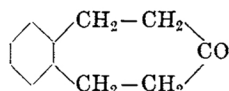


ON THE FORMATION OF BENZENE-(PENTANONE-3-YLENE)<sub>1,2</sub>

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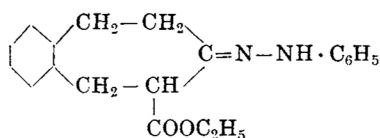
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With the view of inquiring into the conditions of the formation of rings which can be attached to the ortho-positions of benzene nucleus, and the effects of benzene nucleus on the odour of alicyclic poly-membered rings, the synthesis of benzene-(alcanone-x-ylenes)<sub>1,2</sub> was attempted. In the present communication a result of the formation of benzene-(pentanone-3-ylenes)<sub>1,2</sub>



is briefly described.

As to the seven-membered ring compounds of the type above mentioned, A. F. Titley<sup>(1)</sup> had previously showed, in the course of his investigations of conditions of formation of rings attached to the *o*-, *m*-, and *p*-positions of the benzene nucleus, the synthesis of phenylhydrazone of ethyl 3-ketophenheptamethylene-2-carboxylate



by the application of the Dieckmann reaction (the action of sodium on *o*-phenylenedipropionic ester in toluene at 100°), though the pure ketone-carboxylate had not been isolated. Thus the formation of benzene-(pentanone-3-ylenes)<sub>1,2</sub> was examined by means of dry distillation of thorium salt of *o*-phenylenedipropionic acid. The *o*-phenylenedipropionic acid was prepared by Perkin's method<sup>(2)</sup>, but as it was found after a few experiments that the large excess of concentrated alkali solution did not act to give a good yield of the acid, the method was slightly modified as described in the experimental part. The action of alkali on ethyl *o*-xylenedimalonate was precisely investigated by Mr. H. T. Lo who previously reported the results in this Bulletin.<sup>(3)</sup> Being carefully saponified with a dilute potassium hyd-

(1) Titley, *J. Chem. Soc.*, **1928**, 2571.

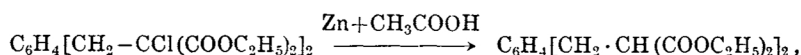
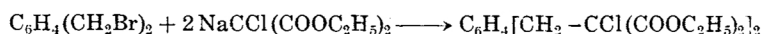
(2) Perkin, *J. Chem. Soc.*, **53** (1888), 18; Titley, *J. Chem. Soc.*, **1928**, 2578.

(3) This Bulletin, **5** (1930), 326.

roxide solution, acidified with a dilute sulphuric acid, and then extracted with either, *o*-xylenedimalonate gives really *o*-xylenedimalonic acid which crystallises from the mixture of chloroform and benzene in colourless microscopic crystals melting at 156° with decomposition. When the thorium *o*-phenylenedipropionate, which was prepared by neutralising the acid with a caustic soda solution and then adding a thorium chloride solution, was subjected to the dry distillation in diminished pressure, it begins to decompose at 200° in the temperature of the oil bath and a yellowish oil which distils between 155 and 175° are collected. The product is soluble in almost all common organic solvents and recrystallised with much difficulty from petroleum ether. It crystallises in large plates melting at 41–42°. On elemental analysis of itself and its phenylhydrazone, and the determination of the molecular weight, it proved to be nothing but benzene-(pentanone-*x*-3-ylene)<sub>1.2</sub>. As Ruzicka<sup>(1)</sup> showed in his excellent researches on higher carbonatom rings that alicyclic ketones which have carbon atoms from C<sub>5</sub> to C<sub>12</sub> have the odour of bitter almond and peppermint. It may be seen somewhat interesting to indicate that the ketone obtained also has the striking smell of them, though we must naturally have many further investigations in order to know what influences are exerted upon the odour of alicyclic rings by an aromatic one consolidated into them.

### Experimental.

**Ethyl *o*-xylenedimalonate.** The preparation of this ester was carried out exactly as described by Perkin,<sup>(2)</sup>



but, as it was found difficult to isolate *o*-phenylenedipropionic acid from ethyl *o*-xylenedimalonate in the quantity showed by the author and also found that the cause was to use concentrated alcoholic potash, the investigation of which was previously reported by Mr. H. T. Lo in this bulletin,<sup>(3)</sup> the method of its preparation was modified as described below.

