



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

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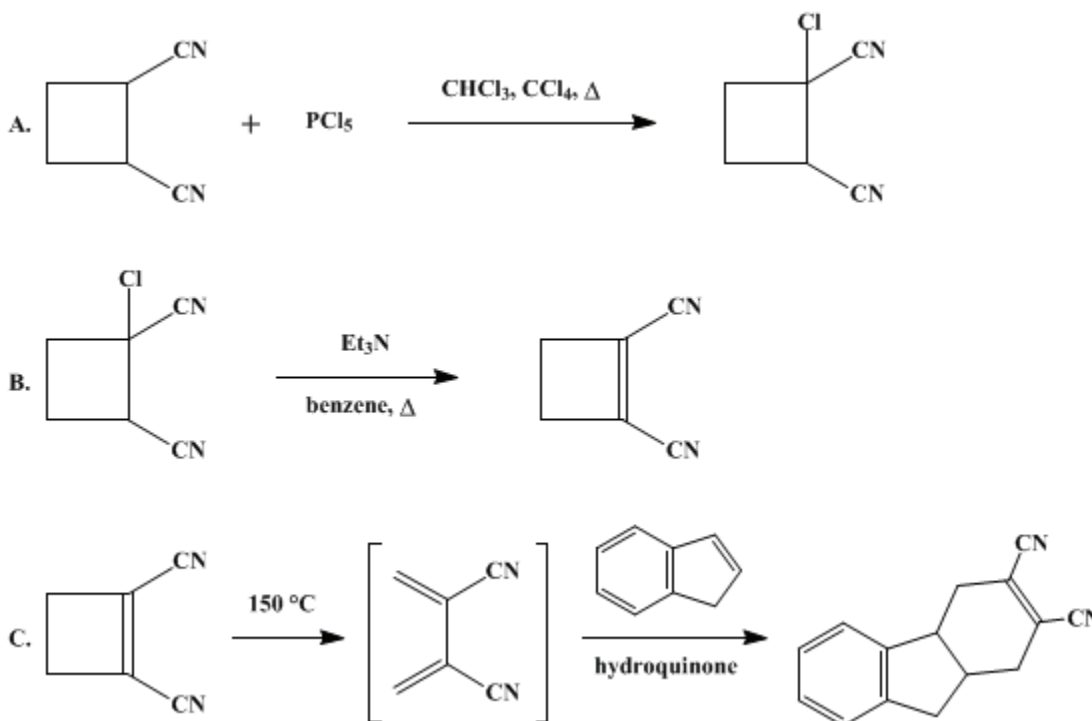
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## 2,3-DICYANOBUTADIENE AS A REACTIVE INTERMEDIATE BY *in situ* GENERATION FROM 1,2-DICYANOCYCLOBUTENE: 2,3-DICYANO-1,4,4a,9a-TETRAHYDROFLUORENE

### [2,3-Fluorenedicarbonitrile, 1,4,4a,9a-tetrahydro-]



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Checked by A. J. Arduengo and William A. Sheppard.

### 1. Procedure

*Caution! 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. *1-Chloro-1,2-dicyanocyclobutane* (1). A 2-l., three-necked flask is equipped with a mechanical stirrer, a 500-ml. pressure-equalizing funnel, and an efficient reflux condenser provided with a gas-outlet tube connected by plastic tubing to a conical funnel inverted over a 5-l. beaker containing aqueous sodium hydroxide, for absorption of the evolved hydrogen chloride. The flask is charged with 562 g. (2.70 moles) of phosphorus pentachloride and 750 ml. of carbon tetrachloride. The rapidly stirred suspension is heated to reflux, and a solution of 159 g. (1.50 moles) of 1,2-dicyanocyclobutane (Note 1) in 120 ml. of chloroform is added dropwise over a period of 40 minutes (Note 2). After addition is complete, the solvents and the phosphorus trichloride formed during the reaction are removed by distillation at 100–150 mm. over a period of 40–60 minutes, with a bath temperature not exceeding 80° (Note 2). The residual liquid is cooled to room temperature and dissolved in 400 ml. of diethyl ether (Note 3). The ethereal solution is placed in a 500-ml. dropping funnel and added over a period of 3 hours to a stirred slurry of 1.7 kg. (12 moles) of sodium hydrogen carbonate, 800 g. of crushed ice, and 500 ml. of water. During the addition the temperature is maintained between –5° and 0° with an external ice-salt bath, and after the addition, stirring is continued for 1 hour at the same temperature. The

