

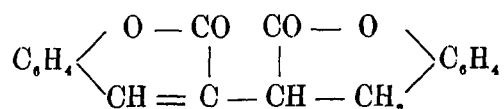
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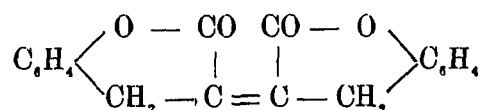
Chemistry. — “*Action of Solar Light on Cumarin*”. By A. W. K. DE JONG. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of Nov. 24, 1917).

GIACOMO CIAMICIAN and SILBER¹⁾ have communicated that cumarin in solid state and also in aqueous and alcoholic solution changes by solar light into hydrodicumarin, which substance was synthetically obtained by FITTIG and DYSON²⁾, starting from salicylaldehyde and succinic acid. According to the last investigators the formula of the hydrodicumarin was the following:



CIAMICIAN and SILBER write, that when we do not wish to assume a tetramethylene ring in the polymerised cumarin, the following formula is to be preferred in their opinion to that given by FITTIG and DYSON:



This formula, however, does not take the properties of hydrodicumarin into account. According to FITTIG and DYSON this substance is namely converted into hydrodicumaric acid, a mono-basic acid, by long boiling with “ziemlich concentrirten freien Alkalien”.

The cumarin ring is difficult to open by boiling with alkalis, so that this property of the hydrodicumarin is in perfect agreement with the formula given to it by the two investigators. A substance that should possess the formula given to hydrodicumarin by CIAMICIAN and SILBER, should easily give a di-basic acid on being heated with alkalis, as there are here no cumarin rings, but hydro-cumarin rings present, which are easily opened when the substance is heated with alkalis.

In connection with the possible structure of the truxillic acids, two of which arise by the action of light from the normal cinnamic

¹⁾ Ber. 35, 4130 (1902); Ber. 47, 642 (1914).

²⁾ Ann. 255, 280 (1889).

acids, it seemed not impossible to me that there occurred a tetramethylene ring in the product of illumination of cumarin. If this were the case, however, the substance would have to yield not a mono-basic, but a di-basic acid on treatment with alkalis, and the product of illumination of cumarin would not be identical with the hydrodicumarin of FITTIG and DYSON.

The possibility of this was not excluded, as CIAMICIAN and SILBER give 262° as melting point of their product, FITTIG and DYSON having found 256° for the hydrodicumarin.

I have prepared the product of illumination of cumarin by illumination of an aqueous solution that was *not* covered by glass, while the hydro-dicumarin was made according to the directions of FITTIG and DYSON. The melting-points of the substances agreed with those given by the investigators. A mixture of the two substances melted, however, already at 225° . This proves that the substances differ.

This may be confirmed by what follows. The product of illumination of cumarin crystallizes from chloroform in microscopic plates, which often look like rectangles; hydrodicumarin separates out of the solvent mentioned in microscopic needles joined to sheaves.

The product of illumination of cumarin dissolves in sodium hydroxide of about 30 % in a few minutes at the ordinary temperature. Through hydrochloric acid it is precipitated from this solution unchanged. When the alcalic solution is boiled for an hour with an ascending still-head, then on addition of hydrochloric acid to the cooled solution a di-basic acid separates, which first crystallizes in fine microscopic needles, which, however, are soon transformed to thicker needles that join to stars and crosses. The acid melts at 245° ; the melt smells strongly of cumarin, and easily dissolves in alcohol at the ordinary temperature. Also in a sodium-carbonate solution the melt is readily soluble.

As has already been communicated by FITTIG and DYSON, the hydrodicumarin gave after being heated for a long time with alkalis, a mono-basic acid, the hydrodicumaric acid, which when heated to the melting point, was again converted to hydrodicumarin, which is insoluble in alcohol, and also in a sodium-carbonate solution.

It appears, therefore, clearly from this that the product of illumination of cumarin is no hydrodicumarin.

I hope shortly to give a fuller discussion of the structure of the product of illumination of cumarin.

Buitenzorg, July 1917.