CONDENSATION OF ETHYL ACETOACETATE WITH SODIO-MALONITRILE. A VIEW ON THE EXPLANATION OF SIMILAR REACTIONS.

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Received September 22, 1927. Published November 28, 1927.

H. Rogerson and J. F. Thorpe(1) showed that ethyl sodio-cyanoacetate condenses with ethyl acetoacetate giving the sodium derivative of diethyl α-cyano-β-methylglutaconate $C_2H_5OOC(CN)CH{\cdot}C(CH_3){=}CHCOOC_2H_5$, but diethyl sodio-malonate does not react with ethyl acetoacetate. They explained the reactive nature of the sodium derivative of ethyl cyanoacetate on the assumption that this sodium compound reacts in the enolic form, whereas the corresponding sodium derivative of diethyl malonate is in the ketonic form. Further they indicated that so long as one of the methylene hydrogen atoms in ethyl acetoacetate remains unsubstituted, that is, so long as it is capable of reacting in an enolic form, it possesses the power of combining with ethyl sodio-cyanoacetate.

According to this indication ethyl sodio-cyanoacetate should give diethyl α,γ-dicyano-β-methylglutaconate $C_2H_5OOC(CN)C{=}C(CH_3)\text{-}CH(CN)COOC_2H_5$, condensing with ethyl cyanoacetoacetate $CH_3CO{\cdot}CH(CN)COOC_2H_5$; and triethyl α-cyano-γ-carboxy-β-methylglutaconate $(C_2H_5OOC)_2C = C(CH_3)-CH(CN)COOC_2H_5$, condensing with diethyl acetylmalonate $CH_3CO\text{-}CH(COOC_2H_5)_2$. In this way some of the nitrile-esters of the β-methyldicarboxyglutaconic acid might be obtained, which the author intended to synthesize for the studies associated with the investigations on the nitrile-esters of the dicarboxyglutaconic acid.(2)

But from the reaction mixture of ethyl sodiocyanoacetate with ethyl cyanoacetoacetate in absolute alcohol or in benzene the free ethyl cyanoacetate and the sodium derivative of ethyl cyanoacetoacetate were obtained, and no condensation product. The migration of the sodium atom from ethyl cyanoacetate to ethyl cyanoacetoacetate can be explained on the consideration of the relative acidity(3) of these two compounds, the former being less strong than the latter. Hence, though it may be a necessary condition, it is not sufficient for the condensation with ethyl sodio-cyanoacetate that ethyl acetoacetate or its substituted derivatives can react in an enolic form. It

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(1) *J. Chem. Soc.*, 87 (1905), 1685. Further cf. *Proc. Chem. Soc.*, 28 (1912), 51 and *J. Chem. Soc.*, 121 (1922), 2216.

(2) This journal, 2 (1927), 278.

(3) " Acidity " means the power of combining with sodium.

must be weaker in acid character than ethyl cyanoacetate. For this reason the condensation which can proceed between ethyl sodio-cyanoacetate and ethyl methyl- or ethyl-acetoacetate(1) did not occur between ethyl sodio-cyanoacetate and ethyl cyanoacetoacetate. The realisation of the condensation seems to depend not so much on the fact that the ethyl cyanoacetate exists in its sodium derivative at the first moment of the reaction, as on the fulfilment of the above condition. Thus Rogerson and Thorpe obtained the same condensation product by the reaction of ethyl cyanoacetate and ethyl sodio-acetoacetate, although in a small yield, as that from ethyl sodio-cyanoacetate and ethyl acetoacetate.

In the previous paper(2) the author showed that the sodium derivative of diethyl $\alpha,\alpha(=\gamma,\gamma)$-dicyanopropylene-$\gamma,\gamma(=\alpha,\alpha)$-dicarboxylate gives an oily substance on acidifying its aqueous solution, but soon the oil dissolves in the mother liquor and colourless crystalline compound is precipitated which is the diethyl α, $\alpha(=\gamma$, $\gamma)$-dicarbamylpropylene-γ, $\gamma(=\alpha$, $\alpha)$-dicarboxylate, $(H_2NCO)_2\text{-}CH\text{–}CH{=}C(COOC_2H_5)_5$. In order to investigate whether the combination with water will occur in a compound constituted similarly, it was necessary to synthesize a suitable compound. If ethyl cyanoacetate in Rogerson and Thorpe's condensation can be replaced by malonitrile without causing the hindrance of the reaction, ethyl α, α-dicyano-β-methylpropylene-γ-carboxylate $(CN)_2CH\text{–}C(CH_3){=}CHCOOC_2H_5$ is to be formed, which will resemble in constitution with the above-mentioned compound. Really the condensation of ethyl acetoacetate with sodio-malonitrile gave a sodium compound, which, on treating with acid in an aqueous solution, was transformed into a free nitrile-ester. The latter is an oily substance and has the composition $C_9H_{10}O_2N_2$ as expected from the above constitutional formula. It possesses no tendency of combining with water to form a diamide.

The sodio-malonitrile can not react in the enolic form, but is capable of condensing with ethyl acetoacetate. Therefore, Regerson and Thorpe's explanation of the reactive nature of the sodium derivative of ethyl cyanoacetate does not seem to be appropriate. The sodium derivative of diethyl malonate did not condense with ethyl acetoacetate probably because diethyl malonate is weaker in acid character than ethyl cyanoacetate and was deprived of sodium atom by the latter.

Experimental Part. *Synthesis of Ethyl α,α-dicyano-β-methylpropylene-γ-carboxylate.*

Sodium (2.0 gr.) was dissolved in a small quantity of absolute alcohol and malonitrile (5.6 gr.) was introduced, when a part of the formed sodio-malonitrile crystallised out. On adding ethyl acetoacetate (11.0 gr.) to the

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(1) Rogerson and Thorpe, loc. cit

(2) This journal, 2 (1927), 278.

sodio-malonitrile, a clear solution resulted and a large quantity of heat was evolved. The solution was boiled for half an hour on the water bath and evaporated to dryness. A crystalline mass was obtained, which was recrystallised twice from a small amount of water. The aqueous solution of this sodium compound reacts alkaline. The purified sodium compound was dissolved in water and the solution was covered with ether and acidified with dilute hydrochloric acid. The ethereal extract was washed with water and dehydrated with calcium chloride. On evaporating the ether in vacuo, a brown coloured oily substance was obtained, which was well dried in vacuo. 0.3258 Gr. of the substance gave 46.5 c.c. of nitrogen at 26° and 758 mm. 0.2325 Gr. of the substance gave 0.5138 gr. of CO_2 and 0.1169 gr. of H_2O. (Found : $N=15.71$; $C=60.29$; $H=5.63$. $C_9H_{10}O_2N_2$ requires $N=15.73$; $C=60.65$; $H=5.66\%$.)

The author expresses his hearty thanks to Prof. K. Matsubara for his kind inspection of this paper.

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