precipitated salts are removed by suction filtration through a sintered-glass funnel of medium porosity and are thoroughly washed with 300 ml. of ether. The organic layer is separated, and the aqueous filtrate extracted with three 200-ml. portions of ether. The combined ether extracts are dried over anhydrous magnesium sulfate, filtered, and concentrated on a rotary evaporator, yielding 166–174 g. (79–83%) of a yellow oil consisting of an isomeric mixture of crude cyclobutane **1** (Note 4).

B. *1,2-Dicyanocyclobutene* (**2**). A 2-l., three-necked, round-bottomed flask fitted with a 500-ml. pressure-equalizing dropping funnel, a mechanical stirrer, and a reflux condenser protected from moisture by a calcium chloride tube is charged with 131 g. (1.30 moles) of triethylamine (Note 5) and 400 ml. of benzene. The stirred solution is heated to gentle reflux, and a solution of 168.5 g. (1.199 moles) of crude cyclobutane **1** in 200 ml. of benzene is added dropwise over a period of 30 minutes. After addition is complete, the mixture is stirred under reflux for an additional 2 hours; the precipitated triethylamine hydrochloride is filtered from the cold solution and washed with 150 ml. of benzene. The combined filtrates are washed twice with 200-ml. portions of water and evaporated using a water aspirator at a bath temperature of 35°. The residue is distilled, yielding 105–110 g. (83–87%) of crude cyclobutene **2**, b.p. 55–60° (0.06 mm.) (Note 6).

C. *2,3-Dicyano-1,4,4a,9a-tetrahydrofluorene* (**3**). A 100-ml., round-bottomed flask equipped with a reflux condenser under nitrogen pressure is charged with 10.4 g. (0.100 mole) of crude cyclobutene **2**, 23.3 g. (0.201 mole) of indene (Note 7), and 0.3 g. of hydroquinone. The reaction mixture is stirred and heated at 150° for 4 hours under nitrogen. The reflux condenser is replaced by a still head, and 6.3 g. (0.053 mole) of indene is distilled from the flask at a bath temperature of about 95° (11 mm.) (Note 8). The dark-colored reaction mixture is transferred to a 500-ml., round-bottomed flask, diluted with 200 ml. of benzene followed by 1 g. of decolorizing carbon, and the resulting mixture is refluxed for 2 hours. After the mixture is cooled to room temperature, the carbon is removed by filtration, and the benzene is distilled. The residual oily residue solidifies on standing and is recrystallized from 45 ml. of ethanol, yielding 15.4–15.9 g. (70–72%) of crystalline fluorene **3**, m.p. 98.5–100° (Note 9).

## 2. Notes

1. *1,2-Dicyanocyclobutane* (*cis*- and *trans*-isomer mixture) was purchased from Aldrich Chemical Company, Inc., and used without further purification.

2. The addition and distillation must be accomplished within the specified period of time; otherwise the amount of dichlorinated *1,2-dicyanocyclobutane* increases considerably. The submitters found that an 80% molar excess of phosphorus pentachloride is optimum. A molar excess less than specified (under given experimental conditions) gives considerable unreacted starting material. Under forcing experimental conditions, such as longer reaction times and/or higher temperatures, the starting material can be completely consumed, even with less than 80% molar excess of phosphorus pentachloride, but a considerable amount of dichlorinated products is formed.

3. The checkers found that, because of the time required for completion of this step, a convenient modification is to cool the ether solution to –78° in dry ice and store overnight at –78°. A solid complex of phosphorus pentachloride and cyclobutane **1**, m.p. 88–91°, precipitates in the cold ether solution. This complex may not redissolve on warming to room temperature, but the suspension in ether can be used to proceed with the second half of Step A.

4. The checkers obtained the cyclobutane **1** as a colorless crystalline solid, m.p. 45–47° (a mixture of major and minor isomers), that is relatively free of *1,2-dichloro-1,2-dicyanocyclobutane*. The product had the following spectral properties: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (multiplicity): 2.35–3.15 (m), 3.40–4.20 (m); <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ: major isomer 21.58 (t), 38.41 (d), 37.24 (t), minor isomer 22.48 (t), 36.72 (d), 36.91 (t).

