opening the stopcock and allowing the mercury level to rise by this amount. The solution was therefore open to the atmosphere only at the instant the tube was filled, then the tube was sealed immediately. Runs were carried out using approximately 0.1 *M* methyl chloride sealed in Pyrex tubes each containing 2 ml. At suitable times tubes were removed from the thermostat, quenched in ice-water, and broken into excess silver nitrate solution, and chloride determined by the Volhard method.

The hydrolysis of methyl iodide was studied in a similar manner except that stock solutions of the compound were prepared by weighing the ice-cold liquid into water.

The reaction of methyl iodide with pyridine was studied in an apparatus consisting of a bulb of about 40-ml. capacity joined at the top through a stopcock to a length of capillary bent so that the tip pointed downwards and at the bottom to a mercury reservoir which could be raised or lowered. The reaction solution was introduced into the bulb by filling both the bulb and capillary with mercury and then lowering the reservoir after the capillary had been inserted in the solution. The bulb could be filled quite rapidly by suction in this way. Pyridine and methyl iodide solutions were prepared by weighing into 50-ml. volumetric flasks and making up to that mark with light or heavy water. The initial concentration of methyl iodide was assumed to equal the concentration of iodide found after ten or more half-lives had elapsed. The solutions to be used were warmed to the temperature at which the reaction was to be studied, mixed rapidly, and introduced into the reaction vessel, the bulb of which was immersed in a thermostat. The stopcock was closed and the mercury reservoir raised to prevent loss of methyl iodide during the course of the run. About 2.5 ml. was run out at intervals by opening the stopcock and 2 ml. immediately pipetted into 5 ml. of standard silver nitrate solution which was back-titrated with ammonium thiocyanate using ferric alum indicator. Although methyl iodide reacts with silver nitrate,[11] we have found that, under the conditions used, it is so slow that after 10 minutes the titration with thiocyanate has not altered to any appreciable extent.

(11) Moelwyn-Hughes, ref. 2.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

Vinylidene Cyanide. VI. The Aluminum Chloride Catalyzed Reaction with *t*-Alkanes

BY J. C. WESTFAHL AND T. L. GRESHAM

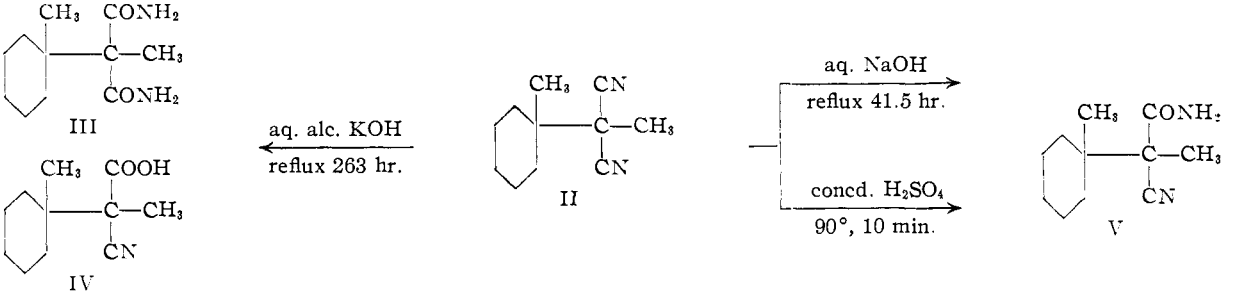
RECEIVED JULY 19, 1954

Vinylidene cyanide reacts, in the presence of two equivalents of anhydrous aluminum chloride, with methylcyclohexane to give 1-methylcyclohexyl-(methyl)-malononitrile. The structure of this substance was proved by degradation and synthesis of a degradation product. Reaction with isopentane gave a product which has been assigned the structure *t*-amyl-(methyl)-malononitrile.

As a continuation of the study of the reactions of vinylidene cyanide (I),[1] the reaction of I with *t*-alkanes was studied. This paper reports the synthesis of two *t*-alkyl(methyl)-malononitriles and their structural study.

