SUPPLEMENTARY STUDIES ON THE NITRILE-ESTERS OF THE DICARBOXYGLUTACONIC ACID.(2)

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Received August 21, 1928. Published September 28, 1928.

Methyl Ethyl Dicyanoglutaconate.(3) The sodium derivative of this mixed ester is to be obtained (I) by the condensation of ethyl ethoxy-methylene-cyanoacetate with methyl sodio-cyanoacetate, and (II) by the condensation of methyl ethoxy-methylene-cyanoacetate with ethyl sodio-cyanoacetate, according to the following equations :

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(2) For the completion of the studies published in this journal, **2** (1927), 278.

(3) Diethyl and dimethyl compounds: this journal, **2** (1927), 26, 236, 283.

$$\text{(I)}\quad C_2H_5OCO(CN)C{=}CH{-}OC_2H_5 + HCNa(CN)COOCH_3$$
$$= C_2H_5OCO(CN)C{=}CH{-}CNa(CN)COOCH_3 + C_2H_5OH,$$
$$\text{(II)}\quad CH_3OCO(CN)C{=}CH{-}OC_2H_5 + HCNa(CN)COOC_2H_5$$
$$= CH_3OCO(CN)C{=}CH{-}CNa(CN)COOC_2H_5 + C_2H_5OH.$$

As is evident from the above equations, the products of the two reactions are apparently different in the positions of the sodium atom and the double union, but it can be expected that they will prove to be identical as in the other cases.

Each of the condensations (I) and (II) was carried out (a) in ethyl alcohol and (b) in methyl alcohol. The experimental procedure common to these four kinds of reactions was as follows: Metallic sodium (1 mol) was dissolved in alcohol, the cyanoacetic ester (1 mol) was added, and then the ethoxy-methylene-compound (1 mol) was introduced. The sodium derivative of the dicyanoglutaconic ester separated out in yellow crystals. It was recrystallised from water, when it became nearly colourless, and then was transformed into the semihydrate by the action of dilute hydrochloric acid, which was examined.

(Ia) The product was wholly *diethyl* dicyanoglutaconate semihydrate $(C_{11}H_{12}O_4N_2)_2H_2O$ with the melting point 184°.

(Ib) The product was found to be *methyl ethyl* dicyanoglutaconate semihydrate with the melting point 197° (corr.). 0.2232 Gr. of the substance gave 23.6 c.c. of nitrogen at 18.5°, 761.0 mm. (Found: $N=12.14$. $(C_{10}H_{10}O_4N_2)_2H_2O$ requires $N=12.12\%$.)

(IIa) The product was the same as that of (Ib). 0.1754 Gr. of the substance gave 18.45 c.c. of nitrogen at 18°, 762.4 mm. (Found: $N=12.13\%$.) The specimens of (Ib) and (IIa) and their mixture melted at the same point 197°.

(IIb) The product was wholly *dimethyl* dicyanoglutaconate semihydrate $(C_9H_8O_4N_2)_2H_2O$ with the melting point 224°.

Thus it has been found that the cyanoacetic ester exchanges its alcohol group when it is converted into the sodium derivative by the action of sodium alcoholate. The exchange of the alcohol group can not take place in the products of the above condensations, for, when dimethyl sodio-dicyanoglutaconate was dissolved in ethyl alcohol, and the solution was boiled for one hour, none of the methyl groups was replaced by an ethyl group.

Mixed Esters of Dicarboxyglutaconic Acid. The condensation of dimethyl malonate with diethyl ethoxy-methylene-malonate was carried out (a) in ethyl alcohol, and (b) in methyl alcohol. The formed sodium compounds were recrystallised from ethyl alcohol. The free esters were obtained by the action of dilute hydrochloric acid in the aqueous solutions. In analysis, the product of (a) gave approximately the numbers calculated for *methyl triethyl* ester. (Found: C=53.67; H=6.51. $C_{14}H_{20}O_8$ requires C=53.14; H=6.38%.) The product of (b) gave nearly the numbers for *dimethyl diethyl* ester. (Found: C=51.16; H=5.91. $C_{13}H_{18}O_8$ requires C=51.64; H=6.01%.)

The malonic ester also exchanges one of its alcohol groups when it is converted into the sodium derivative by the action of sodium alcoholate. Thus, after dimethyl malonate was acted by sodium ethylate, it reacted as if it were methyl ethyl malonate.

