THE NITRILE-ESTERS OF 2-METHYLPROPENE-1,1,3,3-TETRACARBOXYLIC ACID.

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Introduction. One of the authors revealed the true nature of the so-called diethyl dicyano-glutaconate,⁽¹⁾ and then carried out a series of condensations to synthesize other nitrile-esters of propene-1,1,3,3-tetracarboxylic acid (α,γ-dicarboxy-glutaconic acid).⁽²⁾ The introduction to the present paper must be begun with summarizing these previous studies.

The sodium derivative of diethyl 1,3-dicyano-propene-1,3-dicarboxylate (diethyl α,γ-dicyano-glutaconate) (VI or $C_{11}H_{11}O_4N_2Na$) is formed by the reaction of ethyl cyanacetate, chloroform, and sodium ethylate, or by the condensation of ethyl ethoxymethylene-cyanacetate $C_2H_5OCO(CN)C{=}CHOC_2H_5$ and ethyl sodio-cyanacetate $CHNa(CN)COOC_2H_5$, and it crystallizes in needles (colourless when pure) with two molecules of water of crystallization. It is transformed into a yellow crystalline substance on acidifying its aqueous solution. The latter had been long considered diethyl dicyano-glutaconate (H for Na in VI or $C_{11}H_{12}O_4N_2$) corresponding to the sodium compound, but it is really a more complicated compound with formula XV or $(C_{11}H_{12}O_4N_2)_2 \cdot H_2O$.

Nine cases are possible for the condensation of the ethoxymethylene compound $XYC{=}CHOC_2H_5$ with the sodium derivative of the methylene compound $CH_2X'Y'$, where X,Y,X', and Y' represent independently either cyano-group CN or carbethoxy-group $COOC_2H_5$, and the products of the nine cases would be different from one another, including all the possible nitrile-esters (in the form of the sodium derivatives) of propene-1,1,3,3-tetracarboxylic acid $(HOOC)_2C{=}CH{-}CH(COOH)_2$, if the condensation could be expressed simply by the following equation:

$$XYC{=}CHOC_2H_5 + CHNaX'Y' = XYC{=}CH{-}CNaX'Y' + C_2H_5OH.$$

Nevertheless, if the condensation is carried out in alcoholic solution, the product of the reaction to be represented by the above equation is the same as that of the reaction to be represented by the following equation:

$$X'Y'C{=}CHOC_2H_5 + CHNaXY = X'Y'\overset{1}{C}{=}\overset{2}{C}H{-}\overset{3}{C}NaXY + C_2H_5OH.$$

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(1) Y. Urushibara, this Bulletin, **2** (1927), 26, 236.

(2) Y. Urushibara, this Bulletin, **2** (1927), 278; **3** (1928), 219; **5** (1930), 1.

(If $X = X'$ and $Y = Y'$, the two equations are identical, but this is of course not meant here.) The common product of the two different reactions is one of the two required by the above equations, and the one that possesses more carbethoxy-groups in carbon atom 3 than in carbon atom 1. There are three of such pairs among the nine cases, and, therefore, only six compounds, namely I, III, V, VI, VIII, and IX, can be obtained. In the cases where the above equations require the products II, IV, and VII, they are supplanted by III, V, and VIII respectively.

(I)	$(C_2H_5OCO)_2C{=}CH{-}CNa(COOC_2H_5)_2$
(II)	$(C_2H_5OCO)_2C{=}CH{-}CNa(CN)COOC_2H_5$
(III)	$C_2H_5OCO(CN)C{=}CH{-}CNa(COOC_2H_5)_2$
(IV)	$(C_2H_5OCO)_2C{=}CH{-}CNa(CN)_2$
(V)	$(CN)_2C{=}CH{-}CNa(COOC_2H_5)_2$
(VI)	$C_2H_5OCO(CN)C{=}CH{-}CNa(CN)COOC_2H_5$
(VII)	$C_2H_5OCO(CN)C{=}CH{-}CNa(CN)_2$
(VIII)	$(CN)_2C{=}CH{-}CNa(CN)COOC_2H_5$
(IX)	$(CN)_2{=}CH{-}CNa(CN)_2$

No ambiguity is involved in the formulation of compounds I, VI, and IX(3) with cyano- and carbethoxy-groups arranged symmetrically. Sodium compound I and the corresponding free ester (X) give a colouration (blue) with ferric chloride in alcoholic solution, while VI and IX not. Thus it is shown that only the compound in which carbon atom 3 possesses two carbethoxy-groups can exist in the enolic form and gives the colour reaction with ferric chloride. The common product of the condensation of ethoxymethylene-malonitrile with diethyl sodio-malonate and the condensation of diethyl ethoxymethylene-malonate with sodio-malonitrile is V and not IV, because it gives a violet colouration with ferric chloride. The sodium derivative of triethyl cyano-propene-tricarboxylate obtained by the condensation of ethyl ethoxymethylene-cyanacetate with diethyl sodio-malonate and by the condensation of diethyl ethoxymethylene-malonate with ethyl sodio-cyanacetate gives a violet colouration with ferric chloride and formula III can thus be ascertained. The above two examples suggest that carbon atom 3 generally retains more carbethoxy-groups than carbon atom 1. For this reason the constitution of ethyl sodio-tricyano-propene-carboxylate can be assumed to be VIII.