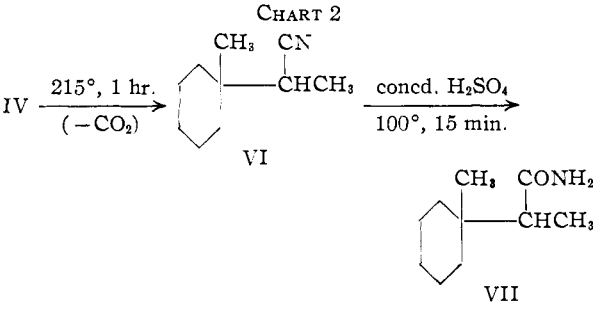
Addition of a solution of equimolar amounts of I and methylcyclohexane in *sym*-tetrachloroethane to a stirred suspension of two equivalents of anhydrous aluminum chloride in *sym*-tetrachloroethane gave a flocculent aluminum chloride complex. When the reaction mixture was stirred with an acidified ice and water mixture, hydrolysis of the complex occurred and a *sym*-tetrachloroethane solution of 1-methylcyclohexyl(methyl)-malononitrile (II) resulted. II, isolated in 42.8% yield, was a colorless liquid which was insoluble in aqueous base and which hydrolyzed with great difficulty. The major hydration and hydrolysis products are shown in Chart 1.

CHART 1



The solid acid, IV, was degraded further as shown in Chart 2. The solid amide, VII, was synthesized as shown in Chart 3.

CHART 2

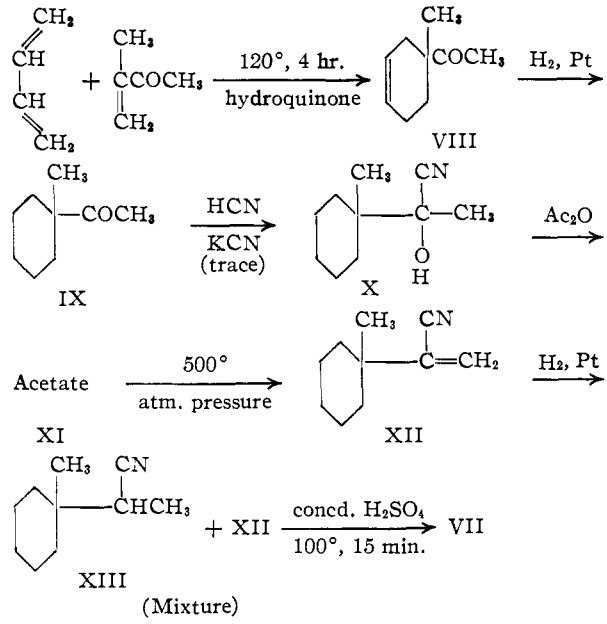


The samples of VII prepared by degradation of II and by the synthesis shown in Chart 3 were shown to be identical by comparison of their infrared absorption spectra and by the melting point of a mixture.

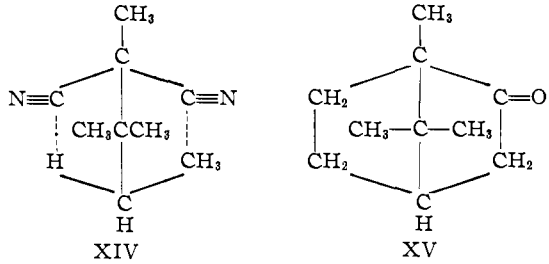
Reaction of I with isopentane gave a 29.7% yield of *t*-amyl-(methyl)-malononitrile (XIV). Pure XIV

(1) Paper V in this series, THIS JOURNAL, 76, 1076 (1954).

CHART 3



was a waxy crystalline solid with an odor virtually indistinguishable from camphor (XV). The similarity of odor may be due to a considerable structural similarity.



