PECULIARITY IN THE FORMATION OF THE NITRILE-ESTERS OF DICARBOXY-GLUTACONIC ACID.

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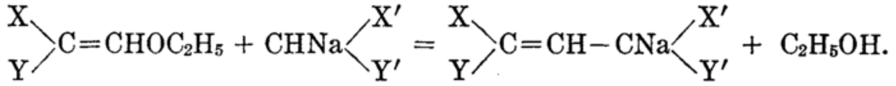
As the introduction to the present paper the previous studies on the synthesis of the nitrile-esters of dicarboxy-glutaconic acid⁽¹⁾ will be outlined. The condensation of the ethoxymethylene compound $XYC=CHOC_2H_5$ with the sodiomethylene compound $CHNaX'Y'$ can occur in nine different combinations if each of X, X′, Y, and Y′ represents either $-CN$ or $-COOC_2H_5$; and the products of the nine cases should be different from one another, including all the possible nitrile-esters of dicarboxyglutaconic acid $(HOOC)_2C=CH-CH(COOH)_2$, if the condensation proceeds as follows:



$$\substack{X \\ Y}{>}C=CHOC_2H_5 + CHNa{<}\substack{X' \\ Y'} = \substack{X \\ Y}{>}C=CH-CNa{<}\substack{X' \\ Y'} + C_2H_5OH.$$

Nevertheless, if the nine condensations are carried out in alcoholic solutions, more than six compounds can not be obtained, for among the nine condensations three pairs yield respectively only one and the same product. In precise expression, the following pair of reactions does not yield two different products which can be expected by the equations:

$$XYC=CHOC_2H_5 + CHNaX'Y' = XYC=CH-CNaX'Y' + C_2H_5OH,$$
$$X'Y'C=CHOC_2H_5 + CHNaXY = X'Y'C=CH-CNaXY + C_2H_5OH.$$

The constitution of the only product has been determined. The sodium atom is always situated at the carbon atom to which the more carbethoxy-groups are attached. The six really obtained compounds are, therefore, as follows:

$(C_2H_5OCO)_2C=CH-CNa(COOC_2H_5)_2$, $C_2H_5OCO(CN)C=CH-CNa(COOC_2H_5)_2$,
$C_2H_5OCO(CN)C=CH-CNa(CN)COOC_2H_5$, $(CN)_2C=CH-CNa(COOC_2H_5)_2$,
$(CN)_2C=CH-CNa(CN)_2$, $(CN)_2C=CH-CNa(CN)COOC_2H_5$.

The following three can not be obtained:

$(C_2H_5OCO)_2C=CH-CNa(CN)COOC_2H_5$, $(C_2H_5OCO)_2C=CH-CNa(CN)_2$,
$C_2H_5OCO(CN)C=CH-CNa(CN)_2$.

Similarly, by the condensation of ethyl ethoxymethylene-cyanoacetate with methyl sodio-cyanoacetate in methyl alcohol and by the condensation

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

of methyl ethoxymethylene-cyanoacetate with ethyl sodio-cyanoacetate in ethyl alcohol, the same methyl ethyl sodio-dicyanoglutaconate and from it the same methyl ethyl dicyanoglutaconate semihydrate are obtained.

By and by, the author became aware of the studies on xanthophanic acids by Feist and his co-workers.⁽¹⁾ They describe γ-methyl α-ethyl α, γ-diacetyl-glutaconate and α-methyl γ-ethyl α, γ-diacetyl-glutaconate as different substances. They obtained the former by the condensation of methyl ethoxy-methylene-acetoacetate with ethyl sodio-acetoacetate in ether, and the latter by the condensation of ethyl ethoxy-methylene-acetoacetate with methyl sodio-acetoacetate.

The above two condensations carried out by the present author and giving the same methyl ethyl dicyanoglutaconate are not more different from those by Feist than that cyano-groups took the place of the acetyl-groups and methyl and ethyl alcohols were used as the solvents instead of ether. Thus, to make matters clear, it seemed important to try the synthesis of the nitrile-esters of dicarboxyglutaconic acid in the ethereal medium. For this purpose it is unnecessary to synthesize those compounds with equal attachments at the both ends of the propylene nucleus. The eight condensations shown later were tried; and if the results are collected it can be deduced that four kinds of products are possible in each reaction, and that in the condensation of $XYC=CHOC_2H_5$ with $CHNaX'Y'$, are possible the following four products:

$XYC=CH-CNaX'Y'$, the product of the 1st kind;
$X'Y'C=CH-CNaXY$, the product of the 2nd kind;
$X'Y'C=CH-CNaX'Y'$, the product of the 3rd kind;
$XYC=CH-CNaXY$, the product of the 4th kind.

If $X=X'$ and $Y=Y'$, the four formulae are the same; and in such cases, if the experiment were carried out, only one product would be obtained. The table shows the results of the eight condensations. Individual compounds found in each condensation are placed in the forms of the sodium derivatives under the general formulae showing the kinds. Compounds corresponding to the blank spaces could not be found. Unfortunately, in no reaction all of the possible products could be isolated. Probably, those formed in relatively large quantities or those easy of separation could be isolated. Besides, at the beginning of the experiments on this series of condensations it was beyond expectation that each reaction would give four kinds of products. It was after studying many of the reactions that possibility of four kinds of products was found.

