[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, UNIVERSITY OF NOTRE DAME]

The Thermal Reaction of Formaldehyde with Allyl Cyanide

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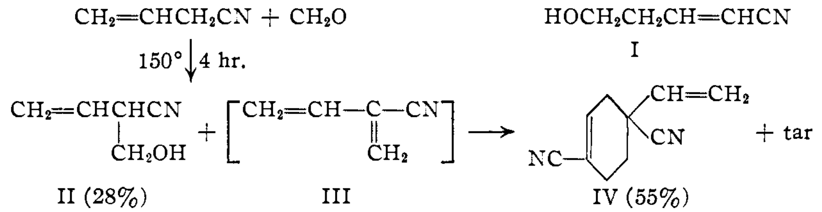
Thermal condensation of formaldehyde with allyl cyanide at temperatures above 130° occurs primarily at the active methylene group. After four hours at 150°, a 28% yield of 2-hydroxymethyl-3-butenonitrile and a 55% yield of the dimer of its dehydration product, 2-cyanobutadiene, were obtained.

A previous report[3] has shown that attempts to carry out acid-catalyzed condensation of formaldehyde with the double bond of allyl cyanide failed because of more rapid reaction of the aldehyde with the nitrile group. Since some substances, such as β-pinene[4] and methylenecyclohexane,[5] have been shown to react with formaldehyde thermally, this reaction has been investigated for allyl cyanide. If reaction had occurred as for β-pinene, the primary product of the reaction would have been 5-hydroxy-2-pentenonitrile (I). All evidence indicates, however, that primary condensation occurred not at the double bond, but at the active methylene group to yield 2-hydroxymethyl-3-butenonitrile (II).



In preliminary experiments, allyl cyanide and paraformaldehyde were heated at reflux temperature with stirring for many hours at atmospheric pressure without any reaction occurring. When aluminum chloride or stannic chloride was added as catalyst, a low-melting white crystalline solid first formed, probably a complex of the metal halide with the allyl cyanide, and then a violent reaction took place. Even when hydrocarbon diluents were used and external cooling was applied only orange or brown polymers could be isolated from the reaction.

The thermal reaction without catalysts was next studied in small sealed glass tubes containing 0.001 mole each of allyl cyanide and paraformaldehyde placed in an oil-bath at constant temperature and agitated occasionally for varying lengths of time. The tubes, when removed from the bath, were cooled in Dry Ice and then broken open. The contents were analyzed for formaldehyde using the method of D'Alelio.[6] Working with such small quantities it was not possible to attain the highest accuracy in these experiments, but checks within a few per cent. were usually obtained. The results for the two temperatures studied are given in Table I.

TABLE I

SEALED-TUBE REACTIONS OF EQUIMOLAR QUANTITIES OF ALLYL CYANIDE AND PARAFORMALDEHYDE

Temperature 150 ± 5°		Temperature, 170 ± 5°	
Time, hr.	Paraformaldehyde consumed, %	Time, min.	Paraformaldehyde consumed, %
1.0	23,25	25	45
2.0	35,41	45	60
4.33	62,63	90	68
8.25	70	140	70
9.25	70	215	80
22.0	87	320	88

As a result of these experiments two large runs were made at 150° in a rocking, stainless steel bomb. One reaction was stopped after four hours, the other was carried on for 30 hours. The product from these reactions was a heavy, yellow, homogeneous liquid, effervescing unreacted formaldehyde. Vacuum distillation of this liquid gave water, unreacted allyl cyanide containing some paraformaldehyde, two main fractions (A and B), and some resinous material.

The higher-boiling fraction B was induced to crystallize by cooling in ice-water. Recrystallized from an ethanol–water solution, it melted sharply at 54.5°. Analysis and molecular weight determination indicated that it was a dimer of cyanobutadiene. Saponification with aqueous alkali produced an acid whose analysis and neutral equivalent were in accord with this. Catalytic hydrogenation showed this acid had two carbon–carbon double bonds. The first mole of hydrogen was absorbed very rapidly and the second mole was added more slowly.

The melting point of the unsaturated acid (238°) was nearly the same as that reported[7] for the acid obtained from saponification of the dimer of 2-cyano-1,3-butadiene (m.p. 236°). However, since the dimer of 2-cyano-1,3-butadiene has a melting point (55–56°) very near that of the dimer[8] of 1-cyano-1,3-butadiene (53–54°) and since no acid has been obtained from the latter, further identification was undertaken.

The unsaturated dibasic acid was heated with palladium-on-charcoal catalyst containing a little copper–chromite catalyst. Carbon dioxide and hydrogen were evolved and pure *p*-ethylbenzoic acid was isolated from the residue. In addition,

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[1] General Tire and Rubber Company Fellows (I. V. K., 1946–1948; G. A. C., 1949–1950).