The Constitutions of the Sodium Derivatives of the Nitrile-esters of Dicarboxyglutaconic Acid. Those having symmetrical arrangement of cyano- and carbethoxy-groups afford no problem concerning their constitutions, and they are:

(I) $(C_2H_5OCO)_2C=CH-CNa(COOC_2H_5)_2$;
(II) $C_2H_5OCO(CN)C=CH-CNa(CN)COOC_2H_5$;
(III) $(CN)_2C=CH-CNa(CN)_2$.

The free ester, tetraethyl dicarboxyglutaconate, obtained by acidifying the aqueous solution of the sodium compound (I), gives blue colour on adding ferric chloride to its alcoholic solution, showing that it is, at least partly, in the enolic form.(1) Tetracyanopropylene $(CN)_2C=CH-CH(CN)_2$ obtainable in solutions from the sodium derivative (III) was found to give no colouration with ferric chloride. Since the free nitrile-ester corresponding to the sodium compound (II) is not obtainable,(2) another compound is to be examined instead of it, in order to know whether it would give colouration with ferric chloride or not, if it should exist. Fortunately, diethyl α, γ-dicyano-β-methyl-glutaconate $C_2H_5OCO(CN)C=C(CH_3)-CH(CN)COOC_2H_5$ is obtainable from its sodium derivative.(3) This substance was found to give no colouration with ferric chloride. Thus the compounds in which the carbon atom retaining the sodium atom possesses two carbethoxy-groups are characterised with the colouration. The ferric chloride test carried out directly on the sodium compunds (I), (II), and (III) in their alcoholic solutions led to the same conclusion.

Now, the constitutions of the sodium derivatives of the other nitrile-esters of dicarboxyglutaconic acid can be determined by the reaction with ferric chloride. By the previous investigation it was found that the condensation of diethyl ethoxy-methylene-malonate with sodio-malonitrile, and the condensation of ethoxy-methylene-malonitrile with diethyl sodio-malonate give the same sodium compound, from which the same diethyl dicarbamyl-proplylene-dicarboxylate is obtained. Then it was shown that the sodium

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(1) H. Stobbe u. F. Wildensee, *J. prakt. Chem.*, **115** (1927), 163.
(2) This journal, **2** (1927), 26.
(3) This journal, **3** (1928), 102.

compound formed in the two reactions must have one of the two following formulae.

(IV) $(CN)_2C=CH-CNa(COOC_2H_5)_2$,

(V) $(CN)_2CNa-CH=C(COOC_2H_5)_2$;

but it was not decided which is the constitution of the substance. This sodium compound gives an oily deposit on acidifying its aqueous solution, which dissolves again in the mother liquor when it is left there for a while and is transformed into the crystals of diethyl dicarbamyl-propylene-dicarboxylate.

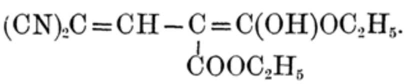
The oily substance deposited from the aqueous solution of the sodium compound was quickly extracted with ether and the ethereal solution was washed with water, dehydrated with calcium chloride, and evaporated in vacuo. The oily residue was dissolved in alcohol. This alcoholic solution gave bluish violet colour on adding ferric chloride, showing that the oily substance is in the enolic form. The sodium compound itself gave violet colour on adding ferric chloride to its alcoholic solution.

The oily substance from both the sodium derivative obtained by the condensation of diethyl ethoxy-methylene-malonate with sodio-malonitrile, and that obtained by the condensation of ethoxy-methylene-malonitrile with diethyl sodio-malonate, gave the same colouration with ferric chloride.

It is evident that the oily substance is the free nitrile-ester corresponding to the sodium compound. If it gives a colouration with ferric chloride, its constitution must be represented by formula (VI), or, in the enolic form, by formula (VII), and its sodium derivative by formula (IV).

(VI) $(CN)_2C=CH-CH(COOC_2H_5)_2$, diethyl γ, γ-dicyano-propylene-α, α-dicarboxylate;

(VII)



$$(CN)_2C=CH-\underset{\displaystyle COOC_2H_5}{\underset{|}{C}}=C(OH)OC_2H_5.$$

The alcoholic solution of this enolic cyano-ester gave a colourless crystalline deposit on standing for a while. After this transformation it gave no colouration with ferric chloride. It was also experienced that the colour given by a fresh alcoholic solution on adding ferric chloride faded gradually. The crystals were collected, washed with alcohol, and dried in a desiccator. This crystalline substance melts at 212°. 0.1149 Gr. of the substance gave 0.2185 gr. of CO_2 and 0.0580 gr. of H_2O; 0.0608 gr. of the substance gave 5.85 c.c. of nitrogen at 18°, 758.5 mm. (Found: $C=51.88$; $H=5.65$; $N=11.03$. $C_{11}H_{12}O_4N_2 \cdot H_2O$ requires $C=51.95$; $H=5.55$; $N=11.03\%$.) The analytical result corresponds to the monohydrate of diethyl dicyano-propylene-dicarboxylate, and one of the cyano-groups is hydrated into a carbamyl-group.

