SOME CONDENSATIONS GIVING DIETHYL DICYANOGLUTACONATE.

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The compound which had been called by the name of diethyl dicyanoglutaconate and to which formula $C_2H_5OCO(CN)C{=}CH{-}CH(CN)COOC_2H_5$ or $C_{11}H_{12}O_4N_2$ had been given, was found by the author to be a more complex compound with formula $(C_{11}H_{12}O_4N_2)_2{\cdot}H_2O$. The author calls it diethyl dicyanoglutaconate semihydrate, because in this compound half a molecule of water is combined with $C_{11}H_{12}O_4N_2$.⁽¹⁾ Many reactions are known, in which diethyl sodio-dicyanoglutaconate $C_{11}H_{11}O_4N_2Na$ is formed; but treated with a dilute acid, it is transformed, not to the corresponding free cyano-ester $C_{11}H_{12}O_4N_2$, but to the semihydrate $(C_{11}H_{12}O_4N_2)_2{\cdot}H_2O$. Hence, the compound with formula $C_{11}H_{12}O_4N_2$, to which the name diethyl dicyanoglutaconate should be given correctly, can not be obtained unless the synthesis is realized without the intermediate formation of the sodium compound. The following condensations were tried, and, in the first two, the formation of diethyl dicyanoglutaconate was ascertained. This compound was not isolated in a pure state, but its presence was proved by the precipitation of diethyl dicyanoglutaconate semihydrate on acidifying the alkali extract of the condensation products, for diethyl dicyanoglutaconate, if present, would dissolve in alkali carbonate forming its own alkali derivative, and the latter, treated with a dilute acid, would give the semihydrate according to the already known process.

(1) *Condensation of ethyl oxymethylene-cyanoacetate* $[HOCH{=}C(CN)COOC_2H_5]$ *with ethyl cyanoacetate* $[CNCH_2COOC_2H_5]$ *by the action of acetic anhydride.* The reaction was expected to proceed as follows:

$$\begin{aligned} &C_2H_5OCO(CN)C{=}CHOH + CH_2(CN)COOC_2H_5 \\ &\quad = H_2O + C_2H_5OCO(CN)C{=}CH{-}CH(CN)COOC_2H_5. \end{aligned}$$

A mixture of ethyl oxymethylene-cyanoacetate, ethyl cyanoacetate, and acetic anhydride in molecular proportions was heated for one hour. Then the whole mass was shaken with an aqueous solution of sodium carbonate and ether. On acidifying the aqueous solution, a crystalline substance separated. This was found to be identical with diethyl dicyano-

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(1) This Bulletin, **2** (1927), 26.

glutaconate semihydrate, for it melted at 182° and could be transformed into the characteristic picrate melting at 197°.(1)

(2) *Condensation of ethyl chloromethylene-cyanoacetate* [$ClCH=C(CN)COOC_2H_5$] *with ethyl chloro-cyanoacetate* [$ClCH(CN)COOC_2H_5$] *by the action of metallic copper.* Ethyl chloromethylene-cyanoacetate had not been known, but was easily obtained by the action of phosphorus pentachloride on ethyl oxymethylene-cyanoacetate. The mixture of ethyl oxymethylene-cyanoacetate and phosphorus pentachloride in molecular proportions was heated on the water bath. From the reaction product hydrogen chloride and phosphorus oxychloride were removed by heating it on the water-bath and sucking with a water jet pump, and the residue was distilled under diminished pressure. The most part distilled at 106–107° under 16 mm. pressure, and by redistillation the pure substance distilling at 105° under 12 mm. pressure was obtained.

Anal. Found: $Cl=22.05$, 21.97%. Calc. for $C_6H_6O_2NCl$: $Cl=22.23\%$.