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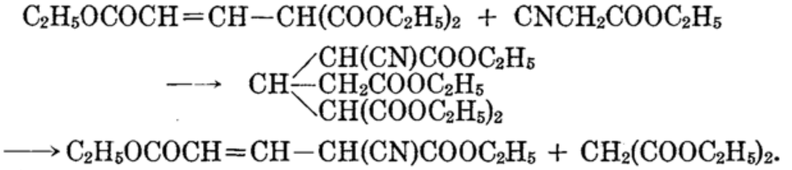
(1) *Ber.*, **59** (1926), 2958.

The mechanism of the reactions can be explained to some extent, if they are compared with the experiments on the synthesis of poly-acetic acids of methane by C. K. Ingold and E. A. Perren.(1) According to them various derivatives of diethyl glutaconate readily react with ethyl sodiocyanoacetate; nevertheless the products of these condensations contain no trace of derivatives of methane triacetic acid, but consist almost wholly of fission products formed from these substances by a decomposition having the character of a retrograde Michael reaction. For instance, triethyl α-carboxyglutaconate gives initially a condensation product, which then undergoes complete fission into diethyl α-cyanoglutaconate and diethyl malonate:



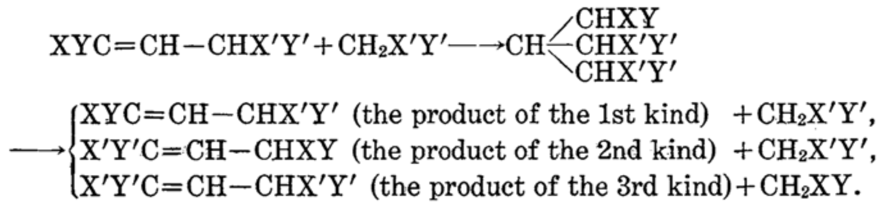
$$C_2H_5OCOCH{=}CH{-}CH(COOC_2H_5)_2 + CNCH_2COOC_2H_5$$
$$\longrightarrow CH\left\langle\begin{array}{l}CH(CN)COOC_2H_5\\ CH_2COOC_2H_5\\ CH(COOC_2H_5)_2\end{array}\right.$$
$$\longrightarrow C_2H_5OCOCH{=}CH{-}CH(CN)COOC_2H_5 + CH_2(COOC_2H_5)_2.$$

In the second reaction the group eliminated from the molecule is usually the largest among the substituted acetic acid residues attached to the same carbon atom.

The mechanism of the reaction of the ethoxymethylene compound $XYC{=}CHOC_2H_5$ with the methylene compound $CH_2X'Y'$ which gives four products can be analysed into several processes. Previously(2) the formation of the intermediate addition compound $XYCH{-}CH(OC_2H_5){-}CHX'Y'$ was supposed, but such a hypothesis is not necessary, because the derivatives of methane triacetic acid act not only in place of it, but also in the formation of such products as not to be explained by the former hypothesis. The reaction begins with the formation of the product of the first kind:

$$XYC{=}CHOC_2H_5 + CH_2X'Y'$$
$$\longrightarrow XYC{=}CH{-}CHX'Y' \text{ (the product of the 1st kind)} + C_2H_5OH.$$

The product of the first kind partly condenses with the methylene compound $CH_2X'Y'$ present in the reaction medium, and then fission follows:



$$XYC{=}CH{-}CHX'Y' + CH_2X'Y' \longrightarrow CH\left\langle\begin{array}{l}CHXY\\ CHX'Y'\\ CHX'Y'\end{array}\right.$$
$$\longrightarrow\left\{\begin{array}{ll}XYC{=}CH{-}CHX'Y' \text{ (the product of the 1st kind)} & + CH_2X'Y',\\ X'Y'C{=}CH{-}CHXY \text{ (the product of the 2nd kind)} & + CH_2X'Y',\\ X'Y'C{=}CH{-}CHX'Y' \text{ (the product of the 3rd kind)} & + CH_2XY.\end{array}\right.$$

