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for osajin and pomiferin and in addition establish the presence of the isopropylidene group COLUMBUS. OHIO

in each of these pigments.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

#### Osage Orange Pigments. X.<sup>1</sup> Oxidation

### BY M. L. WOLFROM AND SAM M. MOFFETT

In continuation of our studies concerning the structure of osajin and pomiferin, the pigments of the fruit of the osage orange (Maclura pomifera Raf.), we have applied to them the CH<sub>3</sub>-C group

analysis of Kuhn and co-workers.<sup>2</sup> The results, shown in Table I, are consistent with the presence of two CH<sub>3</sub>-C groups in the molecule of both pigments. Hydrogenation of the double bonds in the compounds (hexahydro-osajin and tetrahydropomiferin) does not decrease the assay value. The Kuhn procedure involves the use of strong acids (sulfuric and chromic) and under these conditions the pigments are very probably initially isomerized,<sup>3</sup> even in the case of the fully methylated derivatives (osajin dimethyl ether and pomiferin trimethyl ether). This isomerization involves the disappearance of a double bond. 2-Methyl tetrahydro-osajin dimethyl ether<sup>4</sup> shows (Table I) one added increment of methyl

carbon as is required by its structure.

Oxidation of osajetin dimethyl ether<sup>4</sup> (I) and of pomiferitin trimethyl ether<sup>5</sup> (III) by alkaline hydrogen peroxide yielded homoanisic (II) and homoveratric (IV) acids, respectively. Oxidation of the fully methylated ketones, osajetin trimethyl ether (V) and pomiferitin tetramethyl ether (VII), however, yielded anisic (VI) and veratric (VIII) acids, respectively.

Tetrahydro-osajetin<sup>4</sup> dimethyl ether was com-

(1) Preceding publication in this series, M. L. Wolfrom and J. Mahan, THIS JOURNAL, 64, 308 (1942).

(4) M. L. Wolfrom, J. E. Mahan, P. W. Morgan and G. F. Johnson, ibid., 63, 1248 (1941).

(5) M. L. Wolfrom and J. E. Mahan, ibid., 63, 1253 (1941).

pletely methylated to the trimethyl ether (X) and this was oxidized successfully with selenium dioxide<sup>6</sup> to the diketone (XI), designated tetrahydro-osajetinone trimethyl ether. The analogous



derivative of pomiferin, designated tetrahydropomiferitinone tetramethyl ether (XIV), was prepared from tetrahydropomiferitin tetramethyl ether (XIII) in a similar manner. XI also was prepared by the deoximation of the isonitroso derivative (IX) of X.

The two diketones were then oxidized with alkaline hydrogen peroxide.7 Tetrahydro-osajetinone trimethyl ether (XI) yielded anisic acid and an acid (XII), C<sub>16</sub>H<sub>21</sub>O(OCH<sub>3</sub>)<sub>2</sub>COOH, designated tetrahydro-osajylic acid dimethyl ether. This oxidation was effected without carbon loss and the entity XII represents all of the remaining carbon skeleton of the original tetrahydro-osajin,

<sup>(2)</sup> R. Kuhn and F. L'Orsa, Z. angew. Chem., 44, 847 (1931); R. Kuhn and H. Roth, Ber., 66, 1274 (1933).

<sup>(3)</sup> M. L. Wolfrom, F. L. Benton, A. S. Gregory, W. W. Hess, J. Mahan and P. W. Morgan, THIS JOURNAL, 63, 422 (1941).

<sup>(6)</sup> Cf. H. L. Riley, J. F. Morley and N. A. C. Friend, J. Chem. Soc., 1875 (1932).

<sup>(7)</sup> Cf. E. Weitz and A. Scheffer, Ber., 54, 2332 (1921).



