was held at reflux for 200 min. At the start the condensate was not homogeneous but near the end it was clear. By fractionation of the products there was obtained 2.7 g. (12%) of 4-octyne and 25.2 g. (89% if allowance is made for recovered octyne) of 4-octanone, b.p. 126–127°, n^{24}D 1.4173. The semicarbazone[16] melted at 95–96°.

In a similar experiment in which untreated resin was used, after refluxing for 260 min. only a small amount of ketone (less than 25%) was formed. After 16 hr. of reflux, about 69% of 4-octanone was obtained.

3-Hydroxy-3-methyl-2-butanone.—When 20 g. of Hg–resin was added to a stirred solution of 37.3 g. of 2-methyl-3-butyne-2-ol[14] in 100 cc. of ethanol and 15 cc. of water there was spontaneous evolution of heat and darkening of the resin. After a short time the mixture was refluxed for 20 min. The resin was removed and the filtrate vacuum distilled. This distillate, b.p. 36–43° at 10 mm., was rectified in a small column to yield 18.8 g. (42%) of 3-hydroxy-3-methyl-2-butanone,[17] b.p. 137–137.4°, n^{26}D 1.4176. This ketone yielded an oxime,[17] m.p. 86.2–87.8° from water, and a semicarbazone,[17] m.p. 164.0–166.6° dec. The lower boiling fractions undoubtedly contained some unchanged ethynylcarbinol and unsaturated ketone. There was also some higher boiling residue (*ca.* 6 g.). In another experiment in which 39.7 g. of ethynylcarbinol, 150 cc. of water and 15 g. of Hg–resin were held near 80° for 5 hr. there was obtained 33.0 g. (68.5%) of 3-hydroxy-3-methyl-2-butanone b.p. 137–138°, n^{23}D 1.4145.

Hydroxyacetone.—When a stirred solution of 10.4 g. (0.2 mole) of propargyl alcohol[18] in 100 cc. of water at 23° was treated with 2 g. of Hg–resin the temperature rose spontaneously to 55° in 13 min. The temperature was held at 50° for 25 min. by intermittent cooling and then it dropped to 40°. After a total time of 100 min. the resin was filtered and the filtrate made up to 120 cc. with water washings. A 12-cc. aliquot (0.02 mole in theory) was treated with phenylhydrazine hydrochloride and sodium acetate to yield an immediate yellow precipitate which weighed 2.85 g. (87%) and melted alone and mixed with an authentic sample of the phenylhydrazone of hydroxyacetone[19] at 99.0–101.4° dec. The semicarbazone[20] melted at 193–196° dec.

Acetaldehyde.—A slow stream of purified acetylene was passed through a stirred suspension of 2 g. of Hg–resin in 100 cc. of water at room temperature for 20 minutes. The resin was filtered. The filtrate smelled strongly of acetaldehyde which was identified as its 2,4-dinitrophenylhydrazone,[21] m.p. 146–147°.

No attempt was made to determine the efficiency of conversion of acetylene to acetaldehyde, but since it is possible to remove all of the catalyst both acidic and mercurial by filtration of the resin, there may be commercial possibilities in this process.

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[16] E. E. Blaise, *Compt. rend.*, **176**, 1150 (1923).

[17] J. Kapron and J. Wiemann, *Bull. soc. chim.*, **12**, 945 (1945); J. Schmidt and P. Austin, *Ber.*, **35**, 3725 (1902).

[18] We wish to thank the General Aniline and Film Corp., Easton, Penna., for a generous sample of propargyl alcohol.

[19] G. Pinkus, *Ber.*, **31**, 32 (1898).

[20] J. U. Nef, *Ann.*, **335**, 250 (1904).

[21] The 2,4-dinitrophenylhydrazone of acetaldehyde has been shown to exist in two modifications (see W. M. D. Bryant, THIS JOURNAL, **60**, 2814 (1938)). The form isolated in this work melted near 147° and was orange. The infrared absorption spectrum in a Nujol mull was almost identical to that obtained with the yellow, m.p. 168°, form. The main feature of the orange form, m.p. 147°, was a strong absorption at 11.75 μ which was not present in the spectrum of the yellow form. I am indebted to Dr. E. Malmberg and Miss F. Zamnik for this measurement.

