LXXXII.—Action of Light and of Oxygen on Dibenzyl Ketone.

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It was noticed by Professor S. Young in 1896 that a quantity of dibenzyl ketone, which had been prepared by him in 1891 and kept in stoppered vessels, had undergone partial decomposition, and that the action was the greatest in the case of those specimens which had been most exposed to light. At his suggestion, I undertook to investigate the action.

A considerable quantity of an acid yellow liquid had formed in the flasks containing the ketone. This was poured off, treated with sodium carbonate solution, extracted with ether, and the ethereal solution After distilling off the ether, a small quantity of an oily liquid, dried. giving the reactions of benzaldehyde and having its characteristic odour, came over below 250°, after which the temperature rose rapidly to the boiling point of dibenzyl ketone. The solution was acidified with hydrochloric acid, when a white, crystalline precipitate immediately formed; the liberated acids were extracted with ether and the ethereal solution was dried. After distilling off the ether, the residue solidified on cooling, and proved to be a mixture of benzoic and phenylacetic acids. After repeated fractional crystallisation from water, benzoic acid melting at 120° was obtained. Pure phenylacetic acid melting at 76° was also isolated from the mixture by recrystallisation from light petroleum. It seems probable that the ketone is first oxidised to a mixture of phenylacetic acid and benzaldehyde, according to the equation :

 $(C_6H_5 \cdot CH_2)_2CO + O_2 = C_6H_5 \cdot CH_2 \cdot COOH + C_6H_5 \cdot CHO,$

and that the latter is then oxidised to benzoic acid.

In order to test the action of heat in absence of light, a sealed tube containing pure recrystallised dibenzyl ketone and filled with oxygen was heated to 100° in a steam chamber for ten days. The contents of the tube had then become yellow, and gave an acid reaction when tested with litmus. A tube containing dibenzyl ketone, and ex-

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hausted of air, was treated similarly, but the contents remained unchanged. A second exhausted tube was then heated for some days in the vapour of boiling quinoline, but no decomposition of any sort took place. This harmonises with the fact, previously noted by Professor Young, that dibenzyl ketone may be used for some time as a jacketing agent without sensible alteration, the reason no doubt being that the contact with air is so small.

With a view to ascertain whether the oxidation of dibenzyl ketone would take place in absence of moisture, some 'crystals were placed in one limb of a bent tube, the other containing phosphorus pentoxide. After passing a current of dry air, the tube was sealed and kept in the dark for three weeks; it was then exposed to light. In a fortnight's time, the crystals had a decided yellow tinge, and after some months they had become deep yellow, and the liquid had an acid reaction, showing that absence of moisture had not prevented the decomposition of the ketone from taking place. A similar experiment was made, keeping the tube in the dark for nine weeks to ensure complete freedom from moisture, and then sealing off the limb containing the dibenzyl ketone and exposing it to sunlight. The result corroborated that obtained in the former experiment, marked decomposition taking place in a few months' time.

So far the decomposition of dibenzyl ketone observed had been due to the presence of oxygen. An experiment was now made to test the stability of the ketone in the absence of oxygen. Two tubes containing pure dibenzyl ketone were exhausted of air, a third was filled with carbon dioxide in place of air, and, for the sake of comparison, a fourth containing the ketone was filled with oxygen. All four tubes were exposed in a garden for two years. On opening the tubes, they were all found to contain carbon monoxide, which burnt with its characteristic blue flame, and toluene boiling at 110°, and yielding dinitrotoluene on nitration.* In addition, they all contained a white, solid substance, insoluble in water, alcohol, ether, carbon bisulphide, benzene, &c., but readily soluble in chloroform. It melted at 193—194°, and gave the following result on analysis:

0.1464 gave 0.4603 CO_2 and 0.0818 H_2O . C = 85.75; H = 6.21. $C_{30}H_{26}O_2$ requires C = 86.12; H = 6.22 per cent.

The quantity at my disposal was unfortunately too small to allow of an accurate determination of the molecular weight, but it seems most probable that two molecules of the ketone combine together with loss of hydrogen.

^{*} The formation of carbon monoxide and toluene on heating dibenzyl ketone to 360° was observed by Engler and Löw (*Ber*, 1893, **26**, 1438).

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The action may possibly be represented by the equation :

$$3(C_6H_5 \cdot CH_2)_2CO = 2C_6H_5 \cdot CH_3 + CO + (C_{14}H_{13} \cdot CO)_2.$$

This was the only action observed in the case of the dibenzyl ketone in the exhausted tube, and in the tube containing carbon dioxide, the contents of both of which remained colourless, but in the case of the tube filled with oxygen, the ordinary decomposition into benzaldehyde, benzoic acid, and phenylacetic acid had also taken place, and the contents were deep yellow in colour. The tendency of dibenzyl ketone to undergo oxidation is in marked contrast to the behaviour of benzophenone, which is one of the most stable substances known.

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