 $R = C_{10}H_{19}O$ 

less the anisic acid, and the carbon lost as formic acid in the alkaline degradation<sup>4</sup> of the tetrahydro-osajin dimethyl ether to tetrahydro-osajetin dimethyl ether. Tetrahydropomiferitinone tet-

#### TABLE I

Amount of Acetic Acid Produced by the Oxidation of Osajin and Pomiferin (and Derivatives) with Chromic Acid

Substance	Moles AcOH per mole substance
Osajin	1.83
Pomiferin	1.85
Iso-osajin	1.85
Isopomiferin	1.73
Osajin dimethyl ether	1.67
Pomiferin trimethyl ether	1.78
Hexahydro-osajin	1.81
Tetrahydropomiferin	1.87
2-Methyltetrahydro-osajin	
dimethyl ether	2.92
Thymol	1.50

The procedure used was a macro procedure adapted from the micro procedure of Kuhn and Roth<sup>2</sup> and the macro method of Kuhn and L'Orsa.<sup>2</sup> Thymol was run as a control – Kuhn and L'Orsa report the value 1.40 for this substance. ramethyl ether (XIV) yielded veratric acid and the same tetrahydroosajylic acid dimethyl ether.

The carbon nuclei of osaiin and pomiferin are therefore identical. Since it has been demonstrated<sup>1</sup> that both pigments contain one isopropylidene group, they are therefore alike in the position of one of the two double bonds present in each. It is probable that the position of the other double bond likewise is the same, but this will require further proof.

### Experimental

Osajetin Trimethyl Ether (V).—Osajetin dimethyl ether<sup>4</sup> (10 g.) was dissolved in acetone (400 cc.), the solution heated to boiling under reflux (mechanical stirring) and dimethyl sulfate (10 cc.) added. Then over a period of one hour dimethyl sulfate

(110 cc.) and potassium hydroxide (120 cc. of a 42.5% solution) were added dropwise at an equal rate after which the solution was refluxed for fifteen minutes longer. The solution, initially yellow, became colorless when about half of the dimethyl sulfate had been added. The cooled solution was poured into 2.5 liters of ice and water and the resultant suspension made slightly alkaline with potassium hydroxide. After standing over-night, the precipitate was removed by filtration; yield after one recrystallization from methanol (decolorizing charcoal), 9.5 g., m. p. 74.5–75°. Pure material was obtained on further crystallization from methanol; m. p. 75.5–76°, unchanged on further crystallization from petroleum ether.

Osajetin trimethyl ether crystallized in colorless elongated prisms and gave no coloration with ferric chloridealcohol.

Anal. Calcd. for C<sub>24</sub>H<sub>25</sub>O<sub>2</sub>(OCH<sub>3</sub>)<sub>3</sub>: C, 74.27; H, 7.39; OCH<sub>3</sub>, 21.32. Found: C, 74.10; H, 7.33; OCH<sub>3</sub>, 21.60.

Pomiferitin Tetramethyl Ether (VII).—Pomiferitin trimethyl ether<sup>5</sup> (10 g.) was methylated according to the procedure described above for the preparation of osajetin trimethyl ether except that 80 cc. of dimethyl sulfate and 80 cc. of the 42.5% potassium hydroxide solution were employed. The crude oil obtained on pouring the reaction mixture into ice and water was removed by filtration on Super-cel (Johns-Manville) and crystallized from methanol (decolorizing charcoal); yield 6.7 g., m. p. 61.5–63°. Pure Pomiferitin tetramethyl ether crystallized in colorless, mica-like flakes and gave no coloration with ferric chloridealcohol.

Anal. Calcd. for C<sub>24</sub>H<sub>22</sub>O<sub>2</sub>(OCH<sub>3</sub>)<sub>4</sub>: C, 72.06; H, 7.35; OCH<sub>3</sub>, 26.59. Found: C, 71.79; H, 7.12; OCH<sub>3</sub>, 26.56.

Anisic Acid from Osajetin Trimethyl Ether .-- Osajetin trimethyl ether (1 g.) was dissolved in hot acetone (45 cc.) and 25 cc. of a 5% aqueous potassium hydroxide solution added. An amount of 80 cc. of hydrogen peroxide (30%)was then added dropwise under reflux over a period of 5.5 hours with the occasional addition of more acetone and alkali (42.5% potassium hydroxide) as required to maintain the solution alkaline and non-turbid. To the cooled solution was then added 20 cc. of a saturated aqueous solution of sodium bisulfite. The resultant solution was acid to litmus and non-oxidizing toward potassium iodide. The acetone was removed by partial concentration of the solution. Some crude anisic acid separated at this point on cooling and standing: yield 80 mg., m. p. 173-177°. The solution was extracted with ether and the ethereal extract (A) was washed with a saturated aqueous sodium bicarbonate solution. The sodium bicarbonate washings were acidified with hydrochloric acid and extracted with ether. The ethereal extract was concentrated to low volume and crystallization ensued on the addition of ethanol; yield 140 mg., m. p. 177-178°. This material was combined with the previously isolated 80 mg. and further purified from hot water; m. p. 179-180°, unchanged on admixture with an authentic specimen of anisic acid of m. p. 179.6-180°. The ethereal extract A, after removal of the ether soluble acid fraction with sodium bicarbonate, was separated into the ether-soluble neutral and phenolic fractions by extraction with aqueous potassium hydroxide. Only traces of amorphous material were found in these fractions.