Structure XIV was assigned by analogy with II. Some evidence for this structure was obtained from the physical properties of XIV. The fact that the material was not soluble in aqueous base suggested that XIV was not a monosubstituted malononitrile. Comparison of the infrared absorption spectra of XIV with the spectra of II, benzyl-(methyl)-malononitrile (XVI)[2] and 2-naphthylmethyl-(methyl)-malononitrile (XVII) showed that they all exhibit a group of absorption bands between 8.5 and 9.0 μ and a single peak at 20.9 μ. The group of bands between 8.5 and 9.0 μ may be due to the quaternary carbon, whereas the band at 20.9 μ may be characteristic of a large common group such as $CH_3C(CN)_2C$.

In an attempt to increase the yield of *t*-alkyl-(methyl)-malononitriles, the aluminum chloride suspension in *sym*-tetrachloroethane was saturated with anhydrous hydrogen chloride before adding the solution of I and *t*-alkane. No significant increase in yield was observed.

Acknowledgment.—The authors are indebted to J. R. Kubik and A. K. Kuder for the analyses, to J. J. Shipman for the determination and interpretation of the infrared spectra and to W. H. Palmer for carrying out the pressure reaction.

(2) J. C. Hessler, *Am. Chem. J.*, **22**, 194 (1899).

TABLE I

$RC(CN_2)CH_3$

R = *t*-Amyl XIV	R = 1-Methylcyclohexyl II	R = Naphthylmethyl XVII	R = Benzyl XVI
	Wave length, μ[a]		
	8.3 (M)	8.3 (W)	8.4 (W)
8.6 (S)	8.5 (M)	8.7 (S)	8.7 (S)
8.9 (S)	8.9 (S)	8.9 (S)	8.9 (S)
	9.1 (M)		
20.9 (W)	20.9 (W)	20.9 (S)	20.9 (S)

[a] Qualitative intensity—S, M, W = strong, moderate, weak, respectively.

Experimental[3]

Infrared Absorption Spectra.—The spectra were obtained using the B. F. Goodrich Automatic Prism Changing Infrared Spectrophotometer. This instrument was described by J. J. Shipman at the Symposium on Molecular Structure and Spectroscopy at Ohio State University in 1951. A complete description of this instrument will be published elsewhere.

1-Methylcyclohexyl-(methyl)-malononitrile (II).—All apparatus coming in contact with I was dried by passing a current of dry air through it for 30 minutes. A solution of 49.1 g. (0.50 mole) of methylcyclohexane (Paragon Div., Matheson Co., redistilled) and 39.0 g. (0.50 mole) of I in 150 ml. of *sym*-tetrachloroethane (Distillation Products Ind., White Label grade, redistilled) was added dropwise over a 30-minute interval to a stirred suspension of 133.3 g. (1.00 mole) of anhydrous aluminum chloride (Reagent grade, anhydrous sublimed) in 250 ml. of *sym*-tetrachloroethane which was previously saturated with hydrogen chloride by bubbling the anhydrous gas into the stirred suspension for 30 minutes. The temperature during the addition was maintained at 35–40° with a cold water-bath. After the addition, the mixture was stirred without cooling for 70 minutes. The mixture was hydrolyzed by pouring it into 1 l. of ice and water containing 50 ml. of concd. hydrochloric acid and stirring. After filtering with suction to break any emulsion present, the *sym*-tetrachloroethane layer was separated. The aqueous layer was extracted twice with chloroform, the combined organic solution was washed with water and sodium bicarbonate solution, and the organic layer was dried with magnesium sulfate. After filtering, the chloroform was removed by distilling at atmospheric pressure (to 100°) and most of the *sym*-tetrachloroethane was removed at 50° (1.0 mm.) to leave 82.8 g. of brown liquid. Preliminary distillation at 1.0 mm. gave 71.6 g. of yellow distillate and a non-volatile residue. Redistillation gave a forerun consisting largely of *sym*-tetrachloroethane and colorless II boiling at 96–101° (1.0 mm.) weighing 37.8 g. (42.8%), and having $n^{25}D$ 1.4736 and d^{25}_4 0.988. The brown viscous residue weighed 14.8 g. Purer II was obtained if the crude liquid was mixed with phosphorus pentoxide (1.0 g. per 4.0 g. of crude II) and heated with occasional shaking at 130° for one hour. Distillation from the phosphorus pentoxide (1.0 mm.) and redistillation gave II of b.p. 99–99.5° (1.0 mm.) in 25.7% yield and having $n^{25}D$ 1.4751 and d^{25}_4 0.977.

