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Acetylene Polymers and their Derivatives. XXIII. Cyano-4-butadiene-1,3

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Compounds of the formula $CH_2{=}C{=}CHCH_2X$ in which X is Cl, Br, I, OH or OAc survive a series of metathetical reactions without undergoing rearrangement.[1] Of these compounds, the chloride and bromide are readily and irreversibly rearranged to $CH{=}CXCH{=}CH_2$, and the iodide rearranges spontaneously.

Because of the ease with which the chloride, bromide and iodide are rearranged, it appeared likely that the action of sodium cyanide on chloro-4-butadiene-1,2 (I) might yield cyanoprene (II), a compound which should be of especial interest as a precursor of synthetic rubber. As a matter of fact cyano-4-butadiene-1,3 (III), isomeric with (II), is obtained in poor yields when an alcoholic solution of sodium cyanide is allowed to react with (I). The reaction evidently proceeds in a normal metathetical manner and is followed by rearrangement of one of the double bonds. Certain by-products formed during the reaction are indicated in subsequent paragraphs.

(I) $CH_2{=}C{=}CHCH_2Cl$
(II) $CH_2{=}C(CN)CH{=}CH_2$
(III) $CH_2{=}CHCH{=}CHCN$
(IV) $ClCH_2CH{=}CHCH_2CO_2C_2H_5$
(V) $CH_3OCH_2CH{=}CHCH_2CN$

The structure of cyano-4-butadiene-1,3 (III) is established by its analytical composition and by the following reactions.

It is converted to β-vinylacrylic acid by cold acid hydrolysis and it is readily hydrogenated to *n*-amylamine. Alkaline permanganate oxidizes it to oxalic acid. In ethanol solution, the nitrile adds hydrogen chloride. The reaction consists of 1,4-addition and esterification giving rise to ethyl chloro-5-pentenoate-Δ^3 (IV). The ester (IV) is readily oxidized by alkaline permanganate to chloroacetic acid. When cyano-4-butadiene-1,3 is heated with naphthoquinone or maleic anhydride the only evidence of reaction is the formation of a polymeric mass. However, as has already been pointed out,[2] negative results in the Diels–Alder reaction are of no value in the demonstration of structure, since many 1,3-dienes fail to react.

Results already presented[3] show that to obtain a high rate of polymerization, the terminal carbon atoms in a 1,3-diene must be free of any substituents, but the new nitrile nevertheless polymerizes about twenty times as fast as isoprene and gives a rubber-like product. It polymerizes spontaneously on standing, and the polymerization is greatly accelerated at 100°. After three weeks at ordinary temperature, a 5% yield of α-polymer was obtained. On the other hand, after thirteen hours at 100°, the α-polymer was obtained in 14% yield along with a 42% yield of dimer. Antioxidants act as powerful inhibitors for this transformation. The plastic polymer obtained under the influence of heat may be compounded and cured, and, although the plastic properties of the product were never entirely suppressed, the rubber-like material possessed considerable elasticity. Under the influence of light cyano-4-butadiene-1,3 polymerizes to a granular product identical in appearance with ω-polychloroprene.

Under the conditions of preparation cyano-4-butadiene-1,3 is very reactive. It readily adds methanol to form two chemical individuals obtained as by-products.

The first of these is an unsaturated oil corresponding in composition to the addition of one molecule of methanol to the 1,3-diene (III). Oxidation of the oil with permanganate yields methoxyacetic acid. These facts indicate that it has the structure methoxy-1-cyano-4-butene-2 (V). It evidently is formed by the 1,4-addition of methanol.

The second of these is an oil corresponding in composition to the addition of two molecules of methanol to (III) and apparently it is formed by the addition of one molecule of methanol to (V). It is obtained not only as a by-product in the preparation of (III) but also by allowing (III) to react in a methanol solution of sodium methoxide. When hydrolyzed it yields a dimethoxyvaleric acid. Hydrolysis, demethylation by hydrobromic acid, and elimination of two molecules of water produce an unsaturated lactone which on hydrogenation yields δ-valerolactone.

