

CLV.—The Intermolecular Condensation of Methyl Ethyl Ketone in the Presence of Calcium Carbide.

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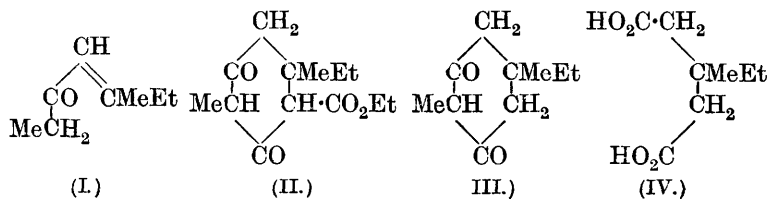
THE experiments described in the communication were undertaken with the object of ascertaining which of the three theoretically possible compounds (I), (V), or (IX) is formed by the condensation of two molecules of methyl ethyl ketone by means of calcium carbide in accordance with the method devised by Bodroux and Taboury (*Bulletin*, 1905, [iv], 3, 831). The question has been left to some extent an open one, and it was necessary, from our point of view, to ascertain the correct answer because dihydroresorcinol derivatives of the type which is formed by the condensation of substituted mesityl oxides with ethyl malonate are now being used extensively in the investigation of *spiro*-compounds which we have in hand.

The condensation proceeds in accordance with the equation :

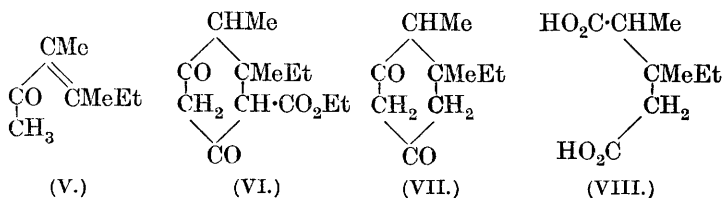


and therefore the possibilities are threefold :

(1) The condensation may proceed to form (I), which on treatment with ethyl sodiomalonate will give (II), and this on hydrolysis will pass into (III), the structure of which will be revealed by its oxidation to β -methyl- β -ethylglutaric acid (IV) :

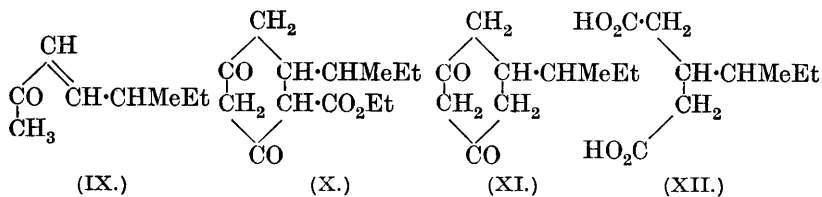


(2) The condensation product may have formula (V), which would give the dihydroresorcinol derivative (VI), yielding on hydrolysis (VII), which on oxidation would give $\alpha\beta$ -dimethyl- β -ethylglutaric acid (VIII) :



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(3) The two molecules may condense to form (IX) which, however, as it is not an $\alpha\beta$ -unsaturated compound, would not condense with ethyl sodiomalonate unless the double bond were transferred to the $\alpha\beta$ -position during the process of condensation. If this were to happen, the product would have the formula (X), the hydrolysis product (XI), and the glutaric acid formed on oxidation (XII) :



The experiments show that, apart from some higher-boiling product, the sole substance produced in the condensation has the structure (I). When condensed with ethyl sodiomalonate, it yields the compound (II), and the dihydroresorcinol derivative (III), produced from this, gives β -methyl- β -ethylglutaric acid on oxidation.

It is worthy of note that, unlike any other derivative of dihydroresorcinol hitherto investigated, the substance (III) is unstable, and rapidly passes from the crystalline form to a resin on keeping.

EXPERIMENTAL.

