A SERIES OF CONDENSATIONS PRODUCING THE ESTERS OF ACETYL-PROPYLENE-CARBOXYLIC ACIDS.

By Yoshiyuki URUSHIBARA.

Received January 16, 1930. Published March 28, 1930.

In the previous paper on "peculiarity in the formation of the nitrile-esters of dicarboxyglutaconic acid"⁽¹⁾ the author pointed out the fact that in the condensation of the ethoxymethylene-compound $XYC=CHOC_2H_5$ with the sodio-methylene-compound $CHNaX'Y'$, if it is carried out in the ethereal medium, the following four products are possible:
$XYC=CH-CNaX'Y'$; $X'Y'C=CH-CNaXY$; $X'Y'C=CH-CNaX'Y'$; $XYC=CH-CNaXY$.

That paper mainly dealt with the cases where each of X, X', Y, and Y' was either CN or $COOC_2H_5$. In the present paper the results of the condensations where the acetyl-group acts in place of the nitrile-group will be reported.

As a whole, similar results have been obtained, which are shown in the table. The found products are placed in the forms of the sodium derivatives under the general formulae showing the kinds, the blank spaces corresponding to those which could not be found inspite of their formation being possible.

But, unfortunately, the products of the first and the second kinds must be considered under the following unfavourable conditions: There have been no method to determine the positions of the sodium atom and the double union; there was no condensation in which both the first and second products were found; and moreover, as shown in the experimental part, it was impossible to determine whether the products of a pair of condensations were identical or not, except condensations 1 and 2. These conditions make the results somewhat indefinite, for it is impossible to determine whether a product belongs to the first kind or the second. In the table such compounds are placed in partly expanded formulae. Nevertheless, the author believes that four products are also theoretically possible in each of these condensations.

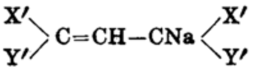
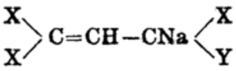
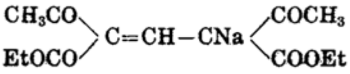
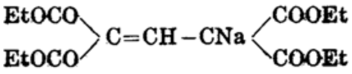
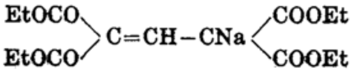
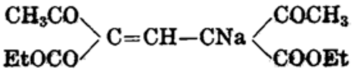
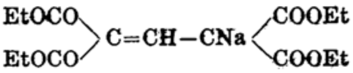
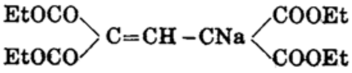
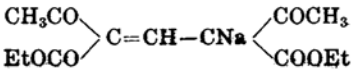
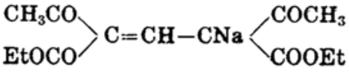
Experimental Part.

Experimental Procedure in General. The methylene compound is converted into the sodium derivative by adding it to finely granulated metallic sodium covered with pure ether. To the sodio-methylene compound in ether a

---

(1) This Bulletin, 5 (1930), 1.

