SYNTHESIS OF THE DIMETHYLETHER OF γ-RESORCYLIC ALDEHYDE.*

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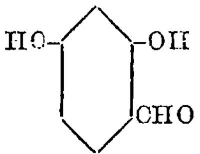
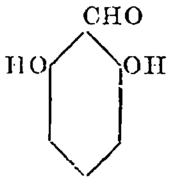
Although the β-resorcylic aldehyde (I) and its derivatives are known since the days of Tiemann (1877), the γ-resorcylic aldehyde (II) and its derivatives have so far withstood synthesis.



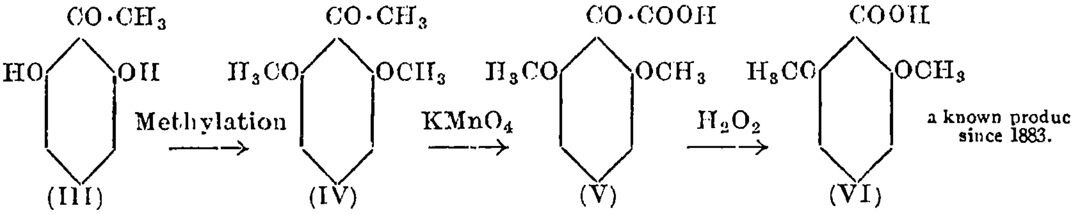
(I)
β-Resorcylic aldehyde.



(II)
γ-Resorcylic aldehyde,

It is intended in this paper to describe the synthesis of the hitherto unknown dimethylether of γ-resorcylic aldehyde (VIII), which is destined to be the precursor of the long-sought γ-resorcylic aldehyde (II) itself and thus to play an important part in the synthesis of some of the natural products.

The series of reactions indicated by the figures (III) to (VI)



(III) m.p. 157° (IV) m.p. 73° (V) m.p. 98° (VI) m.p. 186°

has already been realised and published in abstract form (Limaye and Gangal, Indian Science Congress, 1934, Chemistry Section) and fully described in Mr. Gangal's thesis (now in press).

The 2 : 6-dimethoxyphenyl-glyoxylic acid (V), when heated with aniline (Bouveault, 1896), loses carbon dioxide, in common with other α-ketonic acids, and forms an aldehyde which combines with aniline to give

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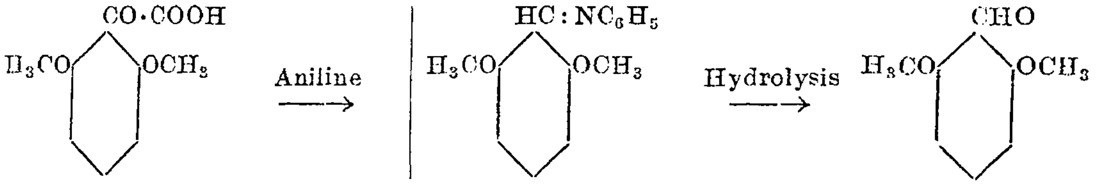
a Schiff's base (VII). This on hydrolysis regenerates 2 : 6-dimethoxybenzaldehyde, *i.e.*, the dimethylether of γ-resorcylic aldehyde (VIII).



(V) (VII) (VIII)

Experimental.

The dimethylether of γ-resorcylic aldehyde (VIII).—2 : 6-Dimethoxyphenyl-glyoxylic acid (V) (1 g.) is heated with aniline (1 c.c.) to 180° for three to five minutes, when a rapid evolution of carbon dioxide and water vapour takes place. On cooling, the mass is transferred to a distilling flask with the help of boiling water, caustic soda (1 g.) added and steam passed in until all the aniline is removed. The contents of the flask are allowed to settle a while and filtered hot, through cotton wool. The oily residue in the flask is again treated with hot water and the solution filtered. The combined filtrates are concentrated to a small volume and cooled, when long, white needles separate. The aldehyde on recrystallisation from boiling water melts at 98-99°. B. P. 285°. Yield—0·45 g.

Analysis:—Found C = 65·2 ; H = 6·1 % ; $C_9H_{10}O_3$ requires C = 65·1 ; H = 6·0 %.

The aldehyde is readily soluble in alcohol, ether and benzene. It dissolves in concentrated sulphuric acid with an orange red colouration, but on dilution with water the major part is precipitated unchanged.

The semicarbazone m.p. 190° is obtained when the aldehyde reacts with semicarbazide acetate. The original aldehyde is regenerated by carefully treating the semicarbazone with hydrochloric acid. Boiling concentrated hydrochloric acid resinifies the aldehyde.

2 : 6-*Dimethoxy-cinnamic acid*, m.p. 146–47°, is obtained when the aldehyde is condensed with malonic acid in pyridine solution. (Found, equivalent, 210. $C_{11}H_{12}O_4$ requires equivalent, 208.) It will be reported upon, in detail, in a separate communication.

Demethylation.—On heating one part of the aldehyde with four parts of aluminium chloride, in benzene solution, on a water bath for two hours, it was observed in one experiment, that although demethylation had taken place, the action of aluminium chloride had gone too far and removed the formyl group with the formation of resorcin. Under a different set of conditions, it has been found possible to bring about demethylation without affecting the aldehyde group and thus yielding a liquid substance, which gives a brown black colour with ferric chloride, is readily soluble in caustic soda solution and reacts with semicarbazide acetate. This indicates the possibility of a partial demethylation to the monomethylether of γ-resorcylic aldehyde or a complete demethylation to γ-resorcylic aldehyde (II) itself, both being unknown.

Mr. S. D. Limaye is working out the best conditions of demethylation of the dimethylether of γ-resorcylic aldehyde, under my guidance.