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

1-Cyano-1,3-butadienes. VI. Copolymerization of the *cis*- and *trans*-1-Cyano-1,3-butadienes with Butadiene[1]

BY H. R. SNYDER, K. CHADWICK MURDOCK AND C. S. MARVEL

RECEIVED APRIL 15, 1953

A technique for the separation of substantial quantities of the labile *trans*-1-cyano-1,3-butadiene from its *cis* isomer is described. Melting point data and infrared spectra determinations have confirmed the assignments of configuration previously given to these isomers. The *cis* compound copolymerized with butadiene about 2.5 times more rapidly than the *trans* isomer. When various mixtures of the isomeric cyanodienes were copolymerized with butadiene, however, it was found that at any given percentage conversion the composition of the copolymer was independent of the *cis–trans* ratio in the monomer charge. Moreover, the geometrical configurations and elastomeric properties of copolymers from the two isomers were practically identical. It was concluded that in their copolymerizations with butadiene both isomers have identical monomer reactivity ratios, but that inhibitors of copolymerization were engendered during copolymerizations involving the *trans* isomer. The Diels–Alder adducts of the *trans* isomer with itself and with butadiene were shown to be powerful polymerization inhibitors.

In previous studies[2–5] the separation of the isomeric forms of 1-cyano-1,3-butadiene and certain of their reactions have been reported. It has been of interest to extend the study of the copolymerization[2] of the pure isomers with butadiene in order to learn whether there are any correlations of the geometrical configuration of the cyanodienes with their reactivities in copolymerization or with the structure and properties of the resulting copolymers. Differences in the physical properties of the copolymers could be due to at least three factors: (1) differences in their structural homogeneity, caused by differences in the monomer reactivity ratios[6,7] of the isomeric monomers, (2) variations in the geometrical configuration about copolymer double bonds, and (3) differences in the ratios of 1,2- to 1,4-addition of the monomer units.

No comparative polymerization studies seem to have been made with geometrically isomeric butadiene derivatives. At least ten terminally substituted butadienes have been allowed to copolymerize with butadiene,[8] but apparently none of these had been separated into its *cis* and *trans* isomers.

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[1] The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

[2] H. R. Snyder, J. M. Stewart and R. L. Myers, THIS JOURNAL, **71**, 1055 (1949).

[3] H. R. Snyder and G. I. Poos, *ibid.*, **71**, 1057 (1949).

[4] H. R. Snyder and G. I. Poos, *ibid.*, **71**, 1395 (1949).

[5] H. R. Snyder and G. I. Poos, *ibid.*, **72**, 4096, 4104 (1950).

[6] T. Alfrey, Jr., J. J. Bohrer and H. Mark, "Copolymerization," Interscience Publishers, Inc., New York, N. Y., 1952.

[7] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

[8] H. W. Starkweather, P. O. Bare, *et al.*, *Ind. Eng. Chem.*, **39**, 210 (1947).

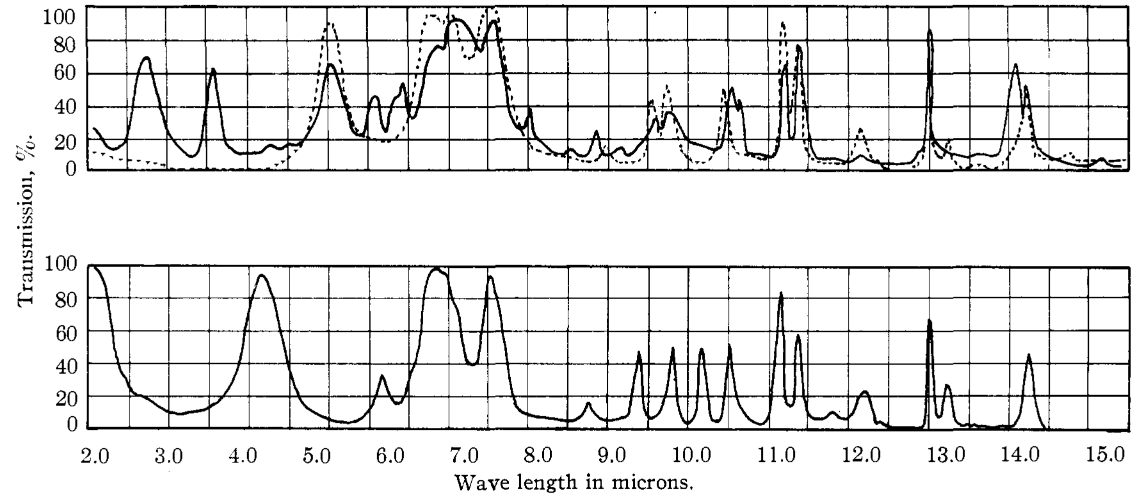
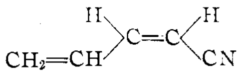


Fig. 1 (top).—Infrared absorption spectrum of *cis*-1-cyano-1,3-butadiene plus dissolved CO_2; KBr cell, cell path 0.0256 mm., Perkin–Elmer model 12B. Fig. 2 (bottom).—Infrared absorption spectrum of *trans*-1-cyano-1-cyano 1,3-butadiene plus dissolved CO_2, dotted line. Same after ten days standing, solid line; KBr cell, cell path 0.0256 mm., Perkin–Elmer model 12B.

