[Contribution from Noyes Chemical Laboratory, University of Illinois]

1-Cyano-1,3-butadienes.[1] V. The Diels–Alder Adducts of 1-Cyano-1,3-butadiene with Ethyl and Methyl Acrylate

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The investigation of the behavior of the geometric isomers of 1-cyano-1,3-butadiene in the presence of unsymmetrical dienophiles was undertaken in connection with a study of the Diels–Alder reactions of 1-cyano-1,3-butadiene. In previous work[2] it was shown that *trans*-1-cyano-butadiene gives addition products with maleic anhydride and butadiene while the *cis*-isomer fails to react with these compounds.

The *cis*-cyanobutadiene did not react with the ethyl or methyl ester of acrylic acid when the materials were heated together at 100° for twelve hours. This result was expected in the light of the non-reaction of the more active dienophile maleic anhydride.[2]

A mixture of the cyanobutadiene isomers gave a 30% yield (based on the *trans*-isomer) of a single product when heated with ethyl acrylate at 50° for five days. With methyl acrylate under similar conditions, an adduct was obtained in 19% yield (based on the *trans*-isomer). A considerable amount of cyanobutadiene dimer[3] was formed in both cases.

Attempts to dehydrogenate the ethyl and methyl acrylate adducts with sulfur were unsuccessful. The methyl acrylate adduct was brominated with N-bromosuccinimide and the crude bromination product treated with isoquinoline in the hope of effecting aromatization. In the dehydrobromination step, the mixture was heated at 180° to insure a complete reaction and only tarry material could be isolated. It appeared that the high temperature had destroyed the product.

Allyl bromination of the ethyl acrylate adduct was effected with two equivalents of N-bromosuccinimide in the same fashion. In this case, the crude dibromo product was dehydrobrominated with triethylamine at low temperatures. By this procedure there was obtained a low-melting solid in 70% yield. Microanalyses of the product agreed with the theoretical values for the expected cyanobenzoic ester. Both ethyl 2-cyanobenzoate[4,5] and ethyl 3-cyanobenzoate[5,6] are known. The melting point of the aromatized ethyl acrylate adduct agreed best with the melting points reported for ethyl 2-cyanobenzoate. However, the ortho- and meta-isomers have similar melting points and there are discrepancies among the values reported in the literature.

The ortho structure was proved by hydrolysis to phthalic acid which was identified by melting point and mixed melting point. Further confirmation of the structure was obtained by the dehydration of the phthalic acid to its anhydride, identified by melting point and mixed melting point.

Both the ethyl and methyl acrylate adducts were hydrolyzed with aqueous ethanolic sodium hydroxide. The same acid was the sole product from both hydrolyses. This acid melted at 206–207° and was found to have the composition of a cyclohexenedicarboxylic acid. The corresponding anhydride was formed by treatment of the acid with acetyl chloride as described by Baeyer,[7] and it had a melting point of 76.5–78°. Although all of the possible cyclohexene-1,2-dicarboxylic acid isomers are reported in the older literature, the early work of Baeyer[7] was partially in error and many of the reports based on his work are misleading. The situation has been clarified recently[8,9] and the most reliable values for the melting points of the isomeric acids and their anhydrides are given in Table I.

TABLE I
The Cyclohexene-1,2-dicarboxylic Acids

Isomer	M. p. acid, °C.	M. p. anhyd., °C.	Ref
1-	120	74	7
2-	215	78	7
cis-3-	174	59	9
trans-3-	218	140	9
cis-4-	166	104	10
trans-4-	172	186	8

From the melting point of the acid obtained from the acrylate adducts and the melting point of its anhydride, the 2-cyclohexene-1,2-dicarboxylic acid structure was assigned. This is the isomer to be expected, for the 1-cyclohexene- and 3-cyclohexene-1,2-dicarboxylic acids are known to isomerize readily to the 2-isomer in the presence of alkali.[7,9]

In order to establish whether the acrylate adducts had the *cis* or *trans* configuration, the direct esterification of the cyano group was investigated. Esterification under conditions that would not cause bond isomerization followed by ammonolysis of the diester to give the cyclic imide[11] was proposed as a route for this proof. When the ethyl and methyl acrylate adducts were

(1) For the previous paper in this series, see Snyder and Poos, This Journal, **72**, 4096 (1950).

