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Synthesis of a Naphthotetrazine from Diethyl Succinylosuccinate and Dicyandiamide.

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SYNTHESIS OF A NAPHTHOTETRAZINE FROM DIETHYL SUCCINYLOSUCCINATE AND DICYANDIAMIDE.

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On account of the ease with which dicyandiamide can be prepared in quantity and at very small cost from the crude calcium cyanamide of commerce, this substance is beginning to find numerous applications in organic syntheses. Among other properties, the amidine structure of dicyandiamide has been taken advantage of for the preparation of certain nitrogen heterocycles. For example, by condensation with such substances as α-ketone acid esters, various pyrimidine derivatives are obtained. Thus, dicyandiamide condenses with amlonic ester derivatives[1] and with acetoacetic[2] ester to form substituted pyrimidines. It is not improbable that dicyandiamide is capable of entering into the same condensation reactions and yielding cyanamino derivatives of the various heterocycles now prepared from guanidine.

The readiness with which dicyandiamide yields pyrimidine derivatives suggested to the writer the possibility of preparing a 1, 3, 6, 8—naphthotetrazine, or symmetrical benzodipyrimidine, by condensation with succinylosuccinic ester. Other amidines have been condensed with succinylosuccinic ester, forming substituted naphthotetrazines. Thus, benzamidine[3] yielded 2, 7—diphenyl—4, 9—diketotetrahydro—1, 3, 6, 8—naphthotetrazine, guanidine[4] the corresponding 2-7—diamino, and acetamidine[5] the corresponding 2-7—dimethyl derivatives. Other derivatives of this heterocycle have been prepared by Bogert and Nelson[6] from p—diaminoterephthalic acid and its derivatives. They all appear to be characterized by insolubility, infusibility and general inertness.

[1]German Patent 165, 223, 1905.
[2]Söll & Stutzer, Ber. 42, 4534, 1910.
[3]Pinner, Ber. 22, 2609, 1889.
[4]Bogert and Dox, J. Amer. Chem. Soc., 27, 1127, 1905.
[5]Bogert & Dox, ibid., 27, 1136, 1905.
[6]Bogert & Nelson, ibid., 29, 729, 1907.

EXPERIMENTAL.

Dicyandiamide was prepared by the method of Söll & Stutzer[7] from commercial calcium cyanamide supplied by the American Cyanamide Co., of Niagara Falls, Ontario. The product was obtained in large white crystals, melting at 209° (corr.). Succinylosuccinic ester, prepared in the usual way from diethyl succinate and sodium, was suspended in ten times its weight of water and an equal volume of 5 per cent sodium hydroxide solution was added. After the ester had dissolved to a bright yellow solution, dicyandiamide, equivalent in amount to two molecules for every molecule of succinylosuccinic ester, was added in the solid form, and the mixture was gradually warmed on an electric stove. As the temperature rose, the dicyandiamide went into solution and at about 50° a pale yellow granular precipitate began to form. Heating was continued until the mixture just began to boil. After cooling, the precipitate was filtered with suction, washed with water, dilute hydrochloric acid, alcohol and finally ether, and dried in the oven at 100°. The yield was 37 per cent of the theory. In a second and third preparation, equal weights of dicyandiamide and succinylosuccinic ester were used, and the yields on the basis of the latter substances were 72 per cent and 61 per cent respectively.

The mother liquor was bright red, the color evidently being due to an oxidation process, since the red appeared first at the surface of the solution in contact with the air. This color turned yellow on acidifying and then back to the original red on the addition of alkali.

Like the other naphthotetrazine derivatives described, this condensation product is characterized by its insolubility in the neutral solvents and by its infusibility. At about 320° it darkens in color without melting. Analysis of the product gave the following results:

	FOUND	CALC. FOR $C_{12}H_8N_8O_2$
N	37.2	37.8
C	48.5	48.6
H	2.7	3.0

The condensation consists in the elimination of two molecules of water and two of alcohol, between one of succinylosuccinic

[7] Söll & Stutzer, loc. cit.

ester and two of dicyandiamide, yielding a substance of the following structural formula:

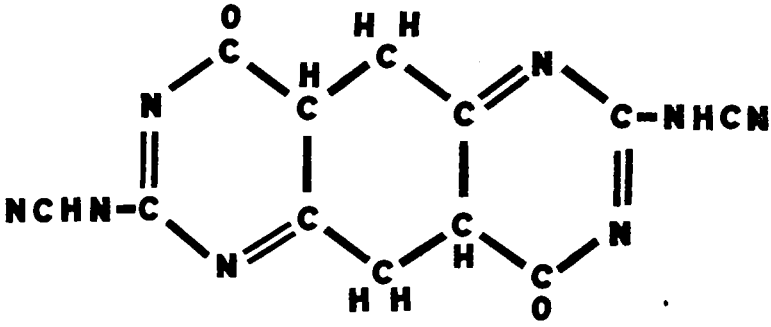

FIGURE 100

The product is therefore 2, 7—dicyanamino—4, 9—diketotetrahydro—1, 3, 6, 8—naphthotetrazine.

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