These facts furnish a basis for a discussion of

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[1] Carothers and Berchet, THIS JOURNAL, **55**, 2807 (1933).

[2] Coffman and Carothers, *ibid.* **55**, 2040 (1933).

[3] Carothers, *Ind. Eng. Chem.*, **26**, 30 (1934).

its structure. Formulas (VI) and (VII) represent the only possibilities consistent with the facts for the structure of a compound formed by the addition of one molecule of methanol to (V).

(VI) $CH_3OCH_2CH_2CH(OCH_3)CH_2CN$
(VII) $CH_3OCH_2CH(OCH_3)CH_2CH_2CN$

No direct experimental method is available for a decision between these two structures since the hydroxy acids derived from each present the possibility of six-membered ring formation required to obtain δ-valerolactone.

Experimental Part

I. **Preparation of Cyano-4-butadiene-1,3.**—Sodium cyanide (250 g.) was dissolved in a solution of 250 cc. of water and 700 cc. of methanol in a 3-liter flask equipped with stirrer and reflux condenser. Chloro-4-butadiene-1,2 (354 g.) was introduced, and the mixture was heated gently with agitation until the reaction became exothermic. After the reaction had proceeded for an hour, the mixture was cooled and the sodium chloride was removed by filtration. The filtrate was poured into 1.5 liters of water, the water-insoluble layer was separated, and the aqueous solution was twice extracted with ether. The water insoluble layer and the ether extracts were combined and dried over calcium chloride. The ether was evaporated and by distillation of the residue 90 g. of crude product boiling from 36° (50 mm.) to 55° (3 mm.) was received. This material was washed once with cold dilute hydrochloric acid and was dried over magnesium sulfate. Distillation of the dried material gave 64 g. of cyano-4-butadiene-1,3 which boiled at 49–53° (30 mm.).

The physical properties of cyano-4-butadiene-1,3 are: b. p. 135–138° (760 mm.) with polymerization; 65–68° (58 mm.), 48–50° (28 mm.); $d^{20}{}_4$ 0.8644; $n^{20}{}_D$ 1.4880; *MR* (obsd.), 24.57; *MR* (calcd.), 24.10.

Anal. Calcd. for C_5H_5N: N, 17.72; mol. wt., 79. Found: N, 17.48; mol. wt., 80.

During the preparation of the nitrile considerable amounts of by-products were formed by the addition of methanol to the 1,3-diene. These products obtained along with some polymeric material account, in part, for the utilization of chloro-4-butadiene-1,2.

II. Proof of Structure of Cyano-4-butadiene-1,3

Hydrolysis to β-Vinylacrylic Acid.—Cyano-4-butadiene-1,3 (10 g.) was introduced into a solution of 60 cc. of concd. hydrochloric acid in 100 cc. of ether. After standing for six days at ordinary temperature the solution was diluted with water to 500 cc. total volume, and the solution was continuously ether extracted for twenty-one hours. Distillation of the dried ethereal extract gave a small amount of β-vinylacrylic acid[4] which melted at 71° after recrystallization from petroleum ether. The distillation residue was a polymeric mass.

Anal. Calcd. for $C_5H_6O_2$: C, 61.22; H, 6.12; neut. eq., 98. Found: C, 61.00; H, 6.16; neut. eq., 100.2.

Conversion to Ethyl β-Vinylacrylate.—To well-cooled ethanol (100 g., 95%) in a liter flask was added 100 g. of concd. sulfuric acid. Cyano-4-butadiene-1,3 (40 g.) was then introduced, and the solution was refluxed for seven hours. After three hours the solution was very viscous. The cooled reaction mixture was poured into ice water, and there separated a large amount of soft, plastic and rubber-like polymer. Ether extraction of the solution and distillation of the dried ethereal extract gave a small amount of ethyl β-vinylacrylate which boiled at 65–67° (30 mm.); $d^{20}{}_4$ 0.9336; $n^{20}{}_D$ 1.4723; *MR* (obsd.) 37.81; *MR* (calcd.), 35.13. The literature[5] records the physical constants of ethyl β-vinylacrylate as b. p. 70–71° (31 mm.); $d^{20}{}_4$ 0.938.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.67; H, 7.94. Found: C, 66.69; H, 7.71.

