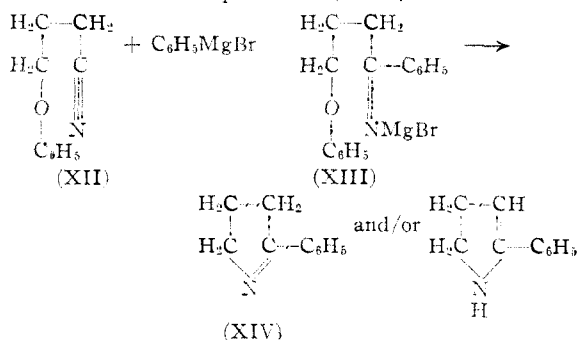


tyronitrile (IV) will react^{1,2} with phenylmagnesium bromide to form an addition product (X), which, when decomposed in liquid ammonia, will give 2-phenyl-4-methylpyrroline (XI). The reaction probably takes place essentially as shown. Whether the pyrroline (XI) should be assigned the Δ^1 or Δ^2 structure has not been ascertained. This pyrroline was synthesized by Sonn¹³ by other methods.

2-Phenylpyrroline (XIV) may be obtained in a small yield by the action of phenylmagnesium bromide on γ -phenoxybutyronitrile (phenyl- γ -cyanopropyl ether) (XII) followed by the heating of the addition product (XIII) in tetralin.^{1b}



In a similar way, 2,3-diphenylpyrroline (XV)^{1b} was obtained^{1b} from α -phenyl- γ -ethoxybutyronitrile (IX). This new method of preparing pyrrolines is a further extension of our γ -chlorobutyronitrile method^{4a} as modified by Craig, Bulbrook and Hixon.¹⁴

III. Other Products from Dichloroisobutane.

--With the expectation of preparing other ether nitriles in addition to (IX) and (XII) for the synthesis of pyrrolines, three chloro-substituted ethers were prepared^{1b} by the reaction of 1,3-dichloro-2-methylpropane with the sodium salts of phenol, *o*-cresol, and *p*-*t*-amyl phenol. Two of these compounds were reported by a somewhat different method¹⁵ after our original work was done.

The small yield of γ -chloro- β -methylbutyronitrile (IV) originally obtained by Stehr^{1a} led to the investigation^{1b} of the effect of cuprous cyanide on the Eastman 1,3-dichloroisobutane.⁵ This gave a liquid chloronitrile (XVI) and some high boiling material. Although (XVI) gave about the same boiling point as (IV) it was soon established that it was a different compound. Subsequently the product was identified¹⁶ as 4-chloro- β -methyl- β -butenenitrile, some of whose properties are reported herein.

Experimental

β -Methyl- γ -chlorobutyronitrile (IV).--To a solution of 294 g. (6 moles) of sodium cyanide in 300 cc. of water under

(13) Sonn, *Ber.*, **72**, 2150 (1939).

(14) Craig, Bulbrook and Hixon, *This Journal*, **53**, 1831 (1931).

(15) Coleman and Moore (to Dow Chemical Company), U. S. Patent 2,159,364. (*C. A.*, **33**, 6877 (1939)).

(16) Aran Mooradian, Thesis, R. P. I., 1941; communication in preparation for *This Journal*.

reflux on a steam-bath a solution of 254 g. (2 moles) of redistilled 1,3-dichloro-2-methylpropane (E. K. C. 1,3-dichloroisobutane)⁶ in 800 cc. of 95% alcohol was added in the course of an hour and the refluxing continued for about twenty-four hours. The solution was then filtered. The solid thus separated was washed with a total of 250 cc. of chloroform, giving extract A. The filtrate was distilled from a Claisen-Vigreux flask under diminished pressure until most of the alcohol had been removed, diluted with 700 cc. of water, and extracted three times with a second 250-cc. portion of chloroform. This extract was mixed with (A), dried and distilled similarly, first at atmospheric pressure and then *in vacuo* whereby 43.6 g. (20.4% yield) of chloronitrile, b. p. 82-83° at 16 mm., was obtained together with an 11.5% yield (20.3 g.) of β -methylglutaronitrile, b. p. 133-137° at the same pressure. In the original work of Stehr,^{1a} wherein the dichloride and cyanide were used in equimolar proportions, yields of only 4-10% of (IV) were obtained, and these were not improved by the use of methyl alcohol, dioxane and potassium iodide.

