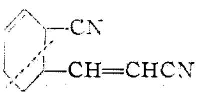
[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

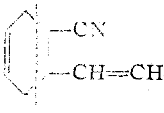
1-Cyano-1,3-butadienes. IV. Diels–Alder Reactions with Dienes

BY H. R. SNYDER AND GEORGE I. POOS

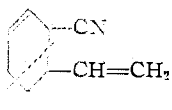
The previous papers of this series have reported the separation of 1-cyano-1,3-butadiene into its geometric isomers,[1] the Diels–Alder reaction of *trans*-1-cyanobutadiene with maleic anhydride and butadiene,[1] the carbon structure of the butadiene adduct[2] and the isolation and characterization of the dimer of 1-cyano-1,3-butadiene.[3] The carbon structure of the dimer (I, dotted line shows orientation of reactants) permits only one interpretation of the dimerization: one molecule acts as a diene and the *terminal* double bond of the other molecule acts as the dienophilic center. It might have been anticipated that the dienophilic molecule would react at the terminal double bond, since reaction at the internal bond undoubtedly would require greater interruption of the resonance within the molecule. The carbon structure of the butadiene adduct of *trans*-1-cyanobutadiene is consistent with either of two interpretations of its formation; the cyanodiene may react as the dienophile, but with the *internal* double bond serving as the dienophilic center (formula II), or it may react as the diene with butadiene functioning as the dienophile (formula III).



I



II



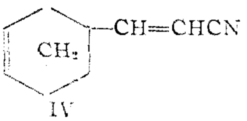
III

These considerations made it desirable to study the reactions of other dienes with the 1-cyanobutadienes. The present paper reports the condensations with cyclopentadiene, 2,3-dimethylbutadiene and isoprene.

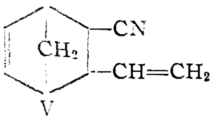
cis- and *trans*-1-cyanobutadiene each yielded a Diels–Alder product when heated with cyclopentadiene. The *cis*-cyanodiene gave an adduct in 58% yield when heated with cyclopentadiene at 50 or 100° for many hours. Under similar conditions *trans*-cyanobutadiene and cyclopentadiene gave a product in 80% yield. The products were shown to have the same composition by microanalysis; however, the material obtained from the *trans*-diene had an appreciably higher refractive index and boiling point (11.5° difference at 4 mm.) than the product from the *cis*-cyanodiene.

In order to establish firmly the difference between the adducts they were hydrolyzed with alkaline hydrogen peroxide to the corresponding amides. These solid amides had similar melting points but were proved to be different by a mixed melting point determination.

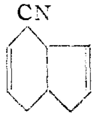
Structures IV, V and VI represent the carbon skeletons of the Diels–Alder products theoretically possible from the condensation of 1-cyanobutadiene and cyclopentadiene. From a consideration of these possibilities, structure VI seemed unlikely because of the inability of *cis*-cyanobutadiene to function as a diene.[1]



IV



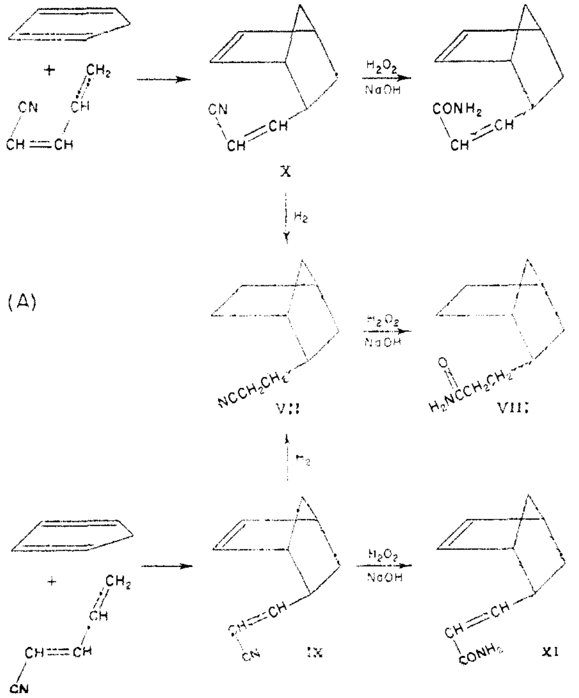
V



VI

Oxidation of the cyclopentadiene adducts with ozone or potassium permanganate led to similar acidic, nitrogen-free products that could not be induced to crystallize. In one ozonization experiment hydrogen cyanide was detected during the decomposition of the ozonide with hydrogen peroxide, and a material that appeared to be cyanuric acid was isolated along with the gummy, acidic product. These results are consistent with structure IV for the cyclopentadiene adducts of both *cis*- and *trans*-1-cyanobutadiene.

That the cyclopentadiene adducts differed only in the spatial arrangement about a carbon–carbon double bond was proved by catalytic hydrogenation to the same nitrile (VII). Both adducts absorbed two moles of hydrogen over 2% palladium on calcium carbonate catalyst at ordinary temperature and pressure. The samples of saturated nitrile obtained from the two adducts were hydrolyzed to the corresponding amide (VIII)



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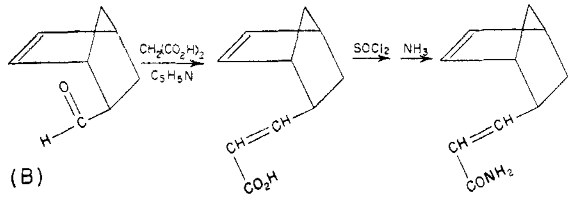
[1] Snyder, Stewart and Myers, THIS JOURNAL, **71**, 1055 (1949).

[2] Snyder and Poos, *ibid.*, **71**, 1057 (1949).

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

with alkaline hydrogen peroxide. The products were proved to be identical by a mixed melting point determination. Since the *cis,trans* isomerism of structure V is due to the rigidity of the ring and would not be affected by catalytic hydrogenation, structure IV was assigned to the adducts. On the basis of the almost invariable stereoselectivity of the diene synthesis involving alicyclic dienes,[4] the *endo* configuration was assigned to the adducts. Since the original space relationships of the cyanobutadienes were retained in the adducts, the higher-boiling adduct (IX) was known to be *trans* (from *trans*-cyanobutadiene) and the lower-boiling product (X), *cis* (from *cis*-cyanobutadiene). The reactions and products involved are outlined in equations A.

This proof for the structure of the cyclopentadiene adducts was substantiated by the preparation of the amide XI from a compound of known structure. The scheme employed is given in equation B. The well-known *endo*-2,5-endomethylene-3-cyclohexene-1-aldehyde (XII) was prepared by the method of Diels and Alder[5] from acrolein and cyclopentadiene. When this aldehyde was condensed with malonic acid in pyridine containing a trace of piperidine according to the procedure of Haworth and co-workers,[6] an 87% yield of *endo*-β-(2,5-endomethylene-3-cyclohexenyl)-acrylic acid (XIII) was obtained. The acid was converted to its chloride with thionyl chloride and the corresponding amide was prepared by treating the acid chloride with ammonia. The resulting amide (XI) proved to be identical with the amide obtained from the hydrogen peroxide–sodium hydroxide hydrolysis of the *trans*-cyanobutadiene-cyclopentadiene adduct. The *trans*-configuration was assigned to acid XIII and its derivatives on the basis of the correspondence with the *trans*-adduct amide.