Now, if the condensation of the ethoxymethylene compound $XYC{=}CHOC_2H_5$ and the sodium derivative of the methylene compound $CHNaX'Y'$ is carried out in ether where the reaction is heterogeneous, four compounds,

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(3) It is not considered here in what manner the sodium atom is combined.

XYC=CH–CNaX′Y′, X′Y′C=CH–CNaXY, X′Y′C=CH–CNaX′Y′, and XYC=CH–CNaXY, may be found side by side in the reaction products. This was deduced by gathering the results of all the cases of condensation except those satisfying the conditions $X = X'$ and $Y = Y'$, where the four compounds are the same. By the condensation in ether the sodium derivative of 3,3-dicyano-propene-1,1-dicarboxylate (IV), which could not be obtained by the condensation in alcoholic solution, was isolated besides its isomeride (V) from the reaction products of diethyl ethoxymethylene-malonate $(C_2H_5OCO)_2C{=}CHOC_2H_5$ and sodio-malonitrile $CHNa(CN)_2$. The theory stated above in general formulæ means that in this case of condensation I and IX also might have been found in the products, althought it was not the case. To give another example, III, I, and VI were isolated from the products of condensation of ethyl ethoxy-methylene-cyanacetate and diethyl sodio-malonate in ether. Compounds II and VII have not yet been obtained even by the reactions in ether.

These sodium compounds behave differently towards acids. The sodium derivative of tetraethyl propene-1,1,3,3-tetracarboxylate (I) gives the corresponding free ester (X), a colourless oily substance insoluble in water. Triethyl 1-cyano-propene-1,3,3-tricarboxylate (XI) is obtained as an oily substance on acidifying the aqueous solution of its sodium derivative (III). It crystallizes gradually on keeping in the desiccator. It has a stronger acid character, but seems to be more easily changeable, than tetraethyl propene-tetracarboxylate (X). The sodium compound (III) forms hygroscopic crystals.

The sodium derivative of diethyl 3,3-dicyano-propene-1,1-dicarboxylate (IV) crystallizes in colourless needles and behaves very similarly to the tetra-cyano-compound (IX). On acidifying its aqueous solution no apparent change is observed. The sodium derivative of diethyl 1,1-dicyano-propene-3,3-dicarboxylate (V), forming nearly colourless crystals with half a molecule of water of crystallization, gives an oily substance on acidifying its aqueous solution. The oily substance can be collected as such by quick extraction with ether followed by also quick dehydration and evaporation of the extract. It is supposed to be diethyl 1,1-dicyano-propene-3,3-dicarboxylate (XII). It gives a bluish-violet colouration with ferric chloride. If the oily substance precipitated is left in the mother liquor, soon it goes again into solution and a colourless crystalline compound separates out. This is diethyl 1,1-dicarbamyl-propene-3,3-dicarboxylate (XIII), and melts at 139–140°, solidifying then and decomposing at higher temperature. When the oily substance is dissolved in alcohol, it is transformed into another crystalline compound, diethyl 1-cyano-1-carbamyl-propene-3,3-dicarboxylate (XIV), melting at 212°.

As mentioned above, the sodium derivative of diethyl 1,3-dicyano-propene-1,3-dicarboxylate (VI) crystallizes with two molecules of water of crystallization and gives a yellow crystalline compound with the formula $(C_{11}H_{12}O_4N_2)_2 \cdot H_2O$ on acidifying its aqueous solution. The yellow compound melts at 183° and its constitution is supposed to be XV. The sodium derivative of ethyl 1, 1, 3-tricyano-propene-3-carboxylate (VIII or $C_9H_6O_2N_3Na$), forming colourless crystals with a molecule of water of crystallization, gives a similar compound $(C_9H_7O_2N_3)_2 \cdot H_2O$, yellow crystals melting at 190°.