Another run, wherein 6 moles of sodium cyanide and 2.5 moles of dichloride were subjected to a somewhat different technique, gave a 26.2% yield (75 g.) of (IV). A further run with 12 moles of cyanide, 5 moles of dichloride and the procedure described above, gave a 21.2% yield of (IV) (115 g.) and 9.2% of the dicyanide (40 g.).

The β -methyl- γ -chlorobutyronitrile obtained above,² whose odor indicated the presence of isonitrile, possessed a density, d^{20}_4 , of 1.012, and an index of refraction, n^{20}_D , of 1.44255.

*Anal.*¹⁷ Calcd. for $\text{C}_5\text{H}_9\text{NCl}$: C, 51.06; H, 6.86; N, 11.91; Cl, 30.17; *MRb*, 29.90. Found: C, 50.45; H, 6.85; N, 11.74; Cl, 30.54; *MRb*, 29.93.

β -Methylglutaronitrile (II).-- β -Methylglutaronitrile was obtained as a by-product as described above.

Anal. Calcd. for $\text{C}_6\text{H}_9\text{N}_2$: N, 25.92. Found: N, 25.15, 25.35.

Alkaline Saponification of β -Methylglutaronitrile (II).--Following the method of Blaise and Gault,⁹ a 5-g. portion of (II) was boiled with a solution of 20 g. of sodium hydroxide in about 90 cc. of water and 40 cc. of ethanol for six hours. The alcohol and part of the water were removed by distillation, the residue cooled and extracted with ether. The aqueous phase was boiled, cooled, acidified with concentrated hydrochloric acid, saturated with salt and extracted with ether. The ethereal solution of β -methylglutamic acid (I) was dried over sodium sulfate, filtered, and evaporated on a steam-bath. Since vigorous scratching and cooling failed to produce the expected crystals, the residue was diluted with 50 cc. of ether and treated with phosphorus pentoxide. When little further reaction with the desiccating agent was observed, the solution was filtered, evaporated on a steam-bath, giving a small amount (less than 1 g.) of mushy crystals after vigorous scratching and a few hours standing at 0°. This product was dissolved in a small amount of 10% hydrochloric acid, treated with decolorizing charcoal, seeded and allowed to crystallize. A further recrystallization gave acid (I) of m. p. 84-85°. The best reported m. p. for β -methylglutamic acid is 85-86°.

Acid Hydrolysis.--Five grams of (II) was refluxed for eight hours with 50 cc. of concentrated hydrochloric acid and 100 cc. of water. The mixture was cooled, saturated with salt, and extracted with ether. The ether extract was dried with phosphorus pentoxide, filtered and evaporated. The residue of 5 g. was boiled with 5 cc. of 10% hydrochloric acid, cooled, and seeded with a crystal of (I). On standing in the ice box at 0° for several hours, the acid (I) was obtained. Two more recrystallizations from 10% hydrochloric acid gave 1.7 g. of (I) of m. p. 84.5-85.5°.

γ -Amino- β -methylbutyric Acid (V).--A mixture of 90 g. of potassium phthalimide and 53 g. of β -methyl- γ -chlorobutyronitrile was heated under an air condenser in an oil-

(17) All analytical data reported herein are micro or semi-micro values.

bath at 170–180° for four and a half hours. The resulting phthalimidonitrile was then extracted with hot water until chloride-free, dissolved in 126 cc. of concd. sulfuric acid with gentle heating and then boiled for three hours with 200 cc. of water. After the hydrolysate had been allowed to stand overnight, the crystalline phthalic acid (45 g.) was removed, the filtrate diluted to a liter and neutralized with about 495 g. of barium carbonate. The mixture was evaporated to dryness on a steam-bath, when the addition of a liter of water and the evaporation were twice repeated. Here the barium sulfate was collected on a filter, washed with hot water, the filtrate evaporated to 200 cc., decolorized with charcoal, filtered and concentrated to a thick syrup, when 450 cc. of absolute alcohol was added, which led to the separation of white crystals after a two day stand in a refrigerator. The crystalline acid was collected on a filter, washed with a little absolute alcohol, giving 12 g. of product. By the evaporation of the mother liquor followed by the addition of more alcohol and a several days stand at 0°, an additional 4-g. portion of acid was obtained. A repetition of this process gave a further 4-g. yield, and thereby a total yield of 20 g., an approximately 40% yield.