Anal. Calcd. for $C_{11}H_{16}N_2$: C, 74.95; H, 9.15; N, 15.90. Found: C, 74.76, 74.77; H, 9.08, 8.93; N, 15.54, 15.65.

1-Methylcyclohexyl-(methyl)-cyanoacetamide (V).—Treatment of 5.0 ml. (4.9 g., 0.028 mole) of II with 20 ml. of concd. sulfuric acid by a standard method[4] gave 2.4 g. (44%) of crude, brown V. Two recrystallizations from benzene–hexane (Norit) gave colorless crystals of m.p. 153.5–154.2°. Further recrystallization raised the m.p. to 154.3–155°.

Anal. Calcd. for $C_{11}H_{18}N_2O$: C, 68.01; H, 9.34; N, 14.42. Found: C, 68.09; H, 9.37; N, 14.34.

Hydrolysis of II. A. Aqueous Alcoholic Potassium Hydroxide.—A solution of 10.0 g. (0.057 mole) of II, 30 g. (0.54 mole) of potassium hydroxide, 30 ml. of water and 125 ml. of ethanol was refluxed for 263 hours in a steel vessel. Ammonia was slowly evolved during the refluxing.

(3) All melting points and boiling points are uncorrected.

(4) S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945, p. 146.

Water was added and the ethanol was distilled off. Unchanged II steam distilled at the end of the distillation. The cooled distilland was acidified, shaken with ether and filtered with suction. The ether and water insoluble III weighed 1.07 g. (8.9%). Recrystallization from ethanol using Norit gave colorless crystals of m.p. 239° (Dennis[5]-Parr Apparatus).

Anal. Calcd. for $C_{11}H_{20}N_2O_2$: C, 62.23; H, 9.50; N, 13.20. Found: C, 62.53, 62.43; H, 9.58, 9.58; N, 13.10.

The filtrate was separated and the aqueous layer was extracted twice with ether. The combined ether solution was washed with water and extracted with saturated sodium bicarbonate solution until free of acid. The bicarbonate extract was washed once with ether, acidified, cooled in ice and stirred. The yellow solid acid, IV, when filtered, washed and dried weighed 6.9 g. (62.2%). Four recrystallizations from hexane–benzene gave 2.7 g. of colorless IV of m.p. 99–104.5°. Further recrystallizations from hexane–benzene failed to raise the m.p. A final recrystallization from carbon tetrachloride gave 2.2 g. of IV of m.p. 99.5–104.5°. When a bit of IV was melted, cooled and powdered, the m.p. was 103.5–104.5°.

Anal. Calcd. for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78; N, 7.17; neut. equiv., 195. Found: C, 67.20, 67.36; H, 8.78, 8.78; N, 7.15; neut. equiv., 198.

Removal of the ether from the ether solution of neutral compounds left 2.1 g. of a mixture of liquid and solid. This is probably a mixture of II, III and V.

B. **Aqueous Sodium Hydroxide.**—A mixture of 6.2 g. (0.035 mole) of II, 7.0 g. (0.17 mole) of sodium hydroxide and 70 ml. of water was refluxed for 41.5 hours during which time the insoluble II was converted to an insoluble yellow solid. The solid isolated by filtering the mixture and washing with water weighed 5.0 g. when dried. One recrystallization from ethanol–water gave colorless crystals of m.p. 149–170°. Most of the solid melted between 149 and 155°. When dissolved in hot benzene–hexane, filtered from a small amount of insoluble solid, and cooled, crystals of V of m.p. 152.3–154.3° were obtained. The m.p. of a mixture of this sample with pure V was not depressed. The impure solid of m.p. 149–170° is probably a mixture of V with a small amount of III.