Of course, it has the configuration of diethyl γ-cyano-γ-carbamyl-propylene-α, α-dicarboxylate, $H_2NCO(CN)C=CH-CH(CO_2C_2H_5)_2$, and, therefore, the dihydrate⁽¹⁾ is diethyl γ, γ-dicarbamyl-propylene-α, α-dicarboxylate, $(H_2NCO)_2C=CH-CH(CO_2C_2H_5)_2$. While the enolic nitrile-ester is gradually transformed into the ketonic form, it is at the same time changed into the dicarbamyl compound in the aqueous solution, and into the monocyano-monocarbamyl compound in the alcoholic solution.

Triethyl cyano-propylene-tricarboxylate (cyano-carboxyglutaconate) gives violet colour on adding ferric chloride to its alcoholic solution. Hence formula (VIII) must be assigned to this cyano-ester, and formula (IX) to its sodium derivative.

(VIII) $C_2H_5OCO(CN)C=CH-CH(COOC_2H_5)_2$, triethyl γ-cyano-propylene-α, α, γ-tricarboxylate ;

(IX) $C_2H_5OCO(CN)C=CH-CNa(COOC_2H_5)_2$, triethyl α-sodio-γ-cyano-propylene-α, α, γ-tricarboxylate.

The examples already described suggest that the sodium atom is generally retained by the carbon atom with the most carbethoxy-groups. For this reason the constitution of the ethyl sodio-tricyano-propylene-carboxylate may be represented by formula (X).

(X) $(CN)_2C=CH-CNa(CN)COOC_2H_5$, ethyl α-sodio-α, γ, γ-tricyano-propylene-α-carboxylate.

The compounds obtained by the action of a dilute acid on the sodium compounds, the free nitrile-esters or the various hydrates,⁽²⁾ may be considered to have the same configurations as the corresponding sodium derivatives. There has been nearly nothing to suggest the configuration of methyl ethyl sodio-dicyanoglutaconate.

The Mechanism of the Condensation of an Ethoxy-methylene Compound $C_2H_5OCH=CXY$ with a Methylene Compound $CH_2X'Y'$ in the Presence of Sodium Alcoholate. In the previous paper on the nitrile-esters of the dicarboxyglutaconic acid, the mechanism of the condensation of an ethoxy-methylene compound with a sodio-methylene compound (or methylene compound in the presence of sodium alcoholate) was explained on the assumption that Thorpe's theory of the normal form can be applied to the derivatives of dicarboxyglutaconic acid. But this theory was found to be based on uncertain evidences and it is natural to consider that the α- and γ-positions in the glutaconic acids are not identical.⁽³⁾ Now that explanation

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(1) This journal, 2 (1927), 281.

(2) Strictly speaking, they should not be called hydrates, for the water combined in those compounds can not be removed, showing that it is not the water of crystallisation.

(3) This journal, 3 (1928), 205.

must be corrected according to this fact. In that and also in this paper 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 any of the negative groups such as CN and $COOC_2H_5$, give one and the same product, while two with the following formulae can be expected:

$$\text{(XI)}\quad XYC{=}CH{-}CNaX'Y',$$
$$\text{(XII)}\quad X'Y'C{=}CH{-}CNaXY.$$

Even a slight difference in the groups attached to each end of the propylene chain caused the seeming migration of the double union, only one compound free from the isomeride being produced in sufficient yield.

On the other hand, Hope⁽¹⁾ found clearly a difference between the two following derivatives of glutaconic acid:

$$\text{(XIII)}\quad C_2H_5OCO(CN)C{=}C(CH_3){-}CH(CH_3)COOC_2H_5,$$
$$\text{(XIV)}\quad C_2H_5OCO(CN)CH{-}C(CH_3){=}C(CH_3)COOC_2H_5.$$

He observed that the former is only very slowly transformed into the latter by the action of ammonia. By the action of sodium ethylate the former is also transformed into the sodium derivative of the latter, but only partly.

