In the 100° run the apparent amount of guanidine as indicated by analysis is larger than that which corresponds to the amount of carbon dioxide, a result which can lead only to the inference that the precipitated picrate was contaminated with picrate of guanylurea and to the conclusion that the figure for carbon dioxide is probably fairly representative of the actual amount of guanidine. In the other runs at higher temperatures, the carbon dioxide exceeds the guanidine. But the reactions (II and III above) which lead to the formation of guanidine and to the destruction of guanidine each produce one mol-equivalent of carbon dioxide. The actual amount of guanidine, therefore, which is produced during the reaction (and in part destroyed) is represented by the arithmetical mean between the value given by analysis and that indicated by the carbon dioxide. Dicyandiamide heated for 6 hours with 4 times its weight of 61% sulfuric acid actually produces at 100° about 34.8%; at 120°, 71.4%; at 140°, 88.0%; at 160°, 88.9% and at 200°, 89.9% of the theoretical amount of guanidine.

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[CONTRIBUTION FROM THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH OF THE UNIVERSITY OF PITTSBURGH.]

BUTYL- AND ISOBUTYL-CYANO-ACETIC ACIDS.[1]

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In continuation of the work already done on the alkylation of cyano-acetic acid ethyl ester, the authors have carried out the Conrad-Limpach reaction with *iso*-butyl alcohol as the solvent and have determined that the *iso*-butyl and di-*iso*-butylcyano-acetic esters formed were *iso-butyl* esters rather than *ethyl* esters. The present paper also describes a number of salts of *iso*-butyl and di-*iso*-butyl-cyano-acetic acids, as well as the preparation of *normal* butyl-cyano-acetic acid and ester and a number of their derivatives.

I. Action of Cyano-acetic Acid Ethyl Ester with Sodium *Iso*-Butylate and *Iso*-Butyl Iodide in *Iso*-Butyl Alcoholic Solution.—A solution of sodium *iso*-butylate was prepared from 6.6 g. of sodium and 185 cc. of absolute *iso*-butyl alcohol. The solution solidified when cold. It was treated with 32.4 g. of cyano-acetic acid ethyl ester dissolved in 65 cc. of absolute *iso*-butyl alcohol, and the mixture was warmed slightly until the solid sodium salt went into solution. The solution was then cooled and 55 g. of *iso*-butyl iodide was added. This is an excess of 2 g.

The solution gradually assumed a deep-red color. After 40 hours the solution was heated to boiling until it was neutral to litmus. The *iso*-

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[1] Most of the work described in this paper was carried out in the Chemical Laboratory of the James Millikin University.

butyl alcohol was distilled off, and the residue was dissolved in water and extracted with ether. The ether solution was then dried, the ether distilled off, and the crude product distilled under 25 mm. pressure. The following fractions were collected (I) up to 50°, 2.35 g.; (II) 50° to 145°, 14.24 g.; (III) 145° to 154°, 15.76 g.; (IV) 154° to 166°, 10.02 g.; total, 42.37 g.

Fraction I consisted of *iso*-butyl alcohol and the excess of the iodide. Fractions II to IV were redistilled under 19 mm. pressure and gave the following (I) up to 125°, 1.96 g.; (II) 125° to 141°, 17.12 g.; (III) 141° to 150°, 15.80 g.; (IV) 150° to 154°, 5.00 g.; total, 39.88 g.

Fraction I was an additional amount of *iso*-butyl alcohol and boiled at 104° to 109° under ordinary pressure. Fraction II was treated with 10% aqueous sodium hydroxide solution, and gave 6 g. *iso*-butyl-cyano-acetic acid, a small amount of *iso*-butyl alcohol, and a considerable amount of di-*iso*-butyl-cyano-acetic acid *iso*-butyl ester, $CN.C(C_4H_9)_2COOC_4H_9$. The latter boiled at 155° to 160° under 25 mm. pressure and at 250° to 260° under 739 mm.; d^{19}, 0.9118.

Calc. for $C_{15}H_{27}NO_2$: C, 71.09; H, 10.68. Found: C, 70.33; H, 10.75.

The ester was a colorless, sirupy liquid; it would not solidify in a freezing mixture of ice and salt.

Fractions III and IV of the reaction products (20.8 g.) were combined and treated with 10% aqueous sodium hydroxide solution. They contained only a little of the *iso*-butyl-cyano-acetic acid *iso*-butyl ester, as was shown by the fact that only 2 g. of the corresponding acid, $CN.CH(C_4H_9)COOH$, was obtained.

The portion neutral to 10% sodium hydroxide solution was extracted with ether, dried, and distilled. The distillation gave a few drops of *iso*-butyl alcohol, formed in the saponification of the *iso*-butyl-cyano-acetic acid *iso*-butyl ester, and 16.31 g. of the unchanged di-*iso*-butyl-cyano-acetic *iso*-butyl ester. The latter boiled at 147° to 153° under 16 mm. pressure and at 255° to 263° under 741 mm. The total yield of di-*iso*-butyl-cyano-acetic acid *iso*-butyl ester, neutral to 10% aqueous sodium hydroxide, was 19.55 g., or 50% of the reaction product.

Di-*iso*-butyl-cyano-acetic acid *iso*-butyl ester was readily saponified by a methyl alcoholic solution of potassium hydroxide; 14.4 g. of it gave 10.85 g. (96% yield) of the corresponding acid, $CN.C(C_4H_9)_2COOH$. This crystallized from petroleum ether in masses of fine needles, and from a mixture of ether and petroleum ether in large, transparent rhombohedra melting at 85° to 86°. Freylon[1] gives the melting point as 90° to 91°.

The *iso*-butyl alcohol obtained was 1.26 g., boiling at 106° to 107°, and having the other characteristic properties of the alcohol.

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[1] Freylon, *Ann. chim. phys.*, [VIII], **19**, 566 (1910).

II. Salts of *iso*-Butyl-cyano-acetic Acid.

(*a*) **The Zinc Salt** was prepared from the acid, mixed with 25 times its weight of water and 4 times the theoretically necessary amount of powdered zinc carbonate. The mixture was heated upon a water-bath until effervescence ceased; it was then filtered, and the filtrate was evaporated to crystallization. The zinc salt was pure white; it crystallized in small rosets of tiny, flat plates.

Analysis. Calc. for $C_{14}H_{20}N_2O_4Zn.H_2O$: Zn, 17.99. Found: 17.95.

(*b*) **The Calcium Salt** was made by a method like that used for the zinc salt. It did not form well-defined crystals, but a solid, white crust which covered the solution as evaporation progressed. This was very soluble in water.

Analysis. Calc. for $C_{14}H_{20}N_2O_4Ca.2H_2O$: Ca, 11.26. Found: 11.08.

(*c*) **The Lead Salt,** made from the acid, water, and lead carbonate, came out of solution as minute, radially grouped, white needles. The salt is difficultly soluble in cold water, but readily in hot water.

Analysis. Calc. for $C_{14}H_{20}N_2O_4Pb.3H_2O$: Pb, 38.23. Found: 38.57.

(*d*) **The Cadmium Salt** was made from the acid, water, and a large excess of cadmium carbonate. The salt separated from solution during evaporation on a boiling water-bath; but it was a gummy mass having, apparently, a considerable amount of free acid. It was, therefore, redissolved in hot water, heated with more cadmium carbonate, and filtered; the filtrate was then allowed to evaporate slowly *in vacuo* over conc. sulfuric acid. In two weeks the salt came out in hard, crystalline form. It was white, very deliquescent, and very soluble in water.

Calc. for $C_{14}H_{20}N_2O_4Cd.H_2O$: Cd, 28.33. Found: 28.21.

III. Salts of Di-*iso*-butyl-cyano-acetic Acid.

(*a*) **The Barium Salt** was prepared from the acid, water, and barium carbonate, which were heated together until effervescence ceased. The mixture was then filtered, and the filtrate concentrated. The salt was obtained as long, colorless needles, some of them over 25 mm. long.

Analysis. Calc. for $C_{22}H_{36}N_2O_4Ba.H_2O$: Ba, 25.08. Found: 25.16.

(*b*) **The Calcium, Cadmium, and Cobalt Salts** were prepared by methods like that used for the barium salt. The calcium salt crystallizes in small, white, lustrous needles.

Analysis. Calc. for $C_{22}H_{36}N_2O_4Ca.2H_2O$: Ca, 8.56. Found: 8.63.

(*c*) **The Cadmium Salt** crystallizes very easily, forming colorless needles arranged in rosets.

Analysis. Calc. for $C_{22}H_{36}N_2O_4Cd.H_2O$: Cd, 21.50. Found: 21.56.

(*d*) **The Cobalt Salt** was obtained by the spontaneous evaporation of its solution in the air. After several days small, purple crystals appeared. As the solution became more concentrated, the crystals became more blue, as though a partial loss of water of hydration were taking place. When allowed to remain *in vacuo* over conc. sulfuric acid, the salt became bright blue.

Analysis. Calc. for $C_{22}H_{36}N_2O_4Co.H_2O$: Co, 12.56. Found: 12.58.

IV. Butyl-cyano-acetic Acid Ethyl Ester.

(a) **Preparation of the Crude Ester.**—Hadley[1] found that when ethyl bromide was used in the alkylation of cyano-acetic acid ethyl ester, practically the same yield was obtained as when ethyl iodide was used. Therefore butyl *bromide* was tried as alkylating agent, instead of the iodide, but the yield was poor.

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[1] Hadley, This Journal, 34, 825 (1912).

A solution of 50 g. of cyano-acetic ethyl ester in 100 cc. of absolute alcohol was treated with the solution of sodium ethylate formed from 10.2 g. of sodium and 350 cc. of absolute alcohol. After 5 minutes 62.6 g. (an excess of 2 g.) of butyl bromide was added. The temperature rose to 33°, and a precipitate formed. After 14 hours the mixture was refluxed in a water-bath until neutral to litmus.

The alcohol and slight excess of butyl bromide were distilled off in a bath heated, finally, up to 150° and the residue was cooled and dissolved in the minimum quantity of water. Two ether extractions were made, and the ether solution was washed with water and dried with calcium chloride; the ether was then distilled. The residue was distilled under reduced pressure, but a yield of only 20.74 g. of crude ester was obtained. The experiment was repeated, but the yield was no better; consequently butyl *iodide* was used, with the result that 55.68 g. of crude product was obtained from 50 g. of cyano-acetic ester. Practically all of this boiled at 138° to 168° under 36 mm., and at 123° to 150° under 25 mm.

(b) **Butyl-cyano-acetic Acid.**—The crude ester obtained in (*a*) was treated 3 times with 10% sodium hydroxide solution, in order that the mono-alkylated product might be separated from the di-alkylated one. From 21.03 g. of crude ester 4.89 g. of substance neutral to alkali was obtained; this was dibutyl-cyano-acetic ethyl ester (*q. v.*). The alkaline solution was acidified and extracted with ether; the ether solution was then dried and distilled. The product, butyl-cyano-acetic acid, weighed 10.2 g. It was a slightly colored, sirupy liquid, with a mild odor. It would not solidify at 0° and was difficultly soluble in water.

(c) **Salts of Butyl-cyano-acetic Acid.**—The *silver* salt was made from the ammonium salt (obtained by neutralization) and silver nitrate solution; it came down as an amorphous, white precipitate. It was analyzed air-dry.

Analysis. Calc. for $C_7H_{10}NO_2Ag$: Ag, 43.51. Found: 43.24.

The *barium* salt was prepared from the carbonate, the acid, and water. The mixture was heated on a water-bath until effervescence ceased; it was then filtered, and the filtrate was allowed to evaporate at room temperature. The resulting crystals were white and very soluble in water.

Analysis. Calc. for $C_{14}H_{20}N_2O_4Ba.H_2O$: Ba, 31.52. Found: 31.94, 32.32, 32.13.

The salt was then dried over conc. sulfuric acid *in vacuo*.

Analysis. Calc. for $C_{14}H_{20}N_2O_4Ba$: Ba, 32.89. Found: 32.67.

The *cadmium* salt of butyl-cyano-acetic acid was prepared from cadmium carbonate, the acid, and water. When the solution was evaporated, the residue was a sirup. After 48 hours' standing over conc. sulfuric acid *in vacuo*, it became a non-crystalline, solid mass. It was very soluble in water.

Analysis. Calc. for $C_{14}H_{20}N_2O_4Cd.3H_2O$: Cd, 25.97, Found: 25.73.

(d) **Butyl-cyano-acetic Acid Ethyl Ester.**—The pure ester was prepared from the silver salt of the acid and an excess of ethyl iodide. The mixture became so hot that the ethyl iodide boiled. The ester obtained was a colorless, sirupy liquid, of faint, agreeable odor, and boiling at

129° to 131° under 22 mm., and at 230° to 233° under 734 mm. Its specific gravity at 18° was 0.9576.

(e) **Butyl-cyano-acetic Acid Butyl Ester.**—The butyl ester was prepared from the silver salt of the acid and butyl iodide, the mixture being heated for the completion of the reaction. The ester was obtained as a sirupy liquid of mild odor. It boiled at 157° to 161° under 30 mm. and at 255° to 260° under 739 mm. Its specific gravity at 21° was 0.9369.

Calc. for $C_{11}H_{19}NO_2$: C, 67.01; H, 9.64. Found: C, 67.01, 66.77; H, 9.68, 9.75.

(f) **Butyl-cyano-acetamide.**—Four g. of butyl-cyano-acetic acid ethyl ester was treated with an excess of conc. ammonia water, and the mixture was shaken frequently. The amide separated out gradually as flat leaflets. Yield 1.5 g. It was recrystallized from hot, dilute alcohol. After being dried *in vacuo* over conc. sulfuric acid, the amide melted at 125°. Its other properties also agreed with those found by Guareschi.[1]

V. Di-butyl-cyano-acetic Acid Ethyl Ester, $CN.C(C_4H_9)_2COOC_9H_5$.—(a) The unsaponified di-butyl-cyano-acetic ethyl ester obtained when crude butyl-cyano-acetic ester (*q. v.*) was treated with 10% sodium hydroxide solution, was subjected to distillation. It was obtained as a colorless, faint-odored liquid. Its boiling point was 154° to 156° under 22 mm. pressure, and 255° to 260° under 738 mm.; its specific gravity was 0.9196 at 23°. The ester did not solidify at —12°.

(b) **Di-butyl-cyano-acetic acid,** $CN.C(C_4H_9)_2COOH$, was obtained by the saponification of its ester by means of potassium hydroxide in cold methyl alcoholic solution. From 19.7 g. of the ester the yield of acid was 16 g., or 93% of the theoretical amount. The acid crystallized from petroleum ether, forming white, silky needles arranged in radiating masses. It had a mild, agreeable odor, melted at 60°, and was difficultly soluble in water.

(c) **The Silver Salt** of di-butyl-cyano-acetic acid was made from its ammonium salt and a silver nitrate solution. It came down as a bulky, white precipitate.

Analysis. Calc. for $C_{11}H_{18}NO_2Ag$: Ag, 35.52. Found: 35.73.

(d) **The Cadmium salt** was prepared from the acid, water, and powdered cadmium carbonate. This mixture was heated at 100° until effervescence ceased, and the solution was filtered and evaporated. The salt crystallized in short, white needles.

Analysis. Calc. for $C_{22}H_{36}N_2O_4Cd$: Cd, 22.27. Found: 22.44.

(e) **Di-butyl Cyano-acetamide.**—Dibutyl-cyano-acetic acid was converted into the acid chloride by treatment with phosphorus pentachloride. The acid chloride was then treated with an excess of conc. ammonia water. The acid amide separated at once in fine needles. When recrystallized from dilute, hot alcohol, it melted at 123°.

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[1] Guareschi, *Ann.*, 325, 221 (1902).