Δ^6 -Hepten- γ -one (I).—Methyl ethyl ketone (500 grams) was treated in the manner described by Bodroux and Taboury (*loc. cit.*), the carbide used being very finely crushed. The operation was continued for eight hours and the product was then fractionated at ordinary pressure. After refractionating, 62.5 grams of distillate were obtained which boiled at 164–166°. This fraction was found to give the semicarbazone, crystallising from alcohol and melting at 119–120°, described by the above investigators.

Condensation with Ethyl Sodiomalonate. Formation of Ethyl 1 : 4-Dimethyl-1-cyclohexane-3 : 5-dione-2-carboxylate (II).—A mixture composed of 7.5 grams of sodium dissolved in 150 c.c. of alcohol, 48 grams of ethyl malonate, and 42.5 grams of Δ^6 -hepten- γ -one was heated on the steam-bath for two hours with frequent shaking. The product was cooled and poured into 1 litre of water, and unchanged material extracted by ether. The aqueous layer was then acidified by means of hydrochloric acid, when an oil was precipitated which would not solidify. It was therefore extracted by ether and obtained as a clear, viscid liquid which gave, in alcoholic solution, a deep red colour with ferric chloride. As the

ester could not be distilled without undergoing decomposition, the specimen analysed was taken from the crude liquid after it had stood in an evacuated desiccator for several days (Found: C = 65.31; H = 8.54. $C_{13}H_{20}O_4$ requires C = 65.0; H = 8.3 per cent.). The ester is readily and completely soluble in dilute aqueous sodium hydroxide solution. The yield was 62 grams.

1 : 4-*Dimethyl-1-ethylcyclohexane-3 : 5-dione* (III).—The crude ester (28.5 grams), mixed with a solution containing 100 grams of crystalline barium hydroxide in 700 grams of water, was heated to the boiling point for twenty hours, and then, while hot, was acidified and filtered. The filtrate was made strongly acid by means of hydrochloric acid and heated to the boiling point for fifteen minutes, during which operation an insoluble oil floated on the surface of the liquid. On cooling, the oil solidified and the aqueous solution deposited well-defined crystals of the dione. The solidified oil was also found to be the dione, the total yield being 9.5 grams. It is very soluble in benzene and alcohol, but crystallises from water or from light petroleum (b. p. 80—100°) as glistening scales which melt at 113—114°. The aqueous or alcoholic solution gives a deep blue-green colour with ferric chloride (Found: C = 71.27; H = 9.49. $C_{10}H_{16}O_2$ requires C = 71.4; H = 9.6 per cent.). The dione was found to be unstable both in the open and in a desiccator, but it can be kept in a vacuum desiccator or in a sealed tube. Decomposition was slow and a viscous oil with an unpleasant smell was formed. An attempt was made to determine the nature of the change by separating the oil from the solid and distilling it under diminished pressure. A fraction boiling at 168—175°/17 mm. was obtained which gave, in alcoholic solution, a deep red colour with ferric chloride. The investigation of this compound is in progress.

The Constitution of the Dione (III). *Formation of β -Methyl- β -ethylglutaric Acid* (IV).—The dione (5 grams), dissolved in 25 c.c. of 10 per cent. aqueous sodium hydroxide solution, was cooled to 0° and an ice-cold neutral solution of 15.5 grams of bromine in 350 c.c. of water added, the neutralisation of the solution having been previously effected by means of 10 per cent. aqueous sodium hydroxide. The mixture was left at 0° for thirty minutes, when a test portion was found to remain clear after acidification by means of hydrochloric acid. After extraction with ether, 2.8 grams of an oil were obtained which solidified on keeping. It was recrystallised from a mixture of benzene and light petroleum (b. p. 80—100°), when it formed plates melting at 82—83° (Found: C = 54.91; H = 8.10. Calc., C = 55.1; H = 8.1 per cent. Found: for the silver salt, Ag = 55.71. Calc., Ag = 55.65 per cent.).

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The acid was proved to be identical with β -methyl- β -ethylglutaric acid by direct comparison with a specimen of the acid which had been prepared through the Guareschi compound.

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