(2) Snyder, Stewart and Myers, *ibid.*, **71**, 1055 (1949).

(3) Snyder and Poos, *ibid.*, **71**, 1395 (1949).

(4) Hoogewerff and van Dorp, *Rec. trav. chim.*, **11**, 97 (1892).

(5) Mueller, *Ber.*, **19**, 1494 (1886).

(6) Bromme, *ibid.*, **20**, 526 (1887).

(7) Baeyer, *Ann.*, **253**, 202 (1890).

(8) Korolev and Mur, *Doklady Akad. Nauk S. S. S. R.*, **59**, 73 (1948); *C. A.*, **42**, 6777 (1948).

(9) Alder, Schumacher and Wolff, *Ann.*, **564**, 79–137 (1949).

(10) Diels and Alder, *ibid.*, **460**, 113 (1928).

(11) Wislicenus and Kiesewetter, *Ber.*, **31**, 194 (1898).

·refluxed in the corresponding alcohol with an equimolar quantity of concentrated sulfuric acid, a low yield of imide was formed directly. Pure diester could not be isolated from the methyl acrylate adduct reaction mixture.

The same imide was obtained from both adducts, as shown by mixed melting point. The microanalysis was correct for a cyclohexene-dicarboximide. Only the 1- and 2-cyclohexene-1,2-dicarboximides are known with certainty.[12,13] Both of these compounds have melting points that are higher than the imide obtained from the ethyl and methyl acrylate adducts. Kuster[12] has described another isomer with a still higher melting point as *trans*-4-cyclohexene-1,2-dicarboximide, but, in the light of recent evidence presented by Alder and co-workers[9] in connection with the corresponding anhydrides, Kuster's highest-melting imide was probably *trans*-3-cyclohexene-1,2-dicarboximide.

Proof of the structure of the imide (I) from the cyanobutadiene-acrylic ester adducts was obtained by the reactions shown in equation A. Imide I was hydrogenated in the presence of platinum catalyst at ordinary temperature and
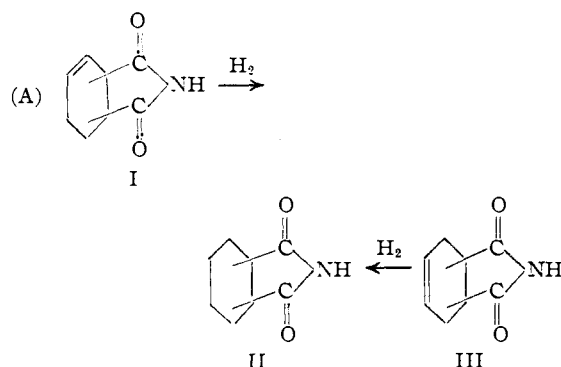
pressure to the known *cis*-cyclohexane-1,2-dicarboximide (II).[14] The preparation of II for comparison was accomplished by a similar hydrogenation of *cis*-4-cyclohexene-1,2-dicarboximide (III). Ammonolysis of the well-known *cis*-4-cyclohexene-1,2-dicarboxylic acid anhydride[10] by the method of Kuster[12] was used to prepare III. Mixed melting point determinations and analysis were used to confirm the identity of the saturated imide II obtained from imide I. This sequence not only proves the *cis*-configuration for imide I but also the 3-cyclohexene structure because of the difference between I and III.
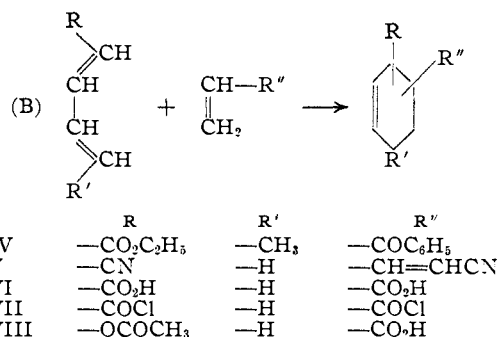
That the acrylic ester adducts of *trans*-1-cyanobutadiene proved to be of the *cis*-ortho-type was somewhat surprising. The product to be expected on the basis of resonance and electronic effects in the reacting molecules would be the meta-type adduct. Apparently ionic influences are of little

importance in determining the orientation of the products from these diene reactions. Although an ionic-type mechanism for Diels–Alder reactions occurring at moderate temperatures has been widely accepted,[15] it is difficult to explain our results by these interpretations. By an application of the principle of "maximum accumulation of unsaturation" (Alder Rule II)[16] it is possible to explain satisfactorily the formation of a *cis*-ortho-type adduct although the rule affords no explanation for the mechanism of the reaction.