Since the crude acid contained inorganic material and did not melt sharply, it was dissolved in methanol and crystallized by the addition of ether, giving a product of m. p. 174° although the m. p. varies a little with the rate of heating. The acid is very soluble in water, moderately so in methyl alcohol, less soluble in ethanol and practically insoluble in ether. When kept in an oven at 80° for several hours, the original white compound became brown. Likewise, during storage for a year in a glass stoppered bottle, a brownish-yellow color developed slowly on the surface of the product.

Anal. Calcd. for $C_6H_{11}O_2N$: C, 51.30; H, 9.40; N, 11.97. Found: C, 50.05; H, 9.17; N, 11.55.

2-Methylcyclopropanecarbonitrile (VI).²—A 1-liter, three-necked, round-bottom flask was fitted with an efficient mechanical stirrer which operated through a mercury seal. A lime tower was attached to the flask, about 500 cc. of liquid ammonia and 0.3 g. of hydrated ferric chloride were introduced, the stirrer was started, and 1 g. of sodium in small pieces was added. As soon as the initial deep blue color had faded to gray, a further quantity of 5 g. of sodium in small pieces was introduced.¹⁸ At this point a solution of 0.2 mole (23.8 g.) of β -methyl- γ -chlorobutyronitrile in 50 cc. of dry ether was run into the sodium amide mixture through a separatory funnel. A total of about 250 cc. of dry ether was added from time to time during the course of an hour and a half while the ammonia was evaporating. Here 2 g. of ammonium chloride was added, the mixture was allowed to stand for two to three hours or until practically all of the ammonia had evaporated, the ethereal solution filtered through a Büchner funnel into a suction flask and concentrated by distillation in a 50 cc. Claisen-Vigreux flask. For this purpose the ethereal solution was run into the flask in small portions while the flask was warmed in a water-bath. Finally, a special receiver, cooled in ice-salt solution, was attached as shown in Fig. 1, and the nitrile was distilled under diminished pressure: The nitrile boiled from 44–45° at 16 mm. and weighed 12.9 g. Redistillation at 754 mm. gave 9.4 g. of product of b. p. 143–146°, a yield of 57.3%.

A second run, carried out as before, gave 9.9 g. or 60.4%. The combined material was redistilled through a 1 × 60 cm. Hempel column, whereby 15.1 g. of nitrile of b. p. 144.5–145.5° at 759 mm. was obtained.

In order to ascertain whether this product contained ethylenic nitrile, 0.2 g. was treated with 3 cc. of 5% sodium carbonate and a drop of 2% potassium permanganate. Since the permanganate color persisted for some time, the absence of ethylenic isomer may be inferred.

The 2-methylcyclopropanecarbonitrile is a mobile colorless liquid with a penetrating odor similar to cyclopropanecarbonitrile and somewhat similar to that of ace-

tone. It possessed a density, d^{20}_4 , of 0.8732 and a refractive index, n^{20}_D of 1.42588, which corresponded to a molecular refractivity of 23.78.

Anal. Calcd. for C_5H_7N : C, 74.03; H, 8.70; N, 17.27; mol. wt., 81. Found: C, 73.54, 73.63; H, 8.88, 8.82; N, 17.47, 17.54; mol. wt. (Rast), 80, 83.

Table I summarizes the observed and calculated values for the molecular refractivities of several cyanocyclopropanes. The calculated values are based on the usual Auwers and Eisenlohr refractivities, including the value 5.459 for the CN group and Östling's¹⁹ value of 0.7 for the exaltation produced by the cyclopropane ring. They do not include any corrections for the presence of the alkyl and aryl groups, such as Le Bas'²⁰ value of 0.39 for the methyl group, which appears to be too large in the light of these data.

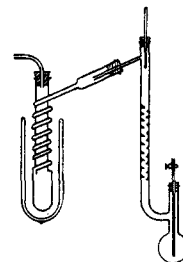


Fig. 1.