[2] Abstracted from the Ph.D. dissertations submitted to the Graduate School by I. V. K. and G. A. C. Presented by title at the XII International Congress, New York, September 10, 1951.

[3] C. C. Price and I. V. Krishnamurti, THIS JOURNAL, **72**, 5334 (1950).

[4] J. P. Bain, *ibid.*, **68**, 638 (1946).

[5] R. T. Arnold and J. F. Dowdall, *ibid.*, **70**, 2590 (1948).

[6] G. F. D'Alelio, "A Laboratory Manual of Plastics and Synthetic Resins," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 111.

[7] C. S. Marvel and N. O. Brace, THIS JOURNAL, **71**, 37 (1949).

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

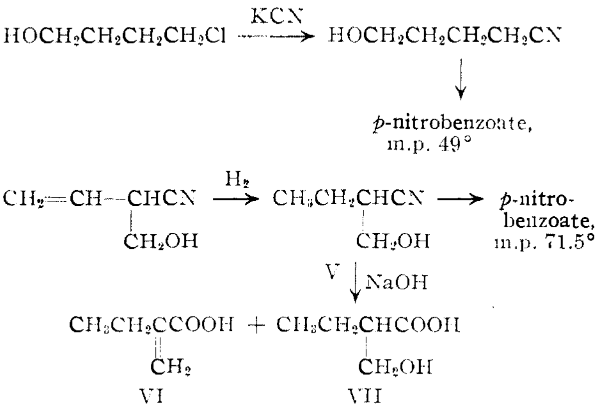
the infrared spectrum of fraction B gave exactly the same five characteristic absorption bands between 4.5 and 6.7 μ as those reported for IV.[7]

The lower-boiling fraction A from the reaction of equal moles of allyl cyanide and paraformaldehyde at 150° was found to give a positive test with ceric nitrate reagent. It decolorized bromine in carbon tetrachloride, was soluble in water and discolored aqueous potassium permanganate. Analysis of the material and of its *p*-nitrobenzoate derivative indicated it was an unsaturated hydroxynitrile formed by the condensation of one molecule of formaldehyde with one molecule of allyl cyanide.

Several attempts to separate the material into individual components with activated alumina and other adsorbents such as "Florosil" and alumina of various degrees of activity failed to give a separation. The material was also carefully distilled under reduced pressure.

Although this distillation indicated a reasonable degree of homogeneity (d^{25} 1.009–1.012, $n^{25}\text{D}$ 1.4635–1.4688, MR^{25} 26.54–26.71) the infrared spectra of several fractions were examined. In the region of the nitrile absorption, a single strong band was observed at 4.48 to 4.52 μ. This is somewhat longer wave length than for a normal nitrile but either conjugation[7] or a β-hydroxyl group[9] promotes a shift in this direction. In the region of the carbon–carbon double bond adsorption, a single strong band was observed at 6.07 μ, clearly indicating lack of conjugation between the nitrile and the double bond. The infrared data therefore support structure II for the lower-boiling product.

Samples of II were catalytically reduced with palladium-on-charcoal catalyst. The required amount of hydrogen was quickly taken up giving a single hydroxy-nitrile, α-hydroxymethylbutyronitrile (V), differing in physical properties and in the properties of its *p*-nitrobenzoate from the isomeric tetramethylene cyanohydrin.



$$HOCH_2CH_2CH_2CH_2Cl \xrightarrow{KCN} HOCH_2CH_2CH_2CH_2CN \longrightarrow p\text{-nitrobenzoate, m.p. } 49°$$

$$CH_2{=}CH{-}\underset{\displaystyle CH_2OH}{CHCN} \xrightarrow{H_2} \underset{\displaystyle CH_2OH}{CH_3CH_2CHCN} \longrightarrow p\text{-nitrobenzoate, m.p. } 71.5°$$

$$\text{V} \xrightarrow{NaOH} \underset{\displaystyle \underset{\text{VI}}{CH_2}}{CH_3CH_2CCOOH} + \underset{\displaystyle \underset{\text{VII}}{CH_2OH}}{CH_3CH_2CHCOOH}$$

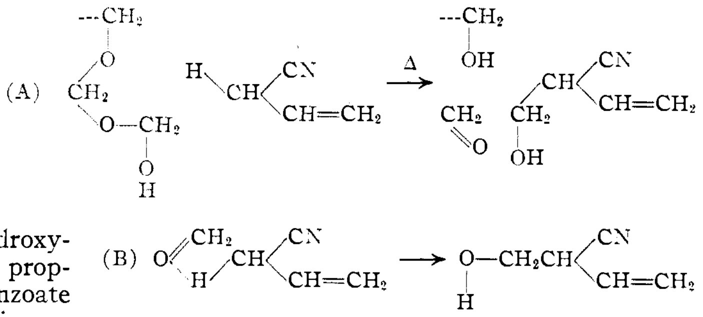
The hydrogenated hydroxynitrile (V) was saponified with aqueous alkali and the free acids were distilled under reduced pressure. Two distinct fractions were obtained. The first fraction distilled at 41° (0.25 mm.); the second fraction, a sirupy liquid, distilled at 102–104° (0.25 mm.). Both liquids had an overpowering odor very similar to that of butyric acid.