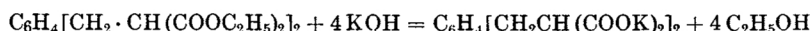
***o*-Phenylenedipropionic acid.** In a flask provided with a reflux condenser, ethyl *o*-xylenedimalonate was boiled with a little excess of dilute

(1) Ruzicka, *Bull. Soc. Chim.*, **43** (1928), 1145.

(2) Loc. cit.

(3) Loc. cit.

alcoholic potash (about 2%) calculated from the following formula for some hours on a water bath and the hydrolysis was completed.



Being added some water, the reaction mixture was carefully evaporated on a water bath until the solution gained the former volume and was acidified with dilute sulphuric acid. *o*-Xylenedimalonic acid thus produced in the solution was extracted three or four times with ether. The ethereal solution was washed with water and the ether was then distilled off, when a slightly yellowish crystalline mass remained, consisting of mainly *o*-xylenedimalonic acid accompanied by a small quantity of *o*-phenylenedipropionic acid and a tarry matter. In preparing *o*-phenylenedipropionic acid, it is enough to heat the product in an oil bath at the temperature between 120° and 165° when a considerable evolution of carbon dioxide takes place and nearly pure *o*-phenylenedipropionic acid is formed, which crystallises from water in small colourless needles melting at 160–162°. Nevertheless when the product consisting of mainly *o*-phenylenedimalonic acid is recrystallised from the mixture of chloroform and benzene, pure *o*-xylenedimalonic acid,  $\text{C}_6\text{H}_4[\text{CH}_2\text{CH}(\text{COOH})_2]_2$ , is obtained. It crystallises in colourless microscopic crystals which melts at 156° with the evolution of carbon dioxide and transforming to *o*-phenylenedipropionic acid.

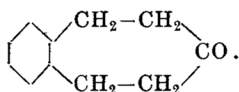
**Seven membered ring.** *o*-Phenylenedipropionic acid is carefully neutralised with a dilute caustic soda solution and a solution of thorium chloride is added, whereby thorium *o*-phenylenedipropionate is precipitated in a voluminous white crystalline mass. It is collected, washed with water, and dried in an air bath at 100°. On dry distillation under diminished pressure (about 0.1 mm.), the salt begun to decompose when the temperature of the oil bath was raised to about 200°, and the following fractions were collected,

- (1) 155–175°                      (2) 174–190°.

The first fraction (1) was a yellowish liquid which crystallised in colourless plates when it was left to cool. The second fraction (2) was a brown liquid which did not crystallise, even if it was left to cool. But when it was fractionated again under the same pressure (0.1 mm.), a yellowish liquid boiling at 155–175° which was quite identical to the first fraction (1) was obtained as the main product.

The product dissolves easily in almost all common organic solvents, though it can be recrystallised with much difficulty from hot petroleum ether, when it forms colourless plates melting at 41–42°. The crystals have

a strong smell of bitter almond and peppermint and on analysis proved to be those of benzene-(pentanone-3-ylene)<sub>1,2</sub>



Anal. Subst. = 2.466;  $\text{CO}_2$  = 7.474;  $\text{H}_2\text{O}$  = 1.775 mg. Found: C = 82.64; H = 7.98 %.  
Calc. for  $\text{C}_{11}\text{H}_{12}\text{O}$ : C = 82.50; H = 7.50 %.

Molecular weight was determined by K. Rast's method, using camphor as solvent, 0.264 mg. in 3.099 mg. of solvent gave  $\Delta t = 21.1^\circ$ . Molecular weight found 166.4.  $\text{C}_{11}\text{H}_{12}\text{O}$  requires 160.

An alcoholic solution of the product produced a white turbidity on the addition of a dilute alcoholic solution of phenylhydrazine hydrochloride and sodium acetate, which being allowed to stand for a few hours, collected into a precipitate. This was filtered and recrystallised from alcohol, when it formed colourless crystals melting at  $85^\circ$  and on analysis it proved to be nothing but phenylhydrazone of benzene-(pentanone-3-ylene)<sub>1,2</sub>.

Anal. Subst. = 2.25 mg.;  $\text{N}_2$  = 0.228 c.c. ( $19^\circ$ , 749.2 mm.) Found:  $\text{N}_2$  = 11.4%. Calc. for  $\text{C}_{17}\text{H}_{18}\text{N}$ : N = 11.2%.

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