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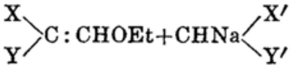
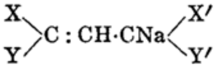
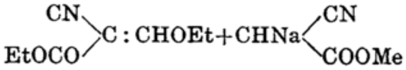
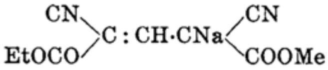
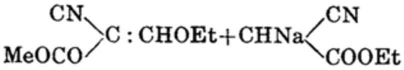
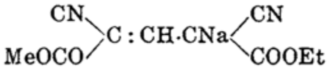
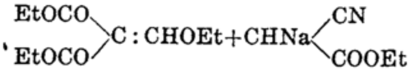
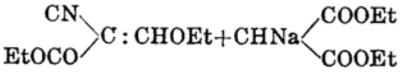
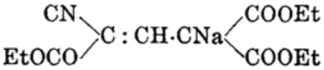
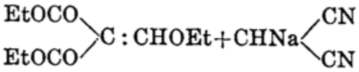
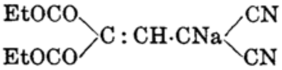
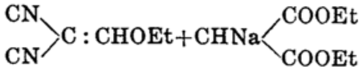
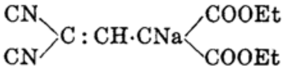
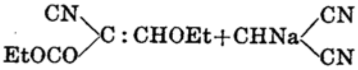
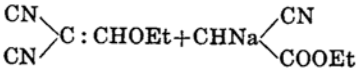
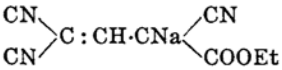
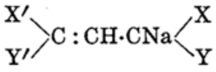
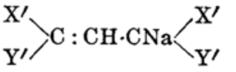
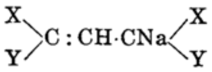
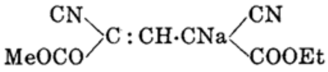
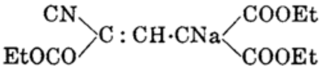
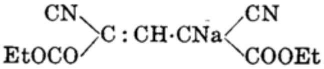
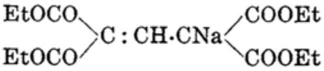
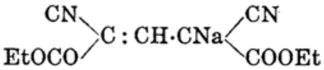
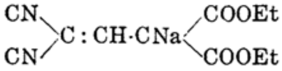
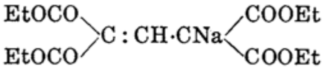
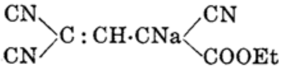
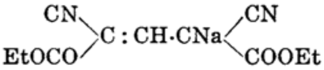
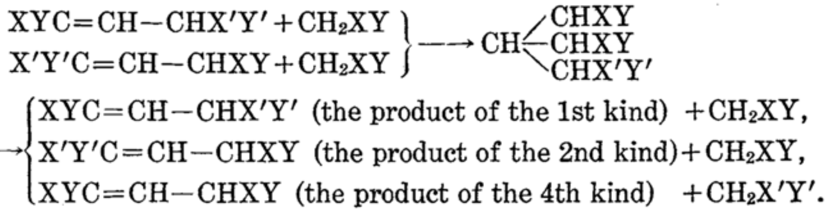
(1) *J. Chem. Soc.*, **119** (1921), 1582.

(2) This Bulletin, **3** (1928), 226.