The *cis*- and *trans*-1-Cyano-1,3-butadienes.—All of the presently available syntheses[2,5,9,10] of 1-cyano-1,3-butadiene produce mixtures of the *cis*-(I) and *trans*-(II) isomers. The *trans* isomer, however, undergoes a Diels–Alder type dimerization[3] so readily that its isolation is difficult. During the removal of the lower-boiling *cis* isomer in the lengthy fractional distillation used to separate the two forms, the *trans* isomer is often almost completely dimerized.



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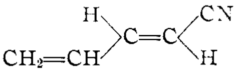

II

A satisfactory isolation of the *trans*-diene has now been achieved by a low-temperature fractional distillation through a Podbielniak column. This distillation was first accomplished in a cold room at 5°, but was later modified so that it could be conducted in an unrefrigerated room. A substantial increase in purity has been attained. Whereas the previously reported refractive indices of the *cis*- and *trans*-cyanodienes were $n^{20}\mathrm{D}$ 1.4852 and 1.4960, the refractive index of the pure *trans*-diene is now thought to be $n^{20}\mathrm{D}$ 1.4986.

Confirmation of the assignment of the *trans*-configuration to the higher-boiling isomer, originally based[2] on its reactivity in the Diels–Alder reaction, has been provided by a comparison of revised melting points of the *cis* and *trans* isomers, which are −64 to −60° and −43°, respectively. The previously assigned value for the melting point of the *trans* isomer[11] was −80°, which, being lower than that of the *cis* form, indicated an apparent anomaly.

Infrared spectrograms of the 1-cyanobutadiene isomers are shown in Figs. 1 and 2. Marked differences are shown between the *cis* and *trans* forms, particularly in the long wave length section. The *trans* form underwent a change as it remained in the spectroscope cell. Several scannings, not plotted, were made between the first and tenth day and were intermediate between the two curves plotted for the *trans* isomer. A progressive change, probably dimerization, was clearly indicated. The *cis* spectrogram is very characteristic[12] of *cis*-olefins.

In contrast to the marked differences of reactivity of the two isomers in the Diels–Alder reaction,[2–5] their densities, thermal stabilities and reactivities toward free radicals appear to be nearly identical. Approximately equal amounts of the two isomers were formed both in their original preparation, *via* the pyrolysis at 575° of crotonaldehyde cyanohydrin benzoate, and in the equilibration at the same temperature of the *cis* isomer to a *cis–trans* mixture. As shown below, it appears that in their copolymerization with butadiene the two isomers add to a growing free radical chain with equal facility.

Polymerization.—Mixtures of the isomeric cyanodienes were copolymerized with butadiene in an emulsion system at 50°. In Fig. 3 are shown copolymerization rate curves for five cyanodiene mixtures ranging from pure *cis*- to essentially pure *trans*-diene. It is seen that the *cis* isomer attains a 53% conversion[13] about 2.5 times as rapidly as does the *trans* isomer. Moreover, the system containing the *cis* isomer immediately approaches its maximum rate, whereas that containing the *trans* isomer attains its maximum rate only after a 16-hour lag.

Of particular interest was the relationship between the *cis–trans* ratio in the comonomer charge and the amount of cyanodiene incorporated into the copolymer at a given percentage conversion. With the aid of a novel and convenient analytical

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(9) P. H. Wise, U. S. Patent 2,473,486, June 14, 1949; *C. A.*, **43**, 7953 (1949).

(10) P. Kurtz, *Ann.*, **572**, 23 (1951).

(11) Office of Synthetic Rubber, private communication.

(12) J. C. Hillyer, Phillips Petroleum Co., private communication.

(13) The conversion of 53% was found to be the optimum for the preparation of copolymer samples. A plot (see Fig. 5) of the viscosity of benzene solutions of the copolymers *versus* percentage conversion exhibited a sharp maximum at this value. At higher conversions the viscosity dropped off rapidly even though the copolymer apparently remained soluble, indicating the presence of micro gel.

