



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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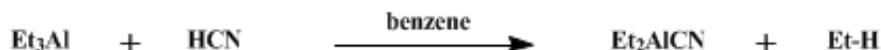
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DIETHYLALUMINUM CYANIDE

[Aluminum, cyanodiethyl-]



Submitted by W. Nagata¹ and M. Yoshioka.

Checked by S. C. Welch, P. Bey, and Robert E. Ireland.

1. Procedure

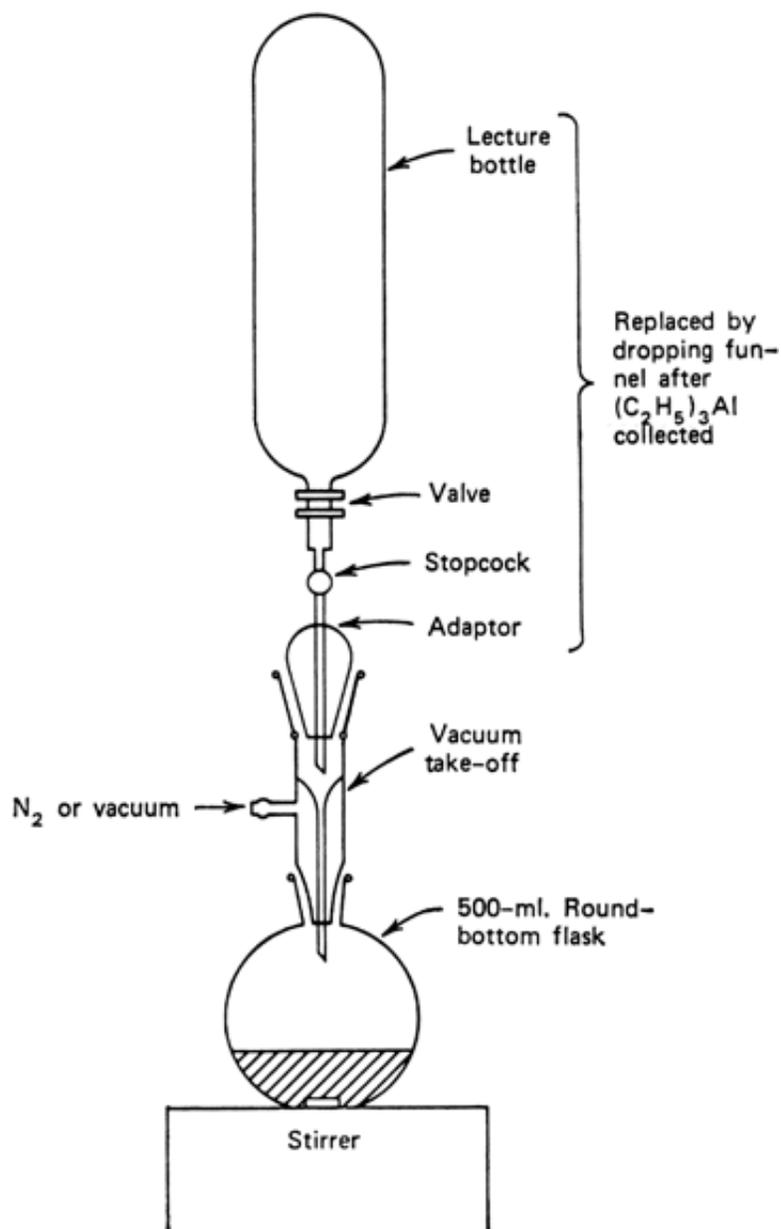
Caution! Dialkylzinc compounds, especially in undiluted form, are pyrophoric and must not be allowed to come into contact with air or moisture. These compounds should only be handled by individuals trained in their proper and safe use. [Note added January 2011]

Caution! This preparation should be conducted in a well-ventilated hood, and neat triethylaluminum must be handled with great care.

Benzene has been identified as a carcinogen. OSHA has issued emergency standards on its use. All procedures involving benzene should be carried out in a well-ventilated hood, and glove protection is required.

