

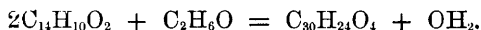
## X.—On Condensation Compounds of Benzil with Ethyl Alcohol.

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IN preparing benzoic acid by heating benzil with alcoholic potash, Jena (*Annalen*, **155**, 79) observed the formation of a neutral compound, melting at  $200^{\circ}$ , to which he ascribed the formula  $C_{14}H_{12}O_2$ , regarding it as isomeric with benzoïn. He assigned to it the name *tolane alcohol*. The quantity at his disposal was insufficient for further investigation.

Limpricht and Schwanert (*Ber.*, **4**, 335) obtained the same compound by heating together benzoïn and alcoholic potash with access of air. They arrive at the conclusion that it is a derivative of benzoïn (although they show in the same experiment that benzil is formed under the above conditions by the oxidising action of the air upon the benzoïn), and state their suspicion that the benzil employed by Jena must have contained benzoïn. On the strength of their analyses (not published) they arrive at the formula  $C_{30}H_{26}O_4$ , and name the compound *ethylidibenzoïn*.

We have found that, by the protracted action of very dilute alcoholic potash on benzil in the cold, the above compound is formed in large quantity. The yield, amounting in one experiment to 6 grams from 10 grams of carefully purified benzil, quite precludes the possibility of a formation from benzoïn present as an impurity. Our analyses lead to the formula  $C_{30}H_{24}O_4$ , which differs from that of Limpricht and Schwanert by containing two atoms of hydrogen fewer. The formation of such a compound from benzil and alcohol might be expressed by the equation—



In order to prepare this compound, 10 grams of caustic potash were dissolved in  $2\frac{1}{2}$  litres of alcohol, and to the solution thus obtained 200 grams of finely powdered benzil were added. The whole was shaken until the liquid was saturated with benzil, after which it was allowed to stand, shaking from time to time. The separation of the compound begins at the end of the first or second day, and is practically complete in about a fortnight. It is thus obtained as a crystalline powder, but, when a larger quantity of alcohol is employed, so as to have all the benzil in solution from the commencement, it separates in moderately large lustrous crystals.

The crude substance was washed with ether, to remove unaltered benzil, and then recrystallised, first from benzene, and afterwards from

alcohol. The latter solvent deposits the compound in small lustrous crystals. These contain alcohol of crystallisation, which they lose only after long heating at  $120^{\circ}$ . At  $100^{\circ}$  they are permanent. The compound, thus freed from alcohol, melted at  $200-201^{\circ}$ , and yielded on analysis numbers agreeing with the formula  $C_{30}H_{24}O_4$ . We append, for the sake of comparison, the theory for Limpricht and Schwanert's formula  $C_{30}H_{26}O_4$  :—

	Substance.	CO <sub>2</sub> .	OH <sub>2</sub> .
I. ....	0.1258	0.3694	0.0612
II. ....	0.1448	0.4260	0.0702
	Calculated for C <sub>30</sub> H <sub>24</sub> O <sub>4</sub> . (Japp and Owens.)	Calculated for C <sub>30</sub> H <sub>26</sub> O <sub>4</sub> . (Limpricht and Schwanert.)	Found.
			I. II.
C .....	80.36	80.00	80.08 80.24
H .....	5.36	5.78	5.41 5.38
O .....	14.28	14.22	— —
	<hr/> 100.00	<hr/> 100.00	

The difference in the percentages required by the two formulæ is certainly rather small for analysis alone to decide between them, but we think that the mode of formation which we have just described renders the first formula the more probable. Further, if the second formula were correct, the errors of analysis, both for carbon and hydrogen, would be in the wrong direction, whereas with the first formula the errors are in the usual direction.

We think that the results obtained by our predecessors are possibly due to their having overlooked the alcohol of crystallisation, or, at all events, to their not having taken into account the difficulty of completely expelling this alcohol. They crystallised the substance from alcohol, but none of them mention the presence of alcohol of crystallisation. Jena appears to have analysed a compound from which only a portion of the alcohol had been expelled. Thus, the formula  $C_{30}H_{24}O_4, C_2H_6O$  requires C 77.73 and H 6.07 per cent., whilst Jena finds C 78.7 and H 5.8 per cent., or values intermediate between the foregoing and those required for the formula  $C_{30}H_{24}O_4$ . A similar, though smaller, error may have lowered the carbon and raised the hydrogen in Limpricht and Schwanert's analyses. The melting point of the substance analysed would probably afford no intimation of the presence of the alcohol, for we have found that the crystals containing alcohol do not, unless the temperature is rapidly raised in determining the melting point, melt lower than those from which the alcohol has been previously expelled.

A determination of alcohol of crystallisation was made, with the following result:—

1·3890 gram of crystallised substance, on heating at 120°, lost 0·1284 gram.