The sodium derivative of 1,1,3,3-tetracyano-propene (IX) forms colourless fine needles with a molecule of water of crystallization. On adding hydrochloric acid to its aqueous solution no apparent change is observed. The unchanged sodium compound (with a molecule of water of crystallization) can be crystallized out from the aqueous solution acidified with hydrochloric acid. But, if the aqueous solution acidified with hydrochloric acid is extracted with ether several times, the aqueous layer leaves sodium chloride alone on evaporation. If the ethereal extract is dried and evaporated in vacuum, a colourless crystalline substance remains, but it decomposes quickly into a brown amorphous mass. The unstable crystalline substance is supposed to be 1,1,3,3-tetracyano-propene (XVI). An aqueous solution can be obtained by evaporating the ethereal extract on water. The substance is stable in solution and behaves as a very strong acid. The electrolytic dissociation of this compound will be dealt with in a separate paper.

(X) $(C_2H_5OCO)_2C{=}CH{-}CH(COOC_2H_5)_2$
(XI) $C_2H_5OCO(CN)C{=}CH{-}CH(COOC_2H_5)_2$
(XII) $(CN)_2C{=}CH{-}CH(COOC_2H_5)_2$
(XIII) $(H_2NCO)_2C{=}CH{-}CH(COOC_2H_5)_2$
(XIV) $H_2NCO(CN)C{=}CH{-}CH(COOC_2H_5)_2$
(XV) $(C_{10}H_{12}O_4N){-}CO{-}NH{-}C(NH){-}(C_{10}H_{12}O_4N)$
(XVI) $(CN)_2C{=}CH{-}CH(CN)_2$

Thus the nature and the arrangement of the four groups, X, Y, X′, and Y′, exert a great influence on the behaviour of the sodium compound of the propene derivative XYC=CH-CHX′Y′.

Now, ethyl ethoxyethylidene-cyanacetate (ethyl α-cyano-β-ethoxy-crotonate) $C_2H_5OCO(CN)C{=}C(CH_3)OC_2H_5$ reacts with the sodium derivative of ethyl cyanacetate in the same way as ethyl ethoxymethylene-cyanacetate, yielding the sodium derivative of diethyl 1,3-dicyano-2-methylpropene-1,3-dicarboxylate (diethyl α,γ-dicyano-β-methyl-glutaconate) (XXVI).⁽⁴⁾ In the same way ethyl α-cyano-β-ethoxy-γ-phenyl-crotonate $C_2H_5OCO(CN)C{=}C(CH_2C_6H_5)OC_2H_5$ and the sodium derivative of ethyl cyanacetate condense to produce the sodium

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(4) Y. Urushibara, this Bulletin, **3** (1928), 102; also compare *ibid.*, **3** (1928), 261.

derivative of diethyl 1,3-dicyano-2-benzylpropene-1,3-dicarboxylate (diethyl α,γ-dicyano-β-benzyl-glutaconate) (XVII).(5) Thus it is shown that $XYC=CROC_2H_5$ and $CHNaX'Y'$ condense in the same way whether R is hydrogen or an alkyl or a similar group.

Sodium compound XXVI(6) gives an oily substance on acidifying its aqueous solution. This oily substance is supposed to be diethyl 1,3-dicyano-2-methylpropene-1,3-dicarboxylate (XVIII), but it is so unstable that it soon changes into a red crystalline mass. Sodium compound XVII gives also an oily substance, which is quickly transformed into a colourless crystalline compound. The latter has the composition of diethyl 1(or 3)-cyano-3(or 1)-carbamyl-2-benzylpropene-1,3-dicarboxylate (XIX or XX).

(XVII) $C_2H_5OCO(CN)C=C(CH_2C_6H_5)-CNa(CN)COOC_2H_5$

(XVIII) $C_2H_5OCO(CN)C=C(CH_3)-CH(CN)COOC_2H_5$

(XIX) $C_2H_5OCO(CN)C=C(CH_2C_6H_5)-CH(CONH_2)COOC_2H_5$

(XX) $C_2H_5OCO(H_2NCO)C=C(CH_2C_6H_5)-CH(CN)COOC_2H_5$

The present paper is concerned with other cases of the condensation of the ethoxyethylidene compound $XYC=C(CH_3)OC_2H_5$ and the sodium derivative of the methylene compound $CHNaX'Y'$, and the comparison of the properties of the produced nitrile-esters of 2-methylpropene-1,1,3,3-tetracarboxylic acid $(HOOC)_2C=C(CH_3)-CH(COOH)_2$ or their sodium derivatives with those of the corresponding compounds of the propene-1,1,3,3-tetracarboxylic acid series.

The Preparation of Ethoxyethylidene Compounds as the Materials of the Condensation. Among three ethoxyethylidene compounds only ethyl ethoxyethylidene-cyanacetate $C_2H_5OCO(CN)C=C(CH_3)OC_2H_5$ is known, and it is obtained by the condensation of triethyl orthoacetate with ethyl cyanacetate by means of acetic anhydride.(7) Ethoxyethylidene-malonitrile $(CN)_2C=C(CH_3)OC_2H_5$ has been obtained by a similar method, malonitrile being used instead of ethyl cyanacetate in the above-mentioned condensation. Ethoxyethylidene-malonitrile forms colourless crystals melting at 91°. In spite of several attempts of synthesis including the condensation of diethyl malonate with triethyl orthoacetate, diethyl ethoxyethylidene-malonate $(C_2H_5OCO)_2C=C(CH_3)OC_2H_5$ has not yet been obtained.