	Condensations	
		The First Kind
	 $\begin{smallmatrix}\mathrm{X}\\ \mathrm{Y}\end{smallmatrix}\!>\mathrm{C:CHOEt+CHNa}<\!\begin{smallmatrix}\mathrm{X'}\\ \mathrm{Y'}\end{smallmatrix}$	 $\begin{smallmatrix}\mathrm{X}\\ \mathrm{Y}\end{smallmatrix}\!>\mathrm{C:CH{\cdot}CNa}<\!\begin{smallmatrix}\mathrm{X'}\\ \mathrm{Y'}\end{smallmatrix}$
1	 $\begin{smallmatrix}\mathrm{CN}\\ \mathrm{EtOCO}\end{smallmatrix}\!>\mathrm{C:CHOEt+CHNa}<\!\begin{smallmatrix}\mathrm{CN}\\ \mathrm{COOMe}\end{smallmatrix}$	 $\begin{smallmatrix}\mathrm{CN}\\ \mathrm{EtOCO}\end{smallmatrix}\!>\mathrm{C:CH{\cdot}CNa}<\!\begin{smallmatrix}\mathrm{CN}\\ \mathrm{COOMe}\end{smallmatrix}$
2	 $\begin{smallmatrix}\mathrm{CN}\\ \mathrm{MeOCO}\end{smallmatrix}\!>\mathrm{C:CHOEt+CHNa}<\!\begin{smallmatrix}\mathrm{CN}\\ \mathrm{COOEt}\end{smallmatrix}$	 $\begin{smallmatrix}\mathrm{CN}\\ \mathrm{MeOCO}\end{smallmatrix}\!>\mathrm{C:CH{\cdot}CNa}<\!\begin{smallmatrix}\mathrm{CN}\\ \mathrm{COOEt}\end{smallmatrix}$
3	 $\begin{smallmatrix}\mathrm{EtOCO}\\ \mathrm{EtOCO}\end{smallmatrix}\!>\mathrm{C:CHOEt+CHNa}<\!\begin{smallmatrix}\mathrm{CN}\\ \mathrm{COOEt}\end{smallmatrix}$	
4	 $\begin{smallmatrix}\mathrm{CN}\\ \mathrm{EtOCO}\end{smallmatrix}\!>\mathrm{C:CHOEt+CHNa}<\!\begin{smallmatrix}\mathrm{COOEt}\\ \mathrm{COOEt}\end{smallmatrix}$	 $\begin{smallmatrix}\mathrm{CN}\\ \mathrm{EtOCO}\end{smallmatrix}\!>\mathrm{C:CH{\cdot}CNa}<\!\begin{smallmatrix}\mathrm{COOEt}\\ \mathrm{COOEt}\end{smallmatrix}$
5	 $\begin{smallmatrix}\mathrm{EtOCO}\\ \mathrm{EtOCO}\end{smallmatrix}\!>\mathrm{C:CHOEt+CHNa}<\!\begin{smallmatrix}\mathrm{CN}\\ \mathrm{CN}\end{smallmatrix}$	 $\begin{smallmatrix}\mathrm{EtOCO}\\ \mathrm{EtOCO}\end{smallmatrix}\!>\mathrm{C:CH{\cdot}CNa}<\!\begin{smallmatrix}\mathrm{CN}\\ \mathrm{CN}\end{smallmatrix}$
6	 $\begin{smallmatrix}\mathrm{CN}\\ \mathrm{CN}\end{smallmatrix}\!>\mathrm{C:CHOEt+CHNa}<\!\begin{smallmatrix}\mathrm{COOEt}\\ \mathrm{COOEt}\end{smallmatrix}$	 $\begin{smallmatrix}\mathrm{CN}\\ \mathrm{CN}\end{smallmatrix}\!>\mathrm{C:CH{\cdot}CNa}<\!\begin{smallmatrix}\mathrm{COOEt}\\ \mathrm{COOEt}\end{smallmatrix}$
7	 $\begin{smallmatrix}\mathrm{CN}\\ \mathrm{EtOCO}\end{smallmatrix}\!>\mathrm{C:CHOEt+CHNa}<\!\begin{smallmatrix}\mathrm{CN}\\ \mathrm{CN}\end{smallmatrix}$	
8	 $\begin{smallmatrix}\mathrm{CN}\\ \mathrm{CN}\end{smallmatrix}\!>\mathrm{C:CHOEt+CHNa}<\!\begin{smallmatrix}\mathrm{CN}\\ \mathrm{COOEt}\end{smallmatrix}$	 $\begin{smallmatrix}\mathrm{CN}\\ \mathrm{CN}\end{smallmatrix}\!>\mathrm{C:CH{\cdot}CNa}<\!\begin{smallmatrix}\mathrm{CN}\\ \mathrm{COOEt}\end{smallmatrix}$

Products		
The Second Kind	The Third Kind	The Fourth Kind
 $\begin{smallmatrix}\mathrm{X'}\\\mathrm{Y'}\end{smallmatrix}>\mathrm{C:CH\cdot CNa}<\begin{smallmatrix}\mathrm{X}\\\mathrm{Y}\end{smallmatrix}$	 $\begin{smallmatrix}\mathrm{X'}\\\mathrm{Y'}\end{smallmatrix}>\mathrm{C:CH\cdot CNa}<\begin{smallmatrix}\mathrm{X'}\\\mathrm{Y'}\end{smallmatrix}$	 $\begin{smallmatrix}\mathrm{X}\\\mathrm{Y}\end{smallmatrix}>\mathrm{C:CH\cdot CNa}<\begin{smallmatrix}\mathrm{X}\\\mathrm{Y}\end{smallmatrix}$
 $\begin{smallmatrix}\mathrm{CN}\\\mathrm{MeOCO}\end{smallmatrix}>\mathrm{C:CH\cdot CNa}<\begin{smallmatrix}\mathrm{CN}\\\mathrm{COOEt}\end{smallmatrix}$		
 $\begin{smallmatrix}\mathrm{CN}\\\mathrm{EtOCO}\end{smallmatrix}>\mathrm{C:CH\cdot CNa}<\begin{smallmatrix}\mathrm{COOEt}\\\mathrm{COOEt}\end{smallmatrix}$	 $\begin{smallmatrix}\mathrm{CN}\\\mathrm{EtOCO}\end{smallmatrix}>\mathrm{C:CH\cdot CNa}<\begin{smallmatrix}\mathrm{CN}\\\mathrm{COOEt}\end{smallmatrix}$	
	 $\begin{smallmatrix}\mathrm{EtOCO}\\\mathrm{EtOCO}\end{smallmatrix}>\mathrm{C:CH\cdot CNa}<\begin{smallmatrix}\mathrm{COOEt}\\\mathrm{COOEt}\end{smallmatrix}$	 $\begin{smallmatrix}\mathrm{CN}\\\mathrm{EtOCO}\end{smallmatrix}>\mathrm{C:CH\cdot CNa}<\begin{smallmatrix}\mathrm{CN}\\\mathrm{COOEt}\end{smallmatrix}$
 $\begin{smallmatrix}\mathrm{CN}\\\mathrm{CN}\end{smallmatrix}>\mathrm{C:CH\cdot CNa}<\begin{smallmatrix}\mathrm{COOEt}\\\mathrm{COOEt}\end{smallmatrix}$		
	 $\begin{smallmatrix}\mathrm{EtOCO}\\\mathrm{EtOCO}\end{smallmatrix}>\mathrm{C:CH\cdot CNa}<\begin{smallmatrix}\mathrm{COOEt}\\\mathrm{COOEt}\end{smallmatrix}$	
 $\begin{smallmatrix}\mathrm{CN}\\\mathrm{CN}\end{smallmatrix}>\mathrm{C:CH\cdot CNa}<\begin{smallmatrix}\mathrm{CN}\\\mathrm{COOEt}\end{smallmatrix}$		 $\begin{smallmatrix}\mathrm{CN}\\\mathrm{EtOCO}\end{smallmatrix}>\mathrm{C:CH\cdot CNa}<\begin{smallmatrix}\mathrm{CN}\\\mathrm{COOEt}\end{smallmatrix}$