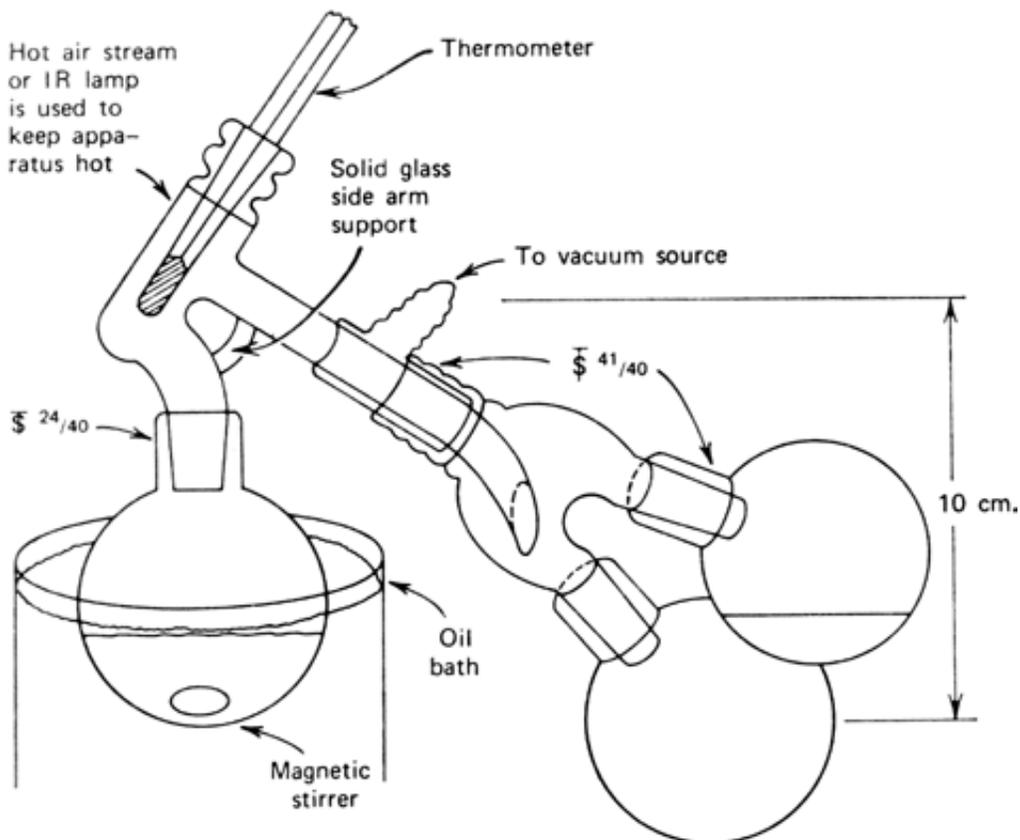
A tared, 500-ml., round-bottomed flask is fitted with a vacuum take-off, and the entire assembly is connected through an adaptor containing a stopcock to an inverted cylinder of triethylaluminum, as shown in Figure 1. The assembly is connected to a nitrogen source (Note 1) through the vacuum take-off, and with the cylinder valve closed but the stopcock open, the system is alternately evacuated and filled with nitrogen four times. With the system filled with nitrogen the cylinder valve is opened and approximately 55 ml. (46 g; 0.40 mole) of triethylaluminum (Note 2) is allowed to flow into the reaction flask. The cylinder valve is then closed; the system is evacuated and filled three times with nitrogen, and the adaptor stopcock is then closed (Note 3). The reaction flask is then quickly removed, stoppered, and weighed to determine the exact amount of triethylaluminum collected. A magnetic stirring bar is added and the flask is fitted with a vacuum take-off and 250-ml., pressure-equalizing dropping funnel. The system is again placed under a nitrogen atmosphere, and the triethylaluminum is dissolved in 150 ml. of anhydrous benzene, added through the dropping funnel. The dropping funnel is charged with a solution of 11.9 g. (0.441 mole) of hydrogen cyanide (Note 4) in 100 ml. of anhydrous benzene, which is added dropwise to the solution of triethylaluminum, with stirring and cooling. Preferably, the addition is carried out at a constant rate such that the hydrogen cyanide solution is added in about 2 hours. The evolution of ethane becomes slow suddenly after one molar equivalent of hydrogen cyanide is added (Note 5). After the addition is complete, the reaction mixture is allowed to stir overnight (Note 6).

Figure 1. Apparatus for collection of triethylaluminum.



After this period, the dropping funnel and the vacuum take-off are replaced by the short-path distillation assembly shown in Figure 2. The system is protected with a Drierite tube, and the benzene is distilled under reduced pressure (water aspirator). After the benzene is removed, the benzene-containing receiver is replaced with a clean, dry flask, and the system is connected to an efficient vacuum pump. The pressure in the system is reduced to 0.02 mm., and the flask is immersed deeply in an oil bath (Figure 2) heated to about 200°. After about 1 ml. of forerun is collected, diethylaluminum cyanide distils at 162° (0.02 mm.) (Note 7) and is collected in a tared, 200-ml. receiver by heating the side arm and the adaptor with a stream of hot air or an IR lamp (Note 8). After all the distillate is collected in the receiver (Note 9), dry nitrogen is admitted to the evacuated apparatus, and the receiver is stoppered, giving 26.7–35.6 g. (60–80%) of diethylaluminum cyanide, usually as a pale, yellow syrup (Note 10) and (Note 11).

>Figure 2. Short-path distillation apparatus.



The stopper of the flask is quickly replaced with the nitrogen adaptor, and after placing the system under a **nitrogen** atmosphere, the **diethylaluminum cyanide** is treated with 130 ml. of dry **benzene**. The resulting mixture is allowed to stand with occasional swirling under **nitrogen** until the syrup goes into solution (Note 12). Sufficient dry **benzene** is then added to make the total volume of the solution 200 ml. After thorough mixing with a magnetic stirring bar, the resulting **diethylaluminum cyanide** solution (13.4–17.8%; 1.2–1.6 M) may be divided and stored in sealed ampoules (Note 13).

