

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  $\text{CH}_3\text{-C}$  groups are present in the molecules of both osajin and pomiferin.

COLUMBUS, OHIO

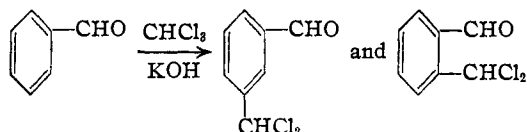
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF EDWARD COLLEGE]

## A New Synthesis of Phthalaldehydes

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Phthalaldehyde has long been obtained by the hydrolysis of *o*- $\text{C}_6\text{H}_4(\text{CHCl}_2)_2$ <sup>1</sup> and isophthalaldehyde from *m*- $\text{C}_6\text{H}_4(\text{CHCl}_2)_2$ .<sup>1,2</sup> 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  $140\text{--}150^\circ$  for about six hours.

The excesses of benzaldehyde and chloroform were dis-

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

(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  $170\text{--}175^\circ$ ; it corresponded to 22% of the total amount. The *m*-dichloromethylbenzaldehyde formed the second and larger fraction, boiling at  $192\text{--}196^\circ$ , 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  $\text{C}_8\text{H}_6\text{OCl}_2$ : 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.  $54^\circ$ ) was obtained as a colorless powder.

*Anal.* Calcd. for  $\text{C}_8\text{H}_6\text{O}_2$ : 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  $\text{C}_8\text{H}_6\text{OCl}_2$ : Cl, 44.65. Found: Cl, 43.91.

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

*Anal.* Calcd. for  $\text{C}_8\text{H}_6\text{O}_2$ : 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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