TABLE I

-Carbonitrile derivative	MR _D		Exaltation
	Obs.	Calcd.	
Cyclopropane-	19.08	18.91	0.17
1-Methylcyclopropane- ¹¹	23.67	23.53	0.14
2-Methylcyclopropane- ^{2,21}	23.78	23.53	0.25
1-Phenylcyclopropane- ^{4b,22}	43.21	43.01	0.20
1-Phenyl-2-methylcyclopropane- ^{4b}	48.03	47.63	0.40
1-Phenyl-2-ethylcyclopropane- ^{4a}	52.70	52.25	0.45

Amide of 2-Methylcyclopropanecarboxylic Acid (VII).²—A mixture of approximately 1.5 g. of nitrile (VI), 20 cc. of water, 20 cc. of alcohol and 10 g. of sodium hydroxide was refluxed for nine hours. Ammonia was evolved slowly but steadily over this period and was still coming off when the boiling was discontinued. The solution was freed of alcohol and part of the water by distillation and then extracted with ether. The aqueous phase was boiled, cooled, acidified with hydrochloric acid and the liberated acid (VIII) removed by extraction with three 50-cc. portions of ether. The combined ethereal extract was dried over sodium sulfate and the filtered solution evaporated to a volume of about 3 cc. This impure acid residue was treated carefully with 15 cc. of thionyl chloride,²³ the mixture refluxed for thirty minutes, and then distilled up to a temperature of 80° in order to remove the excess thionyl chloride.

Approximately one-fourth of the residue was treated with an excess of aqueous ammonia, giving a mush of ammonium chloride crystals. This salt was collected on a filter and the filtrate evaporated on the steam-bath. Benzene was added and boiled down to a small volume in order to remove water. The addition of ligroin followed by cooling gave a precipitate of amide (VII). Treatment with decolorizing carbon and a single crystallization gave a solid of m. p. 99–100°, which m. p. was unchanged by a recrystallization.²⁴

The remaining three-fourths of the acid chloride was diluted with benzene and treated with anhydrous ammonia until no further amount of ammonium chloride was

(19) Östling, *J. Chem. Soc.*, 101, 457 (1912).

(20) Le Bas, *Trans. Faraday Soc.*, 13, 53 (1917).

(21) For the corresponding acid Kishner (ref. 11) reports MR_D obs. 25.36 vs. MR_D calcd. of 25.33, an exaltation of 0.03.

(22) The late Professor K. von Auwers, in a private communication (1932), called our attention to two typographical errors in the reported properties of 1-phenylcyclopropanecarbonitrile.^{4b} The corrected values are d^{20}_4 , 1.0366; n^{20}_D , 1.5386, which give MR_D, 43.21 (J. B. C.).

(23) Purified as described in Fieser, "Experiments in Organic Chemistry," 1935, p. 339.

(24) Kishner, ref. 11, reports a m. p. of 99.5–100° for 2-methylcyclopropanecarboxamide prepared by another method.

(18) Vaughn, Vogt and Nieuwland, *This Journal*, 56, 2120 (1934).

formed.²⁵ The ammonium chloride was collected on a filter, the filtrate evaporated on a steam-bath, the residue dissolved in water and the benzene removed by boiling. The aqueous solution was treated with decolorizing carbon, evaporated, benzene was added and the solution boiled in order to remove water. The benzene solution was decolorized with carbon, giving (VII). Three recrystallizations gave shining white leaflets of the amide (VII) of m. p. 99–100°. Altogether, approximately 400–500 mg. was obtained, a yield of 20–30%.

Anal. Calcd. for C_8H_9ON : N, 14.13. Found: N, 14.42, 14.56.