It may be supposed it is not impossible that the methyl group in the β-position of the compounds investigated by Hope prevented the double union from moving, and enabled the two isomerides to exist, and that, as there is no methyl group in the condensation product of an ethoxy-methylene compound with a sodio-methylene compound, the migration of the double union can easily take place.

But it has been found that this view is contradictory to the fact, for the condensation of methyl ethoxy-ethylidene-cyanoacetate with ethyl sodio-cyanoacetate and the condensation of ethyl ethoxy-ethylidene-cyanoacetate with methyl sodio-cyanoacetate gave the same product, while two corresponding to the following formulae are expected:

$$\text{(XV)}\quad CH_3OCO(CN)C{=}C(CH_3){-}CNa(CN)COOC_2H_5,$$
$$\text{(XVI)}\quad C_2H_5OCO(CN)C{=}C(CH_3){-}CNa(CN)COOCH_3.$$

The details of the experiments will be given later in another paper.

Therefore, it is reasonable to suppose that the double union can not easily move after it has been once formed. Then how is the mechanism of the condensation in question explained? Suppose that an ethoxy-methylene compound and a methylene compound give, in the first place, an addition compound in the presence of sodium alcoholate, the elimination of alcohol and substitution of hydrogen with sodium taking

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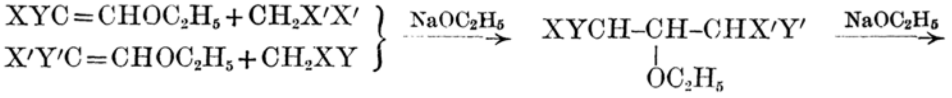
(2) *J. Chem. Soc.*, **121** (1922), 2216.

	Condensations	Sodium compounds obtained by the condensations	Compounds obtained by the action of an acid on the sodium compounds
(1)	$4NaOMe+2CH_2(CO_2Me)_2+CHCl_3$	$(MeO_2C)_2C:CH\cdot CNa(CO_2Me)_2$	$(MeO_2C)_2C:CH\cdot CH(CO_2Me)_2$
(2)	$4NaOEt + 2CH_2(CO_2Et)_2 + CHCl_3$	$(EtO_2C)_2C:CH\cdot CNa(CO_2Et)_2$	$(EtO_2C)_2C:CH\cdot CH(CO_2Et)_2$
(3)	$4NaOEt + 2CH_2(CO_2Et)_2 + CCl_4$		
(4)	$4NaOEt + 2CH_2(CO_2Et)_2 + Cl_3CCO_2Et$		
(5)	$NaOEt + CH_2(CO_2Et)_2 + EtOCH:C(CO_2Et)_2$		
(6)	$NaOMe + CH_2(CO_2Me)_2 + EtOCH:C(CO_2Et)_2$	$C_{13}H_{17}O_8Na$	$C_{13}H_{18}O_8$
(7)	$NaOEt + CH_2(CO_2Me)_2 + EtOCH:C(CO_2Et)_2$	$C_{14}H_{19}O_8Na$	$C_{14}H_{20}O_8$
(8)	$NaOEt + CNCH_2CO_2Et + EtOCH:C(CO_2Et)_2$	$EtO_2C(CN)C:CH\cdot CNa(CO_2Et)_2$	$EtO_2C(CN)C:CH\cdot CH(CO_2Et)_2$
(9)	$NaOEt + CH_2(CO_2Et)_2 + EtOCH:C(CN)CO_2Et$		
(10)	$NaOEt + CH_2(CN)_2 + EtOCH:C(CO_2Et)_2$	$(CN)_2C:CH\cdot CNa(CO_2Et)_2$	$(CN)_2C:CH\cdot CH(CO_2Et)_2$ $H_2NCO(CN)C:CH\cdot CH(CO_2Et)_2$ $(H_2NCO)_2C:CH\cdot CH(CO_2Et)_2$
(11)	$NaOEt + CH_2(CO_2Et)_2 + EtOCH:C(CN)_2$		
(12)	$4NaOMe+2CNCH_2CO_2Me+CHCl_3$	$MeO_2C(CN)C:CH\cdot CNa(CN)CO_2Me$	$(C_9H_8O_4N_2)_2H_2O$
(13)	$4NaOEt+2CNCH_2CO_2Et+CHCl_3$	$EtO_2C(CN)C:CH\cdot CNa(CN)CO_2Et$	$(C_{11}H_{12}O_4N_2)_2H_2O$
(14)	$4NaOEt + 2CNCH_2CO_2Et + CCl_4$		
(15)	$4NaOEt + 2CNCH_2CO_2Et + Cl_3CCO_2Et$		
(16)	$NaOEt + CNCH_2CO_2Et + EtOCH:C(CN)CO_2Et$		
(17)	$NaOEt + CNCH_2CO_2Me + EtOCH:C(CN)CO_2Et$	,,	,,
(18)	$NaOMe + CNCH_2CO_2Me + EtOCH:C(CN)CO_2Et$	$C_{10}H_9O_4N_2Na$	$(C_{10}H_{10}O_4N_2)_2H_2O$
(19)	$NaOEt + CNCH_2CO_2Et + EtOCH:C(CN)CO_2Me$		
(20)	$NaOMe + CNCH_2CO_2Et + EtOCH:C(CN)CO_2Me$	$MeO_2C(CN)C:CH\cdot CNa(CN)CO_2Me$	$(C_9H_8O_4N_2)_2H_2O$
(21)	$NaOEt + CH_2(CN)_2 + EtOCH:C(CN)CO_2Et$	$(CN)_2C:CH\cdot CNa(CN)CO_2Et$	$(C_9H_7O_2N_3)_2H_2O$
(22)	$NaOEt + CNCH_2CO_2Et + EtOCH:C(CN)_2$		
(23)	$NaOEt + CH_2(CN)_2 + EtOCH:C(CN)_2$	$(CN)_2C:CH\cdot CNa(CN)_2$	$(CN)_2C:CH\cdot CH(CN)_2$
(24)	$4NaOEt + 2CH_2(CN)_2 + CHCl_3$	——	$(C_9H_8ON_4)_2H_2O$

