THE IDENTITY OF THE TWO POSSIBLE ISOMERIC METHYL ETHYL β-METHYL-α, γ-DICYANOGLUTACONATES.

By Yoshiyuki URUSHIBARA.

Received September 22, 1928. Published October 28, 1928.

By the previous investigations[1] it was shown that the condensation of $C_2H_5OCH:CXY$ with $CHNaX'Y'$, and the condensation of $C_2H_5OCH:CX'Y'$ with $CHNaXY$, where X, X', Y, and Y' represent negative groups such as CN and $COOC_2H_5$, give the same product, while generally the two compounds corresponding to the following formulae can be expected:

(I) $XYC=CH-CNaX'Y'$,

(II) $X'Y'C=CH-CNaXY$.[2]

(1) This journal, **2** (1927), 278; **3** (1928), 219.

(2) Of course such arrangements of the negative groups that make the two formulae identical are out of the question.

Thus the sodium derivatives of the nitrile-esters of dicarboxy-glutaconic acid can not be obtained in two isomeric forms that differ from each other only in the positions of the double union and the sodium atom, but only one of the two is obtainable. It was already studied which of the two possible formulae must be assigned to the actually obtained substance in individual cases.(1)

In order to make clear the mechanism of the condensations of this kind, it was important to know whether the products would prove also to be identical when two isomeric derivatives of β-methyl-dicarboxy-glutaconic acid which differ from each other only in the positions of the double union and the sodium atom were to be formed.

The author previously succeeded in the synthesis of diethyl β-methyl-α, γ-dicyanoglutaconate $C_2H_5OCO(CN)C:C(CH_3)\cdot CH(CN)COOC_2H_5$.(2) This synthetical method was utilized for the preparation of the two possible isomeric methyl ethyl β-methyl-α, γ-dicyanoglutaconates. The condensation of ethyl ethoxy-ethylidene-cyanoacetate (α-cyano-β-ethoxy-crotonate) and methyl cyanoacetate in the presence of sodium methylate must yield the compound with formula (III), while methyl ethoxy-ethylidene-cyanoacetate and ethyl cyanoacetate must produce the compound with formula (IV) in the presence of sodium ethylate.

(III) $C_2H_5OCO(CN)C=C(CH_3)–CNa(CN)COOCH_3$

(IV) $CH_3OCO(CN)C=C(CH_3)–CNa(CN)COOC_2H_5$

But the experiments showed that the products were the same, and this fact was already cited in a previous paper.(3) The experimental data are given in the following pages.

The sodium compounds formed in the above condensations did not tend to crystallise, while the sodium derivative of the corresponding diethyl compound easily crystallised. Only the silver derivatives, which were obtained by double decomposition of the sodium compounds with silver nitrate in the aqueous solution, crystallised in colourless silky needles from hot alcoholic solution. In order to obtain any of the other metallic derivatives in crystalline form, the experiments on double decomposition of the silver compound with potassium, lithium, barium, and mercuric chlorides were tried without success. On concentrating the aqueous solutions none of the compounds of these metals was brought to crystallisation. It was anticipated that the free compounds, methyl ethyl β-methyl-α, γ-dicyanoglutaconates, which might be obtained from the sodium compounds, would be

(1) This journal, 3 (1928), 221.
(2) This journal, 3 (1928), 102.
(3) This journal, 3 (1928), 224.

too easily changeable to be subjected to the processes of identification, for diethyl β-methyl-α, γ-dicyanoglutaconate itself had been found not to be obtainable in a stable form. Thus the author was obliged to compare the properties of the crystals of the silver compounds.

In the experiment of the refractive indices the silver derivatives of the diethyl compound previously prepared, and of the dimethyl compound newly synthesized were studied side by side with the methyl ethyl compounds.

Preparation. Ethyl ethoxy-ethylidene-cyanoacetate $C_2H_5OC(CH_3)$: $C(CN)COOC_2H_5$ was added to the mixture of methyl cyanoacetate and the methyl alcoholic solution of sodium methylate, the quantities of the three substances being in the molecular proportion. The clear yellow solution was evaporated in vacuo over sulphuric acid to a viscous mass, and it was dissolved in water and the theoretical amount of silver nitrate (in aqueous solution) was added. The silver compound was precipitated in white voluminous powder, which was collected, washed with water, and dried in a desiccator. This silver compound was dissolved in hot absolute alcohol, which was filtered while hot and allowed to crystallise. The recrystallisation was repeated several times. A long boiling in alcoholic solution caused a change of the substance, producing insoluble crystals. Therefore a long heating was avoided in the recrystallisation. The silver compound obtained in this way was long silky needles. It was finely pulverised, dried in a desiccator and analysed. 0.2851 Gr. of the substance gave 20.85 c.c. of nitrogen at 23.5°, 752.8 mm.; 0.2595 gr. of the substance gave 0.3618 gr. of CO_2 and 0.0759 gr. of H_2O. (Found: N=8.10; C=38.03; H=3.27. $C_{11}H_{11}O_4N_2Ag$ requires N=8.16; C=38.48; H=3.23%.) (Specimen A) Considered from the mode of condensation this silver compound must have the following constitution:

$C_2H_5OCO(CN)C=C(CH_3)-CAg(CN)COOCH_3$.