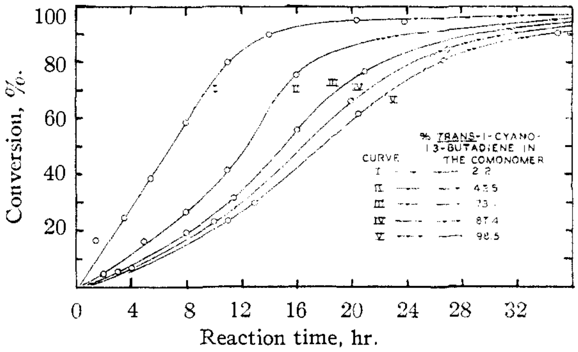


Fig. 3.—Relative copolymerization rates *vs.* composition of *cis–trans* 1-cyano-1,3-butadiene–butadiene/1-cyano-butadiene (90/10); AIBN initiation at 50°.

technique the same reaction mixture aliquots used to determine the first four curves of Fig. 3 were also analyzed for nitrogen. The percentages of combined cyanodiene in these elastomer samples were calculated and have been plotted against percentage conversion in Fig. 4. It was originally expected that four different curves could be drawn corresponding to the four *cis–trans* mixtures, but, surprisingly, it was found that the data could be smoothly fitted by a single curve.

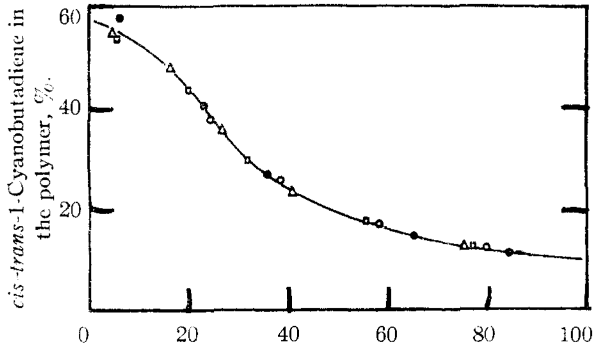
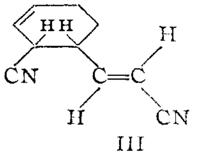


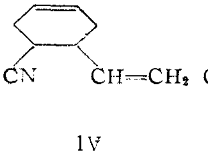
Fig. 4.—% *trans* 1-cyano-1,3-butadiene in the comonomer: ●, 87.4; ○, 2.2; △, 42.5; □, 73.1.

The only reasonable hypothesis which presented itself as an explanation for this phenomenon was that the actual monomer reactivity ratios with butadiene of the *cis-* and *trans*-dienes were identical, but that during the reaction the *trans* isomer engendered a by-product which inhibited the whole copolymerization. The amount of inhibition would then be a function of the concentration of the *trans* isomer in the comonomer charge.

The inhibition was thought to be due to the generation of both the dimer of the *trans*-cyanodiene, *cis*-1-cyano-2-(*trans*-2-cyanovinyl)-5-cyclohexene[14] (III), and the similar Diels–Alder adduct of the *trans*-cyanodiene with butadiene, partially characterized[3] as a 1-cyano-2-vinylcyclohexene



III



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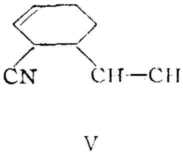


V

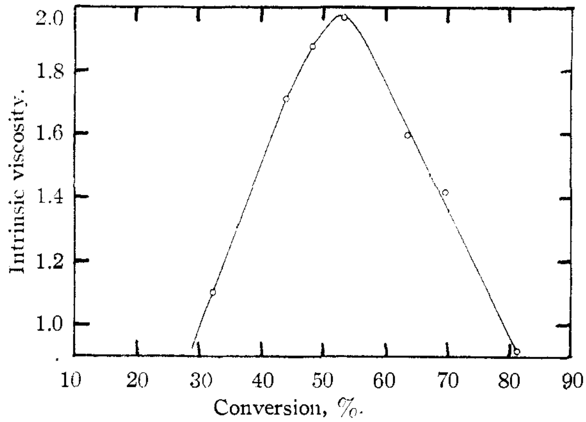


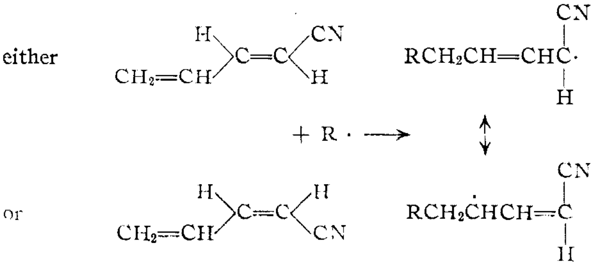
Fig. 5.—Intrinsic viscosity *vs.* percentage conversion in copolymers from 1,3-butadiene–*trans*-1-cyano-1,3-butadiene, 90–10; AIBN initiation at 50°.