The fission is possible in three directions. Now, another methylene compound CH_2XY is ready to condense with the product of the first or the second kind, and fission can yield the fourth product besides others:



$$\left.\begin{array}{l} XYC{=}CH{-}CHX'Y'+CH_2XY \\ X'Y'C{=}CH{-}CHXY+CH_2XY \end{array}\right\}\longrightarrow CH\left\langle\begin{array}{l} CHXY \\ CHXY \\ CHX'Y' \end{array}\right.$$

$$\longrightarrow\begin{cases} XYC{=}CH{-}CHX'Y' \text{ (the product of the 1st kind) } +CH_2XY, \\ X'Y'C{=}CH{-}CHXY \text{ (the product of the 2nd kind)}+CH_2XY, \\ XYC{=}CH{-}CHXY \text{ (the product of the 4th kind) } +CH_2X'Y'. \end{cases}$$

If the sodium atom is taken into consideration the relations are somewhat complicated, but fundamentally not altered. The above mentioned are the necessary processes for the formation of the four products; and the real condensations may include many other similar processes of addition and fission; nevertheless, more than the four products can never be expected. It is noteworthy that there are many chances for the more stable product to grow in amount in the cost of the less stable. It is remarkable that tetraethyl dicarboxyglutaconate having the largest groups attached to the central methenyl carbon atom was produced in many of the condensations⁽¹⁾ where it corresponded to any of the possible four kinds of products; and, therefore, it can not be said that the largest group is eliminated in the form of a methylene compound from the molecule of the intermediate methane triacetic acid derivative.

In the condensation in alcohol one product is prevalent. The reaction is of the homogeneous system, the materials and the products existing both in the dissolved state; and this facilitates the establishment of equilibrium, allowing the product the most table in the condition of that time to prevail. On the other hand, in the reaction in ether only one of the materials, the ethoxy-methylene compound, and none of the products, go into solution, and it is probable that various substances exist in various proportions in various places, and this permits many of the possible products to survive.

The fact that two isomeric compounds which differ from each other only in the position of the double union, and consequently of the sodium atom, the best example being diethyl α-sodio-γ, γ-dicyano-propylene-α, α-dicarboxylate and diethyl α-sodio-α, α-dicyano-propylene-γ, γ-dicarboxylate, are distinctly different is incompatible with the normal theory of J. F. Thorpe, which was already rejected by the present author and others.⁽²⁾

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(1) The synthesis of the esters of acetyl-propylene-carboxylic acids is included, the results of which will be published later.

(2) This Bulletin, **3** (1928), 205; R. Malachowski u. M. Maslowski, *Ber.*, **61** (1928), 2521; R. Malachowski, *Ber.*, **62** B (1929), 1323.

Further the present investigation has thrown light on some obscure points in the previous experiments. The fact that two isomeric derivatives of dicarboxyglutaconic acid which differ from each other only in the positions of the double union and the sodium atom always proved to be identical is nothing but that one of the two possible isomerides was more stable and formed exclusively, the present investigation indicating that sometimes the less stable form can be obtained by the condensation in ether.

Experimental Part.

It seems convenient to begin with describing some of the products, especially concerning the methods of separation and identification, for the same substances may appear in more than one reactions. The following are all the known substances, and new compounds will be described in the places where they are met for the first time.

Tetraethyl α, γ-dicarboxyglutaconate, $(C_2H_5OCO)_2C{=}CH{-}CH(COOC_2H_5)_2$. Its sodium derivative is sparingly soluble in cold water and imparts opacity to water probably owing to its partial hydrolysis. It can be recrystallised from alcohol. The free ester formed by the action of dilute hydrochloric or sulphuric acid on the sodium compound is a colourless oil, and is identified by elementary analysis. It requires $C=54.51$; $H=6.72\%$.

Triethyl γ-cyano-α-carboxyglutaconate, $C_2H_5OCO(CN)C{=}CH{-}CH(COOC_2H_5)_2$. The sodium derivative is easily soluble in water, and its alcoholic solution gives violet colouration with ferric chloride. The free cyano-ester is an oil, requiring $N=4.94\%$. It is easily transformed into diethyl α, α′-dioxypyridine-β, β′-dicarboxylate $C_{11}H_{13}O_6N$ requiring $N=5.49\%$ and melting at 199°.

