ON W. A. NOYES' METHOD OF PREPARING ETHYL CYANACETATE.

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L. Vaninò describes in his "Präparative Chemie" W. A. Noyes' method for the preparation of ethyl cyanacetate.(1) But the condensation of the ester prepared by this method and triethyl ortho-formate by means of acetic anhydride(2) produced a substance which on analysis gave such numbers as if it were the *methyl* ethoxy-methylene-cyanacetate $CH_3OCO-C(=CHOC_2H_5)-CN$, the condensation product of methyl cyanacetate and triethyl orthoformate.(3)

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(1) Original note: *J. Am. Chem. Soc.*, 26 (1904), 1545.

(2) In a manner similar to that described by E. Gregoire de Bellemont, *Bull. Soc. Chim.*, [3], 25 (1901), 18.

(3) *Bull. soc. chim.*, [3], 25 (1901), 21.

	C_2H_5OCO-C $(=CHOC_2H_5)-CN$	CH_3OCO-C $(=CHOC_2H_5)-CN$	Fonnd		
			I	II	III
C	56.77	54.19	54.72	55.21	—
H	6.56	5.81	5.93	6.04	—
N	8.28	9.03	—	—	9.22

Thus it is very probable that this cyanacetic ester contained methyl cyanacetate. This can be easily understood if we consider that the ester was prepared by boiling ethyl chloracetate and potassium cyanide in methyl alcohol. Some of the ethyl group of the ester was replaced by the methyl group of the methyl alcohol, which has been ascertained by the following analysis and measurement of density.

A precise determination of nitrogen content of the cyanacetic ester in question showed that this preparation contained about equal parts of ethyl and methyl esters.

	$CNCH_2CO_2CH_3$	$CNCH_2CO_2C_2H_5$	Found		
			I	II	III
N	14.14	12.39	13.32	13.26	13.28

Methyl cyanacetate was prepared from methyl chloracetate by using methyl alcohol as the solvent.(1)

D_4^{17} of methyl cyanacetate = 1.133

D_4^{17} of the ester prepd. by Noyes' method = 1.114

The real ethyl cyanacetate was prepared from ethyl chloracetate by the action of potassium cyanide in absolute ethyl alcohol.(2)

Potassium cyanide is difficultly soluble in ethyl alcohol, while soluble in methyl alcohol, but the yield of cyanacetic ester is scarcely diminished by replacing methyl alcohol by ethyl alcohol.

D_4^{20} of the ester prepd. by Noyes' method = 1.110

D_4^{20} of ethyl cyanacetate = 1.063

The investigation on the diethyl dicyanoglutaconate, the details of which were given in the previous paper,(3) always started from the cyanacetic ester prepared by Noyes' method. In all cases only the ethyl compound, e.i. diethyl sodio-dicyanoglutaconate, was obtained, the yield being sometimes over 60 % of the theoretical amount. Hence we must consider that the

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(1) and (2). These esters were fractionated two times under diminished pressure and sufficiently pure for synthetical purposes, but probably not for a precise determination of a physical constant.

(3) This Journal, 2 (1927), 26.

methyl ester contained in the ester mixture was again converted into ethyl ester, for the reaction giving diethyl sodio-dicyanoglutaconate was always carried out in ethyl alcohol. As long as the ester prepared by Noyes' method is used in ethyl alcohol, the absurdity of this method cannot be suspected. It can be foreseen that the ester mixture must give the *dimethyl* sodio-dicyanoglutaconate when it reacts with chloroform and sodium methylate in methyl alcohol. This compound, e.i. dimethyl sodio-dicyanoglutaconate had not been known, but was easily synthesised by using methyl cyanacetate in methyl alcohol.(1) The ester mixture prepared by Noyes' method also gave the same dimethyl sodio-dicyanoglutaconate when it was treated with chloroform and sodium methylate in methyl alcohol. J. C. Hessler and R. M. Lamb(2) observed that they obtained *methyl* esters of alkylcyanacetic acids by alkylation of ethyl cyanacetate in methyl alcoholic solution, but when one experiment was carried out on the alkylation of methyl cyanacetate in ethyl alcohol, the products remained methyl esters. But in the present case the replacement of the alcohol group of the cyanacetic ester seems to be reversible.

$$CNCH_2CO_2CH_3 + C_2H_5OH \rightleftarrows CNCH_2CO_2C_2H_5 + CH_3OH.$$

It is also not impossible that the replacement may occur in the reaction product rather than the cyanacetic ester, and a little amount of water or any other substance may act as a catalyser.

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(1) The details will be given in another paper.

(2) *J. Am. Chem. Soc.* 43 (1921), 205.