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

1-Cyano-1,3-butadiene. III. The Dimer of 1-Cyano-1,3-butadiene

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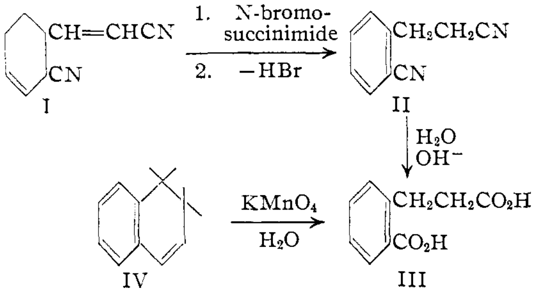
In the course of further studies of the chemistry of 1-cyano-1,3-butadiene,[1,2] a dimer[2a] of the substance has been isolated and characterized. In common with many butadienes, 1-cyano-1,3-butadiene condenses with itself in the Diels–Alder fashion to yield a cyclic dimer,[3] which in this instance proved to be 1-(β-cyanovinyl)-2-cyano-3-cyclohexene (I).

Separation of the *cis* and *trans* forms of the diene by fractional distillation[2] was always accompanied by a considerable loss due to the formation of higher-boiling material in the still-pot. The dimeric compound was isolated by high vacuum distillation of the gummy still residues. After redistillation, the thick oil could be induced to crystallize to a low-melting solid. There was no indication of the presence of more than one dimer. Microanalysis and molecular weight determinations were correct for a dimeric structure.

Attempts to hydrolyze the dimer with alkaline hydrogen peroxide and with acid resulted in the production of intractable materials. Hydrolysis with base of varying strength, with and without a solvent, produced an acidic substance which appeared to be polymeric. It was not possible to effect dehydrogenation of the dimer by heating to 320° with 10% palladium on carbon.

Proof of the dimer structure was obtained by aromatization followed by hydrolysis to a known aromatic acid according to the following scheme (equation A). The dimer (I) was brominated with one equivalent of N-bromosuccinimide and the product was dehydrobrominated by heating with isoquinoline to yield *o*-cyanohydrocinnamonitrile (II). Basic hydrolysis of II yielded *o*-carboxyhydrocinnamic acid (III) which was identified by comparison with an authentic specimen. The preparation of III for comparison was accomplished by oxidizing 1,2-dihydronaphthalene (IV) with cold aqueous permanganate according to the method of Straus and Lemmel.[4]

Equation A



It was of interest to investigate the relative contributions of the *cis* and *trans* isomers in the dimerization of 1-cyano-1,3-butadiene. When the higher-boiling isomer ($n^{20}D$ 1.4960, presumably *trans*) was maintained at 100° for sixteen hours in the presence of a polymerization inhibitor (picric acid), 66% of the material was converted into the dimer, and the remainder could be accounted for as monomer and polymer. On the other hand, in two similar experiments with the lower-boiling isomer ($n^{20}D$ 1.4852, presumably *cis*), heating nine and eighteen hours produced only 13% dimer, the major portion of the diene having been converted into polymer.

The dimer itself is a rather stable compound and shows little tendency to polymerize. Since it might be considered possible that polymerization of the monomer proceeds through the dimer under the conditions described in the experiments above, a sample of the dimer was maintained at 100° in the presence of picric acid for twenty-five hours. When the material was distilled, no polymeric residue remained.

These experiments indicate that I is formed chiefly by the dimerization of the higher-boiling 1-cyano-1,3-butadiene.

Experimental[5,6]

Isolation of the Dimer.—In a short-path distillation apparatus 30 g. of the brown gummy residue from the fractionation of 1-cyano-1,3-butadiene was distilled, yielding 22 g. of a heavy yellow oil, b. p. 122–123° (0.2 mm.), $n^{20}D$ 1.5170, and leaving a hard, polymeric residue in the pot. Redistillation of the oil did not alter its boiling point or index of refraction. However, after standing a portion of the redistilled material solidified.

