2. Methylene iodide has been condensed with methyl and ethyl phenylmalonates and with ethyl phenylcyano-acetate, giving good yields of esters of α,γ-diphenylglutaric acid and α,γ-diphenylglutaronitrile, respectively. These reactions involve the elimination of ester group as carbonic esters.
3. A new isomer of α,γ-diphenylglutaric acid has been obtained.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE ABBOTT LABORATORIES]

PREPARATION AND HYDROLYSIS OF SUBSTITUTED CYANAMIDES: DI-N-BUTYLCYANAMIDE AND DIALLYLCYANAMIDE

BY E. B. VLIET

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In searching for a method of preparing di-*n*-butylamine and diallylamine in relatively pure form, free from primary and tertiary amines, the hydrolysis of disubstituted cyanamides was investigated. Diethylamine has been formed in this manner by the action of acids and alkalies on diethylcyanamide,[1,2] while di-*iso*-amylcyanamide and dibenzylcyanamide have been converted into the corresponding amines by treatment with hydrochloric acid at 140–150°.[3] However, this method of obtaining secondary amines is handicapped by the lack of a practical method for preparing disubstituted cyanamides.

Dialkylcyanamides have been prepared by the reaction of dialkylamines with chlorocyanogen or bromocyanogen,[4,5] the reaction of dialkylchloroamines with potassium cyanide,[6] and the action of bromine on a mixture of dialkylamines and potassium cyanide.[7,8] Dimethylcyanamide has been obtained[9] from dimethylsulfate and free cyanamide, H_2CN_2. It is obvious that these methods are not practical.

Dialkylcyanamides have also been prepared by the action of alkyl halides on disilvercyanamide[10] and on disodiumcyanamide.[2,3] Since disodiumcyanamide cannot be obtained on the market and is difficult to prepare, these methods could not be considered.

[1] Cahours and Cloëz, *Ann.*, **90,** 96 (1854).

[2] Fileti and Schiff, *Ber.*, **10,** 427 (1877).

[3] Traube and Engelhardt, *Ber.*, **44,** 3149 (1911).

[4] Ref. 1, p. 95.

[5] Wallach, *Ber.*, **32,** 1873 (1899).

[6] Berg, *Compt. rend.*, **114,** 483, 1379 (1892); **116,** 327, 887 (1893); *Bull. soc. chim.*, [3] **7,** 548 (1892); *Ann. chim. phys.*, [7] **3,** 352 (1894).

[7] Chancel, *Compt. rend.*, **116,** 329 (1893); *Bull. soc. chim.*, [3] **9,** 239 (1893).

[8] McKee, *Am. Chem. J.*, **36,** 209 (1906).

[9] Diels and Gollmann, *Ber.*, **44,** 3165 (1911).

[10] Lime nitrogen contains approximately 55% of $CaCN_2$, 20% of CaO, 12% of graphite, and small amounts of various impurities. It should be protected from moisture in order to prevent slow polymerization to dicyanodiamide. It is advisable to obtain fresh lime nitrogen for the syntheses reported.

Traube and Engelhardt[8] have treated a suspension of lime nitrogen with dimethyl sulfate and then, without isolating the resulting dimethylcyanamide, have hydrolyzed it to dimethylamine by refluxing with hydrochloric acid. This method cannot be used for preparing the products desired because of the difficulty of obtaining the necessary organic sulfates.

Since lime nitrogen[10] is the only commercially available cyanamide derivative, it would seem to be the logical starting material for synthesizing dialkylcyanamides. Traube and Engelhardt[11] have reported a 45% yield of dibenzylcyanamide by the reaction of benzyl chloride with lime nitrogen suspended in 50% alcohol. However, when this method of preparation was tried with *n*-butyl bromide, only a trace of product was obtained. Various other procedures were tried and a method was finally developed by which di-*n*-butylcyano-amide and diallylcyano-amide can be obtained in fairly good yields using lime nitrogen with *n*-butyl bromide and allyl bromide. A solution of sodium cyanamide is first formed by the action of sodium hydroxide on a suspension of lime nitrogen in water and this, upon the addition of some alcohol, readily reacts with the bromides to give the desired products. This method can undoubtedly be used for the preparation of many other disubstituted cyanamides.

