



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

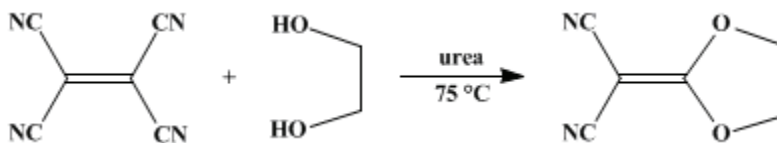
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 4, p.276 (1963); Vol. 39, p.13 (1959).*

## DICYANOKETENE ETHYLENE ACETAL

### [1,3-Dioxolane- $\Delta^{2,\alpha}$ -malononitrile]



Submitted by C. L. Dickinson and L. R. Melby<sup>1</sup>.

Checked by James Cason, Edwin R. Harris, and William T. Miller.

### 1. Procedure

*Caution! This preparation must be carried out in a good hood because hydrogen cyanide is evolved. It is inadvisable to allow contact of tetracyanoethylene with the skin.*

Urea (4.0 g., 0.067 mole) is dissolved in 50 ml. of distilled ethylene glycol (Note 1) contained in a 125-ml. Erlenmeyer flask. Finely divided recrystallized tetracyanoethylene (p. 877) (25.6 g., 0.20 mole) is added, and the flask is heated on a steam bath at 70–75° with frequent stirring by hand with a thermometer until solution is complete (about 15 minutes). The resultant brownish yellow solution is then cooled in ice water, and the precipitated dicyanoketene ethylene acetal is collected on a Büchner funnel. The acetal is first washed with two 25-ml. portions of cold ethylene glycol and then washed thoroughly with cold water to remove the ethylene glycol. The dicyanoketene ethylene acetal, which may be dried in air or in a vacuum desiccator, is obtained in the form of large slightly pink needles, m.p. 115–116.5° (Note 2); yield 21–23 g. (77–85%).

### 2. Notes

1. Moisture in the ethylene glycol leads to lowered yields. Satisfactory results are obtained with glycol collected at 199.5–201° from a simple distillation.
2. The color may be removed by recrystallization from ethanol after treatment with decolorizing carbon; however, the melting point is not improved and occasionally is found to be lowered.

### 3. Discussion

The synthesis of dicyanoketene ethylene acetal described here is a slight modification of one published recently.<sup>2</sup> The procedure has been applied successfully to the synthesis of dicyanoketene dimethyl acetal and dicyanoketene diethyl acetal.<sup>2</sup>

Dicyanoketene ethylene acetal reacts with tertiary amines to give quaternary ammonium inner salts.<sup>2</sup> Similarly, it reacts with sulfides to give sulfonium inner salts.<sup>2</sup> These products are generally solids that can be used to characterize tertiary amines and sulfides. Dicyanoketene acetals can be converted to pyrimidines, pyrazoles, or isoxazoles in one step.<sup>3</sup>

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### References and Notes

1. Contribution No. 481 from Central Research Department, Experimental Station, E. I. du Pont de Nemours & Co., Wilmington, Delaware.
2. Middleton and Engelhardt, *J. Am. Chem. Soc.*, **80**, 2788 (1958).
3. Middleton and Engelhardt, *J. Am. Chem. Soc.*, **80**, 2829 (1958).

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

1,3-Dioxolane- $\Delta^{2,\alpha}$ -malononitrile

ethanol (64-17-5)

hydrogen cyanide (74-90-8)

decolorizing carbon (7782-42-5)

ethylene glycol (107-21-1)

urea (57-13-6)

Dicyanoketene ethylene acetal (5694-65-5)

dicyanoketene dimethyl acetal

dicyanoketene diethyl acetal

Tetracyanoethylene (670-54-2)