

TABLE I.

Ion whose data are employed	Heat of formation of H <sup>+</sup> <sub>(aa)</sub>
SeO <sub>4</sub> <sup>2-</sup>	35 K. cal.
SeO <sub>3</sub> <sup>2-</sup>	39 "
SO <sub>4</sub> <sup>2-</sup>	72 "
SO <sub>3</sub> <sup>2-</sup>	42 "

K. S. GURURAJA DOSS.

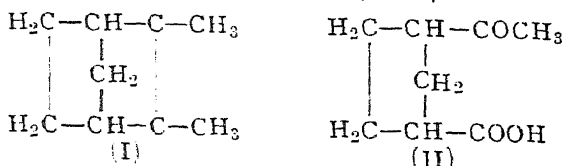
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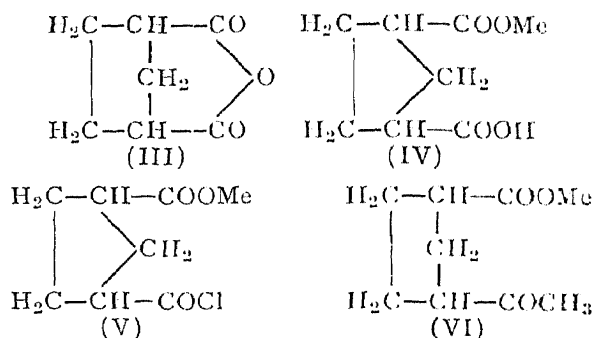
June 24, 1935.

<sup>1</sup> *Proc. Ind. Acad. Sci.*, 1934, 1, 156.*Bicyclo (1:2:3)-octane-2:4-dione.*

ALTHOUGH the constitution assigned to santene (I) by Semmler has been confirmed by direct synthesis,<sup>1</sup> the synthesis of the ketonic acids (II) isolated by Semmler and Bartelt<sup>2</sup> as an oxidation product of santene has not been achieved so far. The acid (II) has now been synthesised starting from *cis-cyclopentane-1:3-dicarboxylic acid* and the investigation continued with a view to synthesising compounds of the type of homonorcarnphor (VIII).

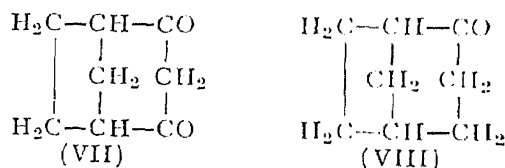


*Cis-cyclopentane-1:3-dicarboxylic anhydride* (III)<sup>3</sup> furnishes the mono methyl ester (IV) in the usual way (b.p. 156°/4 mm.). The mono ester mono-acid chloride (V) prepared from (IV) by treatment with thionylchloride is a colourless mobile liquid (b.p. 109°/3 mm.) which gives by Blaise reaction with zinc methyl iodide the ketonic ester (VI) (b.p. 100°/2 mm. purified through semicarbazone, m.p. 139°). The ketonic acid (II) prepared from (VI) by hydrolysis boils when pure sharply at 155°/5 mm., and not within a range of 30° *vis.*, 175-205°/10 mm. as given by Semmler and Bartelt.<sup>2</sup> They did not analyse this compound and it seems quite probable that their compound was not pure. The semicarbazone melts at 169° (Semmler and Bartelt 168°).



The ketonic ester (VI) on treatment with sodium methoxide in alcoholic solution furnishes a product from which the ketonic acid (II) and a solid m.p. 123°·5 could be isolated by distillation, and subsequent treatment with petrol (obtained in poor yield). The solid gives a semicarbazone m.p. 224°, a brownish colouration with ferric chloride and evolves hydrobromic acid with bromine in chloroform solution and seems in all probability to be the bicyclic diketone (VII).

Experiments are in progress for obtaining the solid m.p. 123°·5 in workable quantities, with a view to confirming its structure as



also to partially reduce it to the monoketone (VIII)—the next higher homologue of *nor-carnphor*.

Full details will be published shortly elsewhere.

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July 3, 1935.