(IV or V). Both compounds are likely constituents of the polymerization mixtures: formation of the butadiene adduct is known[3] to occur at 50°, and the *trans*-cyanodiene slowly dimerizes even when stored at 5°.

Active hydrogen compounds such as 1,4-pentadiene and cyclopentadiene have been shown to be strong inhibitors of polymerization.[15] The dimer III, as well as the adduct V, has a hydrogen atom which not only is allylic, but also is activated by an adjacent cyano group. In a test for inhibitory activity it was found that in a concentration of 0.25% by weight of the monomer charge either the cyanodiene dimer III or the butadiene adduct (IV or V) markedly inhibited the rate of polymerization of butadiene.

Thus it was concluded that in their copolymerization with butadiene the *cis-* and *trans*-1-cyano-1,3-butadienes exhibit identical monomer reactivity ratios. The values for these ratios as determined[11,16] by Wall and co-workers for the *cis*[17] isomer, $r_1 = 1.7$ and $r_2 = 0.0$, would accordingly be applicable to either of the pure isomers or to any of their mixtures.

It is probable that after the addition of isomeric cyanodiene units to corresponding growing polymer chains, the geometrical differentiation between the adducts would be lost due to the indicated allylic resonance



Even the formation of diastereoisomeric polymers

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(14) J. L. Charlish and W. H. Davies, *J. Chem. Soc.*, 1385 (1950).

(15) R. L. Frank, C. E. Adams, J. R. Blegen, R. Deanin and P. V. Smith, *Ind. Eng. Chem.*, **39**, 887 (1947); R. L. Frank, J. R. Blegen, G. E. Inskeep and P. V. Smith, *ibid.*, **39**, 893 (1947).

(16) F. T. Wall, R. W. Powers, G. D. Sands and G. S. Stent, This Journal, **70**, 1031 (1948).

(17) The refractive index of the cyanodiene used[11] was $n^{20}D$ 1.4850, indicating that it was *cis*, and not predominantly *trans* as stated.[14]

would not be expected. Mayo and Wilzbach[18] found that the copolymers of vinyl acetate with the *cis*- and *trans*-1,2-dichloroethylenes were sterically identical, indicating that a free radical has either a planar or a readily reversible pyramidal configuration.

As was expected from the above considerations and from the identities of the monomer reactivity ratios, copolymers with butadiene of the *cis*- and *trans*-cyanodienes (prepared at 51 and 52% conversion, respectively) were found to be essentially identical both in physical properties and in structural characteristics. Vulcanizates of the two copolymers showed no significant differences in their stress-strain, hysteresis, low-temperature or oil resistance properties. Moreover, infrared studies of the copolymers indicated that the modes of addition of their respective monomer units were identical.[19]

Lewis and Mayo studied the copolymerization of several reference monomers with a number of *cis–trans* pairs of monoölefins.[20] They hypothesized that the comparative rates of addition of the isomeric monomers to corresponding free radical polymer chains depended not on the thermodynamic instabilities of the isomers, but on the relative opportunities for resonance stabilization in the activated complexes intermediate in the additions. Thus, as compared with the less stable diethyl maleate, the 20-fold greater reactivity of diethyl fumarate with the terminal styrene radical was related to the ability of both of the ester carbonyl groups to be simultaneously coplanar with the carbon atoms of the central double bond, thereby permitting a maximum of resonance stabilization. With diethyl maleate, however, the proximity of the two ester groups would prevent such a coplanarity. Similar considerations applied to the differences in coplanarities and reactivities of the *cis*- and *trans*-stilbenes. On the other hand, with the pairs of symmetrically substituted dicyano- and dichloroethylenes, no steric restriction upon coplanarity would be expected. Correspondingly, there was no difference in reactivity within either pair.

The identical reactivities of the cyanobutadienes would thus be in agreement with the hypothesis of Lewis and Mayo. Examination of molecular models indicates that coplanarity of the vinyl and cyano substituents with the carbon atoms of the central double bond is possible with both the *cis*-(I) and *trans*-(II) forms. Although the infrared analyses of the structure of the copolymers formed indicates that free radical attack is predominantly on the terminal methylene group rather than on the seat of geometrical isomerism, the resonance stabilization of the activated complexes would be expected to be analogous to that in the above-mentioned systems.

