



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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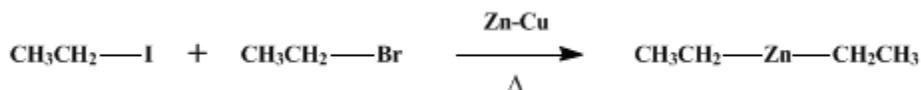
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.184 (1943); Vol. 12, p.86 (1932).

DIETHYL ZINC

[Zinc, diethyl-]



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1. Procedure

In a 500-cc. round-bottomed flask, provided with a reflux condenser (Note 1) and a heavy stirrer (Note 2), is placed 130 g. (approximately 2 gram atoms) of zinc-copper couple (Note 3). To this is added a mixture of 78 g. (0.5 mole) of ethyl iodide and 54.4 g. (0.5 mole) of ethyl bromide (Note 4); the stirrer is started and the mixture heated to refluxing. After one-half hour of refluxing, the reaction starts (Note 5), as is evidenced by the greatly increased rate of refluxing, and the flame is removed. If the reaction becomes too vigorous, the flask is cooled with ice water, but only to the point where the reaction is again under control (Note 6). At the end of one-half hour from the time the flame is removed, the reaction is usually over. The flask is allowed to cool to room temperature (Note 7), connected with a distilling head, condenser, and receiver, and the contents are distilled under reduced pressure (Note 8) directly from the reaction flask into a 200-cc. round-bottomed flask immersed in an ice-salt mixture (Note 9). At the end of the distillation, dry carbon dioxide or purified nitrogen is admitted to the apparatus (Note 10). The yield of crude material, which is sufficiently pure for most purposes, is 53–55 g. (86–89 per cent of the theoretical amount).

For purification, a 30-cm. fractionating column of the Vigreux type is fitted with a condenser and receiving flask provided with a vent. The extension of this vent is covered with a test tube carrying another small tube for admitting carbon dioxide; the end of the test tube is then loosely plugged by a piece of cotton wool (Note 11). The apparatus is swept out with carbon dioxide, and the round-bottomed flask containing the once-distilled diethyl zinc is connected to the column. The diethyl zinc is then redistilled at atmospheric pressure. The yield of material boiling at 115–120° is 50–52 g. (81–84 per cent of the theoretical amount) (Note 5) and (Note 12).

2. Notes

1. The use of dry apparatus and the exclusion of atmospheric moisture are essential to smooth starting of the reaction. Consequently, the top of the condenser is either provided with a drying tube containing calcium chloride or attached to a trap¹ to exclude the atmosphere.
2. A slow-moving stirrer that fits the bottom and sides of the flask is necessary in order to keep the zinc thoroughly agitated.
3. The zinc-copper couple may be prepared by either of the following methods:
 1. (a) A mixture of 120 g. of zinc dust and 10 g. of powdered copper oxide in a 200-cc. round-bottomed flask is heated gently over a free flame in a current of hydrogen with stirring or rotation of the flask until the copper oxide is reduced and a uniform gray mixture is obtained. The temperature should be kept just below the point of fusion during the heating.
 2. (b) A zinc-copper alloy containing 5 to 8 per cent copper is prepared by melting zinc with clean brass turnings and casting into bars. This is turned into fine shavings and is ready for use.

When only small quantities of zinc alkyls are to be prepared, method (a) may be used to advantage. For large quantities it is believed that the zinc-copper alloy turnings (b) are more convenient. Zinc-copper couple prepared by method (a) must be used at once or stored in an atmosphere of dry inert gas, as it rapidly deteriorates on exposure to moist air.

The method recommended by Noyes² does not seem to yield so active a couple as either of the above methods, and, although it gives entirely satisfactory results if pure iodides are used, the yields with a mixture of iodides and bromides are lower.

4. The use of a mixture of alkyl iodide and alkyl bromide is not only less expensive but the reaction is not so vigorous as when the alkyl iodide alone is used. Directions for preparing [ethyl bromide](#) are given in *Org. Syn. Coll. Vol. I*, **1941**, 29, 36.

5. The submitter observed that reaction generally started in twenty to forty minutes after refluxing began. The checkers found that the time for reaction to set in was nearer one and one-quarter hours. Unless all precautions to exclude moisture are exercised, the reaction may not start for several hours. In such cases, after the preliminary period of stirring and heating externally, the mixture can be allowed to stand at room temperature without stirring. Under these conditions the reaction always started spontaneously (sometimes after five hours) and required no attention, for when reaction did set in the refluxing was not sufficiently vigorous to require cooling. When the reaction is slow in starting, the yield of [diethyl zinc](#) is somewhat lower.