XII XIII XI

As with cyclopentadiene, both the *cis*- and *trans*-1-cyanobutadienes gave products when heated with 2,3-dimethyl-1,3-butadiene; however, lower yields of a mixture of products were obtained with both of the cyanodiene isomers. By fractional distillation it was shown that the major product in each case was a homogeneous material. The lower-boiling, lower refractive index product was obtained from *cis*-cyanobutadiene and 2,3-dimethylbutadiene. By a comparison with the results of the work with the cyclopentadiene adducts, it appeared that again a *cis,trans* pair of adducts was involved.

Proof of the 2,3-dimethylbutadiene adduct structures was obtained by the same scheme used for the cyclopentadiene adducts. When reduced over 2% palladium on calcium carbonate catalyst, both adducts absorbed one molar equivalent of hydrogen and yielded the same dihydronitrile, β-(3,4-dimethyl-3-cyclohexenyl)-propionitrile. A confirmation of the identity of the nitrile samples was obtained by alkaline hydrogen peroxide hydrolysis and a mixed melting point comparison of the specimens of β-(3,4-dimethyl-3-cyclohexenyl)-propionamide. The hydrolysis of the *cis*-cyanobutadiene-2,3-dimethylbutadiene adduct with hydrogen peroxide-sodium hydroxide yielded an oil from which only a small amount of crystalline material could be isolated. The homogeneous product from *trans*-cyanobutadiene yielded a different crystalline amide by alkaline hydrogen peroxide hydrolysis.

The mixtures of slightly higher-boiling products obtained from *cis*-cyanobutadiene and 2,3-dimethylbutadiene and the slightly lower-boiling products obtained from the *trans*-isomer were shown to be mixtures of the *cis*- and *trans*-adducts by hydrogenation to the same dihydronitrile that was obtained from both of the adducts and by hydrolysis to an oil and *trans*-β-(3,4-dimethyl-3-cyclohexenyl)-acrylamide.

That the *trans*-cyanobutadiene-2,3-dimethylbutadiene adduct amide was *trans*-β-(3,4-dimethyl-3-cyclohexenyl)-acrylamide was confirmed by synthesis. The acrolein-2,3-dimethylbutadiene adduct[7] was condensed with malonic acid and the resulting *trans*-β-(3,4-dimethyl-3-cyclohexenyl)-acrylic acid was converted to the corresponding amide *via* the acid chloride. Microanalyses and a mixed melting point determination proved the identity of the amide samples.

Both the *cis*- and *trans*-cyanobutadiene isomers yielded rather complex mixtures of products when heated with isoprene at 100° for several days. From the *cis*-isomer there was obtained 36% of a material which was separated by fractional distillation into a single lower-boiling adduct and a mixture of higher-boiling adducts very similar to the product obtained from the *trans*-cyanodiene. As a result of a study of the infrared spectrum of the homogeneous lower-boiling product, it was concluded that *cis*-β-(4-methyl-3-cyclohexenyl)-acrylonitrile (XIV) was the probable structure. Alkaline hydrogen peroxide hydrolysis of XIV yielded an oily product along with a trace of crystalline amide.

Proof of the *cis*-cyanobutadiene–isoprene adduct structure (XIV) was obtained by careful hydrogenation to the dihydronitrile XV and hydrolysis of XV to β-(4-methyl-3-cyclohexenyl)-propionamide (XVI) (equations C). An authentic specimen of XVI was prepared for comparison by

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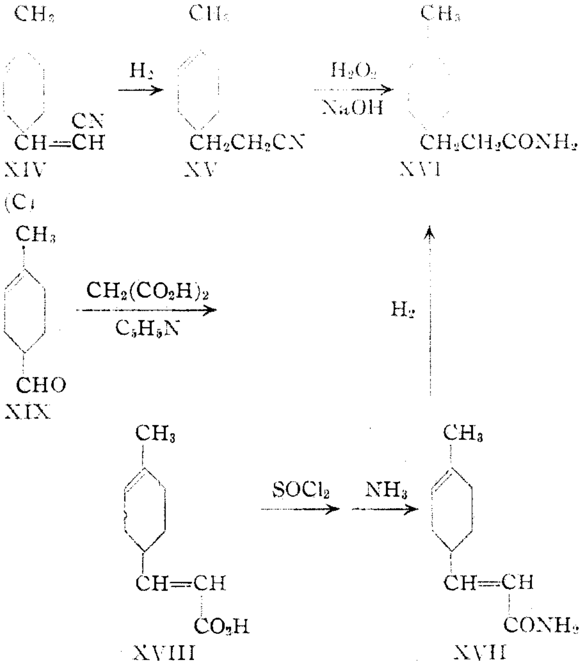
[4] Alder, *et al.*, *Ann.*, **514**, 1 (1934); Alder and Stein, *Angew. Chem.*, **50**, 510 (1937).

[5] Diels and Alder, *Ann.*, **460**, 98 (1928).

[6] Haworth, *et al.*, *J. Chem. Soc.*, **125**, 1693 (1924).

[7] Diels and Alder, *Ann.*, **470**, 62 (1929).

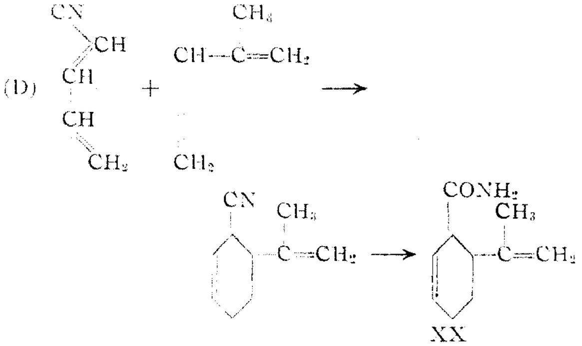
the addition of one mole of hydrogen to *trans*-β-(4-methyl-3-cyclohexenyl)-acrylamide (XVII). The *trans*-amide XVII was prepared from its acid (XVIII) through the acid chloride. The condensation of 4-methyl-3-cyclohexene-1-aldehyde[7,8,9] (XIX) with malonic acid was used to prepare the *trans*-acrylic acid XVIII (equations C).



Isoprene and *trans*-cyanobutadiene yielded 52% of a mixture of adducts from which no single product could be separated by careful fractional distillation through a small Fenske column. The mixture of products was then distilled through a miniature Podbielniak "Hypercal" column in order to effect a more efficient separation. Again no single product was obtained, but, from the physical constants of the various fractions, it appeared that a greater degree of separation had been achieved.

