to complete the reaction, after which the magnesium compound was decomposed by the addition of ice and dilute sulfuric acid, the carbinol separating at once as a white, granular solid. Washed with ether and recrystallized from alcohol, it was obtained in colorless elongated hexagonal crystals, melting sharply at 189°; insoluble in water, nearly insoluble in ether, slightly soluble in ligroin, rather easily soluble in methyl or ethyl alcohol, acetic acid, chloroform or benzene. Yield of carbinol, 25 to 27 grams.

0.1971 g. substance: 0.5452 g. CO_2, 0.1113 g. H_2O. Calcd. for $C_{22}H_{22}O_4$: C, 75.42%; H, 6.28%. Found: C, 75.39%; H, 6.29%.

This carbinol exhibits marked halochromism, dissolving in concentrated sulfuric acid with production of a deep red solution. Examined by the method of von Baeyer and Villiger,[2] its basicity lies considerably below that of *p*-methoxytriphenyl carbinol. While triphenyl carbinol itself

---

[1] *Loc. cit.*

[2] *Ber.*, **35**, 3021 (1902).

requires 4.3 cc. of alcohol, per millimole, to discharge the color of the sulfuric-acetic solution, and *p*-methoxytriphenyl carbinol requires 26.9 cc., the 3,4,5-trimethoxytriphenyl carbinol requires only 15.4 cc. From these figures, the relative basicity of the three carbinols would appear to be *p*-methoxytriphenyl : trimethoxytriphenyl : triphenyl = 6.3 : 3.6 : 1. The presence of the *m*-methoxyl groups therefore seems to reduce the basicity of the *p*-methoxyl group in such carbinols.

3,4,5-Trimethoxytriphenyl Methyl Chloride, $(CH_3O)_3C_6H_2.C(C_6H_5)_2Cl$.—Five grams of the carbinol were suspended in 50 cc. dry ether, the whole cooled to 0°, and dry hydrogen chloride passed in until all was in solution, and the solution thoroughly saturated with the gas. The deep red solution which resulted was dried over calcium chloride, filtered off, the filtrate concentrated and cooled to 0°. The chloride separated in elongated prisms, which were washed with dry ether and dried. Yield, 3 grams. Recrystallized from dry ether, colorless crystals were obtained, melting quite sharply at 110°.

0.5000 g. substance: 0.1928 g. AgCl. Calcd. for $C_{22}H_{21}O_3Cl$: Cl, 9.63%. Found: Cl, 9.54%.

It is readily soluble in ligroin, ether or benzene; in alcohol it dissolves with hydrolysis. On standing in the air, it rapidly assumes a reddish color, as it is very sensitive to moisture. A small amount was shaken for a minute with water, filtered quickly, the filtrate acidified with nitric acid and silver nitrate added. A heavy precipitate of silver chloride resulted.

3,4,5-Trimethoxytriphenyl Methane, $(CH_3O)_3C_6H_2.CH(C_6H_5)_2$. — Two grams of the carbinol were suspended in 15 cc. of absolute alcohol and dry hydrogen chloride passed in to saturation. The resulting deep red solution was heated for a short time under a reflux condenser, the alcohol distilled off, and the yellow residue purified by crystallization from alcohol. Fine, colorless needles were obtained, melting at 133°. Yield, 1.6 grams.

0.2334 g. substance: 0.6768 g. CO_2, 0.1411 g. H_2O. Calcd. for $C_{22}H_{22}O_3$: C, 79.04%; H, 6.58%. Found, C, 78.88%; H, 6.71%.

It is insoluble in water, but readily soluble in alcohol, ether, chloroform or benzene.

This easy reduction of the carbinol was scarcely to be expected in the face of the results recorded by Kauffmann.[1] The latter found that when triphenylcarbinol was boiled for an hour with alcoholic hydrochloric acid, it was only partially reduced, and concluded from other results that a methoxyl group in the para position facilitated but little such a reduction, while in the meta position it had possibly a slight hindering effect.

In the above reduction, we observed no resinification.[2]

---

[1] *Ber.*, **38**, 2702 (1905); **41**, 4423 (1908).

[2] Compare Kauffmann and Pannwitz, *Ber.*, **45**, 766 (1912).