The condensation of ethyl chloromethylene-cyanoacetate and ethyl chlorocyanoacetate was tried at first with so-called molecular silver, but without success. Then metallic copper, which was prepared in fine powder by adding zinc dust to an aqueous solution of copper sulphate, was used. The reaction was too violent, and the whole mass frothed up owing to evolution of an enormous quantity of heat. So in another experiment caution was taken to avoid an excessive rise of temperature. The reaction mass was extracted with ether, and on evaporating the ethereal solution an oily substance was obtained. To examine the presence of diethyl dicyanoglutaconate in this oily substance, it was dissolved in ether, and the ethereal solution was shaken with an aqueous solution of potassium carbonate. A crystalline substance separated from the aqueous solution and proved to be the potassium derivative of diethyl dicyanoglutaconate, for, when its aqueous solution was acidifyed, the yellow crystals of diethyl dicyanoglutaconate semihydrate melting at 182° were obtained, and these gave the characteristic picrate melting at 197°.

The reaction can be represented by the following equation:

$$\begin{aligned} &C_2H_5OCO(CN)C=CHCl + ClCH(CN)COOC_2H_5 + 2Cu \\ &\quad = C_2H_5OCO(CN)C=CH-CH(CN)COOC_2H_5 + Cu_2Cl_2 \end{aligned}$$

(3) *Condensation of ethyl chloromethylene-cyanoacetate* [$ClCH=C(CN)COOC_2H_5$] *with ethyl cyanoacetate* [$CNCH_2COOC_2H_5$] *by the*

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(1) This Bulletin, **5** (1930), 7.

action of pyridine. Because of the strong acid nature of ethyl oxymethylene-cyanoacetate it was expected that ethyl chloromethylene-cyanoacetate would act like an acid chloride, and would condense with ethyl cyanoacetate by the action of pyridine, just as acetyl chloride; that is, there must be an analogy between the following reactions:

$$\mathrm{CH_3COCl + CNCH_2COOC_2H_5 + C_5H_5N = C_5H_5NHCl + CH_3CO{-}CH(CN)COOC_2H_5},$$

$$\begin{aligned}&\mathrm{C_2H_5OCO(CN)C{=}CHCl + CNCH_2COOC_2H_5 + C_5H_5N}\\&\quad\mathrm{= C_5H_5N{\cdot}HCl + C_2H_5OCO(CN)C{=}CH{-}CH(CN)COOC_2H_5}.\end{aligned}$$

To a mixture of ethyl chloromethylene-cyanoacetate and ethyl cyanoacetate, pyridine was added gradually under cooling. The mixture became a dark red pasty mass. Water and ether were added to the mass, and the two liquids were separated. On acidifying the aqueous solution with dilute sulphuric acid a yellow solid was obtained; but this was found not to be diethyl dicyanoglutaconate semihydrate, but its alcoholic solution gave with picric acid the picrate $C_{11}H_{16}O_6N_2{\cdot}C_6H_2(NO_2)_3OH$ which is characteristic to diethyl dicyanoglutaconate semihydrate $(C_{11}H_{12}O_4N_2)_2{\cdot}H_2O$ and to diethyl dicarbamyl-glutaconate $C_{11}H_{16}O_6N_2$. Hence, although the obtained substance were neither of these compounds, it was probably a compound, or a mixture of compounds, which situate between these two in the degree of hydration, and can give the same picrate.

(4) *Condensation of ethyl ethoxymethylene-cyanoacetate* $[C_2H_5OCH{=}C(CN)COOC_2H_5]$ *with ethyl cyanoacetate* $[CNCH_2COOC_2H_5]$ *by the action of acetic anhydride and zinc chloride.* A mixture of ethyl ethoxymethylene-cyanoacetate, ethyl cyanoacetate, and acetic anhydride in molecular proportions was heated. No change was observed. Zinc chloride was added to the mixture, and boiling was continued for two hours. The mixture became very dark in colour, but no trace of diethyl dicyanoglutaconate was found in the reaction mass.

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(1) Cf. this Bulletin, **2** (1927), 239.