Ethyl β-vinylacrylate failed to form an addition compound when heated with naphthoquinone, and polymerized to a rubber-like mass after ten hours at 100°.

Reduction to *n*-Amylamine.—With a platinum catalyst, cyano-4-butadiene-1,3 (10 g. or 0.126 mole) in 25 g. of acetic anhydride absorbed 94% (0.477 mole) of the theoretical amount of hydrogen during eight hours. The reaction mixture was filtered from the catalyst and distilled, the portion boiling from 200–250° being collected. Redistillation gave 10 g. of colorless liquid which boiled at 112–116° (4 mm.); $d^{20}{}_4$ 0.9146; $n^{20}{}_D$ 1.4472; *MR* (obsd.), 37.75; *MR* (calcd.), 37.96.

Anal. Calcd. for C_7H_5ON: N, 10.85. Found: N, 10.92.

Hydrolysis of N-*n*-amylacetamide gave *n*-amylamine which boiled at 102–106°; $d^{20}{}_4$ 0.7584; $n^{20}{}_D$ 1.4093. The literature records the constants for *n*-amylamine as b. p. 104°, d^{19} 0.766. The amine was positively identified by conversion to *p*-bromobenzenesulfon-*n*-amylamide which, after recrystallization from petroleum ether, melted sharply on the block at 54°. The literature[6] records the melting point of *p*-bromobenzene-sulfon-*n*-amylamide as 55°.

Permanganate Oxidation of Cyano-4-butadiene-1,3.—An analytically pure sample of cyano-4-butadiene-1,3 (40 g.) was introduced into an aqueous solution (300 cc.) containing 28 g. of potassium hydroxide. Potassium permanganate (330 g.) was added in small amounts during four hours with vigorous agitation at 30°. The mixture was decolorized with sulfur dioxide, and the manganese dioxide was filtered off and washed with water. The combined filtrates were cooled, strongly acidified and continuously ether extracted. Evaporation of the dried ethereal extract gave a crystalline residue which, after washing with ethyl acetate-petroleum ether mixture, was dissolved in a small amount of water, boiled with Norite, filtered and cooled. The white crystals which separated melted sharply on the block at 101–102° with resolidification either alone or when mixed with an authentic sample of oxalic acid dihydrate.

Neutral equivalent. Calcd. for $H_2C_2O_4 \cdot 2H_2O$: neut. eq., 63.0. Found: neut. eq., 64.0.

Addition of Hydrogen Chloride to Cyano-4-butadiene-1,3.—Cyano-4-butadiene-1,3 (41 g.) was dissolved in 50

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[4] Muskat, THIS JOURNAL, **52**, 326 (1930).

[5] K. v. Auwers, *J. prakt. Chem.*, **105**, 361 (1923).

[6] Demény, *Rec. trav. chim.*, **50**, 51 (1931).

g. of 95% ethanol containing 44 g. of dry hydrogen chloride. After the mixture had stood for sixteen hours at ordinary temperature, it was heated for two hours at 80°. The cooled mixture was poured into ice water, and the water-insoluble layer was separated, washed with water and dried over calcium chloride. Distillation of the crude product (55 g.) in an efficient still gave 21 g. of pure chloro ester and a high boiling residue which could not be distilled without decomposition. The yield of ethyl chloro-5-pentenoate-Δ^3 was 25% of the theoretical amount. It boiled at 67–69° (0.5 mm.), 72–74° (1 mm.), d^{20}_4 1.0862; n^{20}_{D} 1.4612, *MR* (obsd.), 41.08; *MR* (calcd.), 40.58.

Anal. Calcd. for $C_7H_{11}O_2Cl$: Cl, 21.85; mol. wt., 162.5. Found: Cl, 22.02; mol. wt., 159.