	Condensations.	Products	
		The first kind	The second kind
	$\left.\begin{matrix}\mathrm{X}\\\mathrm{Y}\end{matrix}\right\rangle\mathrm{C{=}CHOEt+CHNa}\left\langle\begin{matrix}\mathrm{X'}\\\mathrm{Y'}\end{matrix}\right.$	$\left.\begin{matrix}\mathrm{X}\\\mathrm{Y}\end{matrix}\right\rangle\mathrm{C{=}CH-CNa}\left\langle\begin{matrix}\mathrm{X'}\\\mathrm{Y'}\end{matrix}\right.$	$\left.\begin{matrix}\mathrm{X'}\\\mathrm{Y'}\end{matrix}\right\rangle\mathrm{C{=}CH-CNa}\left\langle\begin{matrix}\mathrm{X}\\\mathrm{Y}\end{matrix}\right.$
1	$\left.\begin{matrix}\mathrm{CH_3CO}\\\mathrm{EtOCO}\end{matrix}\right\rangle\mathrm{C{=}CHOEt+CHNa}\left\langle\begin{matrix}\mathrm{COCH_3}\\\mathrm{COOMe}\end{matrix}\right.$	$\left.\begin{matrix}\mathrm{CH_3CO}\\\mathrm{EtOCO}\end{matrix}\right\rangle\mathrm{C{=}CH-CNa}\left\langle\begin{matrix}\mathrm{COCH_3}\\\mathrm{COOMe}\end{matrix}\right.$	
2	$\left.\begin{matrix}\mathrm{CH_3CO}\\\mathrm{MeOCO}\end{matrix}\right\rangle\mathrm{C{=}CHOEt+CHNa}\left\langle\begin{matrix}\mathrm{COCH_3}\\\mathrm{COOEt}\end{matrix}\right.$	$\left.\begin{matrix}\mathrm{CH_3CO}\\\mathrm{MeOCO}\end{matrix}\right\rangle\mathrm{C{=}CH-CNa}\left\langle\begin{matrix}\mathrm{COCH_3}\\\mathrm{COOEt}\end{matrix}\right.$	
3	$\left.\begin{matrix}\mathrm{EtOCO}\\\mathrm{EtOCO}\end{matrix}\right\rangle\mathrm{C{=}CHOEt+CHNa}\left\langle\begin{matrix}\mathrm{COCH_3}\\\mathrm{COOEt}\end{matrix}\right.$	$\left.\begin{matrix}\mathrm{EtOCO}\\\mathrm{EtOCO}\end{matrix}\right\rangle\mathrm{(C_3HNa)}\left\langle\begin{matrix}\mathrm{COCH_3}\\\mathrm{COOEt}\end{matrix}\right.$	
4	$\left.\begin{matrix}\mathrm{CH_3CO}\\\mathrm{EtOCO}\end{matrix}\right\rangle\mathrm{C{=}CHOEt+CHNa}\left\langle\begin{matrix}\mathrm{COOEt}\\\mathrm{COOEt}\end{matrix}\right.$	$\left.\begin{matrix}\mathrm{CH_3CO}\\\mathrm{EtOCO}\end{matrix}\right\rangle\mathrm{(C_3HNa)}\left\langle\begin{matrix}\mathrm{COOEt}\\\mathrm{COOEt}\end{matrix}\right.$	
5	$\left.\begin{matrix}\mathrm{EtOCO}\\\mathrm{EtOCO}\end{matrix}\right\rangle\mathrm{C{=}CHOEt+CHNa}\left\langle\begin{matrix}\mathrm{COCH_3}\\\mathrm{COCH_3}\end{matrix}\right.$	$\left.\begin{matrix}\mathrm{EtOCO}\\\mathrm{EtOCO}\end{matrix}\right\rangle\mathrm{(C_3HNa)}\left\langle\begin{matrix}\mathrm{COCH_3}\\\mathrm{COCH_3}\end{matrix}\right.$	
6	$\left.\begin{matrix}\mathrm{CH_3CO}\\\mathrm{CH_3CO}\end{matrix}\right\rangle\mathrm{C{=}CHOEt+CHNa}\left\langle\begin{matrix}\mathrm{COOEt}\\\mathrm{COOEt}\end{matrix}\right.$	$\left.\begin{matrix}\mathrm{CH_3CO}\\\mathrm{CH_3CO}\end{matrix}\right\rangle\mathrm{(C_3HNa)}\left\langle\begin{matrix}\mathrm{COOEt}\\\mathrm{COOEt}\end{matrix}\right.$	
7	$\left.\begin{matrix}\mathrm{CH_3CO}\\\mathrm{EtOCO}\end{matrix}\right\rangle\mathrm{C{=}CHOEt+CHNa}\left\langle\begin{matrix}\mathrm{COCH_3}\\\mathrm{COCH_3}\end{matrix}\right.$		
8	$\left.\begin{matrix}\mathrm{CH_3CO}\\\mathrm{CH_3CO}\end{matrix}\right\rangle\mathrm{C{=}CHOEt+CHNa}\left\langle\begin{matrix}\mathrm{COCH_3}\\\mathrm{COOEt}\end{matrix}\right.$		