place subsequently, then how two different condensations give the same prouct will be well understood.



$$\left.\begin{array}{l} XYC=CHOC_2H_5+CH_2X'X' \\ X'Y'C=CHOC_2H_5+CH_2XY \end{array}\right\} \xrightarrow{NaOC_2H_5} XYCH\text{-}\underset{\substack{|\\ OC_2H_5}}{CH}\text{-}CHX'Y' \xrightarrow{NaOC_2H_5}$$

$XYC=CH-CNaX'Y'$ or $X'Y'C=CH-CNaXY$.

The hydrogen in the carbon with less cyano-groups is substituted with sodium, while the hydrogen in the carbon with more cyano-groups is splitted off forming ethyl alcohol with the ethoxy-group.

Summary. The table shows the outlines of synthetical studies made by the present author and others in regard to the nitrile-esters of dicarboxy-glutaconic acid. The water of crystallisation which is present in some of the sodium compounds is omitted. The configurations of those written in molecular formulae are not yet known. As to the constitution of those written in the formula $(\ldots\ldots)_2H_2O$, see this journal, **2** (1927), 29. The details will be found in the following places:

(1) Guthzeit, Weiss and Schoefer, *J. prakt. Chem.*, **80** (1909), 439.
(2) Conrad, Guthzeit, *Ber.*, **15** (1882), 2842; *Ann.*, **222** (1884), 250.
(3) Zelinsky, Doroschewsky, *Ber.*, **27** (1894), 3374; Bischoff, *Ber.*, **28** (1895), 2829.
(4) Ruhemann, *Ber.*, **29** (1896), 1017.
(5) Claisen, Haase, *Ann.*, **297** (1897), 88.
(6), (7) Urushibara, this journal, **3** (1928), 220.
(8), (9) Errera, *Ber.*, **31** (1898), 1243; Urushibara, this journal, **2** (1927), 280; **3** (1928), 223.
(10), (11) Urushibara, this journal, **2** (1927), 281.
(12) Urushibara, this journal, **2** (1927), 240.
(13) Errera, *Ber.*, **31** (1898), 1241; Ruhemann, Browning, *J. Chem. Soc.*, **73** (1898), 282; Urushibara, this journal, **2** (1927), 28, 236.
(14) Dimroth, *Ber.*, **35** (1902), 2882.
(15) Urushibara, this journal, **2** (1927), 237.
(16) Urushibara, this journal, **2** (1927), 240, 283.
(17), (18), (19), (20) Urushibara, this journal, **3** (1928), 219.
(21), (22) Urushibara, this journal, **2** (1927), 284.
(23) Urushibara, this journal, **2** (1927), 285.
(24) Zörnig, *J. prakt. Chem.*, **74** (1906), 435.

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

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