Ethyl chloro-5-pentenoate-Δ^3 was oxidized to chloroacetic acid by potassium permanganate. The chloro ester (32 g.) was introduced into water (250 cc.) and potassium permanganate (85 g.) was added in small amounts during three hours with vigorous agitation. The mixture was decolorized with sulfur dioxide, and the manganese dioxide was filtered off and thoroughly washed with water. The combined aqueous filtrates were strongly acidified, and the aqueous solution was continuously ether extracted. The dried ethereal solution on evaporation and distillation of the residue gave 8 g. of crude chloroacetic acid which, after recrystallization from petroleum ether and chloroform, melted sharply on the block at 60–61°. The literature records its melting point as 61–63°.

Neutral equivalent. Calcd. for $C_2H_3O_2Cl$: neut. eq., 94.6. Found: neut. eq., 93.4.

Chloroacetanilide was prepared as a solid derivative. It melted sharply on the block at 134–135°. The literature records the melting point as 134–135°.[7]

Polymerization of Cyano-4-butadiene-1,3

Light Polymerization.—A sample of cyano-4-butadiene-1,3 in glass exposed to a 200-watt Mazda lamp for 112 hours at 40–50° was completely converted into a colorless granular mass of rubber-like globules. This granular product is identical in appearance with ω-polychloroprene. In a parallel sample isolated from the light, the only change was a slight increase in viscosity and the appearance of a tarry speck of granular polymer.

Heat Polymerization.—(1) Cyano-4-butadiene-1,3 also polymerized spontaneously on standing; after three weeks a sample of the nitrile gave a 5% yield of alcohol insoluble polymer. This soft, plastic, rather rubber-like mass was compounded with 1% of phenyl-β-naphthylamine and 5% of zinc oxide and was heated at 125° for thirty minutes. Vulcanization was apparently far from complete but the product had good elasticity and fair strength. A sample stretched 1400% without breaking; on release it instantly returned to 250% of its initial length and after ten minutes to 200%.

(2) A sample of the 1,3-diene heated in a glass tube at 100° for thirteen hours was converted to a colorless, viscous sirup which contained 14% of alcohol-insoluble polymer, 42% of high-boiling oil, and 21% of unchanged monomer. The high-boiling material had a molecular weight corresponding to a dimer, but its analytical composition indicated that considerable oxygen had been absorbed. The physical properties of the high-boiling oil are: b. p. 150–165° (3 mm.); d^{20}_4 1.0358; n^{20}_{D} 1.5118.

Anal. Calcd. for $C_{10}H_{10}N_2$: N, 17.72; mol. wt., 158. Found: N, 14.68; mol. wt., 160.

The alcohol-insoluble material was a soft, plastic, rubber-like mass. It was compounded with 0.5% of tetramethylthiuram disulfide, 1% benzidine, 3% sulfur, 5% zinc oxide and 1% phenyl-β-naphthylamine and heated at 125° for one hour. The plastic properties were partly suppressed, but the vulcanization was very incomplete. The product could be stretched without breaking to 1800% of its initial length; on release it instantly returned to 400%, and after ten minutes to 200%, its initial length.

(3) Cyano-4-butadiene-1,3 (10 g.) was added to a sodium hydroxide solution (120 g., 17% NaOH), and the mixture was heated to refluxing. During fifteen minutes ammonia was evolved and a polymeric mass commenced to separate from the mixture. After sixteen hours of refluxing all of the nitrile had been converted to a brown, hard, brittle solid (8 g.). The solid was finely ground in a mortar and was repeatedly washed in boiling water. The product after being washed with alcohol and ether was thoroughly dried at 110°. The material was quite hard and very insoluble in common organic solvents.

Anal. Calcd. for $(C_5H_5N)_x$: N, 17.72; C, 75.95; H, 6.33. Found: N, 15.30; C, 76.34; H, 7.38.

