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LVIII.—*Dibenzyl Ketone.*

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DIBENZYL KETONE, $(C_6H_5 \cdot CH_2)_2CO$, was prepared by Popow (*Ber.*, 6, 560) by the action of heat on calcium phenylacetate. The substance was obtained in crystals melting at 30° , and its boiling point was $320-321^\circ$. Calcium phenylacetate crystallises with 3 mols. H_2O , of which $2\frac{1}{2}$ mols. are expelled at 100° ; the remaining water is not easy to remove completely, for the salt becomes viscous if the temperature be raised quickly to about 130° in an ordinary copper air-bath, and in this condition the water is obstinately retained. When heated more strongly in the air, the salt darkens in colour, and evidently undergoes partial decomposition. In order to remove the

water as completely as possible, the temperature should be raised very gradually from 100° to 130°.

A quantity of the dried calcium salt was first heated in a hard glass tube in a combustion furnace, a current of carbon dioxide being passed through the tube, and the temperature kept as low as possible. This method is, however, very tedious, and the product obtained was very far from pure; but by fractional distillation and crystallisation from ether, about 27 per cent. of the theoretical yield was obtained. The melting point of the pure product was 33·85°, and on distillation it boiled quite constantly.

In order, if possible, to discover some better method of preparation, the effect of heat on the calcium salt was more carefully studied. The salt, dried in the steam chamber, was placed in a bulb with a long neck, through which a current of carbon dioxide was constantly passed, and it was heated by the vapours of pure liquids, with the following results:—

At 130° water was expelled, but the salt did not melt.

At 150° more water was expelled, and the salt melted, forming a colourless, very viscous mass.

At 184° and 223° a very little water was expelled, and the salt frothed up slightly.

At 284° a slight turbidity, and a very little discoloration, was observed.

At 360° white fumes were evolved and condensed to a heavy oil, which solidified on the addition of a crystal of dibenzyl ketone. The quantity formed was very small, but after half-an-hour's heating the melted salt had become quite opaque.