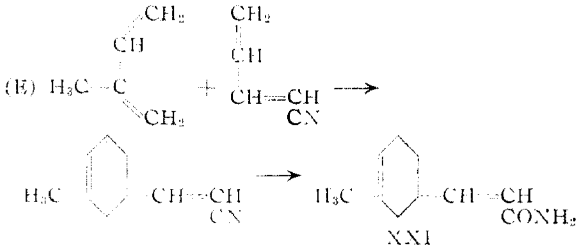
From the boiling point, index of refraction, infrared spectrum and behavior on alkaline hydrogen peroxide hydrolysis, it was concluded that the lowest-boiling material was largely the *cis*-cyanobutadiene–isoprene adduct.

Hydrolysis of an intermediate-boiling fraction with hydrogen peroxide-sodium hydroxide produced an oily material along with a small yield of a single crystalline amide. The purified solid gave a carbon–hydrogen analysis that was correct for a one-to-one adduct amide. This amide was different from all of the other adduct amides obtained from isoprene and cyanobutadiene. The infrared spectrum (curve III) shows absorption bands to be expected for amide carbonyl (1651 cm.$^{-1}$), the second amide band (1621 cm.$^{-1}$) and for the $-NH_2$ group (3207 and 3400 cm.$^{-1}$). The strong absorption band at 899 cm.$^{-1}$ is characteristic for the $R_2C{=}CH_2$ linkage.[10] A structure of the type represented by formula XX is tentatively proposed on the basis of the infrared data. This compound would be formed from a reaction in which cyanobutadiene is the diene and isoprene the dienophile as shown in equation D.



Hydrolysis of the highest-boiling fraction of *trans*-cyanobutadiene–isoprene product with alkaline hydrogen peroxide produced a mixture of amides which was separated into two components by fractional crystallization. The higher-melting amide was present in the smaller proportion and proved to be *trans*-β-(4-methyl-3-cyclohexenyl)-acrylamide (XVII) as shown by mixed melting point and microanalysis.

The major product from this hydrolysis was a lower-melting isomeric amide. From the infrared spectrum of this material (curve II) it is apparent that the compound is very similar to XVII (curve I). These spectra were determined in Nujol suspension. The spectra of the two compounds were also determined in chloroform solution at about the same concentration and were found to be virtually identical. Despite this spectral similarity, the materials proved to be different. A mixture of the two amides melted over a temperature range between the melting points of the compounds both before and after melting together. It appeared unlikely that the compounds being compared were *cis*,*trans* isomers for the lower-melting amide was different from the solid amide obtained from the *cis*-cyanobutadiene–isoprene adduct (XIV) and would not induce the crystallization of the oily product obtained from the hydrolysis of XIV. Since the remaining possibility is position isomerism, structure XXI which would be formed as shown in equation E



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(8) Lehmann and Paasche, *Ber.*, **68**, 1146 (1935).

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

(10) Thompson and Whiffen, *J. Chem. Soc.*, 1412 (1948).

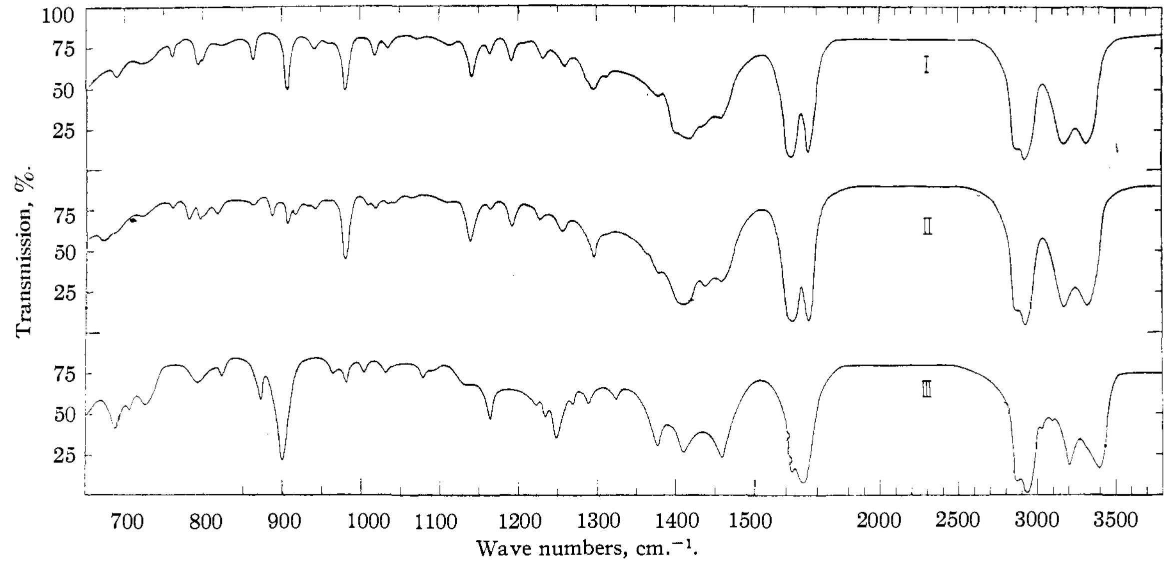

Fig. 1.—Infrared absorption spectra: I, *trans*-β-(4-methyl-3-cyclohexenyl)-acrylamide; II, *trans*-1-cyanobutadiene–isoprene adduct amide, m. p. 115.5–116.5°; III, *trans*-1-cyanobutadiene–isoprene adduct amide, m. p. 113.5–114.5°. All of the spectra were determined in Nujol suspension. The authors are indebted to Miss Elizabeth Petersen for the determination and interpretation of these spectra.

is tentatively proposed for the *trans*-cyanobutadiene–isoprene adduct amide melting at 115.5–116.5°.

It was apparent from this preliminary investigation that a mixture of at least four isomeric adducts is produced by the Diels–Alder reaction of cyanobutadiene and isoprene. From the fact that a number of adducts are produced, it was concluded that isoprene and cyanobutadiene function simultaneously as dienes and dienophiles in the reaction. Thus isoprene and *trans*-cyanobutadiene are apparently of about the same order of reactivity as dienes.

Since none of the adducts from any of the dienes studied appeared to have been formed through dienophilic activity of the internal double bond of either of the 1-cyanobutadienes, it seems highly unlikely that formula II represents the correct interpretation of the reaction of butadiene and *trans*-1-cyanobutadiene. Structure III thus represents the probable mode of combination of these reagents.

Neither of the cyanobutadiene isomers formed a Diels–Alder product with anthracene by prolonged refluxing in benzene. Furan did not react with cyanobutadiene in several experiments in which the materials were heated together for two days at 50°. Maleic anhydride readily gives adducts with both furan[11] and anthracene[12]; therefore, it is apparent that cyanobutadiene is less reactive as a dienophile than maleic anhydride.