By starting from methyl ethoxy-ethylidene-cyanoacetate, ethyl cyanoacetate, and an ethyl alcoholic solution of sodium ethylate, and pursuing the same experimental procedure, another specimen with the same composition was obtained. 0.3252 Gr. of the substance gave 23.75 c.c. of nitrogen at 22.5°, 756.4 mm.; 0.3058 gr. of the substance gave 0.4292 gr. of CO_2 and 0.0903 gr. of H_2O. (Found: N=8.14; C=38.29; H=3.30. $C_{11}H_{11}O_4N_2Ag$ requires N=8.16; C=38.48; H=3.32%). (Specimen B) This compound must have the following constitution:

$CH_3OCO(CN)C=C(CH_3)-CAg(CN)COOC_2H_5$.

Methyl ethoxy-ethylidene-cyanoacetate had not been known, and was synthesised by the action of ethyl iodide on the silver derivative of methyl acetyl-cyanoacetate. It melts at 76–77°, nearly the same temperature at which the ethyl ester melts.

Equal parts of the specimens A and B were dissolved together in hot absolute alcohol and the solution was cooled. Thus the mixed crystals were obtained. (Specimen C).

The sodium derivative of dimethyl β-methyl-α, γ-dicyanoglutaconate was obtained by the condensation of methyl ethoxy-ethylidene-cyanoacetate with methyl sodio-cyanoacetate. On concentrating the methyl alcoholic solution the product crystallised gradually. The crystalline mass was dissolved in water and transformed into the silver derivative by double decomposition with silver nitrate. It was recrystallised from absolute alcohol. 0.3204 Gr. of the substance gave 24.2 c.c. of nitrogen at 22°, 758.2 mm.; 0.3140 gr. of the substance gave 0.4153 gr. of CO_2 and 0.0762 gr. of H_2O. (Found: N= 8.49; C=36.08; H=2.72. $C_{10}H_9O_4N_2Ag$ requires N=8.51; C=36.47; H= 2.76%.)

The preparation of the diethyl compound was already described in the previous paper.[1] The diethyl and dimethyl compounds are represented by the following formulae respectively:

$C_2H_5OCO(CN)C=C(CH_3)-CAg(CN)COOC_2H_5$,

$CH_3OCO(CN)C=C(CH_3)-CAg(CN)COOCH_3$.

Identification. Photographs of X-ray spectra of the specimens A and B were taken by Debye-Scherrer's method. The lines on the two films coincided entirely. The Kα-line of molybdenum was used. The most intense line corresponded to the lattice distance 3.56 Å. This line can not be attributed to metallic silver which might be produced by the decomposition of the substance on exposure to X-rays, for the lattice distance of the metallic silver is 4.06 Å.

The second method of identification was the comparison of the refractive indices. The crystals of all the three specimens A, B, and C gave the same results. They elongate in the direction of the optical elasticity axis X. Therefore n_1 (refractive index for the faster wave) is equal to α and constant around the zone of elongation. $\alpha_D^{27°}$ was determined to be 1.503 ± 0.001 by the immersion method, and the character of zone was found negative.

The crystals of the dimethyl compound elongate also in the direction of the optical elasticity axis X; n_1 is equal to α, and constant around the zone of elongation. $\alpha_D^{27°}=1.518 \pm 0.002$. The character of zone is negative.

The crystals of the diethyl compound elongate in the direction of the optical elasticity axis Z; the character of zone is positive; and $\alpha_D^{27°}$ was found to be nearly 1.580.

No difference has been found between the specimens A, B and C, and this fact reasonably leads to the conclusion that the specimen A, the con-

(1) This journal, 3 (1928), 104.

densation product of ethyl ethoxy-ethylidene-cyanoacetate with methyl cyanoacetate in the presence of sodium methylate, and the specimen B, the condensation product of methyl ethoxy-ethylidene-cyanoacetate with ethyl cyanoacetate in the presence of sodium ethylate, are identical.

Although it is not yet able to decide whether the constitution of the condensation product is the type (III) or (IV), the condensations can be explained similarly as in the cases ef the condensations of ethoxy-methylene compounds with sodio-methylene compounds, the fact that the methyl group in the β-position caused no peculiarity in the condensations being very favorable to this explanation.[1]

The author is much indebted to Dr. I. Okada for photographing the X-ray spectra and measuring the refractive indices.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

(1) See this journal, 3 (1928), 223.