2. Notes

1. The **nitrogen** source described in *Org. Synth.*, **Coll. Vol. 4**, 133 (1963), Figure 5, was used.
2. The exact volume of the **triethylaluminum** added at this point is not critical, since the exact weight is determined later. The use of a 25% solution of **triethylaluminum** in **benzene**, available from the Stauffer Chemical Company, 299 Park Avenue, New York, eliminates the tedious preparation of the **triethylaluminum** solution described in this procedure.
3. These precautions will ensure the removal of any adhering **triethylaluminum** that will flame when the apparatus is disassembled.
4. A 10% molar excess of **hydrogen cyanide** was employed, and the quantity added at this point was determined by the amount of **triethylaluminum** collected. **Hydrogen cyanide** can be prepared as described in *Tetrahedron Lett.*, 461 (1962).
5. The change in the rate of gas evolution is sometimes not clear, especially when the temperature of the hood is high. When the change is recognized distinctly, the addition of **hydrogen cyanide** solution may be stopped.
6. The reaction mixture containing about 13% (1.2 M) of **diethylaluminum cyanide** and a small amount of **ethylaluminum dicyanide** may be used for most hydrocyanation processes without further purification. Care must be taken to have no unchanged **triethylaluminum**, since the submitters have observed that hydrocyanation of Δ^8 -11-keto steroids with **diethylaluminum cyanide** is greatly retarded by the presence of a small amount of unchanged **triethylaluminum**.^{2,3}
7. The checkers collected **diethylaluminum cyanide** at 170–180° (0.35 mm.) and 167–175° (0.25 mm.).
8. Heating of the glassware above 150° with a hot air stream or IR lamp is needed to make the viscous product run into the receiver.
9. The pot residue contains **ethylaluminum dicyanide** as a nonvolatile mass, most of which may be

removed with a spatula and decomposed with [isopropyl alcohol](#) and then water. The flask is then washed with running water and 20% [hydrochloric acid](#) to remove the mass completely.

10. The submitters have obtained an almost colorless syrup by reaction of purified [triethylaluminum](#) with [hydrogen cyanide](#), followed by repeated distillation.

11. The yield depends on the efficiency of the collection of the viscous distillate in the receiver.

12. It takes considerable time (5–10 hours) to dissolve [diethylaluminum cyanide](#). Magnetic stirring is not effective unless most of the material goes into solution.

13. [Diethylaluminum cyanide](#) dissolved in [benzene](#), [toluene](#), [hexane](#), or [isopropyl ether](#) and stored in ampoules is stable for a long period. The cyanide is not stable in [tetrahydrofuran](#). The anhydrous [benzene](#) used in the reaction may be replaced by diethyl or diisopropyl ether. A 1–2 *M* solution of [diethylaluminum cyanide](#) in [benzene](#) is commercially available from Alfa Products, Ventron Corporation, Danvers, Massachusetts.

3. Discussion

Formation of [diethylaluminum cyanide](#) from [triethylaluminum](#) and [hydrogen cyanide](#) was noted initially by the submitters⁴ and later by Stearns,⁵ but isolation and characterization of the product were first performed by the submitters.³ An impractical process comprised of heating [diethylaluminum chloride](#) and [sodium cyanide](#) in [benzene](#) for 21 days has been reported.⁶

[Diethylaluminum cyanide](#) is a useful, potent reagent for hydrocyanation of various compounds. Features of this reagent as compared with the [triethylaluminum–hydrogen cyanide](#) reagent may be obtained from the literature.^{2,3,7}

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 6, 307](#)
- [Org. Syn. Coll. Vol. 6, 520](#)

References and Notes

1. Shionogi Research Laboratories, Shionogi & Co., Ltd., Fukushima-ku Osaka 553, Japan.
2. W. Nagata, "Proceedings of the Symposium on Drug Research," Montreal, Canada, June 1966, p. 188.
3. W. Nagata and M. Yoshioka, *Tetrahedron Lett.*, 1913 (1966); W. Nagata, M. Yoshioka, and S. Hirai, *J. Am. Chem. Soc.*, **94**, 4635 (1972).
4. W. Nagata, M. Yoshioka, and S. Hirai, *Tetrahedron Lett.*, 461 (1962).
5. R. S. Stearns, U.S. Pat. 3,078,263 (1963).
6. R. Ehrlich and A. R. Young, *J. Inorg. Nucl. Chem.*, **28**, 674 (1966).
7. W. Nagata and M. Yoshioka, "Proceedings of the Second International Congress on Hormonal Steroids," Excerpta Medica Foundation, Amsterdam, 1967, p. 327.

Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

diethyl or diisopropyl ether

[hydrochloric acid](#) (7647-01-0)

[Benzene](#) (71-43-2)

[sodium cyanide](#) (143-33-9)

hydrogen cyanide (74-90-8)

nitrogen (7727-37-9)

toluene (108-88-3)

isopropyl alcohol (67-63-0)

ethane (74-84-0)

Tetrahydrofuran (109-99-9)

isopropyl ether (108-20-3)

hexane (110-54-3)

triethylaluminum (97-93-8)

Diethylaluminum cyanide (5804-85-3)

Aluminum, cyanodiethyl-

ethylaluminum dicyanide

diethylaluminum chloride