In order to establish more firmly the configurations of the 1-cyanobutadiene isomers, the pure isomeric nitriles were converted to the corresponding amides by hydrolysis with sodium hydroxide in the presence of hydrogen peroxide. From the lower-boiling nitrile there was obtained an amide melting at 96–97°. The isomeric amide from the higher-boiling isomer melted at 123–124°. The assignment of configuration[1] and these results agree with the usual observation that the *trans*-isomer is the higher-melting of a pair of *cis,trans* isomers.

Experimental[13,14]

The Cyclopentadiene Adducts of 1-Cyano-1,3-butadiene

The *cis*-Cyanobutadiene–Cyclopentadiene Adduct. Preparation.—A mixture of 9.0 ml. (7.8 g., 0.10 mole) of pure *cis*-cyanodiene and 9.0 ml. (7.3 g., 0.11 mole) of freshly prepared cyclopentadiene containing a few crystals of picric acid was sealed in a 4-oz. screw-cap bottle and heated on the steam cone for seven hours. Fractionation of the reaction mixture through a small Fenske column yielded, in addition to unreacted cyanobutadiene and dicyclopentadiene, 8.13 g. (58%) of a water-white oil; b. p. 80° (4 mm.), $n^{20}\mathrm{D}$ 1.5115.

Anal. Calcd. for $C_{10}H_{11}N$: C, 82.71; H, 7.64. Found: C, 82.79; H, 7.92.

The adduct was prepared in 58 and 57% yields by heating the same ratio of reactants together at 50° for twenty-four and one hundred seventy-seven hours, respectively.

Hydrolysis.—A solution of 2.58 g. of the *cis*-cyanobutadiene–cyclopentadiene adduct in 25 ml. of 95% ethanol was treated with 0.71 ml. of 6 *N* sodium hydroxide and 7.1 ml. of 30% hydrogen peroxide. The solution warmed slightly and evolved oxygen. After being kept at 50° for seventeen hours the solution was made exactly neutral with dilute sulfuric acid and then treated with finely divided platinum to decompose the excess hydrogen peroxide. Inorganic material was separated by filtration and the solution was evaporated to a small volume in a stream of air. The white crystals that separated were collected on a filter, sucked free of oil and washed with cold water; 0.56 g. (20%). After four recrystallizations from benzene the amide melted at 139.2–140.7°.

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[11] Diels and Alder, *Ber.*, **62**, 554 (1929).

[12] Bachmann and Kloetzel, THIS JOURNAL, **60**, 481 (1938).

[13] All melting points are uncorrected.

[14] Microanalyses by Mrs. Jane Wood, Misses Emily Davis and Rachel Kopel and Mr. Maurice Dare.

Anal. Calcd. for $C_{10}H_{13}NO$: C, 73.59; H, 8.03. Found: C, 73.47; H, 8.27.

The oil obtained along with the crystalline product was found to consist of about equal parts of the original nitrile and an acid, presumably the corresponding acid.

Hydrogenation.—The adduct (1.44 g.) was reduced to the saturated nitrile in methanol (30 ml.) over 2% palladium on calcium carbonate (0.50 g.) at room temperature and atmospheric pressure. The theoretical amount of hydrogen was absorbed in twenty-two minutes, both bonds reducing with equal ease. After filtration from the catalyst the methanol was boiled away and the residual oil was distilled *in vacuo*. There was obtained 1.29 g. (86.6%) of a colorless product; b. p. 90° (2.5 mm.), $n^{20}D$ 1.4790; it failed to decolorize potassium permanganate.

Anal. Calcd. for $C_{10}H_{15}N$: C, 80.48; H, 10.13. Found: C, 80.50; H, 10.07.

Hydrolysis of the Hydrogenated Adduct.—To a solution of 0.90 g. of the saturated adduct in 10 ml. of 95% ethanol containing 0.24 ml. of 6 *N* sodium hydroxide was added 2.4 ml. of 30% hydrogen peroxide. After being maintained at 50° overnight, the reaction mixture was worked up in the usual fashion. There was obtained 0.69 g. (68%) of an oily solid, m. p. 106–111°. Three recrystallizations from 1:1 benzene–petroleum ether raised the melting point to 111–112.5°.

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.81; H, 10.25. Found: C, 72.07; H, 10.22.

The *trans*-Cyanobutadiene–Cyclopentadiene Adduct. Preparation.—*trans*-1-Cyano-1,3-butadiene (9.0 ml., 7.8 g., 0.10 mole) and freshly prepared cyclopentadiene (9.0 ml., 7.3 g., 0.11 mole) were mixed with a few crystals of picric acid and sealed in a 4-oz. screw-cap bottle. The vessel was rotated in a 50° bath for one hundred and sixty hours. The material was distilled through a small Fenske column, and there was obtained 11.3 g. (80.0%) of colorless adduct, b. p. 91.5° (4 mm.), $n^{20}D$ 1.5165.

Anal. Calcd. for $C_{10}H_{11}N$: C, 82.71; H, 7.64. Found: C, 82.73; H, 7.80.

Hydrolysis.—A 1.18-g. sample of the adduct was hydrolyzed in 10 ml. of 95% ethanol with 0.32 ml. of 6 *N* sodium hydroxide and 3.2 ml. of 30% hydrogen peroxide. The reaction was exothermic. After heating the mixture at 50° for five hours and working up the product in the usual fashion, there was obtained 0.46 g. (35%) of crude amide. The product was recrystallized once from benzene and three times from water; m. p. 135.5–137°.

Anal. Calcd. for $C_{10}H_{13}NO$: C, 73.59; H, 8.03. Found: C, 73.73; H, 8.00.

A mixture with the *cis*-cyanobutadiene–cyclopentadiene adduct amide (m. p. 139.2–140.7°) melted at 100–112°.

Hydrogenation.—A solution of 1.45 g. of the *trans*-cyanobutadiene–cyclopentadiene adduct in 30 ml. of methanol to which 0.10 g. of 2% palladium on calcium carbonate had been added was shaken at room temperature under one atmosphere of hydrogen. The theoretical amount of hydrogen necessary to saturate both double bonds was absorbed in fifty-three minutes; the rate of hydrogen uptake slowed somewhat during the last part of the reaction. The catalyst was removed by filtration and the solvent was boiled away. Vacuum distillation of the pale yellow residual oil yielded 1.29 g. (86%) of a colorless product; b. p. 91° (2.8 mm.), $n^{20}D$ 1.4803.

Hydrolysis of the Hydrogenated Adduct.—One-half gram of the reduced adduct in 10 ml. of 95% ethanol was hydrolyzed with 0.13 ml. of 6 *N* sodium hydroxide and 1.3 ml. of 30% hydrogen peroxide by warming the solution at 50° for twenty hours. After neutralizing, decomposing the excess peroxide and evaporating the solution to a small volume there was obtained 0.48 g. (84%) of white crystals, m. p. 101–110°. One recrystallization from 1:1 benzene–petroleum ether (30–60°) raised the melting point to 114.5–116°. A mixture with the hydrogenated *cis*-cyanobutadiene–cyclopentadiene adduct amide (m. p. 111–112.5°) melted at 112.5–115.5°.