Veratric Acid from Pomiferitin Tetramethyl Ether.— Pomiferitin tetramethyl ether (715 mg.) was oxidized in dilute acetone solution with alkaline hydrogen peroxide as described above for the oxidation of osajetin trimethyl ether. The ether-soluble acid fraction yielded veratric acid; yield 175 mg., m. p. 170–176°. Pure material was obtained on further crystallization from hot water; yield 80 mg., m. p. 178–179°, unchanged on admixture with an authentic specimen of veratric acid of m. p. 179.5°. Only traces of amorphous material were found in the ethersoluble neutral and phenolic fractions.

Homoanisic Acid from Osajetin Dimethyl Ether.—Osajetin dimethyl ether<sup>4</sup> (1 g.) was dissolved in hot acetone (25 cc.) and 25 cc. of a 5% aqueous potassium hydroxide solution added. An amount of 12 cc. of hydrogen peroxide (30%) was then added under reflux. After refluxing for fifty minutes, 5 cc. more of 30% hydrogen peroxide was added and refluxing was maintained for a total of two hours. To the cooled solution was then added 1 cc. of a saturated aqueous solution of sodium bisulfite. The resultant solution was non-oxidizing toward potassium iodide and was made acid to litmus with hydrochloric acid. The acetone was removed by partial concentration of the solution. The ether-soluble acid fraction was isolated as described above under the oxidation of osajetin trimethyl ether; yield 150 mg., m. p. 82-83°. Pure material was obtained on further crystallization from hot water; m. p. 85-85.5°, unchanged on admixture with an authentic specimen of homoanisic acid of m. p. 86°. Only traces of amorphous material were found in the ether-soluble neutral and phenolic fractions.

Homoveratric Acid from Pomiferitin Trimethyl Ether.— Pomiferitin trimethyl ether<sup>6</sup> (1 g.) was oxidized in dilute acetone solution with alkaline hydrogen peroxide as described above for the oxidation of osajetin dimethyl ether. The ether-soluble acid fraction gave homoveratric acid; yield 260 mg., m. p. 94–96°. Pure material was obtained on further crystallization from hot water; yield 200 mg., m. p. 96.5–97°, unchanged on admixture with an authentic specimen of homoanisic acid of m. p. 97–97.5°. Only traces of amorphous material were found in the ethersoluble neutral and phenolic fractions.

Tetrahydro-osajetin Trimethyl Ether (X).—Tetrahydroosajetin dimethyl ether<sup>4</sup> (10 g.) was methylated as described above for the preparation of osajetin trimethyl ether. The crude product obtained on pouring the reaction mixture into ice and water was removed by filtration; yield 10.9 g., m. p. 86-87°. Pure material was obtained on further crystallization from ethanol-water; m. p. 92°, unchanged on further crystallization from petroleum ether.

The substance crystallized in colorless elongated prisms and gave no coloration with ferric chloride-alcohol.

Anal. Calcd. for C<sub>24</sub>H<sub>27</sub>O<sub>2</sub>(OCH<sub>8</sub>)<sub>3</sub>: C, 73.60; H, 8.24; OCH<sub>3</sub>, 21.13. Found: C, 73.44; H, 8.09; OCH<sub>3</sub>, 21.33.

Tetrahydropomiferitin Tetramethyl Ether (XIII).— Tetrahydropomiferitin trimethyl ether<sup>5</sup> (10 g.) was methylated as described above for the preparation of osajetin trimethyl ether. The crude oil obtained on pouring the reaction mixture into ice and water was removed by extraction with ether. The oil obtained from the ethereal extract after solvent removal was boiled with water, isolated by decantation and was obtained crystalline from methanol; yield 7 g., m. p. 40–43°. Pure material was obtained on further crystallization from methanol-water and from methanol; m. p. 48.5–49°, unchanged on further crystallization from pyridine-water.