	Calculated for $C_{30}H_{24}O_4, C_2H_6O$ .	Found.
Alcohol in 100 parts....	9·31	9·24

As the percentage of hydrogen in the compound  $C_{30}H_{24}O_4, C_2H_6O$  differs from that of a compound of the formula  $C_{30}H_{26}O_4, C_2H_6O$ , we analysed a specimen of the air-dried substance containing alcohol of crystallisation:—

Substance.	$CO_2$ .	$OH_2$ .
0·1145	0·3256	0·0619

	Calculated for $C_{30}H_{24}O_4, C_2H_6O$ .		Found.
$C_{32}$ .....	384	77·73	77·55
$H_{30}$ ....	30	6·07	6·01
$O_5$ .....	80	16·20	—
	<hr/> 494	<hr/> 100·00	

The formula  $C_{30}H_{26}O_4, C_2H_6O$ , on the other hand, requires C 77·42 and H 6·45 per cent. The value obtained for hydrogen, coupled with that yielded by the compound dried at 120°, appears to us to afford strong evidence in favour of the formula with less hydrogen.

From a solution in hot benzene, the condensation-product is deposited in minute rhomboidal plates generally grouped in rosettes, and containing benzene of crystallisation. The crystals, when exposed to the air, effloresce and become opaque. A portion of the crystallised substance, freed from adhering benzene by pressure between filter-paper and brief exposure to the air, on heating at 120°, lost 14·96 per cent. of its weight. The formula  $C_{30}H_{24}O_4, C_2H_6O$  requires a loss of 14·83 per cent.

Limpricht and Schwanert (*loc. cit.*) state that by heating "ethyldibenzoïn" with acetyl chloride, a monacetyl-derivative melting at 145° is obtained. We have been unable to confirm this result. The substance may be heated for an hour with acetyl chloride at 100° without undergoing change. Protracted heating, or a higher temperature, produces resinification. We were equally unable to obtain an acetyl-derivative by boiling the substance with acetic anhydride. We have, however, made an observation which, we think, explains the supposed existence of a monacetyl-derivative. When the condensation-product is recrystallised several times from glacial acetic acid, the melting

point sinks each time, until a limit is reached, when a substance is obtained melting at about  $130^{\circ}$ . This limit may be reached in a single crystallisation, by boiling the compound for some hours with the acetic acid. The substance thus obtained is not an acetyl-derivative, but a compound of the condensation-product with acetic acid (or possibly with acetyl and hydroxyl). On exposure to the air, and more rapidly on heating, it parts with acetic acid; and its melting point lies anywhere between  $130^{\circ}$  and  $200^{\circ}$  (the melting point of the original substance), according to the amount of drying to which it has been subjected. It is possible that Limpricht and Schwanert, if they employed acetic acid as a solvent, may have obtained this molecular compound, and analysed a product from which the acetic acid had been only partially expelled. This would account for the melting point found by these investigators; and the substance in this condition would also give figures agreeing more or less with those required for a monacetyl-derivative, seeing that the composition of such a derivative lies almost intermediate between that of the molecular compound and that of the original condensation-product.

	Calculated for		
	$C_{30}H_{24}O_4, C_2H_4O_2$	$C_{30}H_{23}(C_2H_3O)O_4$	$C_{30}H_{24}O_4$
C .....	75.59	78.37	80.36
H .....	5.51	5.31	5.36
O .....	18.90	16.32	14.28
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

A specimen of the molecular compound, melting at  $133^{\circ}$ , gave on analysis C 75.48 and H 5.34 per cent.

As Limpricht and Schwanert publish no details of preparation, or analytical figures, in connection with their acetyl compound, we have no means of testing the correctness of the above supposition.

In the benzene mother-liquors remaining from the purification of the foregoing condensation-product, we found a second substance, which was deposited in minute yellow crystals melting at  $232^{\circ}$ . A larger quantity of this substance was obtained from the original alcoholic potash mother-liquors (after removing the compound  $C_{30}H_{24}O_4$ ), by acidifying with hydrochloric acid, distilling off the alcohol to a small bulk, and precipitating the organic substance by the addition of water. This precipitated substance was treated with alcohol, in order to remove benzoic acid and a soluble resin, and the crystalline residue was dissolved in hot phenol, and reprecipitated with alcohol. By a repetition of this crystallisation from phenol, the substance was

obtained as a yellow crystalline powder, melting as above at  $232^{\circ}$ . Analysis gave numbers agreeing with the formula  $C_{46}H_{34}O_4$  :—

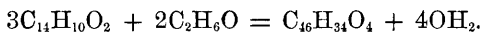
	Substance.	CO <sub>2</sub> .	OH <sub>2</sub> .
I ....	0.1354	0.4204	0.0657
II ....	0.1534	0.4769	0.0742
III ....	0.1492	0.4640	0.0735

	Calculated for $C_{46}H_{34}O_4$ .		Found.		
			I.	III.	III.
C <sub>46</sub> ...	552	84.92	84.67	84.78	84.81
H <sub>34</sub> ..	34	5.23	5.39	5.37	5.47
O <sub>4</sub> ....	64	9.85	—	—	—
	650	100.00			

These analyses were made with different preparations.

The formation of a compound of the above formula from benzil and alcohol may be expressed by the following equation :—



We have also found that dilute alcoholic potash acts slowly on benzoin in the cold, and, when air is excluded during the reaction, gradually converts it into a compound crystallising in silky needles, which melt at  $250^{\circ}$ , and are apparently distinct from any of the compounds hitherto obtained by the action of potash on benzoin. An account of this reaction is reserved for a future communication.

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