There are very few reports in the literature of critical studies of the structures of Diels–Alder adducts obtained from polar unsymmetrical dienophiles with polar 1-substituted butadienes. Ethyl sorbate and phenylvinyl ketone react to give an adduct in which the carbonyl functions are adjacent (IV)[17] (equation B). As in the case of the acrylic ester adducts of 1-cyanobutadiene, compound IV is the reverse of the structure predicted on the basis of the electronic theory. The dimer of 1-cyanobutadiene[3] also has the "reverse" ortho-type structure (V) (equation B).

However, the opposite result is obtained from the reaction of β-chloroethyl sorbate and sorbyl chloride with acrylyl chloride; meta-type adducts are formed.[18] The Diels–Alder dimerization of methyl sorbate yields a complex mixture of products from which both an ortho-type and meta-type adduct have been identified.[19]

Since the completion of the work described in this paper, a series of articles by Alder has appeared in which the adducts of butadiene-1-carboxylic acid (and its chloride) with acrylic acid[9] (VI, equation B) and acrylyl chloride[9] (VII, equation B), and of 1-acetoxybutadiene with acrylic acid[20] (VIII, equation B) are described. All of these adducts were found to have the ortho-structure. Somewhat the same conclusions were presented regarding the mechanism of the reaction. In addition Alder has stated that he

	R	R'	R''
IV	$-CO_2C_2H_5$	$-CH_3$	$-COC_6H_5$
V	$-CN$	$-H$	$-CH=CHCN$
VI	$-CO_2H$	$-H$	$-CO_2H$
VII	$-COCl$	$-H$	$-COCl$
VIII	$-OCOCH_3$	$-H$	$-CO_2H$

(12) Kuster, *Z. physiol. Chem.*, **55**, 524 (1908).

(13) Mazza and Crapetta, *Gazz. chim. ital.*, **57**, 292 (1927).

(14) Willstätter and Jaquet, *Ber.*, **51**, 774 (1918); Hückel and Muller, *ibid.*, **64B**, 1981 (1931).

(15) For leading references, see Kloetzel in Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 8.

(16) Alder and Windemuth, *Ber.*, **71B**, 1939 (1938).

(17) Allen, Bell, Bell and VanAllan, THIS JOURNAL, **62**, 656 (1940).

(18) Wagner-Jauregg and Helmert, *Ber.*, **71B**, 2535 (1938).

(19) Farmer and Morrison-Jones, *J. Chem. Soc.*, 1339 (1940); Wheeler, THIS JOURNAL, **70**, 3467 (1948).

(20) Alder and Schumacher, *Ann.*, **565**, 148 (1949).

believes a radical-type mechanism[21] best explains the course of these diene reactions.

Attempts to obtain Diels–Alder condensation products with 1-cyanobutadiene and other ethylenic dienophiles were mainly unsuccessful. No addition product was formed when acrylonitrile and cis-cyanobutadiene were refluxed in benzene for several days. Mixtures of the cyanodiene isomers or the pure trans-isomer yielded a small amount of high-boiling Diels–Alder product when heated with acrylonitrile. In these experiments a major portion of the trans-cyanobutadiene dimerized. The acrylonitrile adduct boils at a temperature close to the boiling point of the cyanobutadiene dimer and it was not possible to separate the mixture by fractional distillation in sufficient quantity for characterization studies. trans-Cyanobutadiene (in mixture with the cis-isomer) was heated with crotonaldehyde, styrene and ethylenesulfonyl chloride[22] under various conditions without reaction. Dimerization of the trans-diene appeared to proceed more rapidly than Diels–Alder adduct formation with these dienophiles.