Acknowledgment.—The authors are indebted to Dr. J. C. Hillyer and the Chemical Physics Section of the Research Division of Phillips Petroleum Company for the determination and interpretation of the infrared absorption spectra of the *cis*- and *trans*-1-cyano-1,3-butadienes, to Dr. A. W. Meyer, Mr. R. R. Hampton and Dr. J. A. Davison of the U. S. Rubber Company for the infrared analyses of the copolymers, and to Mr. W. K. Taft of the University of Akron for the physical evaluation of these copolymers. Grateful acknowledgment is made for a Research Assistantship, sponsored by the Office of Synthetic Rubber, which supported one of us (K.C.M.) during this investigation.

Experimental

Crotonaldehyde Cyanohydrin Benzoate.[2]—In five 6-molar runs the yields of crotonaldehyde cyanohydrin benzoate, prepared by the reaction of crotonaldehyde with sodium cyanide and benzoyl chloride, ranged from 1035 to 1159 g. (84 to 94%). It was not necessary to fractionate the product, b.p. 125° (1 mm.), $n^{20}\text{D}$ 1.5220. The commercial crotonaldehyde used in the synthesis, stated to be 91% pure, may be purified by distillation, but the yield and quality of the ester obtained are not improved. Moreover, the purification is attended by a loss of about 40% of the aldehyde due to its azeotropic distillation with the water present.

Mixed *cis*- and *trans*-1-Cyano-1,3-butadienes.[2]—In the pyrolysis at 575 ± 10° of the crotonaldehyde cyanohydrin benzoate, conducted by dropping the ester at a rate of one drop per 1.4 sec. through a vertical, 24 mm. × 31 cm. Pyrex tube packed with 6-mm. Pyrex beads, it was necessary to employ a clean tube after each 200 g. of ester had been pyrolyzed, requiring about three hours. As the tube became obstructed and the contact time accordingly increased, the yield and purity of the product dropped. If passage through the tube was once allowed to become blocked completely with a carbon deposit, it was almost impossible to clean.

To minimize dimerization of the *trans*-1-cyano-1,3-butadiene the volatile components of the pyrolysate were distilled at pressure gradually decreasing from 5 to 1 mm. and pot temperatures below 30° in a distillation apparatus in which the condenser-receiver was a 32- × 4.2-cm. test-tube packed in a mixture of acetone and Dry Ice. In seven runs, each utilizing 400 g. of the ester, the yields of the crude mixed dienes averaged 112 g. (80%), $n^{20}\text{D}$ 1.4910.

In one instance a mixture of the *cis*- and *trans*-dienes free from contaminants was desired. From a yield of 81 g. (73%) of crude diene the lower- and higher-boiling contaminants were carefully removed by a fractionation in a 19-inch spinning band column operating at 3450 r.p.m. and rated as having 25 theoretical plates. The column was jacketed, the still-head was well insulated, and the receiver was cooled in a mixture of Dry Ice and acetone. At a pressure of 13 mm., 73 g. (65%) of the diene mixture was collected fairly rapidly from 32 to 38.5°, $n^{20}\text{D}$ 1.4919, $d^{1}{}_{4}$ 0.865.

From many fractionations of the *trans*- from the *cis*-diene (below) small quantities of both lower- and higher-boiling contaminants were accumulated. These were separately fractionated in the spinning band column. From these fractionations, assuming additivity of refractive index contributions in mixtures, it was calculated that in the volatile parts of the pyrolysate the *cis*- and *trans*-dienes are present in equal amounts and comprise about 99% of the material present. Five contaminants were also present, each in amounts less than 0.2%, having boiling points (at 13 mm.) and refractive indices ($n^{20}\text{D}$) roughly estimated as follows: −7°, 1.4362; 13°, 1.4081; 22°, 1.4681; 50°, 1.4848; 50°, 1.4917.

Separation of the *cis*- and *trans*-1-Cyano-1,3-butadienes.[2]—To minimize dimerization of the *trans*-diene the mixture was fractionated as rapidly and at as low a temperature as was practicable. A charge of 105.2 g. of a crude diene mixture, $n^{20}\text{D}$ 1.4914, was stabilized with a pinch of picric acid and fractionated at 13 mm. in a 12″ column made by the Podbielniak Company (No. 1067). This column contains a type of packing (Helipak) in which each unit is a rectangular coil 1 × 2 mm. in cross section consisting of seven turns

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[18] F. R. Mayo and K. E. Wilzbach, This Journal, 71, 1124 (1949).

