



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.

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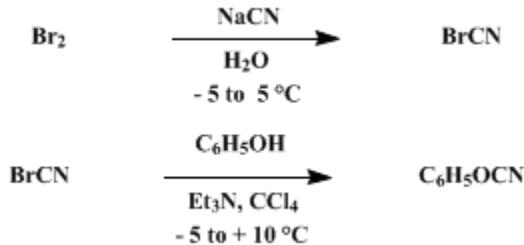
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 7, p.435 (1990); Vol. 61, p.35 (1983).*

## CYANIC ACID ESTERS FROM PHENOLS: PHENYL CYANATE

### [Cyanic acid, phenyl ester]



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Checked by E. R. Holler, Jr. and R. E. Benson.

### 1. Procedure

*Caution! These operations, which involve toxic reagents, should be conducted in an efficient hood.*

A 1-L, three-necked, round-bottomed flask equipped with a mechanical stirrer, thermometer, and a 200-mL pressure-equalizing dropping funnel with a stopper is charged with 160 g (50.9 mL, 1.0 mol) of bromine (Note 1) and 150 mL of water. The mixture is stirred rapidly while cooling in an ice–salt bath to  $-5^\circ\text{C}$ , and a solution of 49.0 g (1.0 mol) of sodium cyanide in 150 mL of water is added dropwise over a 40–50 min period while maintaining the temperature of the reaction mixture at  $-5$  to  $5^\circ\text{C}$ . The resulting solution is stirred an additional 5–10 min (Note 2). A solution of 89.5 g (0.95 mol) of phenol in 300 mL of tetrachloromethane (Note 3) is added in one portion to the flask. The resulting mixture is stirred vigorously while 96.0 g (131 mL, 0.95 mol) of triethylamine is added dropwise over a 30–40-min period at such a rate that the temperature does not exceed  $5$ – $10^\circ\text{C}$ . After an additional 15 min of stirring, the mixture is transferred to a separatory funnel, the organic phase is separated and the aqueous layer is extracted twice with 50-mL portions of tetrachloromethane. The organic phases are combined and washed three times with 50-mL portions of water and then dried over polyphosphoric anhydride ( $\text{P}_2\text{O}_5$ ) (Note 4). The drying agent is removed by filtration and the solvent is removed by distillation under reduced pressure using a rotary evaporator at  $20^\circ\text{C}$  (25 mm). A few drops of polyphosphate ester (Note 5) are added to the remaining liquid and the product is distilled through a 20-cm Vigreux column to give 85–96 g (75–85%) of phenyl cyanate, bp  $77$ – $79^\circ$  (13 mm),  $n_{\text{D}}^{20}$  1.5094–1.5100,  $d_4^{20}$  1.096. The product is a colorless liquid with a pungent odor (Note 6).

### 2. Notes

1. The chemicals used were commercially available products and were used without further purification. The checkers used sodium cyanide, phenol, and tetrachloromethane from Fischer Scientific Company, bromine from Matheson, Coleman and Bell, phosphoric anhydride from J. T. Baker Chemical Co., and triethylamine from Eastman Organic Chemicals.
2. The solution should develop a yellowish color.
3. The procedure can also be conducted using other water immiscible solvents such as ether, trichloromethane, and benzene.<sup>2</sup>
4. Other drying agents such as anhydrous calcium chloride can also be used. The desiccation must be done carefully since water is soluble in the product in the presence of phenol and may cause trimerization of the cyanate to a 1,3,5-triazine derivative.
5. A few drops of polyphosphate ester are a good drying agent and stabilizer.<sup>3</sup> The ester may be prepared by heating polyphosphoric anhydride in dry ether and trichloromethane for 40 hr followed by removal of the solvent.<sup>4</sup> The checkers found that the use of polyphosphate ester was essential to obtain the described yield.

6. The spectral properties of **phenyl cyanate** are as follows. IR ( $\text{CCl}_4$ )  $\text{cm}^{-1}$ : 2235 (m), 2261 (m), 2282 (S) ( $\nu_{\text{C}\equiv\text{N}}$ ).<sup>5</sup> UV (cyclohexane) nm max ( $\log \epsilon$ ): 216 (3.21), 256 (2.58), 262 (2.75), and 268 (2.67).<sup>6</sup> The product was further characterized by vapor-phase chromatography analysis using a 200-cm column containing 10% SE 52 on Chromosorb W/AW/DMCS at 140°C with a **hydrogen** flow rate of 70 mL/min and a retention time of 1.47 min.