5. Reagent grade triethylamine was dried over sodium hydroxide and distilled before use (b.p. 88–89°).

6. The checkers obtained yields of 115 g. (92%) on a 1.2 mole scale and 94 g. (90%) on a 1.0 mole scale.

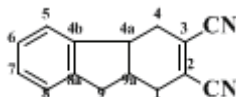
The product was analyzed by GC on a 1.23 m. × 0.65 cm. stainless-steel column of SE-52 on Varoport 30, which was heated to 150° and swept with helium at 60 ml. per minute. Retention times for the various components (minutes) are: cyclobutene **2**, (2.6); *trans-1,2-dicyanocyclobutane*(3.6); two isomeric *1,2-dichloro-1,2-dicyanocyclobutanes* (5.1 and 5.9, respectively); *cis-1,2-dicyanocyclobutane* (9.8).

For most synthetic purposes, such as [4 + 2]- and [2 + 2]-cycloadditions,<sup>2,3,4,5,6,7</sup> ring-opening reactions,<sup>2,8</sup> and hydrolytic reactions,<sup>2</sup> this crude **cyclobutene 2**, which contains approximately 1–3.5% of isomeric mixtures of 1,2-dichloro-1,2-dicyanocyclobutanes, can be used satisfactorily without further purification. Pure cyclobutene **2** can be prepared by treatment of the crude product with Raney cobalt, thereby removing residual quantities of isomeric 1,2-dichloro-1,2-dicyanocyclobutanes. In a typical experiment the crude product is placed in a 250-ml., round-bottomed flask and stirred with 10 g. of Raney cobalt for 4 hours at 70° under nitrogen. Distillation directly from the reaction vessel without filtering off the metal slurry yields 94–98 g. (60–63%) of cyclobutene **2** as a colorless liquid,  $n_D^{20}$  1.4926,  $d_{22}^4$  1.033. The Raney cobalt used by the submitters was obtained from Fluka A G, Buchs, Switzerland, as a suspension in water, and washed with tetrahydrofuran before use. Raney nickel and nickel tetracarbonyl, respectively, are also good dechlorinating reagents. The use of Raney cobalt, however, diminishes the danger of self-ignition during the preparation procedure. The spectral properties are as follows: IR (neat)  $\text{cm}^{-1}$ : 3002, 2957, 2230, 1612, 1422, 1251, 1169, 1003, and 623; UV ( $\text{CH}_3\text{OH}$ ) nm. max. (log  $\epsilon$ ): 235 (4.06), 247 sh (3.90);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  (multiplicity): 2.91 (s).

7. The indene used by the submitters was "practical grade," purchased from Fluka A G, Buchs, Switzerland. The indene used by the checkers was purchased from Aldrich Chemical Company, Inc. Both were distilled (b.p. 60–65°, 11 mm.) before use.

8. Recovered indene may be used for the next batch without further purification.

9. Fluorene **3** has the following spectral properties: IR (KBr)  $\text{cm}^{-1}$ : 2222, 1608, 1479, 1440, 773, and 742; UV ( $\text{C}_2\text{H}_5\text{OH}$ ) nm. max. (log  $\epsilon$ ): 216 (4.10), 234 (3.99), 261 (3.16), 267 (3.11), and 274 (3.07); mass spectrum  $m/e$ : 220 ( $m^+$ ) and 116 (base peak);  $^1\text{H}$  NMR (100 MHz.,  $\text{CDCl}_3$ ): two complex multiplets for the aromatic and aliphatic protons (360 MHz.,  $\text{CDCl}_3$ ),  $\delta$  (multiplicity, coupling constant  $J$  in Hz., number of protons, assignment): 2.10 [d,  $J = 18$ ; d,  $J = 7$ ; and t,  $J = 3$ ; one H of  $\text{CH}_2(1)$  or one H of  $\text{CH}_2(4)$ ], 2.55–2.70 [m, one H of  $\text{CH}_2(1)$ , one H of  $\text{CH}_2(4)$ , one H of  $\text{CH}_2(9)$  and CH(9a)], 2.88 [d,  $J = 18$ ; d,  $J = 7$ ; d,  $J = 3$ ; and d,  $J = 1.5$ ; one H of  $\text{CH}_2(1)$  or one H of  $\text{CH}_2(4)$ ], 3.11 [d,  $J = 15$ ; d,  $J = 6$ , one H of  $\text{CH}_2(9)$ ], 3.42 [d,  $J = 5$ ; t,  $J = 7$ , CH(4a)], 7.20 (m, 4, aromatic H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  (assignment): 143.8 [C(8a)], 141.3 [C(4b)], 127.6, 127.2, and 125.6 [C(6), C(7), and C(8), not assigned individually], 126.6 and 125.9 [C(2) and C(3), not assigned], 123.2 [C(5)], 115.9 [two nitrile carbons], 40.2 [C(4a)], 38.4 [C(9)], 35.4 [C(9a)], 30.7 and 29.7 [C(1) and C(4), not assigned].