The hydrolysis of these cyanamides to give di-*n*-butylamine and diallylamine of good quality was found to proceed satisfactorily by merely refluxing with dil. sulfuric acid.

Di-*n*-butylcyano-amide and diallylcyano-amide have not been previously described. Di-*n*-butylamine has been prepared by the reaction of a dilute alcoholic solution of ammonia with *n*-butyl chloride[12] and with *n*-butyl bromide[13] while diallylamine has been obtained by the action of mono-allylamine on allyl bromide[14] and allyl chloride.[15] The products resulting from the use of these methods contained relatively large amounts of primary and tertiary amines from which it was difficult to separate pure secondary amine.

Experimental Part

Di-*n*-butylcyano-amide.—A 5-liter round-bottom flask (preferably a 3-neck flask) is fitted with a reflux condenser and a stirrer with a mercury seal. To this is added 666 cc. of cold water and 133 g. of cracked ice. Then 200 g. of lime nitrogen is slowly added while the mixture is stirred. As soon as the solid is thoroughly suspended, a cold solution of 111 g. of sodium hydroxide in 200 cc. of water is added and brisk stirring is continued for one hour. If the temperature goes above 25° during this time a little more ice should be added.

After one hour, 433 g. of *n*-butyl bromide and 666 cc. of 95% alcohol are added,

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[11] Ref. 11. p. 3151.

[12] Berg, *Ann. chim. phys.*, [7] **3,** 289 (1894).

[13] Werner, *J. Chem. Soc.*, **115,** 1010 (1919).

[14] Ladenburg, *Ber.*, **14,** 1879 (1881).

[15] Liebermann and Hagen, *Ber.*, **16,** 1641 (1883).

While the mixture is stirred it is heated on a water-bath until it refluxes gently and the refluxing and stirring are continued for two and one-half hours. At the end of this time the reflux condenser is replaced by one which will permit the alcohol to distil. After about 500 cc. of liquid has been collected (stirring should continue during the distillation), the reaction mixture is cooled to room temperature.

Butyl bromide is recovered from the distillate by adding 670 cc. of cold water and enough hydrochloric acid to make the water layer acid to litmus. The butyl bromide layer is then washed with concd. sulfuric acid to remove traces of alcohol, then with water, and is finally dried and distilled. About 85 g. of butyl bromide is recovered.

The cold reaction mixture is filtered with suction and the residue washed with alcohol. The filtrate, which is in two layers, is extracted twice with benzene, first using 270 cc. and then 130 cc. The benzene is distilled from the combined extracts at atmospheric pressure and the dibutylcyanamide is then distilled in a vacuum. About 100 g. of product boiling at 147–151° under 35 mm. pressure or 187–191° under 190 mm. is obtained. This corresponds to a yield of 52%, based on the amount of butyl bromide used.

Di-*n*-butylcyanamide is a clear, slightly viscous liquid, insoluble in water, but soluble in alcohol, benzene and the usual organic solvents. It is readily hydrolyzed by boiling with dil. mineral acids and alkalies.

Diallylcyano-amide.—Diallylcyano-amide can be obtained by following a similar procedure. The amounts of materials used are the same as those for di-*n*-butylcyanoamide with the exception that 382 g. of allyl bromide is used instead of 433 g. of butyl bromide. No allyl bromide is recovered from the alcohol distillate. About 98 g. of diallylcyanamide is obtained. This corresponds to a yield of 50%.

Diallylcyanamide boils at 105–110° under 18mm. pressure, at 128–133° under 57 mm. and at 140–145° under 90 mm. It is a colorless liquid, insoluble in water but soluble in alcohol, benzene and the usual organic solvents. It is readily hydrolyzed upon boiling with dilute mineral acids and alkalies.

