[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

THE PREPARATION OF ZINC METHYL.[1]

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Apparently the greatest difficulty in the preparation of zinc alkyl compounds is in obtaining a highly active zinc-copper couple. A number of investigators have made recommendations for its preparation, but in the judgment of the writers, as matters stand, the accomplishment is an art rather than a science. In general, the inexperienced worker will at first find difficulty in preparing couples as active as those described by Lachman[3] and by Gladstone and Tribe.[4]

This difficulty, while not of great significance in the preparation of zinc ethyl, is serious when one attempts to prepare the methyl derivative, for the velocity of the reaction between methyl iodide and the zinc-copper couple is very much less than that with ethyl iodide; Gladstone and Tribe[4] estimate it as hundreds of times less.

A number of experiments were carried out under various heat treatments, using commercial zinc dust directly with copper oxide and also acid washed zinc dust with finely divided, precipitated copper. Couples were obtained which were fairly active with ethyl iodide, but none of them was as active as the products prepared later from 30-mesh zinc and precipitated copper, nor were they nearly as active as the couples prepared from zinc filings by Gladstone and Tribe.[4] In the absence of a catalyst they were all acted on very slowly by methyl iodide. At least a partial explanation of the greater activity of the granulated zinc couples is believed to lie in the greater porosity, which allows a better penetration of the iodide.

As might have been expected from the fine subdivision of the zinc in the zinc dust as compared with the filings, relatively more copper oxide than that used by Lachman was found to increase the activity.

Experiments were carried out with the idea of being able to define the conditions of heat treatment for the most active couple. This was done by placing the well-mixed material in a 25 mm. glass tube which was imbedded in a trough full of sand and heated over a combustion furnace, while a current of dry hydrogen was passed through the tube. The temperature of the sand throughout the length of the trough was difficult to maintain uniform. It appeared that the best temperature was about 400°, but without special apparatus, as for instance an auto-

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[3] Lachman, *Am. Chem. J.*, **24**, 31 (1900).

[4] Gladstone and Tribe, *J. Chem. Soc.*, **35**, 569 (1879).

clave heated to a constant temperature and fitted with a stirrer, it is believed that it is better to judge the desired heating by the appearance of the material. As the change in appearance of the material on heating is so characteristic it is believed that no one will have difficulty in preparing an active couple by using the following directions. The commercial 30-mesh zinc may be used directly if free from grease and not badly oxidized. Otherwise the zinc should be shaken up in a bottle in turn with dil. hydrochloric acid, water, alcohol and ether and then connected to a vacuum pump and the bottle placed in a hot air bath. This treatment is neither laborious nor long. The copper may be prepared by precipitating a 5% copper sulfate solution with zinc. Zinc dust works excellently. The copper is filtered, washed with water, a little alcohol and then with ether and dried by heating under a vacuum. Nine parts of the zinc are then thoroughly mixed with one part of copper and the mixture placed in a long combustion tube. The amount of material should be such as to fill the tube a little less than half full. Plugs of glass wool are placed at both ends to keep the material from rolling out. Dry hydrogen is then passed into the tube and when the air is replaced the tube is heated over the free flames of the combustion furnace and rotated rapidly. If the flames are of equal height, no trouble is experienced in having part of the material fuse while other portions are not sufficiently heated; as the tube becomes hot, the copper appears to separate out and become spongy. This gradually then works into the zinc, giving it a yellowish color and then a little more heat causes the zinc to form little pellets of a tarnished lead color. This is the stage at which to stop. Higher heating causes the pellets to sinter together and take on a reddish color. With care the whole contents of the tube may be converted into uniform, lead-colored pellets. The couple should be allowed to cool in hydrogen and bottled up if not to be used immediately. Batches of 200 g. may be prepared in this manner in 12 to 15 minutes.

The catalytic effect of a few substances was tested roughly. Early experience had confirmed the accelerating effect of dry ether, but small amount of this substance did not have the influence of either acetonitrile or methyl acetate.

The following experiments were carried out with a moderately inactive couple in order to make more pronounced the effect of the catalyst.

1. 2.5 cc. of ethyl iodide and 10 g. of couple when heated in a water bath at 60° under a reflux condenser ceased to return ethyl iodide in slightly over 14 minutes.

2. The same to which 2 drops of acetonitrile were added, ceased within 5.5 min.

3. The same with the addition of 2 drops of methyl acetate ceased within 4.5 minutes.

The Preparation of Zinc Methyl.—The set up of the apparatus was as follows. A short-necked 500 cc. flask containing 300 g. of couple was fitted with a cork bearing a dropping funnel and a 12 mm. glass tube bent at right angles just above the cork. This tube was surrounded by a Leibig's water jacket, and the other projecting end was fitted with a cork and inserted far into a distilling flask. The side tube of the latter was connected to a mercury seal by means of rubber tubing. The flask with its rubber tubing connection and a pinchcock, was weighed. After the air in the apparatus was displaced with carbon dioxide 110 g. of methyl iodide mixed with one cc. of methyl acetate was added to the couple through the dropping funnel. The apparatus was tilted so that the tube acted as a reflux condenser. It was found convenient to set up the apparatus in the late afternoon and allow it to stand overnight and then warm the flask on a water bath at 60° the next day. Usually condensation ceased by late afternoon, *i. e.*, after about 7 hours heating. When the reaction was complete the apparatus was tilted so that the tube acted as a condenser. The distilling flask was packed in ice and the reaction flask heated in an oil bath until zinc methyl no longer distilled off. Carbon dioxide was passed through the dropping funnel slowly during the distillation and more rapidly at the end, in order to drive the zinc methyl out of the apparatus, and also to fill the neck of the receiving flask with this inert gas. Finally the cork attached to the distilling flask was carefully moved down to the end of the tube while the carbon dioxide was passing through and the distilling flask disconnected and a cork fitted with a dropping funnel and previously weighed, was quickly inserted. After closing the pinchcock, the flask and its attachment were weighed and the amount of zinc methyl calculated. The zinc methyl was then directly treated with the desired reagent.

The records of a large number of runs gave weights of the crude zinc methyl obtained varying between 40 and 45 g. The theoretical yield would have been 42.1 g. The weighings were, however, rough and no corrections were made for the difference in weights of the carbon dioxide and the air. Then, too, probably small amounts of methyl iodide were present in some cases.

The literature does not seem to mention one important property of zinc methyl iodide, namely that at ordinary temperatures it dissociates to give enough zinc methyl to cause the vapor above it to inflame spontaneously when exposed to the air.

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