3,4,5-Trimethoxytriphenyl Pyrryl Methane, $(CH_3O)_3C_6H_2.C(C_6H_5)_2.C_4H_4N$.—Two grams of the carbinol and 0.7 gram of pyrrole were dissolved in 10 cc. of glacial acetic acid by warming, and the dirty green solution heated for 15 minutes under a reflux. On cooling, no crystals separated, so the acetic acid and excess of pyrrole were removed by distillation under diminished pressure, and the sticky green residue was extracted with boiling ligroin, considerable resinous material remaining undissolved. The ligroin extracts, on evaporation, deposited first some resin, and finally rosettes of white prisms of the pyrryl compound. These latter were separated mechanically and recrystallized from acetic acid, giving colorless hexagonal crystals, melting at 155° (uncorr.). Yield, 0.7 gram.

0.4263 g. substance: 12.45 cc. N_2 (21° and 763 mm, over H_2O). Calcd. for $C_{26}H_{35}O_3N$: N, 3.26%. Found: N, 3.35%.

The compound is readily soluble in alcohol, acetic acid, chloroform or benzene; less soluble in methyl alcohol or ligroin; and insoluble in water.

Attempts to avoid resinification by shorter boiling with acetic acid were unsuccessful, as complete condensation could not be accomplished in less than 15 minutes' heating, whereas much longer boiling caused entire resinification.[1]

3,4,5-Trimethoxy-α-methyl Styrene, $(CH_3O)_3C_6H_2.C(CH_3) : CH_2$.—38 grams of methyl iodide, dissolved in dry ether, were allowed to act upon 6.3 grams magnesium turnings. The reaction was vigorous, with nearly complete solution of the magnesium. When this reaction was over, a suspension of 20 grams of methyl trimethylgallate in 100 cc. of dry ether was added slowly. The mixture was allowed to stand for several hours, and the magnesium compound was then decomposed by ice and dilute sulfuric acid. The ethereal layer was separated, washed with water, dried over calcium chloride, filtered, and the filtrate evaporated. There remained a yellowish oil, which was probably the impure carbinol, since it was only partially volatile with steam, while the styrene itself is quite easily volatile.

All attempts to bring this oil to crystallization having failed, it was distilled under diminished pressure. At 193°, and a pressure of 40 mm., a colorless oil passed over and soon solidified to a colorless crystalline mass. Yield, 12 grams.

Some of this product was subjected to a steam distillation. It passed over completely, solidifying in the receiver to colorless needles, melting sharply at 37°. These were separated, dried and analyzed, with the following results:

0.2867 g. substance: 0.7249 g. CO_2, 0.2000 g. H_2O. Calcd. for $C_{12}H_{16}O_3$: C, 69.24%; H, 7.69%. Found: C, 69.09%; H, 7.74%.

The substance is readily soluble in alcohol, ether, acetone, acetic acid,

---

[1] Compare Patzevitch, *Inaug. Dissert., Grenoble,* 1911.

chloroform, ligroin or carbon disulfide. In chloroform solution, it decolorizes the calculated amount of bromine, but on attempting to remove the solvent, hydrobromic acid is removed also, leaving a brown oily residue.

This styrene is isomeric with the naturally occurring elemicin, and with the isoelemicin obtained by Semmler[1] by distilling elemicin over sodium.

3,4,5-Trimethoxy Acetophenone, $(CH_3O)_3C_6H_2.CO.CH_3$.—Six grams of the above styrene were dissolved in 25 cc. of 70% acetic acid, the solution placed in a Peligot tube, warmed to 50°, and ozone passed through it for four hours. The solution gradually assumed a deep reddish brown color, and the presence of formaldehyde in the escaping gases was indicated by the odor and by the Schiff reagent. The solution was then transferred to a distilling flask and subjected to distillation under diminished pressure. After the removal of the acetic acid, a light yellow oil distilled over at 220–4° and 40 mm. pressure. Some tar remained in the flask at the close of the distillation. The yellow oil soon solidified to a light yellow crystalline mass. Recrystallized from ligroin, it was obtained in colorless glistening needles, melting at 78°. Yield, 2.2 grams.

0.1976 g. substance: 0.4544 g. CO_2, 0.1171 g. H_2O. Calcd. for $C_{11}H_{14}O_4$: C, 62.87%; H, 6.66%. Found, C, 62.70%; H, 6.59%.