6. If the mixture is cooled too much, the reaction may stop entirely and is difficult to start again. If this happens the yield will be considerably lower.

7. On cooling, the reaction mass solidifies (probably on account of the re-formation of $RZnX$) and may be briefly exposed to air without danger. The solid material is much less reactive than [diethyl zinc](#).

8. The pressure should be below 30 mm. of [mercury](#) or decomposition will occur.

9. Either a special adapter with a side arm for applying suction may be used or a piece of right-angled tubing may be inserted in the same stopper with the condenser tube.

10. When the distillation is carried out under reduced pressure there is no need to sweep out the apparatus with inert gas. At other times, exposure to air must be prevented by using an atmosphere of [carbon dioxide](#) or [nitrogen](#).

The checkers carried out this distillation by heating the flask in an oil bath (about 200°) at a pressure of about 8 mm. The distillation was complete in about one hour. The flask can also be heated directly with a full Bunsen flame.

11. This vent can be replaced by a mercury seal formed by connecting a double right-angled glass tube from the upper part of the receiving flask to a container with [mercury](#). The tube is only slightly immersed in the [mercury](#). When a mercury seal is used, the receiver must be removed when distillation is completed in order that [mercury](#) may not be pulled into the receiver when the system commences to cool.

12. Using the same procedure, the yields and boiling points of higher zinc alkyls are as follows: [di-*n*-propyl zinc](#), 85–86 per cent, b.p. 39–40°/9 mm.; [di-*n*-butyl zinc](#), 78–79 per cent, b.p. 81–82°/9 mm.; [di-isoamyl zinc](#), 50–55 per cent, b.p. 100–103°/12 mm. The higher zinc alkyls should always be distilled under reduced pressure.

3. Discussion

[Diethyl zinc](#) has been prepared from [zinc](#) and mercury diethyl,³ and from [ethyl bromide](#) and [zinc-copper](#) couple using a special catalyst.⁴ [Diethyl zinc](#) is usually prepared by the action of [ethyl iodide](#) on specially treated [zinc](#),⁵ the [zinc-copper](#) couple being most useful for this purpose.^{6 7 2 8} The procedure described above has been published.⁹ Arylzinc halides, zinc dialkyls, and zinc diaryls may be prepared by the action of the Grignard reagent on anhydrous [zinc chloride](#) in [ether](#) solution.¹⁰

Attention is called to an improved apparatus for the preparation, purification, and use of zinc ethyl.¹¹

References and Notes

1. Gilman and Hewlett, *Rec. trav. chim.* **48**, 1124 (1929).
2. Noyes, "Organic Chemistry for the Laboratory," 3rd Ed., p. 61, 1916.
3. Frankland and Duppa, *J. Chem. Soc.* **17**, 31 (1864).
4. Job and Reich, *Bull. soc. chim.* (4) **33**, 1424 (1923).
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7. Lachman, Am. Chem. J. **19**, 410 (1897); **24**, 31 (1900).
 8. Renshaw and Greenlaw, J. Am. Chem. Soc. **42**, 1472 (1920).
 9. Noller, J. Am. Chem. Soc. **51**, 594 (1929).
 10. Houben-Weyl, "Methoden der organischen Chemie," 2nd Ed., 1924, Vol. 4, pp. 754, 901; Blaise, Bull. soc. chim. (4) **9**, I-XXVI (1911); Gilman and Brown, J. Am. Chem. Soc. **52**, 4482 (Note 7) (1930).
 11. McCleary and Degering, Proc. Indiana Acad. Sci. **43**, 127 (1934) [C. A. **28**, 7245 (1934)].
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

mercury diethyl

zinc ethyl

calcium chloride (10043-52-4)

ether (60-29-7)

hydrogen (1333-74-0)

Ethyl bromide (74-96-4)

nitrogen (7727-37-9)

mercury (7439-97-6)

carbon dioxide (124-38-9)

copper (7440-50-8)

zinc (7440-66-6)

zinc chloride (7646-85-7)

copper oxide (1317-38-0)

Diethyl zinc,
Zinc, diethyl- (557-20-0)

zinc-copper

Ethyl iodide (75-03-6)

di-isoamyl zinc

di-n-propyl zinc

di-n-butyl zinc (1119-90-0)

