Organic Syntheses

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). 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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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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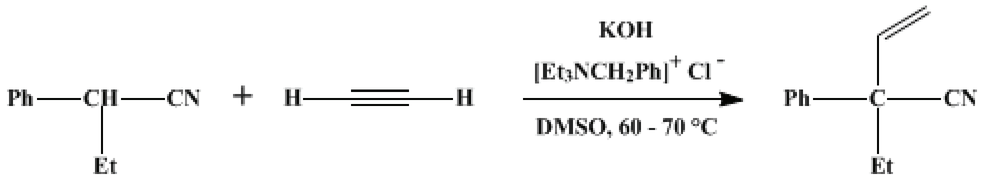
Organic Syntheses, Coll. Vol. 6, p.940 (1988); Vol. 55, p.99 (1976).

2-PHENYL-2-VINYLBUTYRONITRILE

[Benzeneacetonitrile, α-ethenyl-α-ethyl-]



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Checked by John C. Sauer and Richard E. Benson.

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-l., four-necked, round-bottomed flask equipped with a sealed mechanical stirrer, a thermometer, and a gas-inlet tube is charged with 145 g. (1.00 mole) of 2-phenylbutyronitrile (Note 1), 2.3 g. (0.010 mole) of benzyltriethylammonium chloride (Note 2), and 50 ml. of dimethyl sulfoxide (Note 3). The gas-inlet tube is adjusted to extend below the surface of the liquid, and a gas-exit tube is attached to the flask. A slow stream of acetylene (Note 4) is passed through the gas-inlet tube into the flask, removing the air. After 5 minutes, 56 g. of finely powdered potassium hydroxide is added and stirring is begun. Acetylene is introduced at the rate of 15–20 l./hour. An exothermic reaction occurs; the temperature rises to 70–80° and is held in this range with a cold water bath (Note 5). After 40–60 minutes, a warm bath is required to maintain the temperature of the reaction mixture at 60–70°, and stirring is continued for an additional 20–30 minutes (Note 6). The mixture is cooled to room temperature, the inlet tube is replaced with a pressure-equalizing dropping funnel, and 500 ml. of water is added slowly (Note 7). The resulting dark-brown mixture is transferred to a separatory funnel and washed twice with 200-ml. portions of benzene. The benzene layers are combined and washed successively with 200 ml. of water, 100 ml. of 10% hydrochloric acid, and 200 ml. of water. The organic layer is dried over anhydrous magnesium sulfate, and the benzene is removed by distillation at reduced pressure. The residual oil is distilled through a short Vigreux column, giving 125–135 g. of crude product, b.p. 115–125° (13 mm.). Redistillation of this product through a Vigreux column gives 101–107 g. (59–63%) of colorless 2-phenyl-2-vinylbutyronitrile, b.p. 110° (8 mm.), n_{D}^{25} 1.5157 (Note 8).

2. Notes

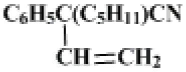
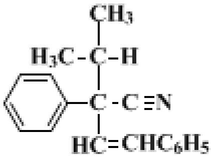
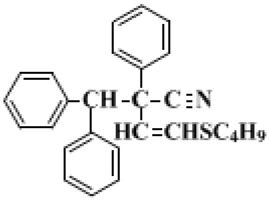
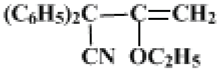
1. The preparation of 2-phenylbutyronitrile is described in *Org. Synth.*, **Coll. Vol. 6**, 897 (1988).
2. The checkers used the product available from Aldrich Chemical Company, Inc. The preparation of this reagent is described in *Org. Synth.*, **Coll. Vol. 6**, 232 (1988).
3. The checkers used the product available from Fisher Scientific Company.
4. The checkers used acetylene available from Matheson Gas Products. The gas was purified by passing it through concentrated sulfuric acid, through a tower filled with potassium hydroxide pellets, then into a 1-l. safety flask which was connected to the gas-inlet tube with rubber tubing. The checkers used a rotameter, calibrated with air, to determine the flow rate of acetylene.
5. The checkers attempted to keep the temperature at 65–70°.
6. The reaction may be monitored by GC. The submitters used a 2-m. column containing silicone oil on diatomite support (190°).
7. The water should be added slowly, since the mixture is saturated with acetylene and the gas may be evolved vigorously.