This ketone was first obtained by Mauthner,[2] by the action of diazo methane upon trimethylgallic aldehyde, and also by the hydrolysis of trimethylgalloyl acetic ester. He describes it as melting at 72°, or 6° lower than our product. The identity of the two, however, was established by the preparation of the *p*-nitrophenyl hydrazone, which Mauthner describes as particularly characteristic. As prepared from our product, this derivative was found to agree in all respects with Mauthner's.

p-Nitrophenyl Hydrazone.—0.2 gram of the ketone was dissolved in 4 cc. of 50% acetic acid and a solution of 0.2 gram of *p*-nitrophenyl hydrazine in 4 cc. of 50% acetic acid was added. On warming, the hydrazone separated in brown needles, which were filtered off when the solution was cold, washed with dilute acetic acid, and recrystallized from alcohol, giving brown needles, melting at 195–6° (uncorr.).

3,4,5-Trimethoxy Chalkone, $(CH_3O)_3C_6H_2.CO.CH : CH.C_6H_5$.—Half a gram of the above acetophenone and 0.25 gram of benzaldehyde were dissolved in 10 cc. of alcohol, and 2.5 cc. of 45% potassium hydroxide solution added. On standing for some time, yellow needles began to separate from the solution. The mixture was left over night, and the separated chalkone then filtered out, washed, and recrystallized from alcohol. Pale yellow needles were obtained, melting at 78–8.5°. Yield, 0.4 gram.

---

[1] *Ber.*, 41, 1769, 1918 (1908).

[2] *J. prakt. Chem.*, [2] **82**, 275 (1910).

0.1297 g. substance: 0.3447 g. CO_2, 0.0704 g. H_2O. Calcd. for $C_{18}H_{18}O_4$: C, 72.49%; H, 6.03%. Found: C, 72.46%; H, 6.04%.

Bargellini and Avrutin[1] have prepared recently the isomeric 2,4,5-trimethoxy chalkone.

3,4,5-Trimethoxyphenyl Diethyl Carbinol, $(CH_3O)_3C_6H_2.C(C_2H_5)_2.OH$.—The necessary Barbier-Grignard reagent was prepared from 6.3 grams of magnesium turnings and 29 grams of ethyl bromide in dry ether. It was acted on by 20 grams of methyl trimethylgallate suspended in 100 cc. of dry ether. After the first vigorous reaction was over, the mixture was allowed to stand for four hours. The magnesium compound was then decomposed, as usual, with ice and dilute sulfuric acid, the ether layer separated, washed with water, dried over calcium chloride, and evaporated to dryness. A light yellow oil remained which partly solidified to a crystalline mass. These crystals were separated, washed with ligroin, and recrystallized from ligroin. As thus obtained, they formed beautiful, blunt, colorless needles, melting at 74°, and decomposing with loss of water at 147°. Yield, 6 grams.

0.1995 g. substance: 0.4831 g. CO_2, 0.1543 g. H_2O. Calcd. for $C_{14}H_{22}O_4$: C, 66.15%; H, 8.68%. Found: C, 66.03%; H, 8.60%.

The substance is easily soluble in methyl or ethyl alcohol, ether, acetone, chloroform, benzene or toluene; moderately soluble in ligroin; insoluble in water. It is quite unstable and passes into the olefin so readily that its isolation and purification were matters of considerable difficulty. In decomposing the above magnesium compound there was always obtained a mixture of the carbinol and olefin.

3-(3,4,5-Trimethoxyphenyl)-pentene(2), $(CH_3O)_3C_6H_2.C(C_2H_5) : CH.CH_3$, was separated in quantity from the mother liquors from the crystallization of the preceding carbinol. These ligroin mother liquors were combined, the ligroin distilled off, and the residual yellow oil distilled under diminished pressure. At 210–20° and 40 mm. pressure, a pale yellow oil passed over. On rectification, the oil was obtained practically colorless, and of the same boiling point as before. Yield, 12 grams.

This olefin resulted also from the following experiment: three grams of the carbinol were dissolved in 30 cc. of ether, the solution cooled to 0° and saturated with dry hydrogen chloride. The ether was then removed at low temperature, the residue taken up with fresh ether, dried over calcium chloride, and the ether again evaporated. This residue contained no chlorine, and proved to be identical with the pentene described above.

The following analyses and experiments were conducted with the product of the first method of preparation.