The substance crystallized in colorless elongated prisms and gave no coloration with ferric chloride-alcohol.

Anal. Calcd. for  $C_{24}H_{25}O_2(OCH_8)_4$ ; C, 71.46; H, 8.14; OCH<sub>3</sub>, 26.38. Found: C, 71.52; H, 8.02; OCH<sub>8</sub>, 26.10.

Tetrahydro-osajetinone Trimethyl Ether (XI) .-- Tetrahydro-osajetin trimethyl ether (2.0 g., 1 mole) and selenium dioxide (1.5 g., 3 moles) were refluxed for one hour with 15 cc. of glacial acetic acid. The precipitated selenium was removed from the cooled solution by filtration through a sintered glass filter and was washed with glacial acetic acid, water and acetone; yield 368 mg., 1.0 mole (solvent blank negligible). The filtrate and the glacial acetic acid washings were poured with stirring into 180 cc. of ice and water. The addition of a little solid sodium bicarbonate caused the resultant suspension to coagulate and the brown precipitate formed was removed by filtration and crystallized from methanol; yield 902 mg., m. p. 100.5-102°. Pure material was obtained in the form of deep yellow prisms on further crystallization from methanol and methanol-water; yield 513 mg., m. p. 103-103.5°, unchanged on further crystallization from petroleum ether.

Anal. Caled. for C<sub>24</sub>H<sub>25</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>3</sub>: C, 71.34; H, 7.54; OCH<sub>3</sub>, 20.48. Found: C, 71.01; H, 7.37; OCH<sub>3</sub>, 20.56.

Tetrahydro-osajetinone trimethyl ether was also prepared from its monoxime, described below, by deoximation with nitrous acid.8 Tetrahydro-osajetinone trimethyl ether monoxime (1.61 g.) was dissolved in glacial acetic acid (95 cc.) and 20 cc. of water added. Solid sodium nitrite (25 g.) was added slowly over a period of one hour. more water (5 cc.) being added when the addition was half completed. After the addition of the sodium nitrite, the solution was allowed to stand for thirty minutes and was then poured into 2 liters of ice and water. The yellow precipitate that formed was removed by filtration and was obtained crystalline from methanol; yield 915 mg., m. p. 97-100°. Pure material was obtained on further crystallization from methanol; yield 812 mg., m. p. 102-103°, unchanged on admixture with the material (m. p. 103-103.5°) prepared as described above by selenium dioxide oxidation.

Tetrahydropomiferitinone Tetramethyl Ether (XIV).--Tetrahydropomiferitin tetramethyl ether (500 mg.) was oxidized in glacial acetic acid with selenium dioxide as described above for the preparation of tetrahydro-osajetinone trimethyl ether except that a twenty-minute reflux period was used; yield of selenium, 77 mg., 0.9 mole. The product was isolated in the same manner; yield 180 mg., m. p. 79-83°. Pure material was obtained in the form of pale lemon-yellow prisms on further crystallization from methanol; yield 98 mg., m. p. 82.5-83°.

Anal. Caled. for  $C_{24}H_{24}O_3(OCH_3)_4$ : C, 69.40; H, 7.49; OCH<sub>3</sub>, 25.62. Found: C, 69.35; H, 7.29; OCH<sub>3</sub>, 25.56.

Tetrahydro-osajetinone Trimethyl Ether Monoxime (IX).---Isoamyl nitrite (8 cc.) was added to a solution of 1.5 g, of sodium in 25 cc. of methanol. To this was added a solution of tetrahydro-osajetin trimethyl ether (2.0 g.) in 35 cc. of warm methanol. The solution was allowed to stand at room temperature for thirty minutes and was then kept at ice-box temperature for two days. At the end of this period the solution was poured into ice and water (450 cc.) and the precipitate that formed was removed by filtration; yield 2 g., m. p. 153-158°. Pure material was obtained in the form of pale yellow prisms on further crystallization from methanol: m. p. 163.5°, unchanged on further crystallization from benzene-petroleum ether.