***trans-endo*-β-(2,5-Endomethylene-3-cyclohexenyl)-acrylic Acid (XIII).**—The combination of acrolein and freshly prepared cyclopentadiene in ether by the method of Diels and Alder[5] was used to prepare *endo*-2,5-endomethylene-3-cyclohexene-1-aldehyde (XII) in 83% yield: b. p. 74° (22 mm.), lit.[5] 70–72° (20 mm.); $n^{20}D$ 1.4883. A mixture of 17.1 g. (0.14 mole) of freshly prepared XII and 31.5 g. (0.30 mole) of malonic acid in 65 ml. of pyridine to which 1 ml. of piperidine had been added was heated on the steam cone for two hours. The evolution of carbon dioxide was almost immediate and continued at a steady rate. The yellow solution was refluxed for five minutes to complete the reaction and then was allowed to cool. The reaction mixture was poured into an excess of dilute hydrochloric acid containing ice. The organic layer was separated and the aqueous layer was extracted with three 100-ml. portions of ether. After combination with the organic layer the ether solution was dried and the ether was removed. Distillation *in vacuo* yielded acetic acid and XIII as a heavy colorless oil, b. p. 107–108°. (0.32 mm.), $n^{20}D$ 1.5260. The yield was 20.0 g. (87%).

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 72.88; H, 7.72.

Acid Chloride and Amide of XIII.—One gram of the pure acid and an equal volume of pure thionyl chloride were slowly heated to 100° in a test-tube protected from moisture by a calcium chloride tube. The solution was kept at 100° for forty-five minutes and then cooled and transferred to a small distillation apparatus. Distillation *in vacuo* yielded *ca.* 0.50 g. of a yellow oil, b. p. 65° (0.4 mm.). A higher boiling residue was discarded. The freshly distilled acid chloride was poured into 3 ml. of concentrated aqueous ammonia containing a little ice. An oil separated which soon crystallized. The white crystals were collected, washed thoroughly and dried; 0.23 g., m. p. 118–127°. After four recrystallizations from water the amide melted at 135.5–136.5° alone or when mixed with the amide obtained from the hydrolysis of the *trans*-cyanobutadiene–cyclopentadiene adduct.

Anal. Calcd. for $C_{10}H_{13}NO$: C, 73.59; H, 8.03. Found: C, 73.66; H, 8.13.

The 2,3-Dimethyl-1,3-butadiene Adducts of 1-Cyano-1,3-butadiene

The *cis*-Cyanobutadiene–2,3-Dimethylbutadiene Adduct. Preparation.—A mixture of 5.0 g. (0.063 mole) of pure *cis*-cyanobutadiene, 5.2 g. (0.063 mole) of 2,3-dimethylbutadiene and *ca.* 0.1 g. of picric acid was sealed in a 4-oz. screw-cap bottle. The vessel was heated at 100° for forty-two hours and then was cooled and opened, and the contents were fractionally distilled. The main fraction was 3.04 g. (30%) of a pale yellow oil, b. p. 70–71° (0.30 mm.), $n^{20}D$ 1.4993. A redistilled sample of this material was colorless; b. p. 66° (0.27 mm.), $n^{20}D$ 1.4992.

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.93; H, 9.38. Found: C, 81.81; H, 9.61.

In addition to this main fraction, there was obtained 1.28 g. of yellow liquid, b. p. 80–115° (0.30 mm.), $n^{20}D$ 1.5072. Redistillation of this material showed that it was probably a mixture of the *cis*-adduct, the *trans*-adduct and cyanobutadiene dimer resulting from isomerization of the *cis*-cyanobutadiene. That isomerization of the *cis*-adduct was not involved was shown by heating the *cis*-adduct at 100° for ninety-six hours, after which it was recovered unchanged by distillation.

Hydrolysis.—A solution of 0.41 g. of the *cis*-cyanobutadiene–2,3-dimethylbutadiene adduct in 5 ml. of 95% ethanol was treated with 0.11 ml. of 6 *N* sodium hydroxide and 1.1 ml. of 30% hydrogen peroxide. The reaction mixture was kept at 50° for twelve hours and then cooled, made neutral with dilute sulfuric acid and stirred with manganese dioxide until the excess hydrogen peroxide was destroyed. After filtration the ethanol was evaporated, whereupon an oily material separated. This oil failed to crystallize when cooled, rubbed with a stirring rod or left to stand for several weeks. The material was heated under reduced pressure in order to remove the nitrile present by distillation. A portion of the residue crystallized. The crystals were collected, sucked free of oil, washed with several portions of cold 50% ethanol and dried; 0.01 g., m. p. 105–111°. There was not enough of this material for purification and analysis.

Hydrogenation.—A solution of 1.72 g. of the adduct in 45 ml. of methanol containing 0.60 g. of 2% palladium on calcium carbonate was hydrogenated at room temperature and a pressure of three atmospheres. In twenty minutes a pressure reduction corresponding to one molar equivalent of hydrogen occurred. The mixture was left on the shaker an additional fifteen minutes but no more hydrogen was absorbed. After filtration from the catalyst and removal of the solvent the residue was distilled under reduced pressure. There was obtained 1.56 g. (89%) of colorless product, b. p. 76° (0.30 mm.), n^{20}D 1.4813.

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.92; H, 10.50. Found: C, 80.79; H, 10.60.

Hydrolysis of the Hydrogenated Adduct.—One gram of the dihydro-adduct in 5 ml. of 95% ethanol was hydrolyzed with 0.26 ml. of 6 *N* sodium hydroxide and 2.6 ml. of 30% hydrogen peroxide by warming at 50° for eighteen hours. The reaction mixture was worked up in the usual manner to yield an oily amide. After one recrystallization from benzene (Darco) there was obtained 0.57 g. (51%) of product melting at 113–115°. An analytical sample was prepared by recrystallizing this material three times from benzene to a constant melting point of 114.5–116°.

Anal. Calcd. for $C_{11}H_{19}NO$: C, 72.88; H, 10.56. Found: C, 72.75; H, 10.53.

The *trans*-Cyanobutadiene–2,3-Dimethylbutadiene Adduct. Preparation.—Cyanobutadiene (5.1 g., n^{20}D 1.4963) and 2,3-dimethylbutadiene (6.4 g.) were mixed with a few crystals of picric acid and sealed in a 4-oz. screw-cap bottle. The bottle was kept at 100° for forty-one hours. A careful fractional distillation of the contents yielded, in addition to unreacted 2,3-dimethylbutadiene, three higher-boiling fractions: I, 0.19 g., b. p. 38° (16 mm.), n^{20}D 1.4852; II, 0.59 g., b. p. 66–72° (0.25 mm.), n^{20}D 1.4990; III, 1.61 g. (15.5%), b. p. 74–76° (0.28 mm.), n^{20}D 1.5048. The highest-boiling fraction (III) appeared to be homogeneous and was taken as the desired product. This material was redistilled several times and submitted for microanalysis; b. p. 77° (0.35 mm.), n^{20}D 1.5053.