The lower-boiling acid was shown to be α-ethylacrylic acid (VI) by its physical constants, neutralization equivalent and preparation of the amide and the phenylhydrazide, both of which were previously reported in the literature.[10]

The higher-boiling acid was shown to be α-ethylhydracrylic acid (VII) by its physical constants, neutralization equivalent and the preparation of its phenylurethan.[11]

Experiment indicated that no appreciable reaction occurred between crotononitrile and formaldehyde under conditions where considerable conversion occurred for allyl cyanide. This rules out as a possible mechanism the isomerization of allyl cyanide to crotononitrile followed by Prins-type condensation at the double bond of the latter.

It also seems unreasonable to believe that the reaction proceeds *via* full ionization of an α-methylene hydrogen, since the resulting anion would presumably isomerize to establish conjugation of the double bond and the nitrile group.[12] Perhaps the most reasonable picture for this process would involve an electrophilic displacement at the α-methylene group, either by a concerted or pseudocyclic process (A) or by a process similar to S_N1 displacement (B). The approximate second-order kinetics of the rough rate measurements in Table I would favor mechanism (B).



Experimental[13]

Allyl Cyanide.—The method of Breckpot[14] was employed in this preparation. In a 5-l. three-necked flask fitted with a mercury-sealed stirrer and two bulb condensers was placed a mixture of 670 g. (10 moles) of allyl alcohol, 845 g. (10.5 moles) of cuprous cyanide, and 1000 cc. of concentrated hydrochloric acid. After the mixture had been stirred for almost an hour the reaction started. Heat was evolved and the flask was cooled from time to time in a water-bath to prevent a violent reaction. The reaction was complete within two hours and the reaction mixture was allowed to stand overnight. One of the condensers was removed and the other was set downward for distillation. The flask was heated and distillation was continued until the temperature reached 95°. Most of the distillate came over between 88 and 92°. The upper organic layer was separated,

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[9] H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., New York, N. Y., 1949, p. 50.

[10] E. E. Blaise and A. Luttringer, *Bull. soc. chim.*, [3] **33**, 761 (1905).

[11] E. E. Blaise and A. Luttringer, *ibid.*, [3] **33**, 638 (1905).

[12] See, *e.g.*, C. K. Ingold, E. de Salas and C. L. Wilson, *J. Chem. Soc.*, 1328 (1936). The author is indebted to Dr. R. N. Lewis for a discussion concerning some aspects of the mechanism of this reaction.

[13] All melting points are corrected; analyses by Micro-Tech Laboratories, Skokie, Illinois.

[14] (a) R. Breckpot, *Bull. soc. chim. Belg.*, **39**, 466 (1930); (b) L. Falaise and R. Frognier, *ibid.*, **42**, 427 (1933).

dried over anhydrous magnesium sulfate, and distilled through a 40-cm. long, helix-packed column. The fraction boiling at 118–119° was collected; n^{25}_D 1.4027; d^{25}_D 0.830; 480 g. (72%) (lit.[14b] b.p. 119–120°; n^{20}_D 1.406; n^{20}_D 1.406; d^{20}_4 0.833 (85–90%)).

Preliminary Investigation of the Thermal Reaction of Allyl Cyanide and Paraformaldehyde (G.A.C.).—The glass tubes used in these small-scale preliminary reactions were made from ordinary 5-mm. diameter Pyrex glass tubing cut in 12-cm. lengths. One end of each tube was sealed and 30.0 mg. (0.001 mole) of paraformaldehyde was weighed into it directly. Then 67.0 mg. (0.001 mole) of allyl cyanide was injected into the bottom of the tube by means of a long thin capillary tube attached to a 1-cc. syringe which has previously been calibrated to deliver the correct weight of material. After the allyl cyanide was added, the lower end of the tube, containing the reactants, was cooled in Dry Ice and the tube was sealed. The tubes were placed in the electrically-heated, thermostatically-controlled oil-bath which was adjusted to the correct temperature and maintained there within ±5°. The tubes were agitated occasionally until the reaction mixture became a homogeneous solution. When a tube was removed from the oil-bath after the proper length of time it was cooled in Dry Ice, broken open, and the contents were dissolved in 150 cc. of hot water.