The Condensations of the Ethoxyethylidene Compounds and the Sodium Derivatives of the Methylene Compounds and the Investigation of the Products. Nine cases are also possible for the condensation of the ethoxy-

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(5) Y. Urushibara, this Bulletin, **3** (1928), 316.

(6) It has not yet been crystallized from water; from alcohol it crystallizes without solvent of crystallization.

(7) Y. Urushibara, this Bulletin, **3** (1928), 103.

ethylidene compound $XYC=C(CH_3)OC_2H_5$ and the sodium derivative of the methylene compound $CHNaX'Y'$, X, Y, X', and Y' representing independently either cyano-group CN or carbethoxy-group $COOC_2H_5$. And, if the reaction proceeded simply to yield the normal product $XYC=C(CH_3)\text{-}CNaX'Y'$, nine compounds XXI–XXIX, the sodium derivatives of all the possible nitrile-esters of 2-methylpropene-1,1,3,3-tetracarboxylic acid, would be obtained. But from the examples of the propene-1,1,3,3-tetracarboxylic acid series it can be naturally expected that compounds XXII, XXIV, and XXVII, which have more cyano-groups in carbon atom 3 than in carbon atom 1, will not be obtained by the condensation in alcoholic solution, compounds XXIII, XXV, and XXVIII appearing as the substitutes respectively.

As diethyl ethoxyethylidene-malonate is not obtainable, three cases of condensation out of the nine can not be realized. The condensation of ethyl ethoxyethylidene-cyanacetate and ethyl sodio-cyanacetate producing compound XXVI has been already described by one of the authors as mentioned above. The remaining five cases have now been studied, all the reactions being carried out in alcoholic solution. If they were carried out in ether, four compounds might be expected from each reaction, that is to say, the condensation of $XYC=C(CH_3)OC_2H_5$ and $CHNaX'Y'$ would give $XYC=C(CH_3)\text{–}CNaX'Y'$, $X'Y'C=C(CH_3)\text{–}CNaXY$, $X'Y'C=C(CH_3)\text{–}CNaX'Y'$, and $XYC=C(CH_3)\text{–}CNaXY$.

From the comparison of VI, XVII, and XXVI, it appeared that the compound represented by the general formula $XYC=CR\text{–}CNaX'Y'$ might behave differently according to the nature of the group R even if the arrangement of the four negative groups was the same, but, so far as the compounds described below are concerned, there is no difference in the chemical behaviour between the propene series ($R = H$) and the 2-methylpropene series ($R = CH_3$).

(XXI) $(C_2H_5OCO)_2C=C(CH_3)\text{–}CNa(COOC_2H_5)_2$
(XXII) $(C_2H_5OCO)_2C=C(CH_3)\text{–}CNa(CN)COOC_2H_5$
(XXIII) $C_2H_5OCO(CN)C=C(CH_3)\text{–}CNa(COOC_2H_5)_2$
(XXIV) $(C_2H_5OCO)_2C=C(CH_3)\text{–}CNa(CN)_2$
(XXV) $(CN)_2C=C(CH_3)\text{–}CNa(COOC_2H_5)_2$
(XXVI) $C_2H_5OCO(CN)C=C(CH_3)\text{–}CNa(CN)COOC_2H_5$
(XXVII) $C_2H_5OCO(CN)C=C(CH_3)\text{–}CNa(CN)_2$
(XXVIII) $(CN)_2C=C(CH_3)\text{–}CNa(CN)COOC_2H_5$
(XXIX) $(CN)_2C=C(CH_3)\text{–}CNa(CN)_2$

(1) *Condensation of Ethyl Ethoxyethylidene-cyanacetate* $C_2H_5OCO(CN)C=C(CH_3)OC_2H_5$ *and Diethyl Sodio-malonate* $CHNa(COOC_2H_5)_2$. The product is expected to be the sodium derivative of triethyl 1-cyano-2-methylpropene-1,3,3-tricarboxylate (XXIII). It is obtained

as hygroscopic crystals. It gives a dark-red colouration with ferric chloride in accordance with the assumed structure (XXIII). On acidifying its aqueous solution the corresponding free ester, triethyl 1-cyano-2-methylpropene-1,3,3-tricarboxylate (XXX), is precipitated as an oily substance. When the oil is collected and kept in the desiccator, it crystallizes slowly. The substance is insoluble in water, but soluble in ether and in alcohol. It dissolves in the aqueous solution of sodium carbonate or hydroxide, and on acidifying the solution it is precipitated. Thus XXIII and XXX manifest behaviours analogous to those of III and XI respectively, and this fact supports the assigned formulæ.