A solution of several grams of the twice-distilled liquid dimer in hot 95% ethanol was treated with Darco, filtered and cooled to about 50°. Water was then added dropwise to cloudiness and the solution was cooled slowly with scratching of the walls of the flask until crystals formed. After drying *in vacuo* the colorless crystals melted at 53–54°. This product was recrystallized twice from absolute ether–petroleum ether (30–60°) and submitted for microanalysis; m. p. 53–54°.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 75.91; H, 6.37; mol. wt., 158.2. Found: C, 76.09; H, 6.59; mol. wt., 136, 142 (ebulloscopic in benzene).

Aromatization of the Dimer. A. Bromination.—To a mixture of 2.00 g. of the crystalline dimer (m. p. 53–54°) and 45 ml. of benzene was added 2.40 g. of N-bromosuccinimide. The mixture was heated with stirring until it became homogenous and then was refluxed until a negative test for active bromine was obtained with acidified potassium iodide solution (three hours). The hot solu-

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(1) For the preceding paper in this series, see Snyder and Poos, THIS JOURNAL, **71**, 1057 (1949).

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

(2a) The same dimer apparently has been isolated in an impure state by Coffman (*ibid.*, **57**, 1981 (1935)).

(3) For the dimer of 2-cyano-1,3-butadiene, see Marvel and Brace, *ibid.*, **71**, 79 (1949).

(4) Straus and Lemmel, *Ber.*, **46**, 239 (1913).

(5) All melting points are uncorrected.

(6) Microanalyses by Miss Emily Davis.

tion was cooled to 0° and the precipitated succinimide was collected on a filter and washed with several portions of cold benzene (wt. 1.19 g., m. p. 123–124.5°).

B. **Dehydrobromination.**—The benzene solution from above was concentrated, transferred to a small flask, and the remainder of the benzene was removed. To the residual yellow oil 8 ml. of isoquinoline was added portionwise with agitation. The flask was then set in an oil-bath and the bath was heated to 180° for twenty-five minutes, then to 190° for five minutes, after which the flask was removed and allowed to cool.

An excess of dilute hydrochloric acid was added to the mixture and the acid solution was extracted thoroughly with benzene. The benzene extracts were combined; the dark solution was washed first with dilute hydrochloric acid and then with water and finally concentrated to a small volume. The resulting black oily solution was transferred to a short-path distilling bulb with benzene and the low-boiling material was distilled at atmospheric pressure. Distillation of the residue yielded 1.50 g. (76%) of a pale yellow oil; b. p. 110° (0.2 mm.), $n^{20}_{\rm D}$ 1.5468. After redistillation the oil was water-white ($n^{20}_{\rm D}$ 1.5468) and a sample of it solidified on standing to a low-melting solid. Another sample of this colorless redistilled oil was then taken up in absolute ether–petroleum ether (30–60°) and the solution was inoculated with the solid and cooled to yield fluffy white needles which were collected on a filter, washed with petroleum ether and air dried; m. p. 41–42.5°. Subsequent hydrolysis of this compound to III identified it as *o*-cyanohydrocinnamonitrile. The crystalline dinitrile was recrystallized two times from absolute ether–petroleum ether (30–60°) and submitted for microanalysis; m. p. 41–42.5°.

Anal. Calcd. for $C_{10}H_8N_2$: C, 76.90; H, 5.16. Found: C, 76.79; H, 5.29.

Hydrolysis of *o*-Cyanohydrocinnamonitrile (II).—A mixture of 0.50 g. of II, 5 ml. of 20% potassium hydroxide and 5 ml. of 95% ethanol was brought to boiling on a steam cone and was allowed to reflux until ammonia evolution had practically ceased (twenty-four hours). Most of the alcohol was distilled, the aqueous residue was cooled and then was neutralized dropwise with concentrated hydrochloric acid. Before the neutral point was reached, a brown solid separated which was collected on a filter, washed with several ml. of water (washings added to the filtrate) and dried; 0.12 g., m. p. 205–215° (dec.). This basic substance was not identified. Acidification of the basic filtrate from above yielded 0.07 g. of an infusible, neutral solid which was presumed to be the diamide of III. After standing overnight, the acidic filtrate had deposited crystals of acid which were collected, washed and dried; 0.14 g., m. p. (155°) 164–166°. Concentration of the mother liquors yielded an additional 0.14 g. of crude acid. One recrystallization from water (Darco) raised the melting point to 166.5–168°. After two more recrystallizations from water the product melted at 166.5–168° alone or when mixed with authentic III prepared as described below.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.99; H, 5.29.