IV. By-Products in the Preparation of Cyano-4-butadiene-1,3

In the preparation of cyano-4-butadiene-1,3 large amounts of by-products are formed. The aqueous alcoholic solutions from six preparations of the nitrile (as already described) were continuously ether extracted for twenty-four hours. Fractionation by careful distillation of the dried ethereal extract showed it to consist essentially of three constant-boiling fractions having the compositions of (V) C_6H_9ON, (VI) $C_7H_{13}O_2N$, and (VIII) $C_7H_{10}O_2N$. Considerable amounts of material were discarded as foreshots obtained during the distillation.

(1) Proof of Structure of Methoxy-1-cyano-4-butene-2. Oxidation to Methoxyacetic Acid.—The first fraction (C_6H_9ON) consisted of 63 g. of colorless oil which boiled at 65–67° (7 mm.); d^{20}_4 0.9318; n^{20}_{D} 1.4397; MR (obsd.), 31.40; MR (calcd.), 30.90.

Anal. Calcd. for C_6H_9ON: C, 64.86; H, 8.11; N, 12.61; mol. wt., 111. Found: C, 65.40; H, 8.01; N, 12.58; mol. wt., 112.

Methoxy-1-cyano-4-butene-2 (44 g.) was introduced into 200 cc. of water and potassium permanganate (127 g.) was added in small portions during four hours with vigorous agitation. The mixture was decolorized by sulfur dioxide, and the manganese dioxide was filtered off and macerated in a mortar with water. The combined aqueous filtrates, strongly acidified with sulfuric acid, were subjected to continuous ether extraction. The dried ethereal extract was evaporated, and by distillation of the residue there was received 5 g. of organic acid which boiled at 115–117° (29 mm.). The acid was positively identified as methoxyacetic acid by conversion to methoxyacetamide. The amide, after recrystallization from absolute ethanol,

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(7) Meyer, *Ber.*, **8**, 1153 (1875).

melted sharply on the block at 95–96° either alone or when mixed with an authentic specimen of methoxyacetamide. Methoxyacetamide is reported in the literature[8] as melting at 96.5°.

(2) **Conversion of Dimethoxyvaleronitrile to Dimethoxyvaleric Acid and to δ-Valerolactone.**—The second fraction ($C_7H_{13}O_2N$) consisted of 288 g. of colorless oil which boiled at 70–73° (1 mm.); d^{20}_4 0.9788; n^{20}_D 1.4288; MR (obsd.) 37.68; MR (calcd.), 37.63.

Anal. Calcd. for $C_7H_{13}O_2N$: C, 58.74; H, 9.09; N, 9.79; mol. wt., 143. Found: C, 58.82; H, 8.81; N, 10.13; mol. wt., 143.

This same nitrile was obtained by the addition of methanol to cyano-4-butadiene-1,3 with sodium methoxide as catalyst. Cyano-4-butadiene-1,3 (79 g.), stabilized by hydroquinone, was added dropwise during half an hour to a vigorously agitated solution of 2 g. of sodium in 64 g. of anhydrous methanol at 60°. After an hour the reaction mixture was cooled, diluted with water and ether extracted. The ethereal solution was washed with dilute acid and dried. From the dried ethereal solution there was received by distillation in an efficient column 32 g. of dimethoxyvaleronitrile which boiled at 72–74° (1 mm.); d^{20}_4 0.9777; n^{20}_D 1.4289. The yield was 23% of the theoretical amount. In the absence of alkaline catalysts, the addition of methanol to cyano-4-butadiene-1,3 does not take place. The nitrile (40 g.) and absolute methanol (40 g.) were heated for four hours at 90° in a sealed tube. By distillation there was recovered 32 g. of methanol and 22 g. of nitrile. The residue was polymeric material.

Hydrolysis to Dimethoxyvaleric Acid.—Into a solution of 67 g. of concd. sulfuric acid in 100 cc. of water was introduced 53 g. of dimethoxyvaleronitrile. The solution was refluxed vigorously for four hours and was then repeatedly ether extracted. Evaporation of the dried ethereal solution and distillation of the residue through an efficient column gave 23 g. of recovered nitrile and 15 g. of dimethoxyvaleric acid which boiled at 119–122° (1 mm.); d^{20}_4 1.0800; n^{20}_D 1.4428; MR (obsd.), 39.75; MR (calcd.), 39.35.