(2) *Condensation of Ethoxyethylidene-malonitrile* $(CN)_2C{=}C(CH_3)OC_2H_5$ *and Diethyl Sodio-malonate* $CHNa(COOC_2H_5)_2$. The product is expected to be the sodium derivative of diethyl 1,1-dicyano-2-methylpropene-3,3-dicarboxylate (XXV). From water it crystallizes in light-yellow needles with half a molecule of water of crystallization. It is easily soluble in water and in alcohol. It gives a dark-red colouration with ferric chloride in accordance with the assumed structure (XXV). On acidifying the aqueous solution of this sodium compound an oily substance is formed, which is supposed to be diethyl 1,1-dicyano-2-methylpropene-3,3-dicarboxylate (XXXI or $C_{12}H_{14}O_4N_2$). The oily substance is easily transformed into two crystalline compounds, one melting at 232° and the other at 164°. Both are insoluble in water and in ether. The compound melting at 232° has the composition $C_{12}H_{14}O_4N_2{\cdot}H_2O$ and formula XXXII may be given to it in analogy to compound XIV. The compound melting at 164° possesses the composition $C_{12}H_{14}O_4N_2{\cdot}2H_2O$, and formula XXXIII may be given to it in analogy to compound XIII. These compounds may be called respectively diethyl 1-cyano-1-carbamyl-2-methylpropene-3,3-dicarboxylate and diethyl 1,1-dicarbamyl-2-methylpropene-3,3-dicarboxylate. The fact that the difference in the melting points between XIV [212°] and XXXII [232°] is nearly equal to the difference between XIII [140°] and XXXIII [164°] justifies the assigned relationship of analogy and homology. Here again exists a perfect parallelism of behaviours between the compounds of the propene series and the compounds of the 2-methylpropene series: the sodium compounds (V and XXV) crystallize with half a molecule of water, and the free compounds (XII and XXXI) are easily combined with a molecule of water (giving XIV and XXXII respectively) and also with two molecules of water (giving XIII and XXXIII respectively). These circumstances reciprocally strengthen the grounds for assigning formulæ XXV, XXXI, XXXII, and XXXIII respectively corresponding to formulæ V, XII, XIV, and XIII, which have been established on a stronger basis by the synthesis of compound IV.

(XXX) $C_2H_5OCO(CN)C{=}C(CH_3){-}CH(COOC_2H_5)_2$
(XXXI) $(CN)_2C{=}C(CH_3){-}CH(COOC_2H_5)_2$
(XXXII) $H_2NCO(CN)C{=}C(CH_3){-}CH(COOC_2H_5)_2$
(XXXIII) $(H_2NCO)_2C{=}C(CH_3){-}CH(COOC_2H_5)_2$

(3) *Condensation of Ethoxyethylidene-malonitrile* $(CN)_2C{=}C(CH_3)OC_2H_5$ *and Ethyl Sodio-cyanacetate* $CHNa(CN)COOC_2H_5$. The product is expected to be the sodium derivative of ethyl 1,1,3-tricyano-2-methylpronene-3-carboxylate (XXVIII), because this structure not only corresponds to the normal product of the condensation, but also possesses more carbethoxy-groups in carbon atom 3 than in carbon atom 1. Further, its behaviour, being very similar to that of compound VIII, are in accordance with the assumed structure: The sodium compound crystallizes in colourless needles with a molecule of water of crystallization ($C_{10}H_8O_2N_3Na{\cdot}H_2O$). On acidifying its aqueous solution a nearly colourless crystalline substance separates out gradually. It is insoluble in water and in ether, but soluble in alcohol, from which it can be recrystallized in colourless crystals. It melts at 212–213° with decomposition, and has the composition $C_{10}H_9O_2N_3{\cdot}{}^1/_2H_2O$ or $(C_{10}H_9O_2N_3)_2{\cdot}H_2O$.

(4) *Condensation of Ethyl Ethoxyethylidene-cyanacetate* $C_2H_5OCO(CN)C{=}C(CH_3)OC_2H_5$ *and Sodio-malonitrile* $CHNa(CN)_2$. If the reaction proceeded as follows:

$$C_2H_5OCO(CN)C{=}C(CH_3)OC_2H_5 + CHNa(CN)_2$$
$$= C_2H_5OCO(CN)C{=}C(CH_3){-}CNa(CN)_2 + C_2H_5OH,$$

a product with formula XXVII would be formed. But the sodium compound produced behaves unlike the 3,3-dicyano-compounds, VII, IX, and XXIX (see below), and manifests the same properties as XXVIII obtained by the condensation of ethoxyethylidene-malonitrile and ethyl sodio-cyanacetate: The present sodium compound crystallizes in colourless needles with a molecule of water of crystallization ($C_{10}H_8O_2N_3Na{\cdot}H_2O$), and, on acidifying its aqueous solution, yields a light-yellow crystalline compound. The latter is insoluble in water and in ether, but can be recrystallized in colourless crystals from alcohol, melts at 227–228° with decomposition, and gives analytical results corresponding to formula $C_{10}H_9O_2N_3{\cdot}{}^1/_2H_2O$ or $(C_{10}H_9O_2N_3)_2{\cdot}H_2O$. Therefore, in spite of a small difference in the melting points of the two specimens of the crystalline derivative, it is very probable that the product of the present condensation is the sodium derivative of ethyl 1,1,3-tricyano-2-methylpropene-3-carboxylate (XXVIII), the same as obtained by the preceding condensation.

There exist analogies in all respects between the propene series and the 2-methylpropene series: by the condensation in alcoholic solution the 1,1,3-tricyano-3-carbethoxy-compounds, VIII and XXVIII, are exclusively formed, even when the 1, 3, 3-tricyano-1-carbethoxy-compounds, VII and XXVII respectively, may be expected as the normal products; the sodium compounds obtained, VIII and XXVIII, crystallize with a molecule of water, and, on acidifying their aqueous solutions, yield the crystalline compounds with similar compositions, $(C_9H_7O_2N_3)_2 \cdot H_2O$ and $(C_{10}H_9O_2N_3)_2 \cdot H_2O$ respectively.

Nevertheless, there is one point of disagreement: the compound $(C_9H_7O_2N_3)_2 \cdot H_2O$ is yellow, while the compound $(C_{10}H_9O_2N_3)_2 \cdot H_2O$ is colourless. It has been repeatedly experienced that the sodium derivatives of the nitrile-esters of dicarboxy-glutaconic acid appear often coloured (mostly yellow), the same compound sometimes being tinged with different colours,⁽⁸⁾ while it is very probable that they must be all colourless when pure, because most of them have been really obtained in colourless state. The colouring, and even the colourless, impurities of the sodium compounds may affect the colour of the compounds derived from them.⁽⁹⁾ Thus it is not impossible that the colour of such derivatives may not be essential. But, without any further investigations, there may be no saying what is the fact with the compounds in question.

(5) *Condensation of Ethoxyethylidene-malonitrile* $(CN)_2C{=}C(CH_3)OC_2H_5$ *and Sodio-malonitrile* $CHNa(CN)_2$. The sodium derivative of 1,1,3,3-tetracyano-2-methylpropene (XXIX) separates out in light-yellow crystals from the alcoholic reaction mixture without evaporation. It is recrystallized from water in colourless silky crystals with a molecule of water ($C_8H_3N_4Na \cdot H_2O$). When its aqueous solution is acidified with hydrochloric acid nothing separates out. On evaporating the acidified solution over sulphuric acid in vacuum, the sodium compound is recovered unchanged. But, if the acidified solution is shaken repeatedly with ether, and the combined ethereal extract is dried with calcium chloride and evaporated in vacuum, colourless silky crystals remain. This crystalline compound is supposed to be 1,1,3,3-tetracyano-2-methylpropene (XXXIV), but it is very unstable and decomposes quickly into a dark-red amorphous substance. It is, however, stable in solution. Its aqueous solution behaves as a very strong acid; it dissolves zinc and magnesium with the evolution of hydrogen gas. The electrolytic dissociation of this compound will be dealt with in a separate paper.

(XXXIV) $(CN)_2C{=}C(CH_3){-}CH(CN)_2$

Thus XXIX and XXXIV behave so much similarly to IX and XVI respectively, that the two series can not be distinguished from each other except by the analytical results. The parallelism goes farther: A sodium-free by-product

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(8) Y. Urushibara, this Bulletin, **2** (1927), 28, 238, 284.

(9) Y. Urushibara, this Bulletin, **2** (1927), 284.

is formed by the condensation of ethoxymethylene-malonitrile and sodio-malonitrile, and is obtained from the mother liquor of the sodium derivative of 1,1,3,3-tetracyano-propene C_7HN_4Na. It has the composition $C_7H_2N_4 \cdot C_2H_5OH$ and melts at 211–212° without decomposition.(10) Similarly from the mother liquor of the sodium derivative of 1,1,3,3-tetracyano-2-methylpropene $C_8H_3N_4Na$, a compound with formula $C_8H_4N_4 \cdot C_2H_5OH$ and melting point 226° is obtained.