2-Phenyl-4-methylpyrrolone.^{1b}—A Grignard solution was prepared from 3 g. of magnesium, 22 g. of bromobenzene and about 150 cc. of anhydrous ether. To this was added drop by drop a solution of 12 g. of β -methyl- γ -chlorobutyronitrile (IV) in 100 cc. of absolute ether. The mixture was heated for eight hours, concentrated to about 150 cc., and then slowly added to 500 cc. of liquid ammonia, after which the latter was allowed to evaporate, which required about twenty-four hours. The solid was collected on a filter, washed with ether, and the washings combined with the first filtrate. The ether was removed from the combined filtrate and the residue heated at 100° for fifteen minutes. The residue was again dissolved in ether, the ether solution extracted three times with hydrochloric acid, and the combined extract, in turn, made alkaline with sodium hydroxide. The liberated pyrrolone was extracted with ether, and the ether evaporated leaving 9 g. of residue of b. p. 119.4–119.7° at 5 mm. The pyrrolone, a colorless liquid, had a density, d^{20}_4 , of 1.009 and index of refraction, n^{20}_D of 1.55519, which give MR_D , 50.66. The calculated MR_D for the Δ^2 formula, assuming the atomic refractivity of 2.502 for the N, is 50.332. The MR_D for the Δ^1 structure, assuming the value of 3.776 for the N, is 49.873.

Anal. Calcd. for $C_{11}H_{13}N$: N, 8.80. Found: N, 8.29, 8.29.

Hydrochloride.—The pyrrolinium chloride was precipitated by the action of dry hydrogen chloride on an ether solution of the base, and recrystallized three times from alcohol and ether. The solid²⁶ melted at 183–187°.

Anal. Calcd. for $C_{12}H_{15}NCl$: N, 7.16; Cl, 18.13. Found: N, 7.13, 7.27; Cl, 18.11, 18.83.

Chloroplatinate.—The chloroplatinate was precipitated by the mixing of alcoholic solutions of chloroplatinic acid and pyrrolinium chloride. The compound after recrystallization from water appeared as deep orange crystals which began to turn brown at about 180° and melted at 201°.

Anal. Calcd. for $C_{22}H_{23}N_2PtCl_6$: Pt, 26.81. Found: Pt, 26.71.

Picrate.—The picrate was obtained by the interaction of a few milligrams of the hydrochloride and picric acid in 3 cc. of acetic acid. The solution was heated and water added until a precipitate appeared, which was redissolved by heating and the solution allowed to cool. The precipitate was removed, dissolved in dilute alcohol and reprecipitated by the addition of water. The tan colored picrate of Stehr melted at 188.4° with decomposition. Steadman obtained 188–189° uncor. (193–194° cor.).²⁷

Anal. Calcd. for $C_{11}H_{13}N \cdot C_6H_3O_7N_3$: N, 14.43. Found: N, 14.14, 14.20.

2-Phenylpyrrolone.^{1b}—A Grignard solution was prepared in the usual way from 4 g. of magnesium, a bit of iodine, 27 g. of bromobenzene and 100 cc. of ether. To this was added 20 g. of Eastman Kodak Co. γ -phenoxybutyronitrile (XII) in 75 cc. of anhydrous ether. The mixture

(25) During the course of this process, the mixture became reddish-brown, indicating the occurrence of undesirable side reactions which were not encountered in the aqueous ammonia method.

(26) Mooradian, B.S. Thesis, R. P. I., 1938, obtained a hydrochloride of m. p. 174–175° by the pyrolysis of the 2-methylcyclopropyl phenyl ketimine.

(27) Sonn, ref. 13, reports a m. p. of 192°.

was refluxed for eighteen hours, the ether removed by evaporation, 200 cc. of anhydrous tetralin added, and the flask heated for twenty-two hours at 165–170°. The cooled product was treated four times with dilute hydrochloric acid, the combined acid solution extracted seven times with ether, then made alkaline, and the pyrrolone extracted with ether. The ethereal solution was dried over anhydrous sodium sulfate, and the pyrrolone precipitated as the hydrochloride with dry hydrogen chloride. This and a second similar run gave yields of about 11%.

α -Phenyl- γ -ethoxybutyronitrile.^{1b}—A two-liter, three-neck flask was provided with stirrer, dropping funnel, condenser and calcium chloride tube. A slurry prepared by the grinding of 40 g. of sodium amide in 400 cc. of anhydrous benzene was transferred to the dry flask, 120 g. of benzyl cyanide in an equal amount of benzene was added slowly with stirring and the mixture refluxed for three hours. The flask was then cooled in an ice-salt bath and 152 g. of cellosolve bromide²⁸ was added drop by drop with stirring, which was continued until the ice melted and the temperature rose to that of the room. Finally, the benzene mixture was gradually heated to the boiling point and refluxed for twenty hours. About 500 cc. of water was then added; the benzene layer separated; the water layer extracted with more benzene; the combined benzene extract distilled on the water-bath; and the residue distilled under diminished pressure, giving 92 g. (32.5%) of liquid of b. p. 147–148.4° at 12 mm.; d^{20}_4 , 0.9951; n^{20}_D , 1.49823.