---

[1] *Gazz. chim. ital.*, 40, II, 346 (1910).

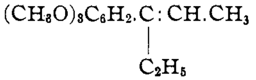
0.2739 g. substance: 0.7121 g. CO_2, 0.2057 g. H_2O. Calcd. for $C_{14}H_{20}O_3$: C, 71.19%; H, 8.47%. Found: C, 70.82%; H, 8.35%.

The substance is easily soluble in alcohol, ether, ligroin, chloroform or benzene; insoluble in water; $n_D^{20} = 1.53600$; $d_{20} = 1.0462$.

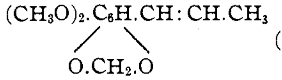
From the equation

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d_t} = MR,$$

the observed molecular refraction is 70.37; while that calculated from the Brühl-Conrady tables is 67.9. The compound thus shows an exaltation in molecular refraction of 2.47, corresponding rather closely to the exaltation of 2.3 shown by isapiol,[1] a body of somewhat similar structure:



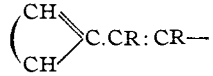
$(CH_3O)_3C_6H_2.\underset{C_2H_5}{C}:CH.CH_3$



$\underset{O.CH_2.O}{(CH_3O)_2.C_6H}.CH:CH.CH_3$

(Isapiol)

It should be noted that this exaltation is considerably greater than was to have been expected from the observation of Eisenlohr,[2] who states that the exaltation from a molecule of the general structure



lies in the neighborhood of 0.45.

The behavior of this olefin with bromine is much like that of the styrene already described. Two grams of the pentene and the calculated amount of bromine were brought together in chloroform solution. The bromine was absorbed and the solution remained momentarily colorless; but on standing hydrobromic acid was given off quite rapidly, the color of the solution passing through reddish violet to a final dirty green. On evaporating the chloroform, there remained a dark green oily residue which was not further examined.

3,4,5-Trimethoxy Propiophenone, $(CH_3O)_3C_6H_2.CO.C_2H_5$.—Eight grams of the above pentene were dissolved in 25 cc. of 70% acetic acid and ozone passed through the warm solution for four hours. A deep reddish brown solution resulted, and the presence of acetic aldehyde was indicated in the escaping gases. This solution was then distilled under reduced pressure. After the removal of the acetic acid, a heavy yellow oil passed over at 210° and 40 mm. This oil solidified to a brownish crystalline mass on standing. It was recrystallized from ligroin and then appeared in glistening colorless needles, melting at 53.5°. Yield, 3.4 grams.

0.2014 g. substance: 0.4740 g. CO_2, 0.1290 g. H_2O. Calcd. for $C_{12}H_{16}O_4$: C, 64.30%; H, 7.14%. Found: C, 64.19%; H, 7.15%.

The compound is easily soluble in alcohol, ether, chloroform, acetic acid or benzene; moderately soluble in ligroin; insoluble in water.

---

[1] Eykmann, *Ber.*, **23**, 863 (1889).

[2] "Spectrochemie organischer Verbindungen," Stuttgart, **1912**.

p-Nitrophenyl Hydrazone.—0.2 gram of the above ketone and a similar amount of *p*-nitrophenyl hydrazine were each dissolved in 4 cc. of 50% acetic acid, the two solutions mixed and the mixture warmed for 30 minutes at 100°. The hydrazone separated in dark reddish brown crystals. When the solution had been thoroughly cooled, the separated hydrazone was filtered out, washed with acetic acid, and recrystallized from alcohol. It was thus obtained in dark reddish brown needles, somewhat resembling chromic anhydride, and melting at 183–4°. Yield, 0.22 gram.

0.1627 g. substance: 16.65 cc. N_2 (21° and 773.5 mm. over H_2O). Calcd. for $C_{18}H_{21}O_5N_3$: N, 11.70%. Found: N, 11.57%.

4 - (3,4,5 - Trimethoxyphenyl) - heptene(3), $(CH_3O)_3C_6H_2.C(CH_2.C_2H_5):$-$CH.C_2H_5$.—The necessary Barbier-Grignard reagent was prepared from 6.3 grams of magnesium turnings and 40 grams of normal propyl iodide, and 20 grams of methyl trimethylgallate were condensed with it in the manner already described in the preceding pages. The magnesium compound was decomposed with ice and dilute sulfuric acid, the ether layer separated, washed, dried, and evaporated. The light yellow oil which remained could not be crystallized, so it was distilled under diminished pressure. It distilled almost completely at 215–8° at 40 mm. pressure, as a pale yellow oil.

