

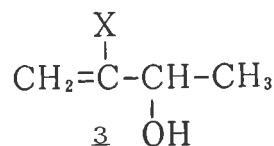
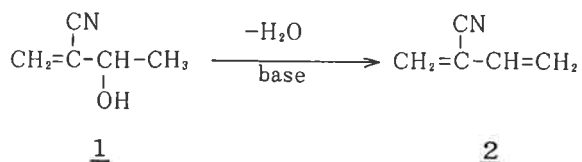
## A Novel Synthesis of 2-Cyano-1, 3-butadiene

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Although 2-cyano-1,3-butadiene (2) bears a structural similarity to chloroprene, its polymer chemistry remains almost unexplored because of the difficult access. We now report a novel and convenient route to 2, which involves the base-catalyzed dehydration of 2-cyano-3-hydroxybutene-1 (1) at temperatures 80–120° C under pressures 30–50 mmHg, the product being continuously removed from the reaction system as it is formed. Of fifteen base catalysts used, potassium carbonate supported on  $\alpha$ -alumina was found to work best.

2-Cyano-1,3-butadiene (2) bears a close structural similarity to chloroprene. In spite of the resemblance, only a little study has been carried out on the polymerization of the former. This lack of the study may be attributable to the fact that the monomer has not been readily available. For the synthesis of 2, several methods are known.<sup>1~6)</sup> These procedures, however, are not convenient since they involve gas phase reactions and the yields are usually very poor.

In this communication, we report a novel of 2 by base-catalyzed dehydration of and convenient method for the synthesis 2-cyano-3-hydroxy-butene-1 (1). The reaction can be carried out conveniently in a laboratory with very good yield.



(wherein X =  $-\text{CO}_2\text{CH}_3$ ,  $-\text{CO}_2\text{C}_2\text{H}_5$ ,  $-\text{COCH}_3$   
and  $-\text{CON}(\text{CH}_3)_2$ )

The catalytic dehydration of 1 is very unique. The closely related compounds having the formula 3 could not be converted to the corresponding dienes under the conditions same as those for 1. The starting material 1 can be easily obtained by reacting acrylonitrile with acetaldehyde in the presence of a donor catalyst such as tertiary phosphines<sup>7)</sup> or amines<sup>8)</sup>. The dehydration takes place at an elevated temperature and under a reduced pressure. The products are continuously removed from the reaction system by distillation.

The bases used as catalysts were alkali and alkali earth metals, their hydroxides and salts, alkoxides, organic amines and phosphines. The representative results are summarized in the table. Among the catalysts, potassium carbonate appears to be the best. When aqueous or  $\alpha$ -alumina supported potassium carbonate was used, 2 was obtained in better yield than

when used directly.

The following is a typical procedure (expt. No. 13 in the table). A mixture of 50 g of 1 and 1 g of anhydrous potassium carbonate in a 100 ml round bottom flask equipped with a distillation condenser was heated with magnetic stirring at 105° and 30 mmHg for 48 minutes, during which time the products were continuously distilled out. Two layers of the distillate, 7.4 g of the water layer and 23.5 g of the organic layer, were then separated. Gas chromatogram of the organic layer showed this to be almost pure 2 (98.3 wt%). The following impurities were also detected; 0.35 wt% of acetaldehyde, 1.0 wt% of acrylonitrile, 0.1 wt% of 1 and 0.2 wt% of crotonaldehyde. (GC conditions; Silicone DC 550 (15 wt%) / Celeite 545, 3 mm I.D. × 5 m, 119°, He 30 cc/min.) Each components were confirmed by NMR and IR analyses. Aldehydes in the product could be removed by washing with 10% aqueous sodium hydroxide at 0°. Pure 2 was obtained by further distillation in the presence of a polymerization inhibitor such as phenothiazine at low temperature and high vacuum (b. p. 34–36°/33 mmHg, lit.<sup>3)</sup> 30–40°/40 mmHg).

**Table** Synthesis of 2-Cyano-1,3-butadiene by Base-catalysed Dehydration of 2-Cyano-3-hydroxybutene-1<sup>a)</sup>

No.	Catalyst	Amount of Catalyst (g)	Reaction Temperature (°C)	Pressure (mmHg)	Reaction Time (min.)	Yield (mol%) <sup>b)</sup>
1	Na-metal	0.85	80–90	30	60	27.0
2	KOH	0.9	80	30	200	27.0
3	Ca(OH) <sub>2</sub>	20	150	120–140	210	55.5
4	Ba(OH) <sub>2</sub>	5	85–90	30	240	37.6
5	NaHCO <sub>3</sub>	3	105–110	30	330	42.5
6	50% NaOCH <sub>3</sub> – CH <sub>3</sub> OH – Soln.	4.8	80	30	105	27.0
7	CH <sub>3</sub> CO <sub>2</sub> K	13	90–140	30–80	240	47.4
8	n-Bu <sub>3</sub> P	2	80	30–40	330	10.7
9	n-C <sub>9</sub> H <sub>19</sub> NH <sub>2</sub>	19	105–110	30–40	330	9.0
10	n-Bu <sub>3</sub> N	29	105–110	30–40	330	4.1
11	DBO <sup>c)</sup>	8	105–110	30–40	330	32.7
12	DBU <sup>d)</sup>	10	105–110	30–40	90	43.3
13	anhydrous K <sub>2</sub> CO <sub>3</sub>	1	105	30	48	59
14	33 wt% K <sub>2</sub> CO <sub>3</sub> aq.	3	105	30	34	72
15	K <sub>2</sub> CO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> <sup>e)</sup>	4	105	40–50	60	78

a) The amount of 2-cyano-3-hydroxybutene-1 used was 150 g for No. 1–12 and 50 g for No. 13–15.

b) Based on 2-cyano-3-hydroxybutene-1.

c) Diaza-bicyclo [2.2.2]-octane.

d) 1.8-Diaza-bicyclo [5.4.0] undecene-7.

e) 20 wt% K<sub>2</sub>CO<sub>3</sub>/Granular α-Alumina (5 mmφ).

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