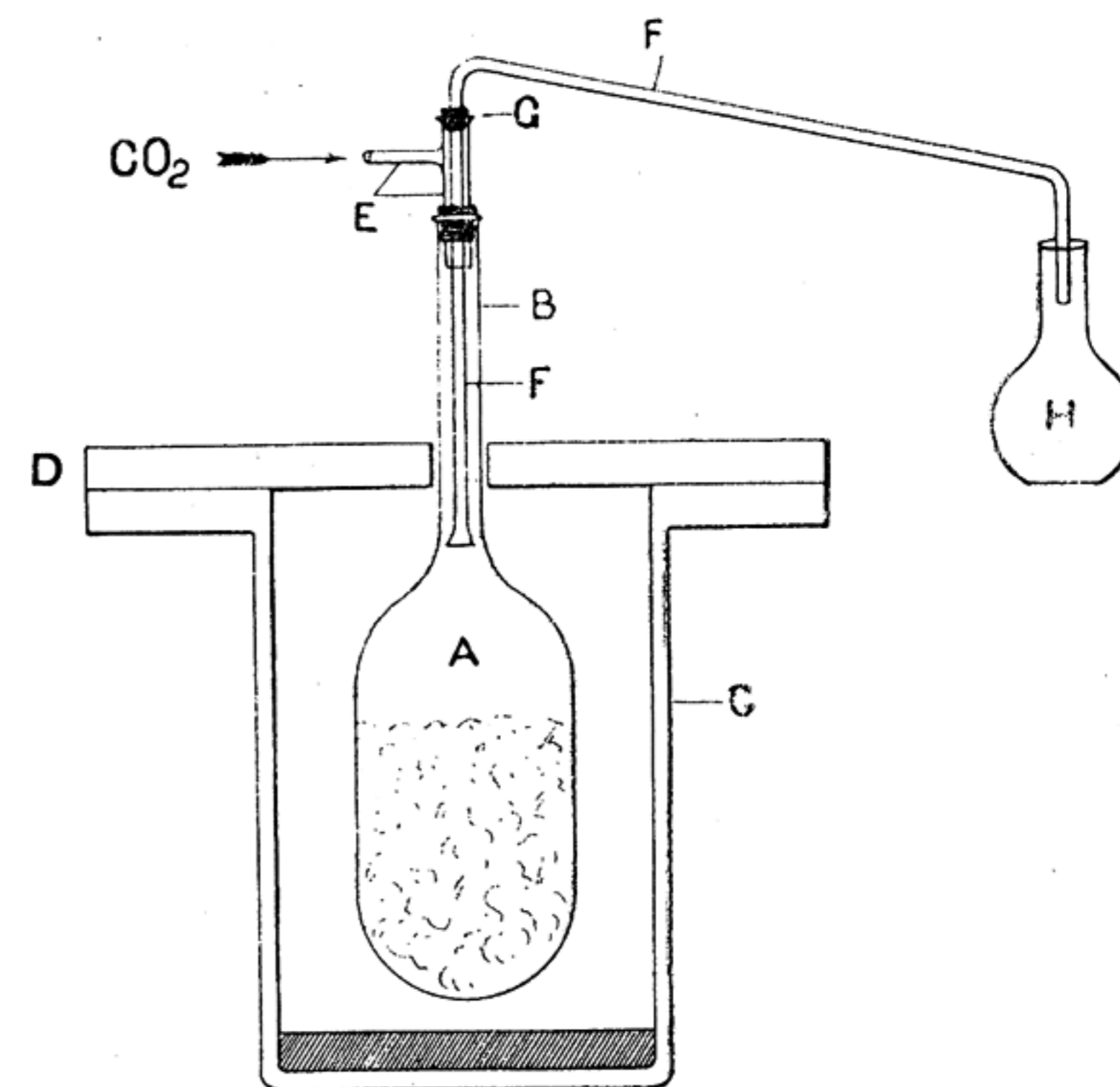
At 446° the ketone came over freely, and condensed as a clear liquid, colourless at first, but gradually becoming yellow, orange, and finally brown, as the distillation proceeded. The residue in the bulb consisted of calcium carbonate, together with a little dark, oily substance.

From these results it appears that it is necessary to heat the calcium salt above 360°, but that a temperature of 450° should not be exceeded.

The apparatus finally adopted is shown in vertical section in the diagram.

The calcium salt, dried at 130°, was placed in the wide, cylindrical glass bulb A, sealed to the narrower tube B. This was heated in the flanged iron vessel, C, provided with the heavy iron cover D (this iron vessel had previously been employed by Dr. Richardson as a sulphur-bath, in his research on the dissociation of nitrogen peroxide). The tube B was provided with an indiarubber cork, through

which the T-tube E passed. A piece of barometer tubing, FF', enlarged conically at its lower end, passed through the T-tube and the tube B, and was attached to the T-tube by an ordinary cork, G, which the T-tube E passed. A piece of barometer tubing, FF', enlarged conically at its lower end, passed through the T-tube and the tube B, and was attached to the T-tube by an ordinary cork, G,



the temperature being too high to admit of an indiarubber cork being employed. The barometer tube was bent, as shown in the diagram, after the T-tube and the cork G had been placed in position. The vessel AB, containing the salt, was first placed in the bath, and the perforated iron cover passed over the tube B; the tubes E and F were then placed in position, and the vessel AB secured by means of a retort stand and clamp. The iron bath, containing sulphur, rested on a tripod, and was heated by a Bunsen burner below and a couple of burners at the sides. A slow current of dry carbon dioxide was passed constantly through the apparatus, entering the T-tube E, passing between the tubes B and F', and finally escaping through the tube FF'.

In this way, all vapour that was evolved from the calcium salt was forced into the barometer tube, where it condensed, and was carried into the receiver H.

The heavy iron cover D never became heated to the boiling point of sulphur, and acted as a very efficient condenser, the escape

of sulphur vapour being extremely small, and causing no inconvenience.