The esters of α, γ-dicyanoglutaconic acid, $ROCO(CN)C{=}CH{-}CH(CN)COOR$. Their sodium derivatives are all fine needle crystals, easily soluble in hot water. The corresponding free cyano-esters can not be obtained, but instead of them their semihydrates are always formed. Dimethyl, diethyl, and one of the methyl ethyl compounds have been obtained. The semihydrates are all yellow crystalline substances and can be identified by analysis and melting points.

Dimethyl compound:	$(C_9H_8O_4N_2)_2\cdot H_2O$,	[225°]	$N=12.90\%$;
Methyl ethyl compound:	$(C_{10}H_{10}O_4N_2)_2\cdot H_2O$,	[197°]	$N=12.12\%$;
Diethyl compound:	$(C_{11}H_{12}O_4N_2)_2\cdot H_2O$,	[183°]	$N=11.43\%$.

Further the diethyl compound gives a picrate of formula $C_{11}H_{16}O_6N_2\cdot C_6H_2(NO_2)_3OH$ melting at 196-197°.

Diethyl γ, γ-dicyano-propylene-α, α-dicarboxylate, $(CN)_2C=CH-CH(COOC_2H_5)_2$. The sodium derivatite is easily soluble in water. On acidifying its aqueous solution an oily substance is precipitated. This is the free cyanoester, but after a short time it changes into colourless crystals of diethyl γ, γ-dicarbamyl-propylene-α, α-dicarboxylate $(NH_2CO)_2C=CH-CH(COOC_2H_5)_2$ which melts at 139-140°, changing opaque on prolonged heating. The free cyano-ester dissolved in alcohol changes into diethyl γ-cyano-γ-carbamylpropylene-α, α-dicarboxylate $NH_2CO(CN)C=CH-CH(COOC_2H_5)_2$ melting at 212°.

Ethyl α, γ, γ-tricyano-propylene-α-carboxylate, $(CN)_2C=CH-CH(CN)COOC_2H_5$. The free cyano-ester can not be obtained, but the semihydrate $(C_9H_7O_2N_3)_2 \cdot H_2O$ melting at 190° and requiring $N=21.21\%$.

α, α, γ, γ-Tetracyano-propylene, $(CN)_2C=CH-CH(CN)_2$. This compound can be isolated only in its sodium derivative, which crystallises in needles from the aqueous solution. The aqueous solution produces no precipitation on acidifying, and if the aqueous solution acidified with hydrochloric acid is evaporated up in vacuum in the desiccator furnished with sulphuric acid and soda-lime, the crystals of the original sodium compound can be recovered. On adding a silver nitrate solution to the aqueous solution of the sodium compound a white precipitate is produced which is insoluble in dilute nitric acid.

Experimental Procedure. The first course of the reactions is to prepare the sodium derivatives of the methylene compounds. The sodium derivative of diethyl malonate was prepared by adding an excess (ten percent more than the theoretical quantity) of this ester to finely granulated metallic sodium covered with a large amount of pure ether. When the evolution of hydrogen is over and sodium disappears, the reaction is completed, and a paste of diethyl sodio-malonate is obtained.

Methyl sodio-cyanoacetate is prepared similarly, except that a small quantity of methyl alcohol is added to accelerate the reaction, and after the reaction is completed the solid is collected, dried in vacuum over sulphuric acid, weighed, and mixed with pure ether.

Ethyl sodio-cyanoacetate is prepared by adding the free ester to an alcoholic solution of sodium ethylate, the white crystals being collected, washed with pure ether, and well dried in vacuum. Sodio-malonitrile is prepared similarly.

In every case the sodio-methylene compound is mixed with pure ether and the calculated amount of the ethoxymethylene compound is added gradually under constant stirring. The reaction mass is from pale yellow to dark red. After standing for a length of time, the solid is separated from ether by filtration or by dissolution in water. Then the solid or the aqueous solution is subjected to the process of separation and identification.

(1) *Condensation of ethyl ethoxymethylene-cyanoacetate with methyl sodio-cyanoacetate.* The semihydrate of the free cyano-ester obtained from the crude condensation product melted at 193°. Then the crude sodium compound was recrystallised four times from water, and the purified substance was transformed into the semihydrate, the latter being recrystallised once from absolute alcohol. It melted at 190°. Anal. Found: N=12.06, 12.23%. Nevertheless, this specimen is not identical with the already known methyl ethyl dicyanoglutaconate semihydrate, because there is a remarkable difference not only in the melting points, but also in the solubilities in absolute alcohol, the already known compound being insoluble in boiling alcohol while the new tolerably soluble in hot alcohol.

The author believes that the crude product was a mixture of the two isomeric methyl ethyl sodio-dicyanoglutaconates, and the specimen melting at 193° was the corresponding mixture of the semihydrates. The substance obtained by recrystallisation of the crude sodium compound was one of the isomerides, and that different from the already known.