Experimental[23,24]

The Ethyl Acrylate Adduct of 1-Cyano-1,3-butadiene. Preparation.—A mixture of 5.5 ml. of cyanobutadiene (n^{20}D 1.4942, 83% trans) and 10.8 ml. (two equivalents) of ethyl acrylate was sealed in a 4-oz. screw-cap bottle along with a few crystals of picric acid to inhibit polymerization. The bottle was heated at 50° for one hundred and sixteen hours and then opened, and the contents were fractionally distilled. Unreacted ethyl acrylate and cyanobutadiene (mainly the cis-isomer) distilled first, followed by 2.7 g. (30% based on trans-cyanobutadiene) of adduct, b.p. 77–78° (0.20 mm.), n^{20}D 1.4727. A higher-boiling material remained in the still-pot and was assumed to be cyanobutadiene dimer. A portion of the product was redistilled and submitted for microanalysis; n^{20}D 1.4729.

Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31. Found: C, 67.17; H, 7.42.

Aromatization of the Ethyl Acrylate Adduct.—Into 30 ml. of benzene were introduced 1.32 g. (0.0073 mole) of the cyanobutadiene–ethyl acrylate adduct and 2.60 g. (0.0146 mole) of N-bromosuccinimide. The mixture was heated with stirring until homogeneous and then was refluxed for ten hours. A positive active bromine test (acidified potassium iodide solution) was obtained throughout. After standing overnight, the reaction mixture was cooled to 0° and the precipitated succinimide was collected by filtration (1.08 g., m.p. 121–125°).

Benzene was removed from the filtrate by distillation. The residue consisted of an orange oil which gave off hydrogen bromide very readily. This crude bromination product was treated at ice temperature portionwise with 4.1 ml. of triethylamine. The resulting mixture was treated with benzene and then with 10% hydrochloric acid. After separating the benzene layer and extracting the acid solution with benzene, the combined organic solution was washed with water and dried. The benzene

(21) For discussions and leading references, see Kloetzel in Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 8; Branch and Calvin, "The Theory of Organic Chemistry," Prentice–Hall, Inc., New York, N. Y., 1945, p. 488.

(22) Snyder and Anderson, unpublished observation.

(23) All melting points are uncorrected.

(24) Microanalyses by Misses Emily Davis and Rachel Kopel and Mrs. Jane Wood.

was evaporated and the residual brown oil was distilled in vacuo to yield 0.91 g. (70%) of a light-yellow oil, b. p. 93° (0.5 mm.), n^{20}D 1.5252. This product solidified after standing a short time; m. p. 54–61°. Repeated recrystallizations from petroleum ether (30–60°) gave a material with a melting point of 63.5–64° (lit.[4,5] 65–66°, 70°).

Anal. Calcd. for $C_{10}H_9NO_2$: C, 68.56; H, 5.18. Found: C, 68.77; H, 5.36.

Hydrolysis of the Aromatized Adduct.—One-tenth gram of ethyl o-cyanobenzoate from the ethyl acrylate adduct was hydrolyzed by refluxing in a solution of 5 ml. of 95% ethanol and 2 ml. of 6 N sodium hydroxide for three days. The alcohol was removed by distillation and the basic solution was acidified to yield 0.09 g. (91%) of tan crystals, m. p. 191–194° (dec.). After one recrystallization from water (Darco) the acid melted at 206–207° (dec.) alone or when mixed with authentic phthalic acid. Twenty milligrams of the acid was sublimed yielding the characteristic long needles of phthalic anhydride, m. p. 130–131° alone or when mixed with an authentic sample.

Hydrolysis.—A solution containing 1.91 g. of the adduct in 10 ml. of 95% ethanol and 10 ml. of 3 N sodium hydroxide was refluxed until ammonia was no longer evolved (four days). The ethanol was distilled and the hot aqueous solution was treated with Darco, filtered and cooled. Concentrated hydrochloric acid was added to the cold solution until it was strongly acid. Brown crystals of acid separated which were collected, washed with water and dried; 0.90 g., m. p. 175–178° (dec.). An additional 0.25 g. of product was obtained by concentrating the mother liquor. The total yield of crude acid was 64%. Partial purification was achieved by recrystallizing the product from water. A more suitable solvent was sought in order to eliminate the difficulties associated with the presence of an impurity less soluble in water than the product. 1-Nitropropane was found to be satisfactory and after repeated recrystallizations from this solvent, the acid had a constant melting point of 206–207° (dec.), lit.[7] 215° (dec.) with rapid heating.

Anal. Calcd. for $C_9H_{10}O_4$: C, 56.46; H, 5.93. Found: C, 56.38; H, 6.07.