[19] In a private communication, A. W. Meyer, R. R. Hampton and J. A. Davison, of the United States Rubber Co., reported the structural composition of each of two butadiene copolymers (one from the *cis*- and the other from the *trans*-cyanodiene) as follows: *cis*-1,4-units, 11 ± 1%; vinyl (1,2-) units, 13 ± 1%; *trans*-1,4-units, 65 ± 5%.

[20] F. M. Lewis and F. R. Mayo, This Journal, 70, 1533 (1948).

of fine Nichrome wire. A stream of ethanol at −10 to −20° was pumped through the cold finger condenser of the variable reflux still-head used. In the still-head the section enclosing the cold finger as well as the glass tubing leading to the receiver were insulated with a layer of bright tinfoil covered with Pyrex wool. A small piece of Dry Ice was kept buried near, but not against, the top end of this tubing. The receiver was cooled in a mixture of Dry Ice and acetone.

The charge was ebulliated with air and heated with an oil-bath whose temperature was gradually raised from 75 to 80°. The reflux ratio was maintained at 7:1 until the refractive index of a sample of the distillate indicated that it was essentially pure *trans*-cyanodiene. The reflux ratio was then lowered to 1:1 and the pressure reduced to 7 mm. All but about 2 ml. of the remaining volatile material was collected in this fraction: 21.3 g. (41% of the *trans*-diene estimated to have been present in the charge), b.p. 41.2° (13 mm.), $n^{20}\mathrm{D}$ 1.4984. It is imperative that this stage of the distillation be conducted rapidly.

The total time of heating was 6.2 hours. The viscous residue (5.8 g.) crystallized on standing. From 38.5 g. of such residues there was obtained after recrystallizations from ether–petroleum ether and from ethanol–water 14 g. of *cis*-1-cyano-2-(*trans*-2-cyanovinyl)-5-cyclohexene, m.p. 53–54° (lit.[14] m.p. 53–54°).

Pure *cis*-cyanodiene was obtained by refractionating an accumulation of fractions rich in that isomer. Because of its relatively greater stability it was conveniently distilled at higher temperatures; b.p. 50° (30 mm.).

The best values for the physical constants of the two isomers are now thought to be: *cis*: b.p. 32.5° (13 mm.), $n^{20}\mathrm{D}$ 1.4855 (lit.[2] 1.4852), m.p. −64 to 60°, d^{1}_{4} 0.866, d^{26}_{4} 0.8541; *trans:* b.p. 41.0° (13 mm.), $n^{20}\mathrm{D}$ 1.4986 (lit.[2] 1.4960), m.p. −43°, d^{1}_{4} 0.865, d^{25}_{4} 0.8576.

The *trans* isomer was stored without decomposition either under Dry Ice or in a refrigerator at −45°. At 5° a sample was 11% dimerized after five days. At 5° and in the presence of picric acid the *cis*-diene is stable.

Pyrolytic Equilibration of *cis*- to *cis-trans*-1-Cyano-1,3-butadiene.—A sample of 9.9 g. of *cis*-diene, $n^{20}\mathrm{D}$ 1.4850, was stabilized with *p*-*t*-butylcatechol and pyrolyzed at 575° using the same apparatus and technique previously described for the synthesis of the mixed cyanodienes. The yield of the volatile part of the pyrolysate was 7.0 g. (71%), b.p. (3.5 mm.) 16–19°, $n^{20}\mathrm{D}$ 1.4908.

Copolymerization.—A 4-oz., screw-top bottle was rinsed with water redistilled from glass and to it were added the following ingredients in the indicated order: 0.060 g. of recrystallized azo-bis-isobutyronitrile (AIBN), 35.0 g. of 3% soap solution, 0.044 g. of dodecyl mercaptan, 2.00 g. of 1-cyano-1,3-butadiene, 18.0 g. of 1,3-butadiene. The soap solution was made with water redistilled from glass and with Office of Synthetic Rubber soap (sodium salts of fatty acids). The dodecyl mercaptan (Hooker lauryl mercaptan), used as a modifier, was delivered as three drops. The isomer or mixture of isomers of 1-cyano-1,3-butadiene, stored either at −45° or under Dry Ice, was allowed to warm to 0°, placed (still in its container) in a Dewar flask and then delivered from a pipet as 2.31 ml. Twenty-two grams of redistilled butadiene (Phillips Special Purity grade) was added; 4.0 g. was allowed to boil away to sweep the air from the bottle. The bottle was sealed with a perforated cap fitted with a self-sealing rubber gasket and tumbled end over end at 28 r.p.m. for the specified period of time in a water-bath maintained at 50 ± 0.5°.