The analysis for formaldehyde was carried out using the method of D'Alelio.[6] The aqueous solution was adjusted to neutrality by the addition of dilute hydrochloric acid and 7 cc. of a 10% solution of hydroxylamine hydrochloride was added. The mixture was allowed to stand for one-half hour and was then titrated to the brom phenol blue end-point with standardized sodium hydroxide.

The reliability of the method was tested by comparing the analysis of 30.0 mg. of stock paraformaldehyde with that of like amounts of paraformaldehyde which had previously been heated for a number of hours in sealed tubes of the type used for the reaction. Individual tubes heated for 2 and 4 hours at 150 ± 5° and for 3 hours at 170 ± 5° checked within 2% with the analysis of an unheated paraformaldehyde sample. The results of the series of tests at the two temperatures are summarized in Table I.

The addition of solvent to the reaction was shown to have a marked effect on the reaction rate. Two tubes which contained 0.10 cc. of dioxane each in addition to the usual 0.001 mole each of allyl cyanide and paraformaldehyde, analyzed at the end of one and two hours at 150 ± 5°, showed that only 4 and 12%, respectively, of the paraformaldehyde had been used. Identical reactions run without added solvent showed 25 and 40% of the paraformaldehyde had been used at the end of one and two hours, respectively.

Reaction of Allyl Cyanide and Paraformaldehyde at 150° (GAC).—Two large-scale reactions (4 hours and 30 hours) were carried out in a 1-l. stainless steel reaction bomb which was tilted in a rocking motion of one cycle per second. The bomb was electrically-heated and the temperature maintained constant at 150° within ±2° by an automatic control. A pressure gage attached only during the 30-hour run indicated a pressure of 90 pounds per square inch at 150°.

The charge used in the bomb for the 4-hour reaction consisted of 268 g. (4 moles) of allyl cyanide and 120 g. (4 moles) of paraformaldehyde. A 170-g. sample of the homogeneous yellow liquid obtained from this reaction was distilled at a pressure of about 12 mm. A very low-boiling fraction (45–50°) condensed in the Dry Ice cooled traps and was found to consist of 10.8 g. of water and 46.2 g. of recovered allyl cyanide. Two main fractions were collected. The first (28.6 g.) boiled from 125–145°, and the second (46.0 g.) boiled in the range 145–195°. About 18 g. of tar remained in the distilling flask at the end of the distillation. Almost 20 g. of solid paraformaldehyde was recovered from the sides of the Dry Ice cooled traps. The 61.6% conversion of allyl cyanide into product was in good agreement with the results of the preliminary experiments.

The starting material for the 30-hour reaction consisted of 201 g. (3 moles) of allyl cyanide and 75 g. (2.5 moles) of paraformaldehyde. Distillation at reduced pressure of the liquid obtained in this reaction gave fractions similar to those of the 4-hour reaction. In addition to the 40% of tar remaining after distillation, the product consisted of 15.5% of the lower-boiling fraction and 44.5% of the higher-boiling fraction. The conversion of allyl cyanide into product in this reaction was 83.9%.

Examination of Higher Boiling Product.—The higher-boiling product from the 4-hour reaction at 150° was redistilled, b.p. 141–144° (2–3 mm.), n^{25}_D 1.5012. White crystals formed when the solution was cooled. They were recrystallized twice from an ethanol–water mixture, m.p. 54.5°. The compound was soluble in absolute ethanol, benzene, dioxane, ether and acetone and insoluble in water and petroleum ether. In acetone solution it rapidly decolorized a dilute solution of potassium permanganate.

Anal. Calcd. for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71; mol. wt., 158.2. Found: C, 75.84; H, 6.46; N, 17.84; mol. wt. (cryoscopic in benzene), 154.

Hydrolysis of Dimer of Cyanobutadiene.—Five grams of the dimer of cyanobutadiene was refluxed with 40 cc. of 10% sodium hydroxide for 6 hours by which time ammonia ceased to be evolved. The solution was twice extracted with ether to remove unreacted nitrile and was then acidified with concentrated sulfuric acid. Removed by filtration and dried at 100°, the tan colored crude acid weighed 2.2 g. Purification by sublimation at 215° (4 mm.) produced 1.8 g. of unsaturated acid, m.p. 238° (lit.[7] 236°). The acid was soluble in ethanol and hot water and slightly soluble in ether and benzene. It decolorized potassium permanganate in 95% ethanol.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; N, 6.17; neut. equiv., 98.1. Found: C, 61.00; H, 6.16; neut. equiv., 98.5, 98.9, 98.9.

