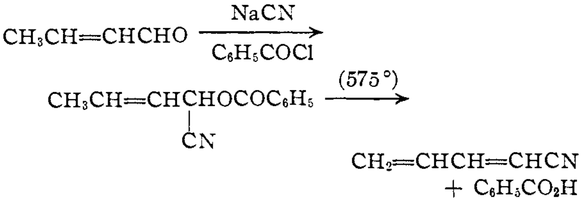
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

1-Cyano-1,3-butadienes: *cis, trans*-Isomers of 1-Cyano-1,3-butadiene[1]

BY H. R. SNYDER, JOHN M. STEWART[2a] AND ROBERT L. MYERS[2b]

In a study of the possible use of certain cyanodienes as replacements for styrene in butadiene–styrene copolymers, 1-cyano-1,3-butadiene has been prepared in quantity sufficient to permit the separation of the *cis*- and *trans*-forms. This substance has been studied previously,[3-15] but apparently only as a mixture of geometric isomers. In the present work the mixture was prepared by the pyrolysis[4-8] of the benzoate or acetate of crotonaldehyde cyanohydrin; the synthesis *via* the benzoate proved the more convenient. 1-Cyano-2-methyl-1,3-butadiene was prepared similarly from tiglic aldehyde.

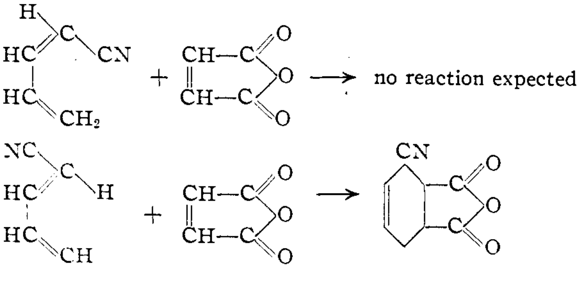


$$CH_3CH{=}CHCHO \xrightarrow[C_6H_5COCl]{NaCN} CH_3CH{=}CH\underset{\underset{CN}{|}}{C}HOCOC_6H_5 \xrightarrow{(575°)} CH_2{=}CHCH{=}CHCN + C_6H_5CO_2H$$

The first indications that the 1-cyano-1,3-butadiene so prepared was a mixture were found in the slight variations in boiling point and index of refraction of the products of various runs and in the concomitant variations of reaction rates observed with samples of the different lots in copolymerizations with butadiene. Separation of the isomers was achieved by fractionation of the mixture through a twenty-five plate, helix-packed column. Two different fractions (I, b.p. 49.5° (31.5 mm.), $n^{20}D$ 1.4852; II, b.p. 57.3° (31.5 mm.), $n^{20}D$ 1.4960) were obtained. In the polymerization studies it was observed that the higher-boiling fraction underwent copolymerization with butadiene at a faster rate than the lower-boiling fraction. Of the two dried rubber-like polymers made in these copolymerizations only the one from the higher-boiling fraction had the strong odor previously associated with all the butadiene copolymers made from the mixture of cyanodienes.

The formation of a by-product of sufficient volatility to possess an odor, in the copolymerization of the higher-boiling isomer, suggested that a Diels–Alder reaction with butadiene might have occurred. In tests with liquid butadiene at 50°, in the absence of polymerization catalysts, only the higher-boiling 1-cyano-1,3-butadiene underwent reaction; the product was a liquid of a very strong, unpleasant odor (somewhat similar to that of isonitriles). The higher-boiling 1-cyano-1,3-butadiene also gave an adduct with maleic anhydride, whereas the lower-boiling isomer failed to react.

The observation of the greater reactivity of the higher-boiling 1-cyano-1,3-butadiene with maleic anhydride permits the tentative assignment of the *trans*-configuration to this isomer. This assignment is made on the basis of the analogy with the closely related piperylenes[16]; only the *trans*-piperylene undergoes Diels–Alder reactions with maleic anhydride, acrylonitrile or with a second molecule of the diene (dimerization).[17] The failure of the *cis*-isomer to react with maleic anhydride is ascribed to the fact that the shape of the molecule is such as to prevent close approach of the dienophile to the ends of the conjugated system of the diene.