(2) *Condensation of methyl ethoxymethylene-cyanoacetate with ethyl sodio-cyanoacetate.* The specimen of the semihydrate obtained from either the crude or the recrystallised sodium compound melted at 196°. It can be said that the product was pure and unique; and, therefore, it is very natural to consider it the product of the first kind, that is γ-methyl α-ethyl α-sodio-α, γ-dicyanoglutaconate.

The sodium compound obtained in condensation 1 and giving the semihydrate melting at 190° is the α-methyl γ-ethyl compound. The only product of the condensations in alcohol is the γ-methyl α-ethyl compound, for it gives the semihydrate with the higher melting point.

(3) *Condensation of diethyl ethoxymethylene-malonate with ethyl sodio-cyanoacetate.* The yellow pasty mass obtained by the reaction was dissolved in water. After a short time a crystalline substance separated from the solution. This was identified with diethyl α-sodio-dicyanoglutaconate by its transformation into diethyl dicyanoglutaconate semihydrate. Anal. Found: N=11.52%.

On acidifying the aqueous solution filtered from the above crystalline substance two kinds of substances separated, one being crystalline and the other oily. The former was identified with diethyl dicyanoglutaconate semihydrate. Anal. Found: N=11.50%. Melting point: 183°. The latter was collected by dissolving it in ether and evaporating the ethereal solution. On standing for three weeks the oil was partly changed into crystals. The part which remained oily was purified by dissolving it in ether, extracting with a ten percent solution of sodium carbonate, acidifying the soda solution, extracting the oil with ether, and evaporating the dried ethereal solution. This was found to be nearly pure triethyl cyano-carboxy-glutaconate. Anal. Found: N=4.82%. Its alcoholic solution gave dark brown colouration with ferric chloride, which showed that the compound was triethyl γ-cyano-α-carboxy-glutaconate.⁽¹⁾ The crystalline part contained 5.71% of nitrogen and melted at 190–195°. It was probably diethyl α, α′-dioxy-pyridine-β, β′-dicarboxylate formed by the transformation of the triethyl cyano-carboxy-glutaconate.

(4) *Condensation of ethyl ethoxymethylene-cyanoacetate with diethyl sodio-malonate.* The crude mass obtained by the reaction was dissolved in water, and the aqueous solution was acidified with dilute hydrochloric acid. The whole was shaken with ether, and the ethereal and the aqueous solutions were treated separately.

The aqueous solution gave a small amount of a yellow crystalline substance. This was identified with diethyl dicyanoglutaconate semihydrate. Anal. Found: N=11.61%. Melting point: 183°.

The ethereal solution was shaken with a ten percent solution of sodium carbonate. The soda solution gave an enormous quantity of sparingly soluble solid, which contained 5.81% of nitrogen and seemed to consist mainly of diethyl α, α′-dioxy-pyridine-β, β′-dicarboxylate. The solid was digested with cold hydrochloric acid, washed, and dried. This was found to be the above pyridine derivative. Anal. Found: N=5.62%. Melting point: 199°.

The presence of alcohol in the mother liquor could be detected by its odour, indicating that the above pyridine derivative was formed from triethyl cyanocarboxyglutaconate according to the following equation:

$$C_{13}H_{17}O_6N + H_2O = C_{11}H_{13}O_6N + C_2H_5OH.$$

This triethyl cyanocarboxyglutaconate can be assumed to be the γ-cyano-α-carboxy-compound, that is the product of the first kind and more stable than the α-cyano-γ-carboxy-compound.

The mother liquor was acidified. The oily drops were collected, and transformed into a yellow crystalline sodium compound by shaking with a soda solution. This was identified with tetraethyl α-sodio-dicarboxy-glutaconate by the analysis of the free ester obtained from it. Anal. Found: C=54.60; H=6.74%.

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(1) Cf. this Bulletin, **3** (1928), 221.

(5) *Condensation of diethyl ethoxymethylene-malonate with sodio-malonitrile.* The condensation mass was dissolved in water. Crystals separated from the aqueous solution. These crystals and the mother liquor were treated separately.

The crystalline sodium compound was recrystallised from alcohol. Its alcoholic solution gave reddish violet colouration with ferric chloride. On acidifying its aqueous solution it was transformed into a colourless crystalline substance, which was identified with diethyl γ, γ-dicarbamyl-propylene-α, α-dicarboxylate by its melting point. Further the sodium compound could be transformed into diethyl γ-cyano-γ-carbamyl-propylene-α, α-dicarboxylate. Hence, it is diethyl α-sodio-γ, γ-dicyano-propylene-α, α-dicarboxylate.

The aqueous mother liquor filtered from the above crystalline sodium compound was acidified, and shaken with ether. The two liquid layers were treated separately.

On evaporating the ethereal solution a small amount of oil was obtained, which was then transformed into a crystalline sodium compound by shaking with a soda solution. This was probably tetraethyl α-sodio-dicarboxy-glutaconate, but the substance was not sufficient in purity and quantity for analysis.