Anal. Calcd. for $C_{12}H_{15}ON$: N, 7.41; MR_D , 55.43. Found: N, 7.27, 7.38; MR_D , 55.26.

2,3-Diphenylpyrrolone.^{1b}—A Grignard solution was prepared from 3 g. of magnesium, 22 g. of bromobenzene and about 125 cc. of anhydrous ether. To this was added 18.9 g. of α -phenyl- γ -ethoxybutyronitrile dissolved in 100 cc. of anhydrous ether and the mixture heated for eight hours. The ether was removed by distillation while 150 cc. of anhydrous tetralin was added simultaneously. The tetralin mixture was heated at 165–175° for eighteen hours, cooled and extracted three times with 1:3 hydrochloric acid. The combined acid solution was extracted six times with ether, and then made alkaline with sodium hydroxide solution. The pyrrolone was extracted with ether, giving 2.7 g. (12%) of free base on evaporation. The properties of the free base as well as those of the hydrochloride, picrate and chloroplatinate were compatible with those of α,β -diphenylpyrrolone and its corresponding derivatives made by Knowles^{4b} using other methods.

1-Chloro-2-methyl-3-aryloxypropanes.^{1b}—Three compounds of this type were prepared with the expectation of transforming them into the corresponding aryloxynitriles. However, the compounds failed to react with sodium cyanide or cuprous cyanide under the conditions used.

1-Chloro-2-methyl-3-phenoxypropane.—For the preparation of this compound the general method described by Lohmann²⁹ for a related reaction was employed. A solution of sodium phenoxide was prepared by the action of 23 g. of sodium on 600 cc. of absolute alcohol followed by the addition of 94 g. of phenol. The phenoxide solution was added slowly with stirring and gentle heating to one consisting of 381 g. (3 moles) of Eastman Kodak Co. 1,3-dichloroisobutane in 200 cc. of absolute alcohol, the gentle refluxing continued for forty hours, and the alcohol removed by distillation. The residue was treated with about 400 cc. of 30% potassium hydroxide, the solution extracted with ether, the ether solution washed with water and distilled under diminished pressure from a Claisen-Vigreux flask. The portion of b. p. 100–130° at 12 mm. was refractionated and gave 128 g. (70%) of 1-chloro-2-methyl-3-phenoxypropane, b. p. 118.5–119.5° at 10.5 mm.; d^{20}_4 , 1.1145; n^{20}_D , 1.53653.

Anal. Calcd. for $C_{10}H_{13}OCl$: Cl, 19.24; MR_D , 51.29. Found: Cl, 19.23; MR_D , 51.67.

Since subsequent work on the Eastman Kodak Co. 1,3-

(28) Prepared by Marsland, B.S. Thesis, R. P. I., 1932.

(29) Lohmann, *Ber.*, **24**, 2632 (1891).

dichloroisobutane has shown it to contain an unsaturated impurity,⁵ the aryloxy derivatives prepared by us probably contain some ethylenic admixture, as would be indicated by the molecular refractivities.

1-Chloro-2-methyl-3-*o*-cresoxypropane.—The procedure described above but with 108 g. of *o*-cresol in place of the phenol gave 117 g. (59%) of product of b. p. 112.8–114.5° at 6 mm.; d_{20}^4 1.0898; n_D^{20} 1.53377.

Anal. Calcd. for $C_{11}H_{15}OCl$: Cl, 17.86; MRD, 55.91. Found: Cl, 17.91; MRD, 56.53.

1-Chloro-2-methyl-3-*p*-*t*-amylphenoxypropane.—The use of 164 g. of *p*-*t*-amylphenol gave 81 g. of product of b. p. 135–147° at 3 mm.

Anal. Calcd. for $C_{15}H_{23}OCl$: Cl, 13.96. Found: Cl, 14.18.