Experimental

Crotonaldehyde Cyanohydrin Benzoate.—To a well-stirred mixture of 420 g. (6 moles) of freshly distilled crotonaldehyde and 1200 ml. of benzene, maintained at −10°, was slowly added 843 g. (6 moles) of benzoyl chloride. Then 392 g. (8 moles) of reagent grade sodium cyanide in 2 l. of distilled water was added dropwise while the reaction mixture was kept at the same temperature. After the cyanide had been added the mixture was stirred for two

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[2] (a) Present address: Department of Chemistry, Montana State University, Missoula, Montana. (b) Present address: Research Laboratory, General Electric Company, Schenectady, New York.

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hours at $-10°$ and then was allowed to warm to room temperature. The organic layer was separated, washed with two 200-ml. portions of 5% sodium carbonate solution, and dried over anhydrous magnesium sulfate. After distillation of the benzene, the residue was fractionated through a 12-inch, helix-packed, jacketed column. The fraction boiling at 125° (1 mm.), $n^{20}_{\rm D}$ 1.5220, was collected. The yield was 1085 g. or 89%.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.62; H, 5.51. Found: C, 71.75; H, 5.58.

Crotonaldehyde cyanohydrin acetate was prepared by the same method with the substitution of acetic anhydride for the benzoyl chloride. From 271 g. (3.88 moles) of crotonaldehyde, 395 g. (3.88 moles) of acetic anhydride, and 275 g. (5.6 moles) of sodium cyanide there was obtained 371 g. (70%) of the crotonaldehyde cyanohydrin acetate, b.p. 78.5° (4 mm.), $n^{20}_{\rm D}$ 1.4340.

Anal. Calcd. for $C_7H_9O_2N$: C, 60.42; H, 6.52. Found: C, 60.34; H, 6.57.

1-Cyano-1,3-butadiene.—Pyrolysis of either the benzoate or acetate of crotonaldehyde cyanohydrin produced 1-cyano-1,3-butadiene. Pyrolysis of the benzoate was found to be more satisfactory because the separation of the cyanodiene from benzoic acid was much more convenient than separation from acetic acid. The esters were pyrolyzed by passage through a vertical, 18-mm. Pyrex tube packed for a distance of about 30 cm. with 4-mm. glass beads and heated to 575 ± 10° by means of a combustion furnace. The temperature was indicated by a thermocouple inserted in the tube. The material was introduced at a rate of one drop per second. A cooled distilling flask connected to the pyrolysis tube by a ground-glass joint served as the receiver for the pyrolysate. The yield of cyanodiene could be increased by the addition of an efficient polymerization inhibitor (such as picric acid) to the ester and the receiving flask. It was necessary to heat the tube (conveniently with an infrared lamp) between the furnace and the receiver to prevent the benzoic acid produced from solidifying. The 1-cyano-1,3-butadiene was separated from the benzoic acid by a flash distillation at reduced pressure. Redistillation through a 12-inch, helix-packed column yielded 1-cyano-1,3-butadiene; b.p. 49.5–53° (31 mm.), $n^{20}_{\rm D}$ 1.4852–1.4895. Coffman[2] reported b.p. 49–53° (30 mm.), $n^{20}_{\rm D}$ 1.4880, d^{20}_4 0.8644.

The yield of redistilled material from the pyrolysis of the benzoate was 70%; from the acetate 55% (based on the recovery of 34% of the unchanged ester). A sample was redistilled for analysis.

Anal. Calcd. for C_5H_5N: C, 75.92; H, 6.37. Found: C, 75.90; H, 6.48.

1-Cyano-1,3-butadiene was separated into its geometric isomers by fractionation of the mixture through a twenty-five plate, helix-packed column at a reflux ratio of about 15:1. The two fractions (I, b.p. 49.5° (31.5 mm.), $n^{20}_{\rm D}$ 1.4852; II, b.p. 57.3° (31.5 mm.), $n^{20}_{\rm D}$ 1.4960) had nearly identical microanalyses.

Anal. Calcd. for C_5H_5N: C, 75.92; H, 6.37. Found (fraction I): C, 75.90; H, 6.48; (fraction II): C, 75.97; H, 6.50.

Maleic Anhydride Adduct of 1-Cyano-1,3-butadiene.—In two 2-oz., screw-cap bottles were placed 6.2 g. of maleic anhydride and 25 ml. of dry benzene. In the first bottle (A) was placed 5.0 g. of 1-cyano-1,3-butadiene (fraction I, $n^{20}_{\rm D}$ 1.4852). In the second (B) was placed 5.0 g. of 1-cyano-1,3-butadiene (fraction II, $n^{20}_{\rm D}$ 1.4960). A few crystals of picric acid were added to each bottle to prevent polymerization. The bottles were capped and placed in a 50° water-bath and rotated for forty-eight hours. The vessels were removed from the bath and cooled, and about 10 ml. of low-boiling petroleum ether was added to each. From bottle A only unchanged maleic anhydride, m.p. 58–59°, was isolated. From bottle B there was obtained a yellow oil, which was induced to crystallize by rubbing it against the side of the container. After six recrystallizations from dry benzene, the material had a constant melting point of 110–111°.