It was expected that the aqueous solution might contain sodio-tetra-cyano-propylene. It was evaporated to a brown mass in vacuum over sulphuric acid and soda-lime. The brown mass was digested with alcohol, and the alcoholic solution was evaporated in vacuum to a crystalline mass. This was recrystallised twice from a small amount of water, animal charcoal being used to decolourize the solution. In this way nearly colourless needle crystals of a sodium compound were obtained. This substance resembles the sodium derivative of tetracyanopropylene as regards the properties, so that it was considered to be the expected substance until it was analysed. Anal. Found: $N = 10.6\%$. The nitrogen content is equal to that of diethyl α-sodio-γ, γ-dicyanopropylene-α, α-dicarboxylate ($N = 10.9\%$), but the properties unequal, the new sodium compound being apparently unchangeable by acidifying its aqueous solution, just as same as sodio-tetracyano-propylene. The compound in question, therefore, can be nothing but diethyl α-sodio-α, α-dicyano-propylene-γ, γ-dicarboxylate $(C_2H_5OCO)_2C{=}CH{-}CNa(CN)_2$, the product of the first kind of this condensation.

(6) *Condensation of ethoxymethylene-malonitrile with diethyl sodio-malonate.* The condensation mass was dissolved in water and the solution was acidified. Most of oil which separated out changed into colourless crystals after a short time, but among them some brown oil drops remained. The crystalline part was collected, washed with water, and then with ether,

the oily part being collected in the wash ether. The crystalline substance, the ethereal solution, and the aqueous mother liquor were treated separately.

The crystalline substance was identified with diethyl γ, γ-dicarbamyl-propylene-α, α-dicarboxylate. Hence, the original sodium compound is diethyl α-sodio-γ, γ-dicyano-propylene-α, α-dicarboxylate.

The ethereal solution gave an oil on evaporation. It was then transformed into a yellow crystalline sodium compound by shaking with a soda solution. This was identified with tetraethyl α-sodio-dicarboxyglutaconate by the analysis of the free ester obtained from it. Anal. Found: C=54.38; H=6.75%.

The aqueous mother liquor was expected to contain diethyl α-sodio-α, α-dicyanopropylene-γ, γ-dicarboxylate or more possibly sodio-tetracyano-propylene. But only a crystalline substance containing about 16% of nitrogen was isolated. It was probably a decomposition compound of either of them.

(7) *Condensation of ethyl ethoxymethylene-cyanoacetate with sodio-malonitrile.* The condensation seemed not to take place at the ordinary temperature, for on mixing these substances in pure ether no apparent change was observed. The mixture was heated for some time, and after evaporating most of ether it was kept at the room temperature for some ten days. Then the solid was dissolved in water and the aqueous solution was acidified, when dark brown oil separated out, which was extracted with ether.⁽¹⁾ From the ethereal solution, on drying with calcium chloride, yellow crystals separated. Anal. Found: N=18.95%. It seemed to be a mixture of ethyl tricyanopropylene-carboxylate semihydrate and diethyl dicyanoglutaconate semihydrate. Then it was recrystallised from alcohol. Anal. Found: N=17.41%. After recrystallisation the nitrogen content decreased, indicating that a mixture was being handled. It was easily found that the mixture contained diethyl dicyanoglutaconate semihydrate, for the alcoholic mother liquor of the above recrystallisation gave the characteristic picrate. The authentic specimen of ethyl α, γ, γ-tricyano-propylene-α-carboxylate semihydrate gives no product with picric acid. Another component of the mixture is believed to have been ethyl α, γ, γ-tricyanopropylene-α-carboxylate semihydrate, its mother substance being ethyl α-sodio-α, γ, γ-tricyanopropylene-α-carboxylate, the product of the second kind of this condensation. If it were the product of the first kind,

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(1) None of the nitrile-esters of dicarboxyglutaconic acid which give semihydrates has ever separated in the form of oil, the present case being the only exception; but it can be considered that the separation of oil was due to the presence of malonitrile which would be formed from the sodio-malonitrile.

ethyl α-sodio-α, α, γ-tricyano-propylene-γ-carboxylate, it would be stable to acid, for the two known α-dicyano compounds are so.

(8) *Condensation of ethoxymethylene-malonitrile with ethyl sodio-cyano-acetate.* The crude product was purely white. On acidifying its aqueous solution a yellow crystalline substance was obtained, which was found to be nearly pure ethyl α, γ, γ-tricyanopropylene-α-carboxylate semihydrate. Anal. Found: N=20.72, 20.75%. The only product is, therefore, ethyl α-sodio-α, γ, γ-tricyano-propylene-α-carboxylate, the product of the first kind.

Summary.

From the results of eight reactions it was deduced that the four compounds,

$XYC=CH-CNaX'Y'$,
$X'Y'C=CH-CNaXY$,
$X'Y'C=CH-CNaX'Y'$,
$XYC=CH-CNaXY$,

can be produced in the condensation of the ethoxymethylene compound $XYC=CHOC_2H_5$ with the sodio-methylene compound $CHNaX'Y'$, where each of X, X′, Y, and Y′ represents either -CN or $-COOC_2H_5$.

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