This method possesses the following advantages:—

(1.) Larger quantities can be heated than by the ordinary method, from 40—50 grams of the crude ketone being obtained in each operation with the apparatus actually employed, and there seems no reason why a larger one should not give good results. (2.) The temperature does not rise above 450°, and serious loss, owing to decomposition of the ketone, is thus avoided. (3.) The condensed liquid is prevented, to a great extent, from flowing back into the hot bulb, and this seems to be of considerable importance, for the large surface of strongly heated calcium carbonate would otherwise cause a considerable amount of decomposition. (4.) The hot, condensed liquid does not come in contact with any cork or indiarubber. (5.) There is very little fear of breakage, for the bulb A is gradually and uniformly heated, and the hot liquid does not come in contact with any sealed joint, as in the ordinary distillation apparatus. (6.) A partial separation of the distillate into fractions is carried out in the preparation of the substance.*

1 kilogram of phenylacetic acid should give 772 grams of dibenzyl ketone. In the actual experiments, 928 grams of the acid (obtained from Kahlbaum) were converted into calcium salt and subsequently heated, but as the amount of acid was not far short of a kilogram, I have corrected all the weights of the ketone obtained to what they would have been if a kilogram had actually been employed.

The distillate was collected in each operation in four fractions: the first was nearly colourless, but contained some water; the colour of the second was pale-yellow, of the third brownish-yellow, and of the last a deep reddish-brown. The second fraction solidified almost completely, the third contained some liquid after cooling, the fourth gave a considerable crop of crystals, but the solidification was far from complete.

The results obtained (calculated for 1 kilo. of acid) are given below:—

Fraction.	I.	II.	III.	IV.	Total.
Weight in grams ..	36.5	289.5	273.0	120.5	719.5
Melting point	not observed	29.5°	28.0°	not observed	—

The first fraction was then pressed between filter paper in a copying press; the second was gently warmed and the liquid poured off; the third and fourth were filtered by means of a filter pump. The

* It is possible that still better results might be obtained at a somewhat lower temperature with an air-bath of the form devised by Lothar Meyer.

quantities and melting points after this preliminary purification were as follows:—

Fraction.	I.	II.	III.	IV.	Total.
Weight	32.5	232.5	242.0	75.5	582.5
Melting point	32.6°	32.25°	31.4°	31.2°	—

The four fractions were melted together, a little ether added, and the ethereal solution allowed to crystallise slowly. Beautiful large crystals were thus obtained, and, after pouring off the mother liquor, these were melted again and recrystallised from ether, the process being repeated several times. Part of the ether from the mother liquors was in each case removed by distillation, fresh crops of crystals being thus obtained, and these were further purified by recrystallisation from ether.

The recrystallised product was finally distilled, and was found to boil quite constantly at 330.55° (corrected to 760 mm. at 0°). The melting point, obtained by immersing a thermometer in the solidifying liquid, was 33.9°.

The weight of ketone obtained in this manner without any fractional distillation was 404.5 grams, or 52.4 per cent. of the theoretical yield.

The filtrates from the original fractions III and IV, the liquid poured off from II, and the residual ethereal mother liquors were subjected to fractional distillation, and the purest fraction recrystallised from ether. In this way a further yield of 187 grams of the pure product, melting and boiling at the same temperature, was obtained.

The total amount of pure ketone obtained was thus 591.5 grams out of a possible 772 grams, or 76.6 of the theoretical yield.

The remaining distillates, after being pressed between filter paper, melted at 33.1° and weighed 26 grams.

The residues in the bulb A were treated with hydrochloric acid to dissolve the calcium carbonate (a little alcohol being added towards the end to complete the solution), and the dark, oily residues were separated from the solutions of calcium chloride. The total weight, after washing with water, and while still moist, was 77.5 grams.

On distillation, the oil yielded small quantities of toluene, a liquid boiling, after purification, at 226—227° (corrected), about 12 grams of undecomposed phenylacetic acid, a little dibenzyl ketone (fractionated with the larger quantity of ketone), and a tarry residue.

The liquid boiling at 226—227° was examined by Mr. R. M. Prideaux and Mr. G. L. Thomas in this laboratory, with the following results:—