Anal. Calcd. for  $C_{21}H_{45}O_4N$ : C, 69.06; H, 7.51; N, 2.98. Found: C, 68.98; H, 7.69; N, 2.91.

Tetrahydro-osajylic Acid Dimethyl Ether (XII).—Tetrahydropomiferitinone tetramethyl ether (122 mg.) was dissolved in 7 cc. of boiling acetone and 2.7 cc. of 5% aqueous potassium hydroxide was added to the refluxing solution followed by the dropwise addition, over a period of seventy minutes, of 5 cc. of hydrogen peroxide (30%). Before the end of the addition (at fifty minutes), 1 cc. more of the 5% potassium hydroxide solution was added to maintain the alkaline reaction. To the cooled and practically colorless solution was added 7 cc. of a saturated solution of sodium bisulfite. The solution was then non-oxidizing to potassium iodide and was made acid with hydrochlorie acid. The acetone was removed by partial concentration and the

solution was extracted with ether and the ethereal extract (A) was washed with a saturated aqueous sodium bicarbonate solution, the latter acidified with hydrochloric acid and again extracted with ether (acid fraction). The solid obtained on ether removal from this acid fraction was extracted with hot petroleum ether. The petroleum ether extract yielded crystals on cooling; yield 26 mg., m. p. 170-177°. Pure material was obtained on further crystallization from water; yield 6 mg., m. p. 177-178°, unchanged on admixture with an authentic specimen of veratric acid (m. p. 179.5°). This fraction was therefore veratric acid.

The petroleum ether filtrate from the above procedure was concentrated to dryness and crystallized from a small amount of hot ethanol by the addition of water; yield 44 mg., m. p. 116–119°. Pure material was obtained on further crystallization from ethanol-water; m. p. 122– 122.5°, unchanged on further crystallization from benzenepetroleum ether.

The ethereal extract A, after removal of the acid fraction, was extracted with a 5% aqueous potassium hydroxide solution, the latter acidified with concentrated hydrochloric acid and again extracted with ether. The ether was removed and the solid obtained was crystallized from petroleum ether; yield 10 mg., m. p. 122–122.5°, unchanged on admixture with the material of like melting point obtained from the acid fraction.

The substance of melting point 122–122.5°, designated tetrahydro-osajylic acid dimethyl ether, crystallized in colorless, clear flakes.

Anal. Caled. for  $C_{16}H_{21}O(OCH_3)_2COOH$ : C, 67.83; H, 8.39; OCH<sub>3</sub>, 18.45; neut. equiv., 336.4. Found: C, 67.64; H, 8.37; OCH<sub>3</sub>, 18.36; neut. equiv., 334.

Tetrahydro-osajylic acid dimethyl ether also was obtained on similar treatment of tetrahydro-osajetinone trimethyl ether. An amount of 500 mg, of the latter compound yielded 50 mg, of anisic acid (m. p. 179.5–180°, mixed m. p. unchanged) and 92 mg, of tetrahydro-osajylic acid dimethyl ether of melting point 122–122.5°, unchanged on admixture with the product of like melting point obtained from tetrahydropomiferitinone tetramethyl ether.

We are indebted to Mr. Bernard S. Wildi (N. Y. A. Project O. S. U. 169) for assistance in preparing the plant material.

#### Summary

1. The trimethyl ethers of osajetin and tetrahydro-osajetin and the tetramethyl ethers of pomiferitin and tetrahydropomiferitin have been prepared.

2. On oxidation with alkaline hydrogen peroxide, osajetin dimethyl ether yielded homoanisic acid and osajetin trimethyl ether yielded anisic acid.

3. On oxidation with alkaline hydrogen peroxide, pomiferitin trimethyl ether yielded homoveratric acid and pomiferitin tetramethyl ether yielded veratric acid.

<sup>(8)</sup> L. Claisen and O. Manasse, Ber., 22, 530 (1889); M. L. Wolfrom, L. W. Georges and S. Soltzberg, THIS JOURNAL, 56, 1794 (1934)

4. Tetrahydro-osajetinone trimethyl ether (XI) was prepared from tetrahydro-osajetin trimethyl ether by two procedures.

5. Tetrahydropomiferitinone tetramethyl ether (XIV) was prepared from tetrahydropomiferitin tetramethyl ether.

6. XI was oxidized to anisic acid and tetra-

hydro-osajylic acid dimethyl ether (XII). XIV was oxidized to veratric acid and XII. This demonstrates that osajin and pomiferin have identical carbon nuclei.