If the reaction of ethoxyethylidene-malonitrile and sodio-malonitrile is carried out without cooling, the yield of the sodium-free by-product $C_8H_4N_4 \cdot C_2H_5OH$ increases at the cost of the sodium compound $C_8H_3N_4Na$, and the reaction mixture or the mother liquor of the sodium compound shows a stronger alkaline reaction than when the yield of the by-product is smaller.

Experimental Part.

Preparation of the Ethoxyethylidene Compounds. (1) *Ethoxyethylidene-malonitrile.* A mixture of triethyl orthoacetate (1 mol), malonitrile (1 mol), and acetic anhydride (2 mols) was heated in a flask with an upright condenser, the cooling water being stopped from running. Ethyl acetate formed was collected through a bent tube attached at the top of the condenser. When it reached the required amount, the mixture in the flask was distilled, under the ordinary pressure until the temperature reached 140°, and then under diminished pressure. Ethoxyethylidene-malonitrile distilled constantly at 120° under 2 mm. Melting point 91°. Easily soluble in alcohol, difficultly soluble in ether, and insoluble in water. (Found: N, 20.68. Calculated for $C_7H_8ON_2$: N, 20.59%.)

(2) *Attempted Preparation of Diethyl Ethoxyethylidene-malonate.* Following reactions were attemped all in vain: (a) Condensation of triethyl orthoacetate and diethyl malonate by means of acetic anhydride. (b) The same with the addition of zinc chloride. (c) Diethyl acetyl-malonate prepared according to the directions of H. Lund(11) was transformed into its silver derivative through the sodium derivative, and the silver compound and ethyl iodide were heated in alcohol. (d) The same reaction in ether instead of alcohol. (e) Action of ethyl iodide on the potassium derivative of diethyl acetyl-malonate. (f) Hydrolysis of ethyl ethoxyethylidene-cyanacetate by sulphuric acid in alcohol. (g) Transformation of the cyano-group of ethyl ethoxyethylidene-cyanacetate into a carbethoxy-group through $-C(NH)OC_2H_5$ and $-C(OC_2H_5)_3$. (h) Action of diazomethane on diethyl acetyl-malonate in ether.

Condensations of Ethoxyethylidene Compounds and the Sodium Derivatives of Methylene Compounds. Sodium (1 mol) was dissolved in absolute alcohol, the methylene compound (1 mol) was added to the alcoholic sodium ethylate, and the ethoxyethylidene compound (1 mol) was introduced gradually under cooling. The reaction liquor was evaporated to crystallization over sulphuric acid in vacuum at the ordinary temperature.

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(10) Y. Urushibara, this Bulletin, **2** (1927), 286.

(11) *Ber.*, **67** (1934), 935.

(1) *Condensation of Ethyl Ethoxyethylidene-cyanacetate and Diethyl Sodio-malonate.* The product (XXIII) was obtained as a crystalline mass by evaporating the reaction liquor over sulphuric acid in vacuum and washing the residue with ether. The substance obtained was very hygroscopic, so that it was not recrystallized. It gave a dark-red colouration with ferric chloride. The crude substance was dissolved in water and the solution was acidified with dilute hydrochloric acid, when an oily substance separated out. The oily substance was extracted with ether, the ethereal solution was shaken with aqueous sodium carbonate, the aqueous solution was acidified, and the oil was collected by extraction with ether followed by evaporation of the solvent in vacuum. The oily substance thus obtained was orange-coloured, and when it was kept in a sulphuric acid desiccator, crystals appeared slowly. After dried in vacuum, the substance was analysed (Found: C, 56.33; H, 6.81; N, 5.02. Calculated for XXX or $C_{14}H_{19}O_6N$: C, 56.97; H, 6.40; N, 4.71%).

(2) *Condensation of Ethoxyethylidene-malonitrile and Diethyl Sodio-malonate.* The product (XXV) was obtained as a crystalline mass by evaporating the reaction liquor. It was readily soluble in alcohol. It was recrystallized from water in light-yellow needles with half a molecule of water of crystallization (Found: H_2O, 3.02. Calculated for $C_{12}H_{13}O_4N_2Na \cdot {}^1/_2 H_2O$: H_2O, 3.20%. Found for anhydrous substance: N, 10.02. Calculated for XXV or $C_{12}H_{13}O_4N_2Na$: N, 10.29%). The substance gave a dark-red colouration with ferric chloride.

On adding dilute hydrochloric acid to an aqueous solution of the sodium compound, an orange-red oily substance separated out immediately. The oil was extracted with ether, the ethereal solution was shaken with 10% aqueous sodium carbonate, and the aqueous solution was acidified and shaken with ether. A small amount of a crystalline substance soluble in neither the aqueous nor the ethereal layer was collected, washed with water and ether, and dried. It was obtained as colourless crystals melting at 232° (Found: C, 53.67; H, 6.28; N, 10.64. Calculated for XXXII or $C_{12}H_{14}O_4N_2 \cdot H_2O$: C, 53.73; H, 5.97; N, 10.44%). On evaporating the ethereal layer without drying, another colourless crystalline substance separated out, which did not dissolve again in ether. It was collected, washed with ether and water, and dried, melting point 164° (Found: C, 50.18; H, 6.66; N, 10.07. Calculated for XXXIII or $C_{12}H_{14}O_4N_2 \cdot 2H_2O$: C, 50.35; H, 6.29; N, 9.79%).