Anal. Calcd. for $C_7H_{14}O_4$: C, 51.85; H, 8.64; neut. eq., 162. Found: C, 52.40; H, 8.79; neut. eq., 162.

Conversion to δ-Valerolactone.—Dimethoxyvaleronitrile (71 g. or 0.5 mole) was refluxed for eighteen hours with 300 g. of 48% hydrobromic acid. The mixture was diluted to 500 cc. and was continuously ether extracted for seventy hours. The dried ethereal solution was evaporated, and the residue (42 g.) on distillation gave 20 g. of lactone which boiled at 83–85° (3 mm.). The remainder of the material was high boiling, acid to litmus, and contained halogen. The properties of the lactone are: b. p. 226–228° (760 mm.), 83–85° (3 mm.); d^{20}_4 1.1439; n^{20}_D 1.4869; MR (obsd.), 24.64; MR (calcd.), 22.43.

Anal. Calcd. for $C_5H_6O_2$: C, 61.22; H, 6.12; mol. wt., 98. Found: C, 60.86; H, 6.33; mol. wt., 100.

The lactone was faintly acid to litmus, but could not be titrated directly with alkali. It absorbed bromine readily, forming a liquid bromide which was not characterized. No solid polymer separated from a sample of lactone heated at 140–150° during eight hours.

The unsaturated lactone (0.234 mole) and a platinum catalyst in 25 cc. of absolute ethanol absorbed 79% (0.184 mole) of the theoretical amount of hydrogen during twenty minutes. The reaction mixture was filtered from the catalyst and distilled. There was received 16 g. of colorless pleasant smelling liquid which had the properties of δ-valerolactone. It boiled at 86–89° (5 mm.), 219–222° (760 mm.); d^{20}_4 1.0794; n^{20}_D 1.4503. The lactone formed a solid polymer when heated during eight hours at 150°.

Anal. Calcd. for $C_5H_8O_2$: C, 60.00; H, 8.00. Found: C, 59.76; H, 8.19.

The physical constants for δ-valerolactone as recorded in the literature[9] are b. p. 215–220° (760 mm.), d^{20}_{20} 1.1130; n^{20}_D 1.4600. Those recorded for γ-valerolactone[10] are b. p. 207–208 (760 mm.), d^{25} 1.0465; n^{20}_D 1.4303. The lactone (1 cc.) when heated with 3 cc. of hydrazine hydrate at 120° for two hours gave a crystalline product. After recrystallization from ethanol–ethyl acetate mixture the product melted sharply on the block at 105° and it had a composition corresponding to the hydrazide of δ-hydroxyvaleric acid.

Anal. Calcd. for $C_5H_{12}O_2N$: N, 21.21. Found: N, 20.97.

(3) The third fraction ($C_5H_{12}ON_2$) was not identified. It consisted of 123 g. of oil which boiled at 131–134° (0.5 mm.); d^{20}_4 1.0293; n^{20}_D 1.4480.

Anal. Calcd. for $C_7H_{10}ON_2$: C, 60.89; H, 7.25; N, 20.29; mol. wt., 138. Found: C, 61.76; H, 7.42; N, 19.38; mol. wt., 147.

Summary

The action of alcoholic sodium cyanide on chloro-4-butadiene-1,2 yields cyano-4-butadiene-1,3. The compound polymerizes much faster than isoprene and yields a rubber-like product. It readily undergoes 1,4-addition with hydrogen chloride and with methanol. The transformation products are ethyl chloro-5-pentenoate-Δ³ and methoxy-1-cyano-4-butene-2.

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[8] Sulo Kilpi, *Z. physik. Chem.*, **80**, 182 (1912).

[9] Marvel and Birkhimer, THIS JOURNAL, **51**, 260 (1929).

[10] Schuette and Thomas, *ibid.*, **52**, 3010 (1930).