For elastomer evaluation studies the latex was coagulated[21] when the percentage conversion was estimated to be 53%.

Rate and Composition Studies.—A total of five 1.0- to 1.5-g. aliquots from each 4-oz. reaction bottle were removed at intervals during the polymerization by inserting the needle of a 2-ml. hypodermic syringe through a hole in the bottle cap and through the rubber gasket. To cope with the pressure exerted by unreacted butadiene the needle was connected to the syringe by a lock valve and the lightly greased plunger was constrained from being ejected by a looped strip of 50-mesh brass gauze fastened to the barrel of the syringe with a cylindrical, screw-type tubing clamp.

The loaded syringe was weighed on the analytical balance and its contents were ejected into a tared, 10-ml. Pyrex beaker containing 2 ml. of a coagulant–antioxidant solution made by dissolving 1.20 g. of N-phenyl-2-naphthylamine and 0.80 g. of 2-naphthol in 1 l. of alcohol. Immediately after weighing the empty syringe the material in the beaker was first frozen over Dry Ice and then lyophilized for 16–24 hours in a vacuum desiccator at 0.5 mm.

The percentage conversions were calculated as follows

$$\%\ \text{conversion} = \frac{\text{dried aliquot} - \text{antioxidant} - \dfrac{\text{wet aliquot}}{\text{reacn. mixt.}} \times \begin{matrix}(\text{soap} + \text{modifier} \\ + \text{initiator})\end{matrix}}{\text{monomers} \times \dfrac{\text{wet aliquot}}{\text{reacn. mixt.}}} \times 100$$

A shallow, vertical groove had been pressed into the inside of the middle third of the beaker in order to allow vapors to pass the plug of coagulated polymer during the lyophilization. Also it was necessary to flatten off the lip of the beaker in order to ensure its passage down the neck of an 800-ml. Kjeldahl flask. Kjeldahl analyses of the copolymer samples were made using copper sulfate as the digestion catalyst. After the addition of alkali to the digestion mixture the liberated ammonia was distilled into a saturated boric acid solution containing a methylene red–methylene blue indicator. The ammonia was then titrated with 0.1 *N* sulfuric acid, using a 10-ml. microburet. Blanks were run on polybutadiene made in the same way as the copolymer.

Copolymerization Inhibition.—Twenty-gram charges of butadiene were polymerized at 50° for 11.5 hours in the same system described above except for the addition of varying amounts of the dimer, m.p. 53–54°, isolated from the residues from distillations involving *trans*-1-cyano-1,3-butadiene.

Amt. of dimer, g.	Yield, % polybutadiene	Amt. of dimer, g.	Yield, % polybutadiene
0	56.4	0.001	56.0
0	58.2	.050	24.1
0	56.4	.100	12.3
		.300	4.3

Analogous though somewhat lesser inhibitions were shown in a similar series of polymerizations, allowed to proceed for 12.2 hours, involving the Diels–Alder type adduct[3] of 1-cyano-1,3-butadiene with butadiene.

Adduct, g.	Yield, % Poly-butadiene	Adduct, g.	Yield, % Poly-butadiene
0	67	0.050	41
0	67	.054	42
0.003	62	.098	24
.008	62	.124	24
.011	62		

In the preparation of the adduct a mixture of 36.0 g. of butadiene and 4.0 g. of predominantly *trans*-1-cyano-1,3-butadiene, $n^{20}\mathrm{D}$ 1.4969, was sealed in a 4-oz., screw-top bottle (fitted with a rubber gasket) and tumbled in the water-bath at 50° for 48 hours. The unreacted butadiene was allowed to boil away and the residue was fractionally distilled in a Holzman column.[22] The yield of the foul-smelling, oily adduct was 0.45 g. (12%), b.p. 47° (0.25 mm.), $n^{20}\mathrm{D}$ 1.4972 [lit.[3] b.p. 94° (8 mm.), $n^{20}\mathrm{D}$ 1.4940]. The present material may be a 1-cyano-2-vinylcyclohexene which differs from the previously described compound[3] in the location of the internal double bond. It was previously stated[3] that evidence of conjugation in the infrared absorption spectra of the compound indicated that the relatively high distillation temperatures involved in its isolation may have allowed a migration of the internal double bond.

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[21] C. S. Marvel, T. R. Fukuto, J. Berry, W. K. Taft and B. G. Labbe, *J. Polymer Sci.*, **8**, 599 (1952).

[22] C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).