A small amount of the acid obtained above was refluxed in an excess of pure, freshly distilled acetyl chloride for conversion to the acid anhydride by the method of Baeyer.[7] Low-boiling components were removed by vacuum distillation, and the crystalline residue was recrystallized from absolute ether; m. p. 76.5–78°, lit.[7] 78°.

Esterification and Imide Formation.—A solution of 2.02 g. (0.0113 mole) of the ethyl acrylate adduct in 10 ml. of absolute ethanol was treated with 0.60 ml. (1.11 g., 0.0113 mole) of concentrated sulfuric acid and then was refluxed for thirty-six hours. Half of the ethanol was distilled, the solution was cooled and poured into 20 ml. of water. The organic material was taken up in ether and the ether solution was washed with water and dried. The solvent was removed and there remained a yellow oil from which crystals separated at 0°. The crystals were collected on a filter, sucked free of oil and washed once with cold benzene; 0.27 g. (16%), m. p. 145–147°. After one recrystallization from benzene, the imide melted at 147.5–148° alone or when mixed with the imide obtained by a similar treatment of the methyl acrylate adduct. Analytical data are given for the imide sample obtained from the methyl acrylate adduct.

No attempt was made to isolate the diester from the oily material obtained in this experiment.

Proof of the Imide Structure (I). Hydrogenation to cis-1,2-Cyclohexanedicarboximide (II).—One-quarter gram of I in 25 ml. of absolute ethanol was shaken with hydrogen at atmospheric pressure and room temperature in the presence of 0.10 g. of platinic oxide. The theoretical volume of hydrogen was absorbed in ten minutes. After filtration from the catalyst, the ethanol solution was concentrated to ca. 5 ml. From the cold solution there was obtained 0.17 g. of white crystals; m. p. 133.5–136°. Two recrystallizations from ethanol raised the melting point to 136–136.5° (lit.[14] 137°).

Anal. Calcd. for $C_8H_{11}NO_2$: C, 62.72; H, 7.24. Found: C, 63.02; H, 7.39.

There was no depression in the melting point of this sample on admixture with authentic II prepared as described below.

cis-4-Cyclohexene-1,2-Dicarboximide (III).—The maleic anhydride adduct of butadiene[10] was prepared in 65% yield by bubbling butadiene into a warm benzene solution of maleic anhydride. Twenty-five milliliters of absolute ethanol was saturated with ammonia at 0° and then 4.1 g. of *cis*-4-cyclohexene-1,2-dicarboxylic acid anhydride was added to the cold solution in a Pyrex tube. The tube was sealed and heated in an electric furnace at 150–170° for three hours according to the method of Kuster.[12] After being allowed to cool, the tube was opened, and the contents were boiled to expel the excess ammonia. An alcohol insoluble material was removed from the hot reaction mixture by filtration. After washing and drying, the fine white powder amounted to 0.83 g. and melted at 243–245° (dec.). This material was presumed to be an amide and was not investigated further. Evaporation of the ethanolic filtrate left a thick orange residue which deposited large needles after standing overnight. A total of 0.52 g. (12.7%) of crystalline material, m. p. 130–137°, was obtained from the residue. The imide was recrystallized three times from benzene; m. p. 136.5–137.3°.

Anal. Calcd. for $C_8H_9NO_2$: C, 63.56; H, 6.00. Found: C, 63.65; H, 6.18.

Hydrogenation of III.—A solution of 0.25 g. of III in 25 ml. of absolute ethanol containing 0.10 g. of platinum oxide was shaken at room temperature under hydrogen at one atmosphere pressure. The theoretical volume of gas was absorbed in ten minutes. The catalyst was filtered and the solution was evaporated to dryness to yield II as a white crystalline residue melting at 133–136°. One recrystallization from absolute ethanol raised the melting point to 135–136° (lit.[14] 137°). A mixture with the starting imide melted at 119–124°.

The Methyl Acrylate Adduct of 1-Cyano-1,3-butadiene. Preparation.—A mixture of 13.9 ml. of cyanobutadiene ($n^{20}D$ 1.4942, 83% *trans*) and 22.7 ml. (two equivalents) of methyl acrylate containing a small amount of picric acid was sealed in a 4-oz. screw-cap bottle. The vessel was rotated in a water-bath at 50° for ninety-two hours. The bottle was opened and the contents were fractionally distilled. In addition to unreacted acrylic ester and monomeric and dimeric cyanobutadiene, there was obtained 4.0 g. (19%) of a colorless oil, b. p. 81–82° (0.3 mm.), $n^{20}D$ 1.4793.