The third kind	The fourth kind
 $\begin{matrix}X'\\Y'\end{matrix}\rangle C{=}CH{-}CNa\langle\begin{matrix}X'\\Y'\end{matrix}$	 $\begin{matrix}X\\X\end{matrix}\rangle C{=}CH{-}CNa\langle\begin{matrix}X\\Y\end{matrix}$
 $\begin{matrix}CH_3CO\\EtOCO\end{matrix}\rangle C{=}CH{-}CNa\langle\begin{matrix}COCH_3\\COOEt\end{matrix}$	 $\begin{matrix}EtOCO\\EtOCO\end{matrix}\rangle C{=}CH{-}CNa\langle\begin{matrix}COOEt\\COOEt\end{matrix}$
 $\begin{matrix}EtOCO\\EtOCO\end{matrix}\rangle C{=}CH{-}CNa\langle\begin{matrix}COOEt\\COOEt\end{matrix}$	 $\begin{matrix}CH_3CO\\EtOCO\end{matrix}\rangle C{=}CH{-}CNa\langle\begin{matrix}COCH_3\\COOEt\end{matrix}$
	 $\begin{matrix}EtOCO\\EtOCO\end{matrix}\rangle C{=}CH{-}CNa\langle\begin{matrix}COOEt\\COOEt\end{matrix}$
 $\begin{matrix}EtOCO\\EtOCO\end{matrix}\rangle C{=}CH{-}CNa\langle\begin{matrix}COOEt\\COOEt\end{matrix}$	
	 $\begin{matrix}CH_3CO\\EtOCO\end{matrix}\rangle C{=}CH{-}CNa\langle\begin{matrix}COCH_3\\COOEt\end{matrix}$
 $\begin{matrix}CH_3CO\\EtOCO\end{matrix}\rangle C{=}CH{-}CNa\langle\begin{matrix}COCH_3\\COOEt\end{matrix}$	

calculated amount of the ethoxymethylene compound diluted with pure ether is added gradually under constant stirring. The mixture is kept at the room temperature for a length of time, during which the colour of the mass grows from yellow to red, and, after relatively long standing, to dark red. Then water is added to the mass. If the sodium derivative of tetraethyl dicarboxyglutaconate is present in a large quantity, it crystallises from the aqueous solution after a short time. If such is the case, the crystals are collected, and treated separately. The aqueous solution is acidified with dilute hydrochloric or sulphuric acid, and the separating substance is extracted with ether. If any solid substance difficulty soluble in ether be present, it is filtered. The ethereal solution is shaken many times with small volumes of a ten percent aqueous solution of sodium carbonate, and in this way the substance in ether is fractionated into several parts in the grade of acidity. Most of the red colouring matter is taken in the first few fractions. If tetraethyl dicarboxyglutaconate be present, its sodium derivative separates out in yellow crystals towards the end of the fractional extraction with sodium carbonate, and then this is collected. These fractions are separately acidified with hydrochloric acid, when oil or crystals separate out. Here, if it can be considered that some numbers of successive fractions are of the same nature, they are united together, and afterall the whole is divided into five or six fractions. Crystalline substances are purified by recrystallisation from carbon bisulphide and ligroin; oils are extracted with ether and the ethereal solutions are washed with water, dried, and evaporated in vacuum. These purified substances are subjected to analysis and identification. If necessary, oils are dissolved in ether, again fractionated with soda solutions, and the seemingly purest part is analysed.

The red substance in the condensation mass, the crystalline substance separating on acidifying the aqueous solution of the condensation mass and difficulty soluble in ether, and the red colouring matter taken into the soda extracts, are all of the similar nature. These are probably xanthophanic acids(1) or similar compounds; but as they are not the objects of the present investigation, no experiment on these substances was carried out.

1. *Condensation of ethyl ethoxymethylene-acetoacetate with methyl sodio-acetoacetate.*(2) α-Methyl γ-ethyl α,γ-diacetylglutaconate was isolated. The substance, obtained by recrystallising the crude product three times from carbon bisulphide and once from ligroin, melted at 74°. After it was recrystallised twice more from carbon bