[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JAMES MILLIKIN UNIVERSITY.]

ALKYL CYANO-ACETIC ESTERS.[1]

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In a previous paper,[1] describing the work done by several of his students, the senior author describes the benzylation of cyano-acetic acid ethyl ester by the Conrad-Limpach method, with this change: the reaction was carried out in methyl alcoholic solution instead of in ethyl alcohol, the usual solvent. Under these conditions the resulting monobenzylated and dibenzylated products were *methyl* esters rather than ethyl esters, the ethyl group of the ester having been replaced by the methyl group of the methyl alcohol. The following experiments describe 2 alkylations with methyl alcohol and *iso*-amyl alcohol, respectively, as solvents. To illustrate:

$$\text{(A)}\quad 2CN.CH_2.COOC_2H_5 + 2Na \longrightarrow 2CN.CH = C(ONa)OC_2H_5 + H_2$$

$$\text{(B)}\quad CN.CH = C(ONa)OC_2H_5 + C_2H_5I + CH_3OH \longrightarrow CN.CH(C_2H_5)COOCH_3 + NaI + C_2H_5OH$$

$$\text{(C)}\quad CN.CH = C(ONa)OC_2H_5 + C_5H_{11}I + C_5H_{11}OH \longrightarrow CN.CH(C_5H_{11})COOC_5H_{11} + NaI + C_2H_5OH.$$

The products are not merely the mono-alkylated esters shown in the equations, but mixtures of the mono- and di-alkylated bodies, as has been true in other cases of alkylation by the Conrad-Limpach reaction.[2]

One experiment was carried out on the alkylation of cyano-acetic acid *methyl* ester in ethyl alcohol. In this case the products remained methyl esters.

Ethylation of Cyano-acetic Acid Ethyl Ester in Methyl Alcoholic Solution.—Fifty g. of cyano-acetic acid ethyl ester was dissolved in 200 cc. of absolute methyl alcohol, and then treated with the sodium methylate solution obtained from 10.15 g. of sodium and 200 cc. of methyl alcohol. After 15 minutes' standing, during which there was no precipitation of sodium cyano-acetic ester, 44 g. of ethyl iodide (1.25 times the theoretical amount) was added. The solution became orange colored and warm; the highest temperature was 45°. After 36 hours the excess of methyl alcohol was distilled off on an oil-bath heated finally to 120°. When the residue was cool, water was added to it, and the solution was extracted 3 times with ether and dried with anhydrous calcium chloride. The product left after the distillation of the ether was distilled at 24 mm. pressure and gave 24.7 g. of a colorless liquid boiling at 102° to 105° (chiefly 102° to 103°). Much tar remained in the flask.

The distilled product was dissolved in ether, and shaken out twice with 10% sodium hydroxide solution. The ether solution, after being

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[1] THIS JOURNAL, **38**, 909–916 (1916).

[2] *Am. Chem. J.*, **22**, 169–198 (1899).

washed, dried and distilled, left 9.8 g. of a liquid boiling at 103° to 105° under 23.5 mm., and 205° to 206° under 743 mm. The boiling point was too low, by 10°, for the diethylcyano-acetic acid ethyl ester; analysis showed that it was the *methyl* ester, $(C_2H_5)_2C(CN)COOCH_3$:

Calc. for $C_8H_{13}NO_2$: C, 61.94; H, 8.39; N, 9.03. Found: C, 61.73, 61.99; H, 8.87, 8.95; N, 9.72.

The 10% sodium hydroxide solution gave, when acidified and extracted with ether, 9.2 g. of ethylcyano-acetic acid, boiling at 167° under 26 mm.

The diethylcyano-acetic methyl ester is a colorless liquid of fragrant odor, readily soluble in alcohol and ether. Its specific gravity at 21° is 0.977. It was saponified by treatment with caustic potash in anhydrous methyl alcohol, and gave a practically theoretical yield of diethylcyano acetic acid, melting at 64° to 65°[1]. A portion of the acid was converted into the silver salt for further identification.

Calc. for $C_7H_{10}NO_2Ag$: Ag, 43.55. Found: 43.39.

Alkylation of Cyano-acetic Methyl Ester ($CNCH_2.COOCH_3$) in Ethyl Alcoholic Solution.—Twenty g. of cyano-acetic acid methyl ester was alkylated with sodium ethylate and ethyl bromide in absolute alcoholic solution. The yield of crude product was 22 g., boiling at 202° to 205° under ordinary pressure. This was separated, by treatment with 10% aqueous sodium hydroxide solution, into the mono-ethylated and diethylated products. The yield of *diethylcyano-acetic acid methyl ester* was 7.1 g., boiling at 205° to 206° under 742 mm. It was saponified by potassium hydroxide in methyl alcoholic solution and gave the crystalline acid melting at 64° to 65°. The 10% sodium hydroxide solution gave, when acidified and extracted with ether, 5.7 g. of ethylcyano-acetic acid. No exchange between the alkyl radical of the alcohol and the ester had taken place, as was the case when methyl alcohol was the solvent.

Action of Cyano-acetic Acid Ester with Sodium Iso-amylate and Iso-amyl Iodide in Iso-amyl Alcoholic Solution: Formation of Iso-amyl and Di-iso-amylcyano-acetic Acid Iso-amyl Esters.—Twenty-five g. of cyano-acetic acid ethyl ester in 125 cc. of *iso*-amyl alcohol was treated with the sodium *iso*-amylate formed from 5.07 g. of sodium and 100 cc. of *iso*-amyl alcohol. The *iso*-amyl alcohol used was "pyridine-free." Practically no separation of the sodium salt took place, and after 10 minutes 55 g. of *iso*-amyl iodide was added.