Anal. Calcd. for $C_9H_7O_3N$: C, 61.01; H, 3.98. Found: C, 60.86; H, 3.77.

These reactions were repeated several times and in each instance an adduct was obtained only from the higher-boiling fraction, $n^{20}_{\rm D}$ 1.4960.

Diels–Alder Adduct of 1-Cyano-1,3-butadiene with 1,3-Butadiene.—Five-gram samples of 1-cyano-1,3-butadiene, fraction I, $n^{20}_{\rm D}$ 1.4852, and fraction II, $n^{20}_{\rm D}$ 1.4960, an excess of 1,3-butadiene, and a few crystals of picric acid were placed in 2-oz., screw-cap bottles. The bottles were capped and placed in the 50° water-bath and rotated for forty-eight hours. The bottles were removed, and the unchanged 1,3-butadiene was allowed to evaporate. Distillation of the residual liquid from experiments with fraction I resulted only in the recovery of 1-cyano-1,3-butadiene. From experiments with fraction II, along with some unchanged cyanobutadiene, there was obtained a liquid boiling at 94° (8 mm.), $n^{20}_{\rm D}$ 1.4940, d^{20}_4 0.9471. This liquid had the foul odor previously associated with the copolymers of butadiene and 1-cyano-1,3-butadiene (mixture of isomers). A sample of this material was redistilled for analysis.

Anal. Calcd. for $C_9H_{11}N$: C, 81.15; H, 8.33. Found: C, 81.05; H, 8.24.

Attempts to effect dehydrogenation of this compound with sulfur or with palladium-on-carbon at high temperature failed. When 13.3 g. (0.1 mole) of the adduct was reduced over Raney nickel catalyst there was obtained 10.2 g. of an amine, b.p. 96° (22 mm.), $n^{20}_{\rm D}$ 1.4653, d^{20}_4 0.8461.

Anal. Calcd. for $C_9H_{19}N$: C, 76.51; H, 13.55; N, 9.92. Found: C, 76.45; H, 13.38; N, 10.08.

A picrate of this material was prepared, and after three recrystallizations from 95% ethanol it melted at 189–190° (dec.).

In an attempt to identify the adduct, *o*-cyanostyrene was reduced over nickel but it was not possible to prepare a crystalline picrate of the reduction product.

1-Cyano-2-methyl-1,3-butadiene.—The benzoate of tiglic aldehyde cyanohydrin was prepared by the same method used for the benzoate of crotonaldehyde cyanohydrin. From 63 g. (0.75 mole) of tiglic aldehyde (2-methylcrotonaldehyde), 106 g. (0.75 mole) of benzoyl chloride, and 45 g. (0.92 mole) of sodium cyanide there was obtained 120 g. (75%) of tiglic aldehyde cyanohydrin benzoate, b.p. 134° (2 mm.), $n^{20}_{\rm D}$ 1.5200.

Anal. Calcd. for $C_{13}H_{13}O_2N$: C, 72.54; H, 6.09. Found: C, 72.49; H, 6.23.

Pyrolysis of tiglic aldehyde cyanohydrin benzoate in a manner exactly analogous to that employed for the pyrolysis of crotonaldehyde cyanohydrin benzoate yielded 1-cyano-2-methyl-1,3-butadiene. From 120 g. of the benzoate there was obtained 29 g. (56%) of 1-cyano-2-methyl-1,3-butadiene, b.p. 65° (28 mm.), $n^{20}_{\rm D}$ 1.4986.

Anal. Calcd. for C_6H_7N: C, 77.38; H, 7.58. Found: C, 77.37; H, 7.68.

Summary

The *cis*- and *trans*-isomers of 1-cyano-1,3-butadiene have been separated. The higher-boiling isomer undergoes Diels–Alder reactions with maleic anhydride and 1,3-butadiene. This isomer is considered to have the *trans*-structure, on the basis of the reaction with maleic anhydride. 1-Cyano-2-methyl-1,3-butadiene has been prepared, but no stereochemical study of the product has been made.

URBANA, ILLINOIS

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