7. Two  $CH_3$ -C groups are present in the molecules of both osajin and pomiferin.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF EDWARD COLLEGE]

# A New Synthesis of Phthalaldehydes

# By Tarini Charan Chaudhuri

Phthalaldehyde has long been obtained by the hydrolysis of  $o-C_6H_4(CHCl_2)_2^1$  and isophthalaldehyde from  $m-C_6H_4(CHCl_2)_2^{1,2}$  The author has now found that these di-aldehydes can be prepared from benzaldehyde through the action of chloroform and potassium hydroxide. In the presence of chloroform the usual action of potassium hydroxide on benzaldehyde does not occur. Instead, a reaction similar to the Tiemann-Reimer reaction on phenols takes place. The principal product is *m*-dichloromethylbenzaldehyde, accompanied by a small amount of the lower-boiling *ortho* isomer.



By hydrolysis of the dichloro derivatives, phthalaldehyde and isophthalaldehyde were obtained.

These results lend support to the view that in the Tiemann-Reimer reaction on phenols the intermediate products are the dichloro derivatives which are then hydrolyzed to the phenolic aldehydes. In the present synthesis, the dichloro derivatives are more stable and can be isolated.

Preparation of Phthalaldehyde and Isophthalaldehyde.— To a mixture of 10 cc. of pure benzaldehyde and 8 cc. of chloroform in a round-bottomed flask was added a solution of 30 g. of potassium hydroxide in 50 cc. of water. The flask was connected immediately to an upright condenser. A vigorous reaction ensued, and as it subsided the mixture was shaken frequently. When the action had ceased, the mixture was heated in an oil-bath at 140–150° for about six hours.

(2) Meyer, Ber., 20, 2005 (1887).

tilled from the mixture and the residue, after being washed repeatedly with water, was distilled under reduced pressure in Bruhl's apparatus. The *o*-dichloromethylbenzaldehyde was obtained in the first fraction as a slightly yellow viscous liquid boiling at 170–175°; it corresponded to 22% of the total amount. The *m*-dichloromethylbenzaldehyde formed the second and larger fraction, boiling at 192–196°, and was obtained as a thick red oil.

The *o*-dichloromethylbenzaldehyde has a sharp pungent odor. It is insoluble in water, alcohol and ether, but soluble in glacial acetic acid.

Anal. Calcd. for C<sub>8</sub>H<sub>5</sub>OCl<sub>2</sub>: Cl, 44.65. Found: Cl, 43.87.

When it was heated for forty to forty-five minutes with a solution of potassium hydroxide and the mixture was acidified with dilute hydrochloric acid and cooled, phthalaldehyde (m. p. 54°) was obtained as a colorless powder.

Anal. Calcd. for  $C_8H_6O_2$ : C, 71.64; H, 4.49. Found: C, 71.73; H, 4.58.

The m-dichloromethylbenzaldehyde possesses a pleasant odor resembling that of rose. It attacks the sensitive skin and membranes of the nostril, producing a mild burning sensation.

Anal. Calcd. for C<sub>8</sub>H<sub>6</sub>OCl<sub>2</sub>: Cl, 44.65. Found: Cl, 43.91.

Isophthalaldehyde (m. p.  $90^{\circ}$ ) was obtained by hydrolysis of the dichloro derivative.

Anal. Calcd. for C<sub>8</sub>H<sub>6</sub>O<sub>2</sub>: C, 71.64; H. 4.49. Found: C, 71.81; H, 4.61.

### Summary

A study has been made of the action of chloroform and caustic potash on benzaldehyde under certain special conditions. The reaction leads to the formation of o- and m-dichloromethylbenzaldehyde, which can be separated by fractional distillation. By hydrolysis of the dichloro derivatives, phthalaldehyde and isophthalaldehyde are obtained. This procedure represents a new synthesis of dialdehydes.

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The excesses of benzaldehyde and chloroform were dis-

<sup>(1)</sup> Colson and Gautier, Bull. soc. chim., [2] 45, 509 (1886); Ann. chim., [6] 11, 29 (1887).