Quantitative Hydrogenation of the Unsaturated Acid.—The amount of unsaturation was determined by the catalytic hydrogenation of the acid at atmospheric pressure using 10% palladium-on-charcoal catalyst. The 0.1440-g. sample of acid dissolved in about 30 cc. of 95% ethanol absorbed 33 cc. of hydrogen, corrected to standard conditions. The first 15 cc. was rapidly absorbed, the rest was added more slowly. This quantity of hydrogen corresponds to 1.98 moles of hydrogen per mole of $C_{10}H_{12}O_4$.

The catalyst was removed by filtration and the solvent by distillation. The recovered acid was purified by sublimation at 160° (1 mm.) to produce about 80 mg. of a previously-unreported saturated acid, m.p. 188°.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.06. Found: C, 60.13; N, 8.01.

Dehydrogenation of Unsaturated Acid.—A 0.5550-g. portion of the unsaturated acid was mixed with 0.10 g. of 10% palladium-on-charcoal catalyst and 0.01 g. of copper chromite catalyst in a Pyrex test-tube. This test-tube was connected to a gasometer through a tube filled with soda lime as an absorbent for carbon dioxide. The test-tube was heated slowly on a Woods metal-bath from 200 to 295°. After an hour-and-a-half no more gas was evolved and the system was allowed to come to equilibrium at room temperature. A total of 69.5 cc. of gas, corrected to standard conditions, was collected in the gasometer. This was 5.0 cc. more than required for the evolution of one mole of hydrogen per mole of unsaturated acid and was probably caused by the presence of unabsorbed carbon dioxide.

The black residue from the dehydrogenation was dissolved in ether and the catalysts were removed by filtration. When the ether was evaporated, an amorphous mass remained. Sublimation of this material at 100° (5 mm.) produced about 0.3 g. of white crystals which were recrystallized from ethanol–water, m.p. 112°. A mixed melting point with authentic *p*-ethylbenzoic acid (preparation given below) showed no depression.

Preparation of *p*-Ethylbenzoic Acid.—A mixture of 3.5 g. of *p*-ethylacetophenone (b.p. 236°), 150 cc. of 5% sodium hypochlorite solution and 2 g. of sodium hydroxide was heated at 70° with vigorous stirring for 1.5 hours. Concentrated sodium bisulfite solution was added to the cooled reaction mixture until potassium iodide test paper was no longer colored brown by the resulting solution. The solution was made strongly acid by the addition of concentrated hydrochloric acid and the *p*-ethylbenzoic acid was removed by filtration. Recrystallized twice from water it melted sharply at 112° (lit. 110–111°[15] and 112–113°[16]).

Examination of Lower-Boiling Product.—The lower-boiling product from the 4-hour reaction at 150° was redistilled, the record of this distillation is given in Table II. A

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(15) R. Fittig and J. Konig, *Ann.*, **144**, 290 (1867).

(16) H. Aschenbrandt, *ibid.*, **216**, 218 (1882).

portion of fraction number 4, $n^{25}\mathrm{D}$ 1.4642, $d^{25}{}_4$ 1.008, was taken for further examination. It was a clear, colorless liquid with almost no odor and was soluble in water, absolute methanol, chloroform, benzene and ether and insoluble in petroleum ether and carbon tetrachloride. It gave a positive reaction when treated with ceric nitrate reagent and was found to decolorize dilute potassium permanganate solution and bromine in carbon tetrachloride.

Anal. Calcd. for C_6H_7ON: C, 61.83; H, 7.27; N, 14.43. Found: C, 61.72; H, 7.17; N, 14.37.

Preparation of the *p*-Nitrobenzoate of the Unsaturated Hydroxynitrile.—A mixture of 300 mg. of the hydroxynitrile and a slight excess of *p*-nitrobenzoyl chloride was heated over a flame. First, an homogeneous liquid was obtained; then gas was evolved and a solid formed. This mixture was poured into 25 cc. of water and the solid was collected and broken into small pieces. After being stirred with 10 cc. of 5% sodium carbonate solution it was filtered, washed with water, and recrystallized three times from ethanol-water. A 30% yield of slightly yellow needles, m.p. 118°, was obtained.

Anal. Calcd. for $C_{12}H_{10}N_2O_4$: C, 58.53; H, 4.09; N, 11.39. Found: C, 58.60; H, 3.80; N, 11.20.

Reduction of the Unsaturated Nitrile.—An 8.1-g. portion of the nitrile (from combined fractions 2, 3 and 4 of distillation shown in Table II) was dissolved in 90 cc. of 95% ethanol and catalytically hydrogenated using 0.10 g. of 10% palladium-on-charcoal as catalyst. The initial hydrogen pressure was 60 pounds per square inch. The calculated amount of hydrogen was absorbed within 40 minutes. The catalyst was removed by filtration and the solvent by distillation. The residue on distillation at reduced pressure gave 7.1 g. of saturated hydroxynitrile, b.p. 69–71° (0.30 mm.), $n^{25}\mathrm{D}$ 1.4302, $d^{25}{}_4$ 0.973.