From the above basic filtrate, 1.2 g. of a yellow solid acid was isolated. One recrystallization from benzene–hexane gave impure IV of m.p. 96–102.5°.

1-(1-**Methylcyclohexyl)-propionitrile (VI).**—Heating 0.73 g. (3.73 mmoles) of IV for one hour at 215° (oil-bath) gave a 78% yield of light brown. liquid VI. Distillation at atmospheric pressure gave 0.26 g. (46%) of VI boiling at 220–227° and having $n^{25}D$ 1.4631.

1-(1-**Methylcyclohexyl)-propionamide (VII).**—Treatment of 0.26 g. (1.72 mmoles) of VI with 2 ml. of concd. sulfuric acid[4] for 15 minutes at 100° gave VII as a light tan solid. Two recrystallizations from benzene–hexane gave 25 mg. of VII having m.p. 108–108.5°.

Anal. Calcd. for $C_{10}H_{19}NO$: C, 70.95; H, 11.31; N, 8.28. Found: C, 70.70, 71.03; H, 11.33, 11.45; N, 8.14, 8.12.

4-Acetyl-4-methylcyclohexene (VIII).—In a steel bomb was placed 270 g. (5.0 moles) of 1,3-butadiene (commercial, flash distilled), 126.3 g. (1.5 moles) of methyl isopropenyl ketone (Carbide and Carbon Chemicals Co.) and 6.0 g. of hydroquinone. The mixture was heated for four hours at 120° under autogenous pressure. Removal of the excess 1,3-butadiene at room temperature and 5.0 mm. left 205.7 g. of liquid. Distillation gave 119.1 g. of impure VIII at 67–70.5° (5.0 mm.) having $n^{25}D$ 1.4658. This liquid is a mixture of VIII (76.6%) and methyl isopropenyl ketone dimer[6] (2,6-dimethyloctene-1-dione-3,7) as shown by the carbonyl content of 23.26, 23.28% (Hydroxylamine Method).[7]

The semicarbazone of VIII, prepared by a standard method,[8] melted at 162.5–163.5° after two recrystallizations from ethanol–water.[9]

Anal. Calcd. for $C_{10}H_{17}N_3O$: C, 61.51; H, 8.78; N, 21.52. Found: C, 60.91, 60.84; H, 8.61, 8.72; N, 21.73, 21.71.

1-**Acetyl-1-methylcyclohexane (IX).**—A solution of 27.64 g. of impure (76.6%) VIII in 40 ml. of ethanol containing 0.1 g. of platinum oxide absorbed 0.14 mole of hydrogen in 10 minutes at room temperature and an initial pressure of 40 p.s.i.g. (Adams–Parr Hydrogenator). The combined reaction mixture from *four* of the above preparations was filtered, freed of ethanol and distilled to give 77.5 g. of impure IX boiling at 57–59° (5.0 mm.) and having $n^{25}D$ 1.4545. This liquid was a mixture of IX (90.4%) and 2,6-dimethyloctane-3,7-dione as indicated by its carbonyl content of 21.25, 21.19% (Hydroxylamine Method).[7]

The semicarbazone of IX prepared by a standard method,[8] melted at 186–186.8° after three recrystallizations from ethanol–water.

Anal. Calcd. for $C_{10}H_{19}N_3O$: C, 60.88; H, 9.71; N, 21.30. Found: C, 60.86, 60.92; H, 9.68, 9.73; N, 21.46, 21.43.

1-**Hydroxy-1-(1-methylcyclohexyl)-propionitrile (X).**—To 35 ml. (24 g., 0.89 mole) of anhydrous hydrogen cyanide and 0.33 g. (5.1 mmoles) of potassium cyanide at 0° was added dropwise with stirring 35.0 g. of IX (90.4%). The mixture was warmed to room temperature, 0.3 ml. of concd. sulfuric acid was added and the excess hydrogen cyanide was removed *in vacuo* to leave 44.7 g. of crude X.