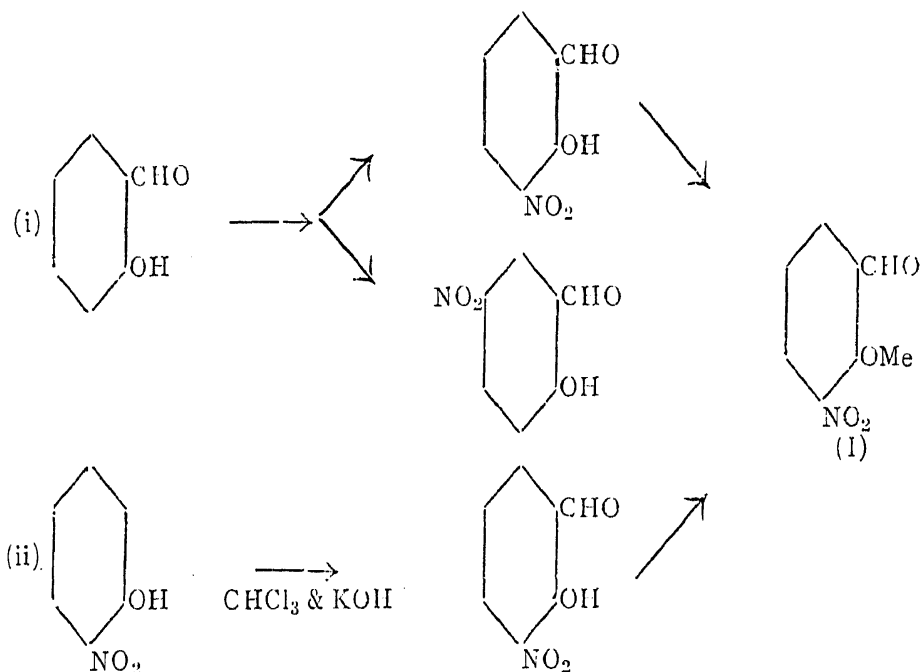
<sup>1</sup> Diels and Alder, *Annalen*, 1931, 486, 205.<sup>2</sup> Semmler and Bartelt, *Ber.*, 1907, 40, 4596; *Ibid.*, 1908, 41, 128, 389, 867.<sup>3</sup> Pospischill, *Ber.*, 1898, 31, 1953; Perkin and Scarborough, *J.C.S.*, 1921, 119, 1400.

#### A Preliminary Note on the Nitration of Methyl-Ether of Salicylaldehyde.

DURING the course of synthetical experiments in the group of alkaloids, we required Iso-Orthovanillin as a starting substance and it was thought that the latter might be obtained from 3-Nitromethyl-salicylaldehyde

(I). 3-Nitromethyl-salicylaldehyde has so far been obtained only from 3-Nitrosalicylaldehyde which in its turn has been synthe-

sed by two entirely different methods indicated below, one due to Miller,<sup>1</sup> and the other due to Sen and Ray<sup>2</sup> :—



Both the methods of preparation of 3-Nitrosalicylaldehyde are very tedious, and the method of Sen and Ray gives exceedingly poor yield. Further 3-Nitrosalicylaldehyde cannot be readily methylated by dimethylsulphate and alkali, and special methods (*viz.*, diazomethane or silver salt) have to be used for this purpose.<sup>3</sup> It was therefore thought desirable to explore methods of direct synthesis of 3-Nitromethylsalicylaldehyde.

Methyl ether of salicylaldehyde was first nitrated by Voswinckel,<sup>4</sup> and then by Schnell.<sup>5</sup> The latter author showed that if nitration were carried out with fuming nitric acid below  $15^\circ$ , then only 5-Nitrosalicylaldehyde-methylether is formed. These results were confirmed by Hodgson and Smith in 1930.<sup>6</sup> These results did not appear to the present author to be quite correct as it was thought that the 3-Nitro-compound should also have been formed just as in the case of the nitration of salicylaldehyde itself. A repetition of Schnell's experiment and careful working up of the nitration product showed that 3-Nitromethylsalicylaldehyde is actually formed in a yield of about 20%. The separation is best effected in the following manner. The

crude solid nitration product is first carefully extracted with *cold* sodium carbonate solution, which extracts the dinitrosalicylic acid which is formed in small quantities at the same time. The dry residue is crystallised from benzene when 5-Nitromethylsalicylaldehyde m.p.  $89^\circ$  separates first. From the benzene mother-liquors petroleum ether (b.p.  $30^\circ$ - $50^\circ$ ) precipitates a mixture m.p.  $40^\circ$ - $50^\circ$ . This is converted into the *p*-toluidide, and the *p*-toluidide subjected to a series of careful fractional crystallisations from alcohol. The *p*-toluidide of the 5-Nitro-compound which is only sparingly soluble in alcohol separates first in needles m.p.  $165^\circ$ , and from the mother-liquors the *p*-toluidide of the 3-Nitro-compound is then obtained in prismatic plates m.p.  $92^\circ$  (identical with the *p*-toluidide obtained from an authentic specimen of 3-Nitrosalicylaldehyde). The latter on hydrolysis gives 3-Nitromethylsalicylaldehyde m.p.  $102^\circ$ , identical in all respects with an authentic specimen of 3-Nitromethylsalicylaldehyde prepared by the older method—the mixed melting point being not lowered.

The results of these experiments may be briefly summarised thus :—