Anal. Calcd. for C_6H_9ON: C, 60.59; H, 9.15; N, 14.14. Found: C, 60.51; H, 9.28; N, 14.53.

Preparation of the *p*-Nitrobenzoate of the Saturated Hydroxynitrile.—The method used for the preparation of the same derivative of the unsaturated hydroxynitrile was again employed. A 30% yield of white crystals, m.p. 71.5° after three recrystallizations from ethanol-water, was produced.

Anal. Calcd. for $C_{12}H_{12}O_4N_2$: C, 58.06; H, 4.88; N, 11.29. Found: C, 58.13; H, 5.25; N, 11.36.

Preparation of Tetramethylene Cyanohydrin.—A mixture of 33 g. (0.5 mole) of potassium cyanide and 22 g. (0.2 mole) of tetramethylene chlorohydrin in 200 cc. of 70% ethanol was heated at reflux temperature for 12 hours. Most of the solvent was removed by distillation and the remaining material was extracted three times with 100-cc. portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate, filtered and the ether was removed by distillation. Distillation of the residue at reduced pressure produced 3.5 g. of colorless liquid, b.p. 77–78° (0.35 mm.), $n^{25}\mathrm{D}$ 1.4360, $d^{25}{}_4$ 0.977.

Anal. Calcd. for C_6H_9ON: C, 60.59; H, 9.15; N, 14.14. Found: C, 60.43; H, 9.21; N, 14.73.

Preparation of the *p*-Nitrobenzoate of Tetramethylene Cyanohydrin.—After three attempts by the method described above, about a 20% yield of white crystals was produced. After five recrystallizations from ethanol–water the derivative melted sharply at 49°.

Anal. Calcd. for $C_{12}H_{12}O_4N_2$: C, 58.06; H, 4.88; N, 11.29. Found: C, 57.90; H, 4.97; N, 11.30.

Conversion to δ-Bromovaleric Acid.—A mixture of 1.5 g. of the tetramethylene cyanohydrin and 10 cc. of 48% hydrobromic acid was heated at reflux temperature for 20 hours in a test-tube fitted with a cold-finger condenser. During the last 10 hours gaseous hydrogen bromide was bubbled through the mixture from a capillary tube which extended to the bottom of the test-tube. At the end of this time the mixture was made alkaline by the addition of sodium hydroxide and was twice extracted with 15-cc. portions of ether to remove unconverted nitrile. The solution was made strongly acid by the addition of concentrated sulfuric acid and was extracted five times with 15-cc. portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate, filtered, and the ether removed by distillation. The remaining liquid solidified when cooled. After being placed on a porous clay plate in a desiccator for a day, the remaining white crystals melted at 38–39° (lit.[17] 39°).

Hydrolysis of the Saturated Hydroxynitrile.—A 9.0-g. portion of saturated hydroxynitrile (V) was heated at reflux temperature with 40 cc. of 20% sodium hydroxide for 7 hours. At the end of this time no more ammonia was evolved. The solution was extracted three times with 25-cc. portions of ether to remove unconverted nitrile. The solution was made acid by the addition of 50% sulfuric acid and was extracted five times with 30-cc. portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate, filtered, and the ether was removed by distillation. Distillation of the residue at reduced pressure gave two distinct fractions. The first fraction (1.7 g.) distilled at 40–41° (0.25 mm.), the second (3.1 g.) distilled from 102–104° (0.25 mm.). Both fractions had an overpowering odor reminiscent of butyric acid.

The lower-boiling acid, b.p. 40–41° (0.25 mm.), $n^{25}\mathrm{D}$ 1.4332, $d^{25}{}_4$ 0.991, m.p. −16 to −15°, and neutralization equivalent 103, was identical with α-ethylacrylic acid. The literature[10] records m.p. −16° for this acid, and the calculated neutralization equivalent is 100.

The higher-boiling acid, b.p. 102–104° (0.25 mm.), $n^{25}\mathrm{D}$ 1.4458, $d^{25}{}_4$ 1.116 and neutralization equivalent 121, was identical with α-ethylhydracrylic acid. The calculated neutralization equivalent for this acid is 118. In accord with its description in the literature[11] this acid was a heavy sirupy liquid which could not be induced to crystallize, even when cooled to −40°.

Preparation of α-Ethylacrylamide.—A mixture of 1 cc. of α-ethylacrylic acid and 3 cc. of thionyl chloride was heated at reflux temperature for 30 minutes. The mixture was cooled and poured slowly into 10 cc. of liquid ammonia. After the excess ammonia had evaporated the remaining solid was recrystallized three times from dilute ethanol and melted at 83° (lit.[10] 83.5–84°).