Preparation of *o*-Carboxyhydrocinnamic Acid[4] (III).—The oxidation of 2.00 g. of 1,2-dihydronaphthalene with aqueous potassium permanganate solution at 9–11° yielded 0.34 g. of III, m. p. 163–167° (lit.[4] 162–164°), along with unchanged hydrocarbon. After several recrystallizations from water (Darco) the pure acid melted at 166.5–168° (lit.[4] 166–167°).

Dimerization Experiments with *cis*- and *trans*-1-Cyano-1,3-butadiene.—Into a small distilling flask was placed 3.0 g. of higher-boiling 1-cyano-1,3-butadiene ($n^{20}_{\rm D}$ 1.4960) and *ca.* 0.1 g. of picric acid. The flask was stoppered and left on a steam cone until the material had thickened to a sirupy consistency (sixteen hours). When the contents of the flask was submitted to high vacuum distillation there was obtained as distillate 2.0 g. (66%) of oily dimer, $n^{20}_{\rm D}$ 1.5172. From the Dry Ice-trap there was recovered *ca.* 0.5 g. (16%) of monomeric cyanodiene. A small amount of polymeric residue remained in the flask.

In a like manner, 3.0 g. of the lower-boiling isomer ($n^{20}_{\rm D}$ 1.4852) was heated for eighteen hours to yield 0.4 g. (13%) of dimer ($n^{20}_{\rm D}$ 1.5112). Recovered monomer amounted to *ca.* 0.5 g. (16%) while the major portion of the material remained as polymer in the flask. From a second experiment with the same quantity of lower-boiling isomer, 0.4 g. (13%) of dimer ($n^{20}_{\rm D}$ 1.5155) and 0.9 g. (30%) of monomer were isolated after nine hours at 100°.

Several grams of once-crystallized dimer was heated with picric acid on the steam cone for twenty-five hours and then distilled. The material was unchanged, and left no polymeric residue upon distillation.

Summary

The cyclic dimer of 1-cyano-1,3-butadiene has been isolated and characterized as 1-(β-cyanovinyl)-2-cyano-3-cyclohexene. The structure was proved by aromatization of the dimer to *o*-cyanohydrocinnamonitrile and hydrolysis of this dinitrile to the known *o*-carboxyhydrocinnamic acid. Experiments with the *cis* and *trans* isomers of 1-cyano-1,3-butadiene indicate that the higher-boiling isomer (presumably *trans*) is the chief source of the dimer.

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[Contribution from the Chemical Laboratories of the University of Maryland]

1,3,5,7-Octatetraene

By G. Forrest Woods and Louis H. Schwartzman[1]

The reaction of 2,4-pentadienal[2] with methylmagnesium bromide was shown to yield 1,3-hexadien-5-ol. This latter substance was dehydrated very readily over activated alumina to yield 1,3,5-hexatriene.[3]

$$\begin{array}{l} CH_2{=}CH{-}CH{=}CH{-}CHO + CH_3MgBr \longrightarrow \\ \quad CH_2{=}CH{-}CH{=}CH{-}CHOH{-}CH_3 \longrightarrow \\ \qquad\qquad H{-}(CH{=}CH)_3{-}H \end{array}$$

Pentadienal has now been utilized as a starting material for the synthesis of 1,3,5,7-octatetraene.

Allylmagnesium bromide (I) reacts very smoothly with 2,4-pentadienal (II) to yield 1,3,7-octatrien-5-ol (III). The possibility of a rearrangement in the reactions leading to (III) or rearrangement of (III) itself had to be considered.[3,4] Accordingly, 1,3,7-octatrien-5-ol was catalytically reduced to the saturated alcohol, 4-octanol (IV) and identified as the α-naphthylurethan, and the

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[1] National Institute of Health Predoctorate Fellow.

[2] (a) Woods and Sanders, This Journal, **68**, 2483 (1946); (b) Woods and Sanders, *ibid.*, **69**, 2926 (1947).

[3] Woods and Schwartzman, *ibid.*, **70**, 3394 (1948).

[4] Heilbron, Jones, McCombie and Weedon, *J. Chem. Soc.*, 84, (1945).