

THE PREPARATION OF INDONES

BY D. DALEV

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THERE are many methods of preparing indones. One of the commonest is that which was given more or less at the same time by Löwenbein and Ulich¹ on the one hand, and by Weiss and Sauermann² on the other. This method is not very convenient because most of the indones produced by it contain much impurity in the form of 3-benzalpthalide and some by-products, and the mixture of the latter with the indones is a sticky, resinous substance which prevents the indones from crystallisation. Weiss and his fellow worker removed the benzalpthalide by saponification with concentrated alcoholic ammonia. Under such conditions the purification of the greater proportion of the indone is difficult. Weiss does not mention the reasons which made him choose ammonia for the saponification of benzalpthalide.

My experiments have shown that dilute aqueous solutions of alkaline hydroxides or carbonates do not change the indones to any marked extent when boiled. The latter do not change even when they are mixed with benzalpthalide. The crude indones which are produced, after they are distilled from the ether-benzene mixture at a temperature below 100° C., form a thick substance resembling molten resin. The by-products of the reaction, such as hydrocarbons and unchanged halogenides, are separated from this mass by steam distillation.

The use of steam has this advantage, that it continuously stirs the resinous substance and almost completely separates the volatile compounds. From this it appeared that the benzalpthalide in the crude indone would be easily soluble under these conditions if the medium was alkaline. Experiment proved that a 1 to 2 per cent. solution of sodium hydroxide is suitable for saponification. An aqueous solution of sodium or potassium carbonate can be used equally successfully. What quantity of unchanged benzalpthalide there is with the different indones is, of course, not known. It can safely be assumed that the hydroxide or the carbonate can be calculated for at least 50 per cent. of unchanged benzalpthalide. The saponification is completed in most cases in about half an hour.

EXPERIMENTAL

General method. The organomagnesium compound is produced from 0.1 g. mol. of halogenide with a corresponding excess according to Gilman's table³ in order to produce a 100 per cent. yield. The ether solution of the organomagnesium compound is transferred to a separating funnel in such a way as to prevent oxidation from the air. The flask is closed with a rubber stopper through which passes a short glass tube. The flask is turned over quickly, the tube is put in the separating funnel and almost all the ether solution is poured out of the flask in which there always remains a little of the ether solution of the organomagnesium com-

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pound and a little magnesium. A solution of 22.2 g. of benzaldehyde in 100 ml. of dry benzene is quickly poured in, followed by the solution, first drop by drop, and then in a thin stream, at the same time continually shaking the flask. Very often the inside of the flask becomes covered with a thick yellow-brown precipitate which fills the whole flask before all the ether solution is added. The temperature rises and the solution in the flask begins to boil. Boiling is prevented by cooling with water from time to time. After adding all the ether solution, the contents are stirred well with a metal rod and boiled over steam for 1 hour. At the bottom of the flask there almost always gathers a dark red sticky substance which is scraped off and stirred with a rod, two or three times while the heating lasts. It is left overnight and decomposed with ice and dilute sulphuric acid. In some cases water followed by sulphuric acid may be used—the temperature does not rise very much. Decomposition is completed in a short time, and the ether-benzene layer, of a colour something between orange and red, is separated. It is washed several times with a dilute alkali and with water and distilled directly in steam. At first the ether and the benzene distil quickly, and afterwards the unchanged halogenide and the other by-products of the reaction which are volatile in steam. The distillation in steam is continued until a clear liquid passes, sometimes over 10 or 12 hours. Distillation is then stopped and, without cooling, a sufficient quantity of dilute sodium hydroxide solution to produce about a 2 per cent. solution is poured in and distillation in steam is continued for another hour. When the resinous substance has deposited, the deep-red aqueous layer is poured off, and the resinous substance is again distilled in steam for another hour. When treated with alkali the indone often turns into a solid mass, and its removal from the flask becomes impossible. The solid mass contains a good deal of water, and for this reason its solubility in ether is very small, but it dissolves easily in chloroform. The chloroform solution is washed with water, and dried with dehydrated sodium sulphate and the chloroform is distilled off.

The following 12 indones have been prepared by this method and identified:—

| | m.pt. |
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| 2:3-diphenylindone ⁴ | 153°C. |
| 2-phenyl-3-tolylindone ⁵ | 123° to 125°C. |
| 2-phenyl-3- <i>m</i> -tolylindone | 113°C. |
| 2-phenyl-3- <i>p</i> -tolylindone ⁷ | 133 to 134°C. |
| 2-phenyl-3- <i>p</i> -bromo-phenylindone ⁷ | 172 to 174°C. |
| 2-phenyl-3- <i>α</i> -naphthylindone | 182 to 183°C. |
| 2-phenyl-3-benzylindone | 135°C. |
| 2-phenyl-3- <i>β</i> -naphthylindone | 132°C. |
| 2-phenyl-3- <i>cyclohexyl</i> indone | 162 to 163°C. |
| 2-phenyl-3- <i>isopropyl</i> indone | 110°C. |
| 2-phenyl-3- <i>isoamyl</i> indone | 74°C. |
| 2-phenyl-3- <i>ethyl</i> indone | 98°C. |