0.1877 g. substance: 0.5001 g. CO_2, 0.1530 g. H_2O. Calcd. for $C_{16}H_{24}O_3$: C, 72.72%; H, 9.09%. Found: C, 72.68%; H, 9.06%.

$n_D^{20} = 1.52877$; $d_{20} = 1.0300$. Molecular refraction: observed, 79.12; calculated, 77.12. Here, too, considerable exaltation is evident.

The heptene dissolves in alcohol, ether, ligroin, acetic acid, chloroform or benzene; but is insoluble in water. With bromine, it shows a behavior similar to that of the pentene already described.

No carbinol at all was encountered among the products of the above reaction.

3,4,5-Trimethoxy Butyrophenone, $(CH_3O)_3C_6H_2.CO.CH_2.C_2H_5$.—Seven grams of the above heptene were dissolved in 35 cc. of dilute acetic acid, the solution warmed, and ozone passed through it for 15 hours, by which time it no longer decolorized a bromine solution. The solution was then subjected to distillation under reduced pressure. After the acetic acid was removed, a heavy, yellow oil distilled over at 218–20° and 40 mm. pressure. This oil slowly solidified to a crystalline, somewhat oily mass. Yield, 4.5 grams.

Great difficulty was experienced in purifying this ketone, as it is easily soluble in methyl or ethyl alcohol, ether, chloroform, carbon tetrachloride, ligroin, carbon disulfide, acetone, ethyl acetate, ethyl bromide, pyridine, benzene or toluene. From dilute methyl alcohol, or dilute acetic acid, it tends to separate as an oil. It was finally obtained in long, colorless needles from dilute methyl alcohol, melting at 51–52.5°, which were still somewhat impure.

p-Nitrophenyl Hydrazone.—Equal weights (0.5 gram of each) of the ketone and of *p*-nitrophenyl hydrazine were each dissolved in 10 cc. of 50% acetic acid, the solutions mixed, and the mixture warmed at 100° for 30 minutes. A heavy, red oil separated and gradually solidified to a crystalline mass. The separated hydrazone was removed, washed with dilute acetic acid, and recrystallized from alcohol. Dark brownish red needles were obtained, melting sharply at 160°. Yield, 0.6 gram.

0.1263 g. substance: 13.1 cc. N_2 (21.5° and 756 mm. over H_2O). Calcd. for $C_{19}H_{23}O_5N$: N, 11.26%. Found: N, 11.40%.

5-(3,4,5-Trimethoxyphenyl)-2,8-dimethylnonene(4), $(CH_3)_2CH.CH_2.CH:C[C_6H_2(OCH_3)_3]CH_2.CH_2.CH(CH_3)_2$.—The reaction was carried out in the usual way, employing 6 grams of magnesium turnings, 47 grams of isoamyl iodide, and 18 grams of methyl trimethylgallate. After decomposing the magnesium compound with ice and dilute sulfuric acid, the ether layer was separated, washed, dried, and evaporated. A yellow oil remained which deposited a few crystals on standing. The addition of ligroin caused a considerable increase in the quantity of these crystals. They were filtered out, washed with ligroin and dried. Yield, 3.5 grams. Recrystallized from benzene, the substance was obtained in colorless rhombohedral crystals, melting at 109–10°, and showing no sign of decomposition at 265°. It distils unchanged at 218° and 40 mm. pressure.

I. 0.2003 g. substance: 0.4148 g. CO, 0.1117 g. H_2O.
II. 0.1983 g. substance: 0.4103 g. CO_2, 0.1031 g. H_2O.
III. 0.1914 g. substance: 0.3981 g. CO_2, 0.1000 g. H_2O.

Found.	Carbon, %.	Hydrogen, %.	Oxygen, %.
I	56.48	6.19	....
II	56.98	5.77	....
III	56.74	5.79	....
Average	56.72	5.92	37.36

Analysis I was run on undistilled material, II and III on the distilled.