8. The checkers found the product to be at least 95% pure on a GC column containing 10% silicone 200 on nonacid washed Chromosorb W operated at 125°. The spectral properties of the product are as follows; IR (neat) cm.$^{-1}$: 1639, 1000, 930 ($CH{=}CH_2$); ^1H NMR (neat), δ (multiplicity, coupling constant J in Hz., number of protons, assignment): 0.92 (t, $J = 7$, 3H, CH_3), 1.87 (q, $J = 7$, 2H, CH_2), 5.00–6.20 (m, 3H, $CH{=}CH_2$), 7.17–7.57 (m, 5H, C_6H_5).

3. Discussion

This procedure, which involves the addition of an anion derived from a nitrile to an unactivated acetylenic bond under rather mild conditions, is a convenient, general method for the synthesis of α-vinylnitriles (see Table I). The reaction proceeds smoothly in either dimethyl sulfoxide or hexamethylphosphoric triamide [*see* J. A. Zapp, Jr., *Science*, **190**, 422 (1975) *for a toxicity warning concerning this compound*] with a tetraalkylammonium salt as catalyst. The products thus prepared are obtained in yields higher[2] than those obtained under conventional conditions, which generally require higher temperatures and elevated pressures.[3,4]

TABLE I
α-VINYLNITRILES DERIVED FROM ACETYLENES

Nitrile	Acetylene	Product	b.p.	Yield (%)
$C_6H_5CH(C_5H_{11})CN$	$HC{\equiv}CH$	 $C_6H_5\underset{\displaystyle CH{=}CH_2}{C}(C_5H_{11})CN$	139° (8 mm.)	88
$C_6H_5CH(2\text{-}C_3H_7)CN$	$HC{\equiv}CC_6H_5$		145° (0.8 mm.)	83
$(C_6H_5)_2CHCH(C_6H_5)CN$	$HC{\equiv}CSC_4H_9$		113°[c]	96
$(C_6H_5)_2CHCN$	$HC{\equiv}COC_2H_5$	 $(C_6H_5)_2\underset{\displaystyle CN}{C}{-}\underset{\displaystyle OC_2H_5}{C}{=}CH_2$	146° (0.6 mm.)	77

[a] Product is a 2:1 mixture of (Z) and (E) isomers; (Z) isomer, m.p. 62°.
[b] Only the (Z) isomer is obtained.
[c] Melting point.

References and Notes

1. Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland.
2. M. Makosza, Pol. Pat. **55113** (1968) [*Chem. Abstr.*, **70**, 106006s (1969)]; M. Makosza, *Tetrahedron Lett.*, 5489 (1966); M. Makosza and M. Jawdosiuk, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **16**, 589 (1968) [*Chem. Abstr.*, **71**, 30193y (1969)].
3. P. P. Karpukhin and A. I. Levchenko, *Zh. Prikl. Khim. Leningrad*, **32**, 1354 (1959) [*Chem. Abstr.*, **54**, 450c (1960)]; P. P. Karpukhin, A. I. Levchenko, and E. V. Dudko, *Zh. Prikl. Khim. Leningrad*, **34**, 1117 (1961) [*Chem. Abstr.*, **55**, 22259f (1961)].
4. M. Seefelder, *Justus Liebigs Ann. Chem.*, **652**, 107 (1962).

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

$HC\equiv CH$

sulfuric acid (7664-93-9)

acetylene (74-86-2)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

potassium hydroxide (1310-58-3)

magnesium sulfate (7487-88-9)

dimethyl sulfoxide (67-68-5)

hexamethylphosphoric triamide (680-31-9)

benzyltriethylammonium chloride (56-37-1)

2-Phenyl-2-vinylbutyronitrile,
Benzeneacetonitrile, α-ethenyl-α-ethyl- (13312-96-4)

2-Phenylbutyronitrile (769-68-6)