### 3. Discussion

Three syntheses of 1,2-dicyanocyclobutene (**2**) have been previously described. The first involves dehydration of cyclobutene-1,2-dicarboxamide, with no specified yield.<sup>9</sup> The second procedure involves a concomitant chlorination and catalytic dehydrochlorination of 1,2-dicyanocyclobutane in the gas phase, yielding 1,2-dicyanocyclobutene (**2**) in a mixture of several other products.<sup>10</sup> The third method consists of dechlorination of 1,2-dichloro-1,2-dicyanocyclobutane using metals, such as zinc copper couple,<sup>11</sup> Raney nickel,<sup>11</sup> and, especially, Raney cobalt.<sup>2</sup> In comparison with the third synthesis, the overall yield of the present procedure is 5–10% higher. Furthermore, the reaction is performed in less time and utilizes considerably cheaper reagents.

Pure, crystalline 2,3-dicyanobutadiene has been prepared in high yield by gas-phase thermolysis of cyclobutene (**2**).<sup>2,8</sup> Analogously, thermolysis of derivatives of cyclobutene-1,2-dicarboxylic acid appears to represent a general procedure for the synthesis of derivatives of butadiene-2,3-dicarboxylic acid, of high purity.<sup>2,12</sup> These butadienes take part in [4 + 2]-cycloaddition reactions either as reactive dienes<sup>2,13,14</sup> or as reactive dienophiles.<sup>2,14</sup> In the pure state, however, they tend to polymerize, and even crystalline 2,3-dicyanobutadiene slowly polymerizes, yielding a highly cross-linked polymer without losing its original crystal form. A [2 + 4]-dimer of a 2,3-dicyanobutadiene is also formed by heating the dicyanocyclobutene in solution with a polymerization inhibitor.<sup>2</sup> Monomeric derivatives of butadiene-2,3-dicarboxylic acid cannot be prepared in solution because of rapid dimerization.<sup>8,14</sup>

The present procedure, *in situ* generation and trapping of 2,3-dicyanobutadiene in the presence of

olefins, overcomes these problems and affords [4 + 2]-cycloadducts in good yields, particularly in the case of olefins possessing a strained double bond.<sup>2</sup> Substituted 1,2-dicyanocyclohexenes, prepared by the *in situ* [4 + 2]-cycloadditions, can be dehydrogenated to new aromatic *ortho*-dinitriles. For example, 2,3-dicyanofluorene is prepared in 56% yield by heating 2,3-dicyano-1,4,4a,9a-tetrahydrofluorene (**3**) at 200° in dimethylmaleate in the presence of 5% palladium on charcoal. Other aromatic *ortho*-dinitriles have also been prepared by this method.<sup>2</sup> Because 2,3-dicyanobutadiene is an electron-deficient diene, it does not react with electron-deficient olefins, such as maleic anhydride and fumaronitrile<sup>2,8</sup> using this procedure. However, by generating the dicyanobutadiene in refluxing chlorobenzene in the presence of maleic anhydride and 2,5-di-*tert*-butylbenzoquinone, as an inhibitor, the [2 + 4]-cyclic dicarbonitrile adduct, m.p. 201–202.5°, was formed in a yield of 38%.<sup>15</sup>