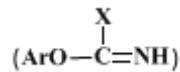
### 3. Discussion

Although isocyanates have been known for some time, the isomeric cyanates were unknown until 1964. The latter were first prepared almost simultaneously by two different methods: (1) thermolysis of 5-aryl- or 5-alkyloxy-1,2,3,4-thiatriazoles<sup>6,7</sup> and (2) by reaction of phenols or alcohols with cyanogen halides.<sup>8</sup> Since their synthesis, cyanates have acquired considerable synthetic significance.<sup>9,10,11,12,13,14</sup> The simplified procedure described here for preparation of **phenyl cyanate** is a combination of the preparation of **cyanogen bromide**<sup>15</sup> and the cyanation of **phenol** in the presence of a base.<sup>8</sup> This procedure is also applicable to many other phenols, bisphenols, naphthols, and some acidic alcohols. Examples are given in Table I.

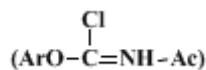
TABLE I  
CYANATES FROM HYDROXY COMPOUNDS

Hydroxy Compound	Cyanate	mp(°C) (bp, °C/mm)	Yield (%)
2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OCN	(88–90/10)	81
4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OCN	(90–91/10)	87
4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> OH	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> OCN	22–26(118–119/10)	91
2-ClC <sub>6</sub> H <sub>4</sub> OH	2-ClC <sub>6</sub> H <sub>4</sub> OCN	(112–113/13)	81
4-ClC <sub>6</sub> H <sub>4</sub> OH	4-ClC <sub>6</sub> H <sub>4</sub> OCN	38–39(100–101/10)	87
2-CH <sub>3</sub> OCOC <sub>6</sub> H <sub>4</sub> OH	2-CH <sub>3</sub> OCOC <sub>6</sub> H <sub>4</sub> OCN	58–60	84
2-Naphthyl-OH	2-Naphthyl-OCN	(162–164/12)	95
4-NCOC <sub>6</sub> H <sub>4</sub> OH	4-NCOC <sub>6</sub> H <sub>4</sub> OCN	107–109	98
CCl <sub>3</sub> CH <sub>2</sub> OH	CCl <sub>3</sub> CH <sub>2</sub> OCN	(77–78/10)	75
CF <sub>3</sub> CH <sub>2</sub> OH	CF <sub>3</sub> CH <sub>2</sub> OCN	(29–30/13)	81

Aryl cyanates have activated cyano groups and undergo many reactions.<sup>14</sup> They are effective dehydrating and hydrogen sulfide-bonding agents in organic synthesis.<sup>9,10,11,13,14</sup> *N*-, *O*-, and *S*-nucleophiles (HX) add to the **carbon** atom of the cyano group to form the corresponding carbonic acid imide esters



<sup>9,10,11,13,14</sup> Transfer of the cyano group to a number of carbon nucleophiles also occurs.<sup>9,10,11,13,14</sup> Acyl halides (AcCl) add to the **nitrogen** atom of the cyano group to give *N*-acylated carbonic acid imide chlorides



<sup>12,13,14</sup> These compounds are useful starting materials for syntheses of heterocyclic compounds. The cyanates also undergo 1,3- and 1,4-dipolar cycloadditions involving the cyano group to give substituted azoles and azines.<sup>9,10,11,13,14</sup> Polycyclic trimerization of dicyanates to poly-*s*-triazines is of considerable importance.<sup>16,17,18</sup>

### References and Notes

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

polyphosphoric anhydride ( $P_2O_5$ )

polyphosphoric anhydride

polyphosphate ester

2-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>OH

4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>OH

4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>OH

4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>OCN

2-ClC<sub>6</sub>H<sub>4</sub>OH

2-ClC<sub>6</sub>H<sub>4</sub>OCN

4-ClC<sub>6</sub>H<sub>4</sub>OH

4-ClC<sub>6</sub>H<sub>4</sub>OCN

2-CH<sub>3</sub>OCOC<sub>6</sub>H<sub>4</sub>OH

2-CH<sub>3</sub>OCOC<sub>6</sub>H<sub>4</sub>OCN

2-Naphthyl-OH

2-Naphthyl-OCN

4-NCOC<sub>6</sub>H<sub>4</sub>OH

4-NCOC<sub>6</sub>H<sub>4</sub>OCN

CCl<sub>3</sub>CH<sub>2</sub>OH

CCl<sub>3</sub>CH<sub>2</sub>OCN

CF<sub>3</sub>CH<sub>2</sub>OH

CF<sub>3</sub>CH<sub>2</sub>OCN

calcium chloride (10043-52-4)

Benzene (71-43-2)

ether (60-29-7)

hydrogen (1333-74-0)

trichloromethane (67-66-3)

phenol (108-95-2)

sodium cyanide (143-33-9)

bromine (7726-95-6)

tetrachloromethane (56-23-5)

nitrogen (7727-37-9)

carbon (7782-42-5)

Cyanogen bromide (506-68-3)

phosphoric anhydride (2466-09-3)

triethylamine (121-44-8)

PHENYL CYANATE,  
Cyanic acid, phenyl ester (1122-85-6)

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