Preparation of the Phenylhydrazide of α-Ethylacrylic Acid.—The method of Blaise[11] was employed in this preparation. Equal quantities of the acid and freshly-distilled phenylhydrazine were mixed and gently warmed. The solid salt which formed was removed and heated at about 150° for 30 minutes to drive off water. The resulting derivative was recrystallized from dilute ethanol and melted at 77° (lit.[10] 77°).

Preparation of the Phenylurethan of α-Ethylhydracrylic Acid.—A mixture of 2 cc. of the α-ethylhydracrylic acid and 1 cc. of freshly distilled phenyl isocyanate was heated for 15 minutes on a steam-bath. The liquid was cooled and a solid formed. Recrystallized twice from ether it melted at 122° (lit.[11] 121°).

Reaction of Allyl Cyanide with Paraformaldehyde in a Sealed Tube at 130–135° (I.V.K.).—A mixture of 34 g. (0.5 mole) of allyl cyanide and 15.5 g. of paraformaldehyde was sealed in a Pyrex tube and heated with shaking at 130–135°. The heating was stopped at the end of 24 hours and the cooled tube was broken open. The clear liquid was cooled in the refrigerator overnight to precipitate as much of the unreacted paraformaldehyde as possible. The filtered liquid was distilled first at 20 mm. to remove the unreacted allyl cyanide (13–14 g.) and then at 0.5 mm. Considerable amounts of formaldehyde were evolved and a total of 16 g. of distillate could be collected. A few grams of tarry residue was left behind. Careful redistillation at 1 mm. of the distillate yielded mainly two fractions, one (6–7 g.) boiling between 80–90° and the other (8 g.) boiling between 120–125°. The refractive index of various samples of the lower-boiling material varied from $n^{20}\mathrm{D}$ 1.4675 to $n^{20}\mathrm{D}$ 1.4800. A sample of the first cut was analyzed.

Anal. Calcd. for C_6H_7ON: C, 61.89; H, 7.26; N, 14.44. Found: C, 61.87; H, 7.27; N, 14.36.

The amount of unsaturation was determined by the catalytic hydrogenation of 0.5278 g. of the substance in about 30 cc. of 95% ethanol at atmospheric pressure in the presence of palladium–charcoal as catalyst. Absorption of 120 cc. of hydrogen, corrected to standard conditions, corresponded to 0.99 mole of hydrogen per mole of C_6H_7ON. The saturated hydroxynitrile was shown to give α-ethacrylic and α-ethylhydracrylic acids on alkaline hydrolysis. Its identity with the lower-boiling 150° product was further checked by preparation of the *p*-nitrobenzoate, which after four recrystallizations from 25% alcohol, melted at 116–118°.

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[17] A. M. Cloves, *Ann.*, **319**, 368 (1901).

Anal. Calcd. for $C_{12}H_{10}O_4N_2$: C, 58.53; H, 4.09; N, 11.39. Found: C, 58.85; H, 3.72; N, 11.30.

The Higher-Boiling Fraction of the Reaction between Allyl Cyanide and Paraformaldehyde in a Sealed Tube at 130–135°.—The high boiling fraction had the following physical constants: $n^{25}D$ 1.4945, d^{25}_4 1.055. The liquid was immiscible with water. It gave the usual tests for unsaturation. It gave off ammonia on boiling with 10% sodium hydroxide. It did not give any test for alcohol or cyclic formal.

Anal. Calcd. for $C_{12}H_{12}ON_2$: C, 68.16; H, 6.86; N, 15.90; *MR*, 48.60. Found: C, 68.90; H, 6.72; N, 15.53; *MR*, 48.72.

Its analysis was not in satisfactory agreement for the dimer (IV) but agreed for a dimer containing one mole of water. This might be the ether of the hydroxy nitrile (I or II) but further work to establish its identity was discontinued.

Isomerization of Allyl Cyanide to a Mixture of *cis*- and *trans*-Crotononitriles.—A mixture of 67 g. of allyl cyanide, 5 g. of phenol and 2 drops of 10% sodium hydroxide was heated on a steam-bath for three hours. The phenol was neutralized with dilute sodium hydroxide. The organic layer was separated, dried over anhydrous sodium sulfate and distilled. The fraction boiling above 107° (60 g.) was collected. This mixture of the two geometrical isomers of crotononitrile had a refractive index $n^{20}D$ 1.4200. The last portion distilling at 119°, which was probably mainly *trans*-crotononitrile, showed $n^{20}D$ 1.4218. The values reported in the literature for the *cis*- and *trans*-isomers are $n^{20}D$ 1.4162 and $n^{20}D$ 1.4216, respectively.