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.93; H, 9.38. Found: C, 81.75; H, 9.57.

Fraction I was cyanobutadiene, presumably the *cis*-isomer. From the boiling point and refractive index it appeared that fraction II was the same as the *cis*-cyanobutadiene–2,3-dimethylbutadiene adduct.

A second preparation was carried out in order to confirm this apparent isomerization of the *trans*-forms to the *cis*-forms. The same quantities of reactants were heated together at 100° for sixteen hours and the product was fractionally distilled. In addition to unreacted 2,3-dimethylbutadiene and cyanobutadiene (n^{20}D 1.4880), there were obtained three fractions of adduct: I, 0.78 g., b. p. 69–71° (0.30 mm.), n^{20}D 1.4990; II, 1.60 g., b. p. 73–75° (0.30 mm.), n^{20}D 1.5025; III, 0.33 g., b. p. 75° (0.30 mm.), n^{20}D 1.5050. The intermediate fraction was hydrogenated to yield the same nitrile (n^{20}D 1.4815) as was obtained from the hydrogenation of both the *cis*- and *trans* - cyanobutadiene–2,3 - dimethylbutadiene adducts. Hydrolysis of the intermediate fraction gave a small yield of the amide obtained by the hydrolysis of the *trans*-cyanobutadiene-2,3-dimethylbutadiene adduct. These experiments indicated that the product obtained was a mixture of the *cis*- and *trans*-adducts.

Hydrolysis.—A solution of 0.52 g. of the adduct (n^{20}D 1.5053) in 5 ml. of 95% ethanol was treated with 0.13 ml. of 6 *N* sodium hydroxide and then with 1.3 ml. of 30% hydrogen peroxide. After the reaction had subsided the mixture was kept at 50° for fourteen hours and then worked up as described previously. There was obtained 0.24 g. (42%) of crude amide, which after three recrystallizations from 95% ethanol melted at 153–155°.

Anal. Calcd. for $C_{11}H_{17}NO$: C, 73.70; H, 9.56. Found: C, 73.69; H, 9.64.

Hydrogenation.—The *trans*-cyanobutadiene-2,3-dimethylbutadiene adduct (0.93 g., n^{20}D 1.5050) in methanol (40 ml.) containing 2% palladium on calcium carbonate (0.50 g.) was shaken at room temperature with hydrogen at three atmospheres pressure. One double bond reduced in three minutes and no more hydrogen was absorbed during the following ten minutes. After removal of the catalyst by filtration the solvent was boiled away. Distillation of the residue yielded 0.85 g. (91%) of the dihydro-adduct, b. p. 77–77.5° (0.32 mm.), n^{20}D 1.4820.

Hydrolysis of the Hydrogenated Adduct.—A solution of 0.79 g. of the nitrile in 5 ml. of 95% ethanol was treated with 0.19 ml. of 6 *N* sodium hydroxide and 1.9 ml. of 30% hydrogen peroxide at 50° for eighteen hours. From the reaction mixture there was obtained 0.46 g. (53%) of amide melting at 111–114°. After one recrystallization from benzene the product melted at 114.5–116° alone or when mixed with the amide obtained from the hydrogenated *cis*-cyanobutadiene-2,3-dimethylbutadiene adduct.

***trans*-β-(3,4-Dimethyl-3-cyclohexenyl)-acrylic Acid.**—3,4-Dimethyl-3-cyclohexene-1-aldehyde[7] was prepared in 70.8% yield by heating acrolein and 2,3-dimethylbutadiene in a sealed bottle at 100° for three hours; b. p. 73° (8 mm.), lit.,[7] 79° (10 mm.), n^{20}D 1.4783. The freshly prepared aldehyde (17.6 g., 0.127 mole) was combined with 28.3 g. (0.272 mole) of malonic acid in 65 ml. of pyridine containing 1 ml. of piperidine. The mixture was heated on the steam cone for two hours and then refluxed for ten minutes to complete the reaction. When the cold solution was poured into an excess of cold dilute hydrochloric acid, an oil separated which soon solidified. The solid cake was broken up, collected on a filter and washed repeatedly with cold water. After thorough drying the product weighed 21.8 g. (95.2%); m. p. 100–103°. A portion of the material was purified by three recrystallizations from 30% ethanol; m. p. 103.5–104.5°.

Anal. Calcd. for $C_{11}H_{16}O$: C, 73.30; H, 8.95. Found: C, 73.13; H, 8.93.

Acid Chloride and Amide of *trans*-β-(3,4-Dimethyl-3-cyclohexenyl)-acrylic Acid.—A mixture of 2.77 g. of the pure dry acid and 3.66 g. of pure thionyl chloride was heated at 100° for one and one-half hours. Excess thionyl chloride was distilled under reduced pressure followed by the product as a pale yellow oil; 1.96 g. (64.5%), b. p. 85–87° (0.25 mm.), n^{20}D 1.5192. There was also obtained 0.57 g. of a higher-boiling material (b. p. 92–93° (0.50 mm.), n^{20}D 1.5282) which was presumed to have resulted from the addition of hydrogen chloride to the molecule and was discarded. The acid chloride was poured into cold concentrated ammonia and the amide collected, washed with water and dried. After four recrystallizations from 95% ethanol and two recrystallizations from benzene the crystals melted at 153–155° alone or when mixed with the amide obtained from the hydrolysis of the *trans*-cyanobutadiene–2,3-dimethylbutadiene adduct.

Anal. Calcd. for $C_{11}H_{17}NO$: C, 73.70; H, 9.56. Found: C, 73.95; H, 9.56.

The Isoprene Adducts of 1-Cyano-1,3-butadiene

The *cis*-Cyanobutadiene–Isoprene Adduct. Preparation.—A mixture of 26.8 g. of *cis*-cyanobutadiene and 277 g. of isoprene to which a small amount of picric acid had been added was heated at 100° for forty-six hours. When distilled, the reaction mixture yielded unchanged isoprene and *cis*-cyanobutadiene along with 13.1 g. of product (26.2% or 36.1% based on cyanobutadiene consumed) boiling at 72–79° (1.5 mm.), n^{20}D 1.4943. By fractional distillation of this mixture, 4.1 g. of a homogeneous material was separated; b. p. 53° (0.23 mm.), n^{20}D 1.4938. The remainder of the distillate consisted of a mixture of higher-boiling, higher refractive index nitriles which was very similar to the product obtained from isoprene and *trans*-cyanobutadiene. The lower-boiling adduct was redistilled twice; b. p. 53° (0.23 mm.), n^{20}D 1.4933.

Anal. Calcd. for $C_{10}H_{13}N$: C, 81.58; H, 8.90. Found: C, 81.45; H, 9.20.