These results correspond quite closely to the formulas $C_{12}H_{14}O_6$ and $C_{12}H_{16}O_6$:

	Carbon.	Hydrogen.	Oxygen.	M. W.
$C_{12}H_{14}O_6$	56.7	5.5	37.8	254
$C_{12}H_{16}O_6$	56.3	6.2	37.5	256

Cryoscopic molecular-weight determinations in benzene solution gave the following results:

I. 0.5026 gram undistilled material, in 17.5735 grams benzene, gave a freezing-point depression of 0.629°. Super-cooling = 0.43°. M. W. = 228.5.

II. 0.5005 gram distilled material, in 17.5735 grams benzene, gave a freezing-point depression of 0.537°. Super-cooling = 0.21°. M. W. = 260.6.

Average of the above determinations, 244.6.

The substance is easily soluble in alcohol, ether, chloroform, or benzene, difficultly soluble in ligroin or water. Its aqueous solution is neutral to indicators, and with dilute neutral potassium permanganate solution in the cold is entirely consumed. It does not decolorize a chloroform solution of bromine. Warmed with phosphorus pentachloride, a reaction occurs. Attempts to form an oxime or a phenylhydrazone failed. The identity of the compound is still undisclosed.

The nonene itself was found in the ligroin mother liquors from the above crystals. It is the chief product of the reaction, no carbinol having been encountered. These ligroin mother liquors were evaporated to dryness and the residual yellow oil distilled under diminished pressure. At 235–7° and 40 mm., a light yellow oil passed over. Yield, 12 grams.

0.2224 g. substance: 0.5930 g. CO_2, 0.1949 g. H_2O. Calcd. for $C_{20}H_{32}O_3$: C, 72.72%; H, 9.69%. Found, C, 72.71; H, 9.71%.

Observed molecular refraction, 96.03; molecular refraction as calculated from the Brühl-Conrady tables, 95.53. This exaltation of 0.50 agrees quite closely with the figure of 0.45 found by Eisenlohr[1] for compounds of this type.

The action of bromine upon a chloroform solution of the nonene was similar to that recorded for the preceding olefins. An attempt to split the nonene with ozone, in the hope of getting the corresponding valerophenone, was discontinued because the oxidation proceeded so slowly that even after passing ozone through the solution for 20 hours, it still decolorized bromine.

3,4,5-Trimethoxyphenyl Dibenzyl Carbinol, $(CH_3O)_3C_6H_2.C(CH_2.C_6H_5)_2.OH$.—The reaction was carried out as described for the other carbinols, using 6.5 grams magnesium turnings, 35 grams benzyl chloride and 20 grams methyl trimethylgallate, in presence of dry ether. After decomposing the magnesium compound with ice and dilute sulfuric acid, the ether layer was separated, washed with water, dried with calcium chloride, and concentrated. On cooling, the carbinol separated practically pure. Recrystallized from methyl alcohol, it formed elongated prisms, melting at 116–7°. Yield, 22 grams.

0.2011 g. substance: 0.5611 g. CO_2, 0.1245 g. H_2O. Calcd. for $C_{24}H_{26}O_4$: C, 76.2%; H, 6.88%. Found: C, 76.11%; H, 6.88%.

It is readily soluble in methyl or ethyl alcohol, chloroform or benzene, sparingly soluble in ligroin or ether, and insoluble in water. Unlike most

---

[1] *Loc. cit.*

of the carbinols described in the foregoing pages, this one is quite stable, showing no tendency to decompose even when heated above 350°.

3,4,5-Trimethoxy-α-benzyl Stilbene, $(CH_3O)_3C_6H_2.C(CH_2.C_6H_5) : CH.-C_6H_5$.—Ten grams of the carbinol were suspended in 50 cc. of dry ether, the whole cooled to 0° and saturated with dry hydrogen chloride. The carbinol dissolved. After allowing the resulting colorless solution to stand for a few minutes, the ether and hydrogen chloride were evaporated at low temperature, the residue dissolved in fresh ether, this ether solution dried with calcium chloride, and the ether driven off again. A viscous light yellow oil remained which, after standing for several weeks, finally crystallized. Recrystallized from ligroin, it formed colorless rhombohedral crystals, which melted sharply at 93°. Yield, 8 grams.

This product, instead of proving to be the expected chloride, turned out to be the stilbene. It contained no chlorine.

0.2003 g. substance: 0.5841 g. CO_2, 0.1193 g. H_2O. Calcd. for $C_{24}H_{24}O_3$: C, 80.00%; H, 6.67%. Found: C, 79.67%; H, 6.62%.