1-**Acetoxy-1-(1-methylcyclohexyl)-propionitrile (XI).**—To 37 ml. (40 g., 0.39 mole) of acetic anhydride at 70–80° was added dropwise with stirring 41.7 g. (*ca.* 0.25 mole) of crude X. The solution was stirred for 1 hour at 70–80°, cooled to 20°, mixed with 150 ml. of water and stirred and cooled to keep the temperature below 25°. After neutralizing with aqueous sodium hydroxide, the ester was taken up in ether and dried with magnesium sulfate. After filtering, the ether was removed *in vacuo* to leave 46.59 g. of crude XI. Distillation gave 32.51 g. (68.8% based on IX) boiling at 106–117° (1.0 mm.). Redistillation gave 15.18 g. (32.2% based on IX) of colorless XI of b.p. 115–116° (1.0 mm.) and having $n^{25}D$ 1.4670 and d^{25}_4 1.026.

Anal. Calcd. for $C_{12}H_{19}NO_2$: C, 68.86; H, 9.15; N, 6.69. Found: C, 68.58, 68.60; H, 9.03, 9.12; N, 6.64, 6.63.

1-(1-**Methylcyclohexyl)-acrylonitrile (XII).**—Through a 22 mm. o.d. Pyrex tube packed with a 30-cm. layer of 6 mm. porcelain Berl saddles at 550° was passed 22.86 g. (0.1092 mole) of XI over a 31-minute interval. A gentle current of carbon dioxide was passed through the apparatus to maintain an inert atmosphere. The product condensed at 0°, weighed 22.35 g. and required 93.8% of the calculated quantity of sodium hydroxide to neutralize the acetic acid present. The product was taken up in ether, dried with magnesium sulfate, filtered and freed of ether at 50° (10 mm.) to leave 14.83 g. (91.4%) of crude XII. Distillation gave 9.19 g. (55.4%) of XII of b.p. 89.5–95° (10.0 mm.) and having $n^{25}D$ 1.4736 and d^{25}_4 0.994. The infrared absorption spectrum of distilled XII had peaks at 6.2 and 11.2 μ characteristic of $-C=CH_2$ and a peak at 4.4 μ characteristic of the nitrile group.

Hydrogenation of XII.—A solution of 8.11 g. (0.0544 mole) of XII in 70 ml. of ethanol was stirred for 30 minutes with *ca.* 5 g. of Raney nickel (Harshaw Chemical Co.) and filtered. The ethanol solution and 0.1 g. of platinum oxide were shaken with hydrogen at room temperature and an initial pressure of 40 p.s.i.g. in the Adams–Parr apparatus. After 4 hours, 75% of the theoretical pressure drop occurred and hydrogenation stopped. The catalyst was filtered and the ethanol was distilled. The residue was taken up in ether and washed three times with dilute hydrochloric acid to remove amines. After drying with magnesium sulfate, the ether was removed *in vacuo* to leave 6.59 g. of crude XIII. The crude XIII distilled largely at 223–226° (734.3 mm.). The distilled XIII had $n^{25}D$ 1.4683. This refractive index lies between that found for VI and that of the unsaturated nitrile XII. This suggested that the hydrogenation product was a mixture of XIII and XII. This was confirmed by the infrared absorption spectrum of the distilled hydrogenation product which had peaks due to $C=CH_2$. The intensity of absorption was considerably less than previously found for the unsaturated starting material XII.

Sulfuric Acid Hydration of Mixture XIII and XII.—A solution of 2.86 g. of the mixture of XIII and XII in 22 ml.

(5) L. M. Dennis and R. S. Shelton, THIS JOURNAL, **52**, 3128 (1930).

(6) German Patent 227,176; *Chem. Centr.*, **81**, II, 1421 (1910).

(7) S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 17.

(8) S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945, p. 198.