Di-*n*-butylamine.—To a solution of 100 g. of concd. sulfuric acid in 300 cc. of water, is added 100 g. of di-*n*-butylcyanamide and the mixture is refluxed for six hours. A homogeneous solution results. It is cooled and a cold solution of 156 g. of sodium hydroxide in 285 cc. of water is added. A condenser is attached and the amine which separates is distilled, together with some water. Distillation is continued until no amine separates from a test portion of the distillate. The amount of water in the distillate is estimated and about one-half this amount of solid potassium hydroxide is added. The solution should be kept cool while this is dissolving. Ammonia gas is evolved. The amine is separated, dried for several hours over solid sodium hydroxide and distilled. About 62 g. of di-*n*-butylamine, boiling at 157–160°, is obtained, accompanied by only a very small amount of low- and high-boiling material. This corresponds to a yield of 75%.

Diallylamine.—For the preparation of diallylamine, 98.5 g. of diallylcyano-amide is refluxed for six hours with a solution of 123 g. of concd. sulphuric acid in 369 cc. of water. After cooling, a cold solution of 192 g. of sodium hydroxide in 350 cc. water is added and the amine is gotten out in the same manner as di-*n*-butylamine. About 68 g. of diallylamine, boiling at 108–111°, is obtained, a yield of 88%.

Summary

1. A method has been described for preparing di-*n*-butylcyano-amide and diallylcyanamide by the reaction of lime nitrogen with *n*-butyl and allyl bromides.

2. Di-*n*-butylamine and diallylamine have been prepared by hydrolyzing the corresponding cyanamides.

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[Contribution from the Chemical Laboratories of Columbia University, No. 442]

RESEARCHES ON THIAZOLES. IV. THE SYNTHESIS OF BENZOTHIAZOLES FROM ORTHO-NITROCHLOROBENZENE

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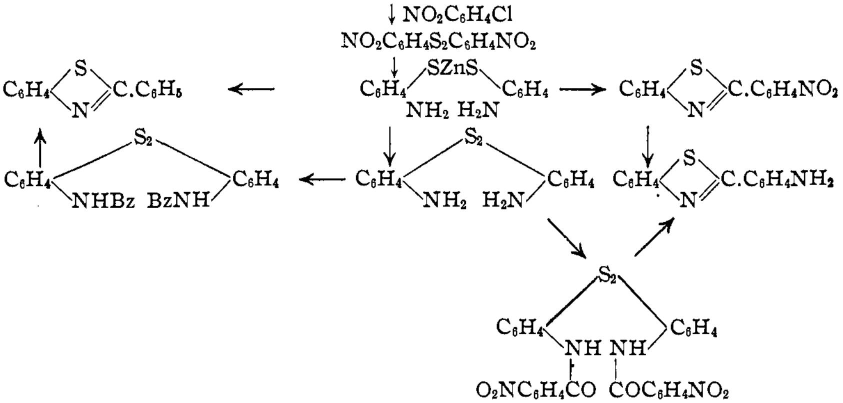
Introductory

Of the many methods which have been utilized from time to time for the preparation of benzothiazoles, one of the simplest and most satisfactory is that discovered many years ago by Hofmann,[1] which depends upon the condensation of acid halides or anhydrides with *o*-aminophenyl mercaptans. Such syntheses have been somewhat infrequent in application because of the non-availability or instability of the requisite thiophenol.

Due to our interest in the benzothiazoles, we have been led to devote some time to the study of methods by which such initial materials can be obtained more easily and used more conveniently, and this paper is a report upon some of the results already attained.

The ground which it covers is represented by the following schematic arrangement.



Free *o*-aminophenyl mercaptan is very sensitive to oxidation, even on standing in the air, rapidly changing to the disulfide. For this reason, the latter has been used often in synthetic work instead of the free thiophenol.[2] Möhlau, Beyschlag and Köhres[3] reduced the nitrophenyl di-

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[1] Hofmann, *Ber.*, **12,** 2362, 2365 (1879).

[2] Kehrmann and Nossenko, *Ber.*, **46,** 2812 (1913).

[3] Möhlau, Beyschlag and Köhres, *Ber.*, **45,** 134 (1912).