TABLE I  
[4 + 2]-CYCLOADDITION REACTIONS OF 2,3-DICYANOBUTADIENE FORMED *in situ*  
FROM 1,2-DICYANOCYCLOBUTENE<sup>2</sup>

Olefin	Product	Yield (%) <sup>a</sup>	Temperature (°C)	Time (hours)
Norbornadiene	4,5-Dicyanotricyclo-[6.2.1.0 <sup>2,7</sup> ]undeca-4,9-diene	79 <sup>b</sup>	150	12
Acenaphthylene	8,9-Dicyano-6b,7,10,10a-tetrahydrofluoranthene	77	138	48
Cyclopentene	3,4-Dicyanobicyclo[4.3.0]non-3-ene	65	135	16
Ethylene	1,2-Dicyanocyclohexene	58	135	16
( <i>E</i> )-Stilbene	1,2-Dicyano-4,5-diphenylcyclohexene	32	138	24
Butyl vinyl ether	1,2-Dicyano-4-butoxycyclohexene	28	155	16
( <i>E</i> )-1,2-Dichloroethylene	1,2-Dicyano-4,5- <i>trans</i> -dichlorocyclohexene	8	135	16
2-Vinylpyridine	1,2-Dicyano-4-(2-pyridyl)cyclohexene	5	138	48

<sup>a</sup> Yields of analytically pure products are given.

<sup>b</sup> A 70:24 mixture of *exo* and *endo* isomers. Some 2:1 cycloadduct was also isolated (2.4% yield).

## References and Notes

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

Raney cobalt

zinc copper couple

ethanol (64-17-5)

hydrogen chloride (7647-01-0)

Benzene (71-43-2)

ether,  
diethyl ether (60-29-7)

sodium hydroxide (1310-73-2)

phosphorus pentachloride (10026-13-8)

chloroform (67-66-3)

hydroquinone (123-31-9)

sodium hydrogen carbonate (144-55-8)

carbon tetrachloride (56-23-5)

nitrogen (7727-37-9)

Raney nickel (7440-02-0)

decolorizing carbon,  
carbon (7782-42-5)

chlorobenzene (108-90-7)

palladium (7440-05-3)

phosphorus trichloride (7719-12-2)

ethylene (9002-88-4)

Triethylamine hydrochloride (554-68-7)

magnesium sulfate (7487-88-9)

Cyclopentene (142-29-0)

indene (95-13-6)

Tetrahydrofuran (109-99-9)

maleic anhydride (108-31-6)

triethylamine (121-44-8)

Fumaronitrile (764-42-1)

helium (7440-59-7)

norbornadiene

cyclobutene (822-35-5)

2,3-DICYANO BUTADIENE

1,2-Dicyanocyclobutene,  
dicyanocyclobutene (3716-97-0)

1,2-dicyanocyclobutane

1,2-dichloro-1,2-dicyanocyclobutane

nickel tetracarbonyl

cyclobutene-1,2-dicarboxamide

cyclobutene-1,2-dicarboxylic acid

butadiene-2,3-dicarboxylic acid

2,3-dicyanofluorene

dimethylmaleate

dicyanobutadiene

4,5-Dicyanotricyclo-[6.2.1.0<sup>2,7</sup>]undeca-4,9-diene

Acenaphthylene (208-96-8)

3,4-Dicyanobicyclo[4.3.0]non-3-ene

1,2-Dicyanocyclohexene

1,2-Dicyano-4,5-diphenylcyclohexene

Butyl vinyl ether (111-34-2)

1,2-Dicyano-4-butoxycyclohexene

2-Vinylpyridine (100-69-6)

1,2-Dicyano-4-(2-pyridyl)cyclohexene

(E)-stilbene (103-30-0)

2,5-di-tert-butylbenzoquinone

1-Chloro-1,2-dicyanocyclobutane (3716-98-1)

2,3-Dicyano-1,4,4a,9a-tetrahydrofluorene,  
2,3-Fluorenedicarbonitrile, 1,4,4a,9a-tetrahydro- (52477-65-3)

cis-1,2-dicyanocyclobutane

(E)-1,2-Dichloroethylene (156-60-5)

1,2-Dicyano-4,5-trans-dichlorocyclohexene

trans-1,2-dicyanocyclobutane

8,9-Dicyano-6b,7,10,10a-tetrahydrofluoranthene