Reaction of Crotononitrile with Paraformaldehyde in a Sealed Tube at 130–135°.—Thirty-four grams of the mixture of geometrical isomers and 15 g. of paraformaldehyde were heated in a sealed tube at 130–135° with shaking. After 24 hours the tube was cooled. The paraformaldehyde remained undissolved. The sealed tube was broken and liquid filtered. On distillation practically the whole of the starting material was recovered unchanged.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON]

Ring Scission During Formation of the Grignard Reagent from 3-Methyl-2-(chloromethyl)-thianaphthene. Ring Closure of *o*-(*α*-Methylallenyl)-thiophenol

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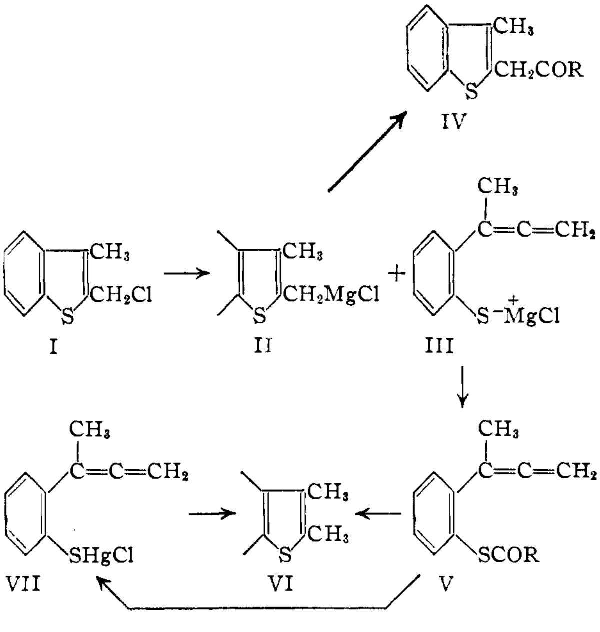
3-Methyl-2-(chloromethyl)-thianaphthene yielded in the cyclic reactor only small amounts of the Grignard reagent, detected by isolation of the expected products in reactions with carbon dioxide, acetyl chloride and ethyl chlorocarbonate. In each case the major product was derived from *o*-(*α*-methylallenyl)-thiophenol. The free thiophenol was labile, undergoing ring-closure to give 2,3-dimethylthianaphthene under a variety of mild conditions. This is the second example of an equilibrium between acyclic and aromatic anions and the first case in which the carbanion has been detected directly.

Although it had been shown that the furan ring in 2-(chloromethyl)-benzofuran was cleaved during an attempt to form the Grignard reagent,[1] the corresponding thianaphthene derivative was converted in fair yield to a normal reagent,[2] underwent abnormal reactions in the same manner as did 2-thenylmagnesium chloride.[3] Since the thianaphthene nucleus seemed stable to such cleavage and its arylmethyl reagents gave very predominantly abnormal reactions with common reactants,[2,4] the investigation has been extended to 3-methyl-2-(chloromethyl)-thianaphthene (I in Chart A) in the hope of observing products with the "isoaromatic" structure, *i.e.*, in which the reactant attacked the ortho-carbon atom bearing the methyl group. However, only traces of products corresponding to *normal* reactions of this Grignard reagent have been isolated, the mere addition of the methyl group resulting in predominant cleavage of the thiophene ring in a manner analogous to the behavior of the benzofuran derivative.

The halide (I) was best obtained preparatively by chloromethylating 3-methylthianaphthene. Its structure was proved by synthesizing it also by the action of thionyl chloride on the corresponding alcohol.[4] I reacted normally in the cyclic reactor and titration after hydrolysis indicated the presence of magnesium hydroxide equivalent to 83% conversion. However, carbonation of this solution gave only a trace of 3-methyl-2-thianaphthenylacetic acid[4] (IV, R = OH), the major product being 2,3-dimethylthianaphthene (VI). It seemed at first that simple hydrolysis of the reagent had occurred before carbonation; this was shown not to be the case by allowing the "reagent" to react with ethyl chlorocarbonate. Although a trace of the ester (IV, R = OC_2H_5) of the acetic acid was

CHART A



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(1) R. Gaertner, THIS JOURNAL, **73**, 4400 (1951).

(2) R. Gaertner, *ibid.*, **74**, 766 (1952). There was no positive evidence for ring-scission in this case, although polymeric by-products may have represented that side-reaction.

(3) R. Gaertner, *ibid.*, **73**, 3934 (1951).

(4) Concerning 3-thianaphthenylmethylmagnesium chloride, see R. Gaertner, *ibid.*, **74**, 2185 (1952).