Action of Cuprous Cyanide on Eastman 1,3-Dichloroisobutane.^{1b,2}—A mixture of 90 g. (1 mole) of cuprous cyanide and 762 g. (6 moles) of Eastman practical 1,3-dichloroisobutane⁶ was stirred and refluxed for twenty-four hours. During the course of the reaction a large lump of tarry material appeared in the flask and the liquid turned dark brown. The liquid was filtered into a distilling flask and the tar washed with a little dichloride. The mixed liquid was distilled at atmospheric pressure to about 140° and the residue fractionated under diminished pressure. In one run in which 2 g. each of the bromides of cobalt, copper and nickel were added, 25.5 g. of liquid 4-chloro-3-methyl-3-butenitrile and 6.5 g. of solid nitrile (m. p. 51.5–52.5°) were obtained.

The liquid chloronitrile, b. p. 69–70° at 10 mm., has a somewhat ethereal odor and lachrymatory effect. In contact with the skin it gives a stinging burning sensation.

Anal. Calcd. for C_6H_8NCl : N, 12.12; Cl, 30.68. Found: N, 11.78, 11.07; Cl, 30.72, 29.79.

Imido-ester.—A mixture of 9.9 g. of chloronitrile and 5 g. of absolute ethanol was treated with dry hydrogen chloride and poured into 100 cc. of absolute ether. A yield of 13 g. (86.8%) of product was obtained. This was recrystallized by dissolving in anhydrous acetic acid and reprecipitated by the addition of anhydrous ether.

Anal. Calcd. for $C_7H_{13}NOCl_2$: N, 7.07. Found: N, 7.46, 7.28, 7.41.

Hartigan by a differential thermocouple method,³⁰ found that the compound melts at 102°, uncor., with decomposition to give an amide, a white crystalline solid of m. p. 156–157°, cor.

Unlike (IV) the new chloronitrile gave a black resinous mass with sodium amide in liquid ammonia and similar material with phenylmagnesium bromide.²

Summary

1. β -Methyl- γ -chlorobutyronitrile and β -methylglutaronitrile may be prepared by the action of sodium cyanide on 1,3-dichloro-2-methylpropane.

2. 2-Methylcyclopropanecarbonitrile, whose structure has been established by its transformation into the corresponding amide, has been made in a 60% yield by the action of sodium amide on β -methyl- γ -chlorobutyronitrile in liquid ammonia solution.

3. β -Methyl- γ -aminobutyric acid and α -substituted- γ -methylpyrrolines may also be prepared from the β -methyl- γ -chlorobutyronitrile.

4. 2-Phenylpyrroline may be obtained in small yield by the action of phenylmagnesium bromide on γ -phenoxybutyronitrile. Similarly, 2,3-diphenylpyrroline is formed by the reaction of this Grignard reagent with α -phenyl- γ -ethoxybutyronitrile, which may be made from benzylcyanide, sodium amide and cellosolve bromide.

5. The 1,3-dichloro-2-methylpropane reacts with sodium aryloxides to give 1-chloro-2-methyl-3-aryloxypropanes.

6. An impurity in the 1,3-dichloro-2-methylpropane will react with cuprous cyanide to give a new chloronitrile and a solid dinitrile.

(30) Hartigan and Cloke. *This Journal*, **67**, 709 (1945).

TROY, N. Y.

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The Chemical Composition of Technical DDT¹

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The recent discovery of the outstanding insecticidal properties of the product known as DDT

(1) These researches were carried out under a transfer of funds to the Bureau of Entomology and Plant Quarantine from the Office of Scientific Research and Development, as recommended by the Committee on Medical Research, and under contracts between Harvard University, University of Maryland, and The Ohio State University, and the Office of Scientific Research and Development, as recommended by the National Defense Research Committee.

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and its successful application against the body louse and other disease-carrying insects have aroused considerable interest. Numerous articles praising its merits have appeared in scientific and trade magazines, as well as in newspapers and popular magazines. These usually include the history of its introduction into this country and, as might be expected, the stories are not always in agreement. Probably the most accurate account is given by Froelicher.⁶ The studies leading to the discovery of DDT as an insecticide are presented by Luger, Martin, and Muller.⁷

The symbol "DDT" is a contraction for di-

(6) Froelicher. *Soap and Sanit. Chem.*, **20** (7), 115 (1944).

(7) Luger, Martin and Muller, *Helv. Chim. Acta*, **27**, 892 (1944).