Anal. Calcd. for $C_9H_{11}NO_2$: C, 65.43; H, 6.72. Found: C, 65.67; H, 6.87.

In another run, a 15.5% yield of the adduct was obtained when the reactants in the same proportion were kept at 50° for six days. A large amount of cyanobutadiene dimer was formed in both cases and it appeared that conversion to dimer was the predominant reaction of the *trans*-cyanobutadiene.

Hydrolysis.—The methyl acrylate adduct (1.32 g.) was hydrolyzed by refluxing in aqueous-ethanolic sodium hydroxide until the evolution of ammonia had practically ceased (forty-eight hours). Alcohol was removed by distillation and the dark aqueous solution was treated with Darco and filtered. Acidification of the basic solution at 0° with concentrated hydrochloric acid yielded 0.94 g. (69%) of brown crystals, m. p. 179–181° (dec.). After being recrystallized twice from 1-nitropropane (Darco) the white powdery acid melted at 198–200° (dec.). A mixture with the pure acid obtained from the ethyl acrylate adduct (m. p. 206–207°, dec.) melted at 199–201° (dec.).

Esterification and Imide Formation.—To 10 ml. of absolute methanol were added 1.94 g. (0.0118 mole) of the methyl acrylate adduct and then 0.65 ml. (1.18 g., 0.012 mole) of concentrated sulfuric acid. After being allowed to stand for thirty-six hours, the solution was refluxed twenty-four hours. The reaction mixture was cooled and poured into 20 ml. of water. A brown oil which separated was taken up in 10 ml. of ether. The aqueous solution was extracted with two 10-ml. portions of ether and the ether solutions were combined, washed with water and dried. Removal of the ether left a yellow-brown oil which was vacuum distilled. The distillate consisted of 1.22 g. of a colorless oil, b. p. 74–75° (0.3 mm.), $n^{20}D$ 1.4745, which contained nitrogen and was apparently a mixture of diester and starting material. The residue from the distillation crystallized on cooling. This solid was taken up in several milliliters of hot ethanol and recovered as white crystals from the cold solution; 0.15 g. (8.3%), m. p. 143–147°. The analytical sample melted at 148° after three recrystallizations from benzene.

Anal. Calcd. for $C_8H_9NO_2$: C, 63.56; H, 6.00. Found: C, 63.66; H, 5.89.

The nitrogen-containing oil obtained from the reaction was again treated with methanol and concentrated sulfuric acid. The reaction mixture was refluxed for one week and then was worked up as before. There was obtained 0.63 g. of oil, b. p. 78° (0.4 mm.), $n^{20}D$ 1.4725, which gave a faint positive test for nitrogen. Crystalline imide was again obtained from the residue.

Summary

trans-1-Cyano-1,3-butadiene condenses in the Diels–Alder fashion with ethyl and methyl acrylate to give ethyl and methyl *cis*-2-cyano-3-cyclohexene-1-carboxylate. The ortho-type structure is proved by aromatization of the ethyl acrylate adduct to ethyl 2-cyanobenzoate which is identified by hydrolysis to phthalic acid. Hydrolysis of both the ethyl and methyl acrylate adducts of 1-cyanobutadiene yields 2-cyclohexene-1,2-dicarboxylic acid which is identified by its melting point and the melting point of its anhydride. The acrylate adducts both give low yields of *cis*-3-cyclohexene-1,2-dicarboximide when refluxed in the corresponding alcohol with concentrated sulfuric acid. Hydrogenation to the known *cis*-cyclohexane-1,2-dicarboximide establishes the structure of this imide.

Acrylonitrile and *trans*-1-cyano-1,3-butadiene evidently react, but the addition product cannot be separated easily from the dimer of the cyanodiene which is formed concurrently. *trans*-1-Cyanobutadiene does not give a product with crotonaldehyde, styrene or ethylenesulfonyl chloride. Dimerization of the cyanodiene appears to proceed more rapidly than adduct formation with these dienophiles.

The *cis*-isomer of 1-cyanobutadiene does not react with ethyl acrylate, methyl acrylate, acrylonitrile, crotonaldehyde, styrene or ethylenesulfonyl chloride.