Hydrogenation.—A solution of 0.36 g. of the *cis*-cyanobutadiene–isoprene adduct (XIV) in 15 ml. of methanol containing 0.20 g. of 2% palladium on calcium carbonate was shaken with hydrogen at 25° and atmospheric pressure. Within twelve minutes the solution had absorbed 65.5 ml. of hydrogen (theoretical for one double bond was 59.8 ml.) at a maximum rate of 7 ml./minute. After fourteen minutes, 68.5 ml. of hydrogen had been absorbed, the rate of hydrogen uptake had slowed markedly and the shaker was stopped. The catalyst was filtered and the methanol was distilled. Upon distilling the residue, there was obtained 0.23 g. of product, b. p. 70° (0.5 mm.), n^{20}D 1.4743.

Hydrolysis of the Hydrogenated Adduct.—The sample of dihydro-adduct described above was hydrolyzed in 5 ml. of 95% ethanol with 0.07 ml. of 6 *N* sodium hydroxide and 0.65 ml. of 30% hydrogen peroxide by heating at 50° for eighteen hours. When processed in the usual fashion, the reaction mixture yielded 0.13 g. (48%) of product. After five crystallizations from petroleum ether (90–100°) containing a few drops of benzene, the dihydro-adduct amide melted at 132–134.5°.

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.81; H, 10.25. Found: C, 71.67; H, 10.28.

***trans*-β-(4-Methyl-3-cyclohexenyl)-acrylic Acid (XVIII).**—4-Methyl-3-cyclohexene-1-aldehyde[7,8,9] was prepared in 78% yield by heating an equimolar mixture of acrolein and isoprene together in the presence of picric acid at 100° for twenty-two hours; b. p. 61–62° (9.0 mm.), lit.[7] 63–64° (10 mm.), n^{20}D 1.4724. To a solution of 15.2 g. (0.123 mole) of the freshly-prepared aldehyde in 60 ml. of pyridine containing 1 ml. of piperidine was added 27.7 g. (0.263 mole) of malonic acid. After heating on the steam cone for two hours and refluxing for thirty minutes, the reaction mixture was poured into a mixture of ice and an excess of hydrochloric acid. An oily solid separated which was collected on a Buchner funnel, washed with cold water and sucked free of oil. The oily material collected in the filtrate failed to crystallize and was apparently the *cis*-isomer. After thorough drying the solid product weighed 15.4 g. (76%); m. p. 90–103°. Four recrystallizations from 30% ethanol raised the melting point to 107–108.5°.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.02; H, 8.76.

Acid Chloride and Amide of XVIII.—Three grams of dry acid, m. p. 102–106°, was heated with 4.3 g. of pure thionyl chloride at 100° for one hour. Distillation of the reaction mixture under reduced pressure yielded, in addition to unreacted thionyl chloride, 1.52 g. (46.5%) of pale yellow product; b. p. 81° (0.23 mm), n^{20}D 1.5174. There was also obtained 0.80 g. of a yellow oil, b. p. 92–105° (0.40 mm.), n^{20}D 1.5207, which was discarded. The freshly prepared acid chloride was poured into 10 ml. of cold concentrated ammonia solution. A solid amide separated which was collected, washed and dried; 0.80 g. (62%), m. p. 150–157°. After four recrystallizations from benzene the product melted at 162.5–163.5°.

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.69; H, 9.15. Found: C, 72.39; H, 9.32.

Hydrogenation of *trans*-β-(4-Methyl-3-cyclohexenyl)-acrylamide (XVII).—A solution of 0.27 g. of XVII (m. p. 157–159°) in 15 ml. of 95% ethanol containing 0.15 g. of 2% palladium on calcium carbonate was shaken with hydrogen at atmospheric pressure and 24°. After five minutes 40.5 ml. of hydrogen had been absorbed (theoretical for one double bond was 39.4 ml.) at a maximum rate of 18.5 ml./minute. The hydrogenation was stopped after six minutes when 42.5 ml. of hydrogen had been absorbed and the rate had slowed to 2 ml./minute. The catalyst was removed by filtration, the solution was evaporated to a small volume and water was added to the hot solution to incipient cloudiness. Upon cooling, crystals separated from the solution. The product was collected, washed with dilute ethanol and dried; 0.20 g. (74%), m. p. 131–134.5°. After three recrystallizations from petroleum ether (90–100°) containing a few drops of benzene the white crystals melted at 132.5–136° alone and at 132–136° when mixed with the amide obtained from the hydrogenated *cis*-cyanobutadiene–isoprene adduct.

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.81; H, 10.25. Found: C, 71.67; H, 10.38.

Hydrolysis of XIV.—To a solution of 0.86 g. of XIV in 10 ml. of 95% ethanol were added 0.24 ml. of 6 *N* sodium hydroxide and 2.4 ml. of 30% hydrogen peroxide. The reaction mixture was kept at 50° for twenty-one hours and then neutralized and treated with manganese dioxide until the excess hydrogen peroxide was destroyed. Evaporation of the ethanol left an oil which could not be induced to crystallize.

Water was added to the oily mixture obtained above and the water-insoluble material was collected in ether. The ether solution was washed with bicarbonate, dried, and the ether was evaporated. The residual oil was transferred to a small distillation bulb and heated to 80–100° at a pressure of 0.25 mm. Several drops of a liquid (n^{20}D 1.4935, presumably XIV) distilled. The residue was very viscous but did not crystallize on cooling. This residue was dissolved in hot dilute ethanol and the solution was allowed to cool. An oil separated from the solution which deposited a small amount of crystalline material on long standing. After two crystallizations from petroleum ether (90–100°) there was obtained 0.01 g. of crystals, m. p. 99–104°. There was not enough of this material for further purification and analysis.

The *trans*-Cyanobutadiene–Isoprene Products.—In the initial investigation of this reaction, pure *trans*-cyanobutadiene and isoprene were heated together at 100° for forty-one hours. The complex reaction mixture was fractionally distilled through a small Fenske column. The various fractions were hydrolyzed with alkaline hydrogen peroxide but only oils and mixtures of oily amides could be obtained. It was not possible to isolate a single amide from the mixtures by fractional crystallization.