It is readily soluble in alcohol, ether, chloroform, carbon disulfide or benzene, moderately soluble in ligroin or pyridine, insoluble in water. It distils with slight decomposition at 320° under a pressure of 20 mm.

When this stilbene and the calculated amount of bromine were brought together in chloroform solution, the color of the bromine immediately disappeared, but on attempting to evaporate the chloroform there was a copious evolution of hydrogen bromide and only a cherry-red tar remained.

In view of the considerable stability of the carbinol, and the evident instability of the dibromide, the production of the stilbene in the above reaction is probably to be ascribed to the intermediate formation of the chloride, with subsequent elimination of hydrogen chloride.

3,4,5-Trimethoxy Desoxybenzoin, $(CH_3O)_3C_6H_2.CO.CH_2.C_6H_5$.—Five grams of the stilbene were dissolved in 35 cc. of 70% acetic acid,[1] the solution transferred to a Peligot tube immersed in a bath at 70°, and ozone passed through it for three hours. The solution gradually turned a reddish brown color and a strong odor of benzaldehyde was noticed. The acetic acid was finally distilled off under diminished pressure and the brown residue crystallized from methyl alcohol. Beautiful, colorless needles were obtained, melting sharply at 99°. Yield, 2 grams.

0.1994 g. substance: 0.5223 g. CO_2, 0.1129 g. H_2O. Calculated for $C_{17}H_{18}O_4$: C, 71.32%; H, 6.29%. Found: C, 71.42%; H, 6.29%.

It is readily soluble in methyl or ethyl alcohol, ligroin, ether, chloroform or acetic acid, but is insoluble in water.

p-Nitrophenyl Hydrazone.—This was prepared by separately dissolving equal amounts (0.2 gram of each) of the ketone and of *p*-nitrophenyl hydrazine, each in 4 cc. of 50% acetic acid, mixing these solutions and

---

[1] Compare Otto, *Ann. chim. phys.*, [8] 13, 77 (1908); D. R. P. No. 97,620.

warming the mixture. The hydrazone separated in orange needles. When the mixture had cooled thoroughly, the crystals were filtered out, washed with dilute acetic acid, and recrystallized from alcohol. Fine orange needles resulted, which sintered at 185° and gave a clear melt at 194.° Yield, 0.19 gram.

0.1147 g. substance: 10.15 cc. N_2 (21° and 773.5 mm. over H_2O). Calcd. for $C_{23}H_{23}O_5N_3$: N, 9.97%. Found: N, 10.00%.

3. Summary.

1. The study of methoxylated carbinols has been extended by an investigation of a series of carbinols obtained by the action of various magnesium reagents upon trimethylgallic ester.

2. The 3,4,5-trimethoxytriphenyl carbinol has been found to be more strongly basic than triphenyl carbinol, but less so than *p*-methoxytriphenyl carbinol.

3. The trimethoxyphenyl dialkyl carbinols are generally unstable, losing water readily to form the olefin; whereas the trimethoxyphenyl dibenzyl carbinol is quite stable.

4. The action of isoamyl magnesium iodide upon trimethylgallic ester appears to follow a somewhat abnormal course, giving an unidentified by-product, in addition to the olefin.

5. Trimethoxyphenyl-diethyl and -dibenzyl methyl chlorides are very unstable.

6. A series of olefins of the type $(CH_3O)_3C_6H_2.CR : CHR$ have been prepared, and it has been shown that these substances do not form stable dibromides. Certain of these hydrocarbons show marked exaltation in molecular refraction.

7. A series of new 3,4,5-trimethoxyphenyl ketones has been obtained and examined.

8. New syntheses are recorded of 3,4,5-trimethoxy cinnamic acid, of syringic acid and of 3,4,5-trimethoxy acetophenone.

ORGANIC LABORATORY, COLUMBIA UNIVERSITY,
NEW YORK.

SOME ORGANIC PREPARATIONS.

BY L. P. KYRIAKIDES.

Received January 2, 1914.

During the past three years we have had the occasion to use many organic reactions, and as the result of our study, we have been able to improve some of them.

The substances prepared and described are mainly related to the synthesis of the unsaturated hydrocarbons with conjugated double bonds, which of late years have become so important in the synthetic production of rubber-like masses.