The mixture was allowed to stand for 2 days, but very little sodium iodide separated from solution. The mixture was then heated at 130° for 2 hours under a reflux condenser. A large quantity of crystalline solid then separated out. The excess of *iso*-amyl alcohol was distilled off from an oil-bath heated up to 170°, water was added to the residue, and the resulting mixture was extracted twice with ether. The ether

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[1] Hessler, This Journal, 38, 909–916 (1916).

solution was then washed with water, dried with calcium chloride, and distilled. There was a dark-colored residue; this was distilled under 25 mm. and gave the following fractions.

		G.
I	50–155° (chiefly 50–80°)	7.2
II	155–165°	18.8
III	165–200°	17.6
		43.6

Fraction I consisted chiefly of *iso*-amyl alcohol, boiling at 130°.

Fractions II and III were redistilled under 15 mm. and gave the following fractions.

		G.
I	up to 142°	0.71
II	142–157°	10.00
III	157–167°	16.31
IV	167–180°	3.18
		30.20

Considerable tar remained in the distilling flask.

Fractions II to IV consist of a mixture of *iso*-amyl and di-*iso*-amylcyano-acetic *iso*-amyl esters, as was proved by the fact that *iso*-amylcyano-acetic acid, di-*iso*-amylcyano-acetic acid, and *iso*-amyl alcohol were obtained from them by saponification.

Thus, 10 g. of Fraction III, boiling at 157° to 167° under 15 mm. pressure, was saponified by potassium hydroxide in cold methyl alcoholic solution. There was obtained 2.3 g. of *iso*-amyl alcohol boiling at 129° to 130°, formed by the saponification of its esters. The theoretical amount is 2.9 g.

By treatment of the remainder of Fractions III and IV (9.5 g.) with cold 10% aqueous sodium hydroxide solution for 15 hours, the *iso*-amylcyano-acetic acid *iso*-amyl ester was separated from the di-*iso*-amyl ester. When the alkaline solution was acidified and extracted with ether, it gave *iso*-amylcyano-acetic acid. The part neutral to 10% caustic soda was distilled under 19 mm. pressure, and gave 8.3 g. of oily liquid boiling at 164–180° (practically all at 164° to 166°). From 7.5 g. of this liquid there was obtained, by treatment with potassium hydroxide in cold methyl alcoholic solution, the theoretical amount (2.1 g. instead of 2.2 g.) of *iso*-amyl alcohol boiling at 129° to 130°.

The di-*iso*-amylcyano-acetic acid obtained by the saponification crystallized in colorless plates melting at 74° to 75°. It was neutralized by means of ammonium hydroxide solution and treated with an excess of a conc. silver nitrate solution. The precipitated silver salt first came out in a sticky, wax-like form, but became granular when ground with water in a mortar. An analysis of the dry salt gave the following results.

Calc. for $C_{13}H_{22}NO_2Ag$: Ag, 32.53. Found: 32.83.

The specific gravity of the di-*iso*-amylcyano-acetic acid *iso*-amyl ester was 0.9074 at 22°. The total amount of this ester obtained from the product of the reaction was 21.5 g., or 70.3% of the whole.

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THE PREPARATION OF 9(10)-PHENANTHRIDONE FROM PHENANTHRENE.

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An attempt was made to prepare a compound similar to the vat dye indanthrene red-violet, 2RN, by the following series of transformations: phenanthrene ⟶ phenanthraquinone ⟶ diphenic acid ⟶ diphenic anhydride ⟶ diphenamic acid ⟶ 1-amino-10-carboxyl-diphenyl and the condensation of this compound with α-chloro-anthraquinone. In attempting to convert the diphenamic acid into 1-amino-10-carboxyl-diphenyl by Hofmann's reaction, 9(10)-phenanthridone was obtained instead of the desired amino acid. The 9(10)-phenanthridone was then condensed with α-chloro-anthraquinone.

Experimental Part.

Phenanthraquinone.—The method used in this oxidation is a modification of the one used by Anschutz and Schultz.[1] One hundred g. of "commercial phenanthrene," supposedly 80% pure, was ground to a very fine powder. This was added with constant stirring to an oxidizing solution, contained in a 12-inch evaporating dish, consisting of 1500 cc. of water, 500 cc. of 96% sulfuric acid and 300 g. of potassium dichromate. When the first brisk reaction had ceased an additional 300 g. of dichromate was added. After being slowly heated to the boiling point the solution was cooled and an equal volume of water added. After standing a few hours the mixture was filtered through glass wool (or asbestos) in a Büchner funnel. The yellow precipitate was washed until the wash water came through colorless. The product was suspended in 500 cc. of conc. sulfuric acid for 12 hours in order to remove resins and other acid-soluble impurities. A liter of water was then added in order to decrease the solubility of the phenanthraquinone,[2] the solution heated to boiling and filtered as before. After thoroughly washing the precipitate with water it was washed with a liter of saturated sodium carbonate solution to re-

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[1] Anschutz and Schultz, *Ann.*, 196, 37 (1878).

[2] *J. Chem. Soc.*, 115, 850 (1919)