A second preparation was carried out in which a mixture of 15.2 g. of cyanobutadiene (n^{20}D 1.4948, predominately *trans*) and 19.7 g. of isoprene with a small amount of picric acid was heated at 100° for forty-six hours. When distilled under reduced pressure, there was obtained 4.13 g. of cyanobutadiene (n^{20}D 1.4875) and 10.7 g. (38% or 52% based on cyanobutadiene consumed) of mixed products, b. p. 55–60° (0.20 mm.), n^{20}D 1.4965. This material was carefully fractionated through a 60-plate Podbielniak "Hypercal" column. The distillation was carried out at a constant pressure of 3 mm. The column was preflooded, and then after equilibrium had been reached, distillate was taken at the rate of one drop every thirty seconds

Fraction	Vapor temp., °C.	Ml.	n^{20}D	Fraction	Vapor temp., °C.	Ml.	n^{20}D
I	73.0	0.10	1.4913	V	84.8	0.12	1.4932
	77.4	0.50			85.0	0.34	
	79.5	1.06			86.5	0.88	
						4.45	
II	79.9	0.26	1.4927	VI	86.3	0.06	1.4961
	80.3	0.55			88.0	0.55	
		1.61			88.8	1.10	
III	80.3	0.12	1.4930			5.55	
	81.2	0.50		VII	89.1	0.60	1.4975
	82.2	0.84				6.15	
		2.45		VIII	89.1	0.15	1.5005
IV	82.0	0.76	1.4933		91.0	0.50	
	84.1	1.12			91.5	1.00	
		3.57				7.15	
				IX	91.8	3.80	1.5023
					91.8	4.05	
						11.20	

with a reflux ratio of about 5:1. The total distillation time was five hours. Indices of refraction and significant boiling data are given for the various fractions in the accompanying table. From the boiling points, it would appear that the mixture was complex and that a poor separation was attained. However, the refractive indices indicate that the mixture was separated into two major components. The fractions were investigated as follows: Fraction II (0.44 g.) was hydrolyzed in 5 ml. of 95% ethanol with 0.13 ml. of 6 N sodium hydroxide and 1.3 ml. of 30% hydrogen peroxide at 50° for eighteen hours. The product was obtained as an oil from which no crystalline material could be isolated. Fraction III was redistilled and submitted for microanalysis; b. p. 56° (0.30 mm.), n^{20}_D 1.4929.

Anal. Calcd. for $C_{10}H_{13}N$: C, 81.58; H, 8.90. Found: C, 81.37; H, 9.08.

The infrared spectrum of this sample was determined. The absorption characteristics were almost identical with those of the *cis*-cyanobutadiene–isoprene adduct (XIV).

Fraction V (0.82 g.) was dissolved in 5 ml. of 95% ethanol and hydrolyzed with 0.23 ml. of 6 N sodium hydroxide and 2.3 ml. of 30% hydrogen peroxide at 50° for nineteen hours. The oily product was collected in ether, washed with bicarbonate solution and recovered from the ether. When this oil was partially distilled *in vacuo*, the residue crystallized. After crystallization from benzene there was obtained 0.07 g. of solid melting at 108–112°. Four recrystallizations from petroleum ether (90–100°) containing a few drops of benzene raised the melting point to a constant value of 113.5–114.5°.

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.69; H, 9.15. Found: C, 72.63; H, 9.02.

When mixed with the amide obtained from XIV (m. p. 99–104°) the material melted at 73–88°.

One gram of fraction IX in 10 ml. of 95% ethanol was treated with 0.27 ml. of 6 N sodium hydroxide and 2.7 ml. of 30% hydrogen peroxide. The reaction mixture was kept at 50° for twenty-four hours and then was neutralized and treated with platinum to destroy the excess hydrogen peroxide. By fractionally evaporating the ethanolic solution, there were obtained 0.26 g. of amide melting at 107–111° and 0.18 g. of amide melting at 128–144°. The lower-melting product was recrystallized once from benzene and three times from water; m. p. 115.5–116.5°.

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.69; H, 9.15. Found: C, 72.77; H, 9.17.

The melting point of this sample was lowered both when mixed with the amide m. p. 99–104° from XIV and when mixed with the amide m. p. 113.5–114.5° from the hydrolysis of fraction V. When this amide was mixed with XVII, the material melted at 120–155°. After these materials were melted together and allowed to solidify, the melting point was 150–157°.

The higher-melting amide from the hydrolysis of fraction IX was recrystallized twice from chloroform–petroleum ether (30–60°), three times from benzene–petroleum ether (90–100°) and once from benzene; m. p. 158–162.5°.

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.69; H, 9.15. Found: C, 72.66; H, 9.25.

A mixture of this sample with XVII (m. p. 162.5–163.5°) melted at 160–163°.

Hydrolysis of the *cis*- and *trans*-1-Cyano-1,3-butadienes. *cis*-β-Vinylacrylamide.—A solution of 3.89 g. of pure *cis*-1-cyanobutadiene in 20 ml. of 95% ethanol was treated with 1.96 ml. of 6 N sodium hydroxide and 19.6 ml. of 30% hydrogen peroxide. Oxygen evolution was immediate and it was necessary to cool the reaction mixture in an ice-bath to keep the vigorous exothermic reaction under control. After the reaction had subsided, the solution was kept at 50° for three hours and then cooled. Dilute sulfuric acid was added to neutrality and the mixture was stirred with finely-divided platinum until a negative peroxide test was obtained. The solution was filtered and evaporated to a small volume. White crystals separated which were collected, washed and dried; m. p. 94–96°. After standing in the air for two days, a portion of this material had polymerized. The monomeric amide was taken up in hot benzene, filtered from the polymer and crystallized, m. p. 96–97°.

Anal. Calcd. for C_5H_7NO: C, 61.83; H, 7.27. Found: C, 61.88; H, 7.29.

***trans*-β-Vinylacrylamide.**—Pure *trans*-cyanobutadiene was hydrolyzed with alkaline hydrogen peroxide in the same manner as the *cis*-isomer. From 3.2 g. of the nitrile there was obtained 1.00 g. (25.8%) of crude amide, m. p. 117–120°. After three crystallizations from benzene, the white crystals had a constant melting point of 123–124°. On standing, the material darkened and rapidly formed a benzene-insoluble polymer.

Anal. Calcd. for C_5H_7NO: C, 61.83; H, 7.27; N, 14.42. Found: C, 61.70, 60.85, 60.95; H, 7.27, 7.21, 7.18; N, 13.50.

Summary

The very active diene cyclopentadiene condenses with the *cis*- and *trans*-1-cyano-1,3-butadienes to give *cis*- and *trans-endo*-β-(2,5-endomethylene-3-cyclohexenyl)-acrylonitriles. The somewhat less active diene 2,3-dimethylbutadiene condenses similarly to give *cis*- and *trans*-β-(3,4-dimethyl-3-cyclohexenyl)-acrylonitriles. In these reactions the terminal double bond of the 1-cyano-1,3-butadienes serves as the dienophilic center. The still less active diene isoprene reacts to give mixtures; evidently, each of the reagents functions both as diene and dienophile. The only pure product which has been isolated from the reaction of isoprene with *cis*-1-cyano-1,3-butadiene is *cis*-β-(4-methyl-3-cyclohexenyl)-acrylonitrile. The corresponding *trans*-adduct has been obtained from *trans*-1-cyano-1,3-butadiene and isolated as the amide along with two other adduct amides for which structures are proposed.

From the course of the reactions of these dienes with the cyanodienes, and from the knowledge of the carbon skeleton of the butadiene–*trans*-1-cyano-1,3-butadiene adduct, it is concluded that this adduct most probably is formed by reaction of butadiene as a dienophile with *trans*-1-cyano-1,3-butadiene as a diene.

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