(3) *Condensation of Ethoxyethylidene-malonitrile and Ethyl Sodio-cyanacetate.* On evaporating the reaction liquor, the product (XXVIII) separated out in crystals. It was easily soluble in water, alcohol, and acetone. Recrystallized from water, it was obtained as colourless needles with a molecule of water of crystallization (Found: H_2O, 7.07. Calculated for $C_{10}H_8O_2N_3Na \cdot H_2O$: H_2O, 7.41%. Found for anhydrous substance: N, 18.48. Calculated for XXVIII or $C_{10}H_8O_2N_3Na$: N, 18.67%).

When an aqueous solution of the sodium compound was acidified with dilute hydrochloric acid, a crystalline substance separated out after a while. It was insoluble in water and in ether. It was recrystallized from alcohol, colourless crystals, melting point 212–213° with decomposition (Found: C, 56.52; H, 4.73; N, 19.94. Calculated for $(C_{10}H_9O_2N_3)_2 \cdot H_2O$: C, 56.60; H, 4.72; N, 19.81%).

(4) *Condensation of Ethyl Ethoxyethylidene-cyanacetate and Sodio-malonitrile.* The product crystallized out on evaporating the reaction liquor in vacuum. By repeated recrystallization from water it was obtained as colourless needles (Found: H_2O, 7.66 Calculated for $C_{10}H_8O_2N_3Na \cdot H_2O$: H_2O, 7.41%. Found for anhydrous substance: N, 18.90. Calculated for $C_{10}H_8O_2N_3Na$: N, 18.67%).

On adding dilute hydrochloric acid to an aqueous solution of the sodium compound a light-yellow crystalline substance separated out slowly. It was insoluble in water and in ether. It was recrystallized from alcohol, colourless crystals, melting point 227–228° with decomposition (Found: C, 56.81; H, 4.99; N, 19.90. Calculated for $(C_{10}H_9O_2N_3)_2 \cdot H_2O$: C, 56.60; H, 4.72; N, 19.81%).

(5) *Condensation of Ethoxyethylidene-malonitrile and Sodio-malonitrile.* The product (XXIX) crystallized out without evaporation. It was recrystallized from water, colourless silky crystals with a molecule of water of crystallization (Found: H_2O, 8.87. Calculated for $C_8H_3N_4Na \cdot H_2O$: H_2O, 9.18%. Found for anhydrous substance: N, 31.54. Calculated for XXIX or $C_8H_3N_4Na$: N, 31.46%).

On acidifying an aqueous solution of the sodium compound with hydrochloric acid nothing separated out. When the acidified solution was evaporated over sulphuric acid in a vacuum desiccator, the original sodium compound remained, the desiccator being filled with the fume of hydrogen chloride. An acidified aqueous solution of the sodium compound was shaken with ether several times, and the ethereal solution was dried with calcium chloride and evaporated by suction, when colourless silky crystals appeared and immediately decomposed into an amorphous substance coloured like red phosphorus.

The mother liquor of the sodium compound was evaporated over sulphuric acid in the vacuum desiccator. The remaining yellow crystalline mass contained light-yellow crystals insoluble in water. They were collected and recrystallized from alcohol. Thus a colourless crystalline compound melting at 226° was obtained (Found: C, 59.27; H, 5.22; N, 27.89. Calculated for $C_8H_4N_4 \cdot C_2H_5OH$: C, 59.41; H, 4.95; N, 27.72%).

When the condensation was carried out without cooling, the reaction mixture was coloured intensely, and the sodium compound (XXIX) did not crystallize out. The crystalline mass obtained by evaporating the reaction liquor consisted mainly of the sodium-free by-product $C_8H_4N_4 \cdot C_2H_5OH$.

Summary.

The sodium derivatives of the nitrile-esters of 2-methylpropene-1,1,3,3-tetracarboxylic acid $(HOOC)_2C{=}C(CH_3){-}CH(COOH)_2$ have been synthesized, and their properties have been compared with those of the corresponding compounds of the propene-1, 1, 3, 3-tetracarboxylic acid series synthesized previously. It has been observed that, with one exceptional case of the 1, 3-dicyano-1,3-dicarbethoxy-compounds, there exist analogies in all respects between the 2-methylpropene-tetracarboxylic acid series and the propene-tetracarboxylic acid series.

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