(9) The reported m.p. of 2,6-dimethyloctene-1-dione-3,7 semicarbazone is 183°, ref. 6.

of concd. sulfuric acid[4] was heated for 15 minutes at 100° and poured on 200 ml. of crushed ice. The sticky semi-solid was taken up in ether, washed with sodium bicarbonate solution and the ether solution dried with magnesium sulfate. After filtering, the ether was removed to leave 2.05 g. of crystalline VII. This amount of amide is equivalent to 1.83 g. of XIII in the mixture taken and suggested that the mixture contained at least 64% of XIII. Repeated recrystallization of the crude VII from hexane–benzene followed by sublimation *in vacuo* gave colorless VII of m.p. 107.5–108.5°.

Anal. Calcd. for $C_{10}H_{19}NO$: C, 70.95; H, 11.31; N, 8.28. Found: C, 70.91, 70.88; H, 11.22, 11.30; N, 8.25.

The infrared absorption spectra of this sample of VII and the sample of VII derived from II were identical. The melting point of a mixture of the two samples of VII was not depressed.

t-Amyl-(methyl)-malononitrile (XIV).—A solution of 36.1 g. (58.2 ml., 0.5 mole) of isopentane (Phillips Commercial grade, dried with phosphorus pentoxide) and 41.5 g. (41.8 ml., 0.5 mole) of 94% I in 150 ml. of *sym*-tetrachloroethane was added dropwise over 47 minutes to a stirred suspension of 133.3 g. (1.00 mole) of anhydrous aluminum chloride in 250 ml. of *sym*-tetrachloroethane at 40°. Occasional cooling was required to keep the temperature below 40°. The reaction mixture was stirred without heating or cooling for a further 30 minutes and hydrolyzed as given for the preparation of II. The hydrolysis mixture was worked up as previously described to give 76.8 g. of crude XIV (freed of solvent at 60° and 4 mm.). A preliminary distillation gave 61.0 g. of colorless, impure XIV (to 80° at 1.8 mm.) and a brown residue weighing 12.5 g. Fractionation gave 30.17 g. of forerun to 70° (2.0 mm.) and a XIV fraction of 22.32 g. (29.7%) of b.p. 70–71° (2.0 mm.). The residue weighed 2.97 g. The XIV of b.p. 70–71° (2.0 mm.) was cooled in ice and filtered with suction to give 8.89 g. of waxy crystals of XIV having a final melting temperature of 41°. The solid was recrystallized from methanol at −78°, dried *in vacuo* and sublimed at 35° (0.02 mm.) to give pure XIV having a final melting temperature of 44.4°.

Anal. Calcd. for $C_9H_{14}N_2$: C, 71.96; H, 9.39; N, 18.66. Found: C, 71.58, 71.56; H, 9.34, 9.50; N, 18.73, 18.64.

t-Amyl-(methyl)-cyanoacetamide (XIX).—Treatment of XIV with concd. sulfuric acid by a standard procedure[4] gave crude XIX. Four recrystallizations from benzene–hexane gave XIX of m.p. 123–124°.

Anal. Calcd. for $C_9H_{16}N_2O$: C, 64.25; H, 9.59; N, 16.66. Found: C, 64.07, 64.04; H, 9.58, 9.56; N, 16.76, 16.75.

Benzyl-(methyl)-malononitrile (XVI).—Reaction of the sodium derivative of benzylmalononitrile in ethanol (Commercial, anhydrous) with methyl iodide by the method of Hessler[10] gave a liquid distilling at 102–106° (0.4 mm.) which partly crystallized on standing. Hessler obtained pure monoimino ester of XVI as a liquid. The mixture of b.p. 102–106° (0.4 mm.) gave a precipitate of ammonium chloride when concd. hydrochloric acid was added to its ethanol solution. This test[10] indicated the presence of the imino ester of XVI. When 5.0 g. of the mixture was refluxed gently, 0.6 g. of ethanol distilled. This corresponded to 56.6% of imino ester in the mixture. The crystalline residue was recrystallized twice from ethanol and once from ethanol–water (Norit) to give XVI of m.p. 94.5–95.5°.[11]

Anal. Calcd. for $C_{11}H_{10}N_2$: N, 16.46. Found: N, 16.41.

2-Naphthylmethyl-(methyl)-malononitrile (XVII).—To a sodium ethoxide solution prepared from 1.8 g. (0.078 atom) of sodium and 40 ml. of ethanol (Commercial anhydrous) was added 16.1 g. (0.079 mole) of 2-naphthylmethylmalononitrile.[1] The mixture was heated to near the b.p. and a solution of 4.9 ml. (11.2 g., 0.079 mole) of methyl iodide in 10 ml. of ethanol was added dropwise over a 5-minute interval. When the spontaneous reaction was over the mixture was refluxed for 30 minutes at which time the mixture was neutral. The ethanol was distilled off, water was added, and the yellow liquid was taken up in ether and dried with magnesium sulfate. After filtering, the ether was removed to leave 20.0 g. of yellow viscous liquid. This liquid contained the monoimino ester of XVII as shown by the precipitation of ammonium chloride when concd. hydrochloric acid was added to an ethanol solution of the liquid.[10] The imino ester present was decomposed by boiling the liquid gently until ethanol no longer distilled. Volume of ethanol distillate was 2.9 ml. The brown residue of XVII weighed 16.6 g. (96.5%) and solidified when cool. One recrystallization from ethanol gave 12.7 g. (73.8%) of light tan XVII of m.p. 128–129.5°. Further recrystallization gave colorless XVII of m.p. 129.2–130°.

Anal. Calcd. for $C_{15}H_{12}N_2$: N, 12.72. Found: N, 12.70.

(10) Reference 2, p. 195.

(11) J. C. Hessler, ref. 2, p. 194, reports m.p. 94–95° for XVI.

BRECKSVILLE, OHIO

[CONTRIBUTION NO. 1922 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Mercury-catalyzed Addition of Acetic Acid to 3-Hexyne[1]

BY HENRY LEMAIRE[2a] AND HOWARD J. LUCAS[2b]

RECEIVED JULY 19, 1954

An equimolar solution of perchloric acid and mercuric acetate in anhydrous acetic acid exhibits a very rapid drop in acidity in the presence of 3-hexyne. This is due to the formation of a stable, reactive complex ion, 3-hexyneacetoxymercurinium ion, $C_6H_{10}\cdot HgOAc^+$. There is also a moderately rapid drop in unsaturation, which soon tapers off to a slow change. The tapering off is believed to be due to a reaction of mercuric ion with a product of the reaction, presumably 3-acetoxy-3-hexene. Since the initial drop in unsaturation is proportional to the concentration of the complex ion rather than to the concentration of 3-hexyne, the rate-determining step is the reaction of this ion, either by solvolysis or by rearrangement, to form 3-acetoxy-3-hexene. Excess perchloric acid causes a marked increase in the rate of change of unsaturation. Excess mercuric acetate has a much smaller effect. Structures are assigned to intermediate complex mercurinium ions.

Usually the addition of reagents to the carbon-carbon triple bond requires a combination of a mercuric salt and a strong acid as catalyst. One kinetic study of this type has been reported on acetylene.[3] The present investigation was undertaken to extend information to disubstituted acetylenes. The addition of acetic acid to 3-hexyne yields 3-acetoxy-3-hexene, as shown by eq. 1.

$$C_2H_5—C\equiv C—C_2H_5 + HOAc \longrightarrow C_2H_5—CH=C(OAc)—C_2H_5 \quad (1)$$

Preparation of Materials.—The preparation of 3-hexyne from ethyl bromide and sodium acetylide

(1) Presented before the Division of Organic Chemistry, 119th Meeting of the American Chemical Society, Cleveland, Ohio, April 11, 1951.

(2) (a) Lever Brothers Research Center, Edgewater, N. J. (b) To whom requests for reprints should be sent.

(3) R. H. Frieman, E. R. Kennedy and H. J. Lucas, THIS JOURNAL, **59**, 722 (1937). A mechanism of addition to the triple bond has been proposed by G. F. Hennion, R. R. Vogt and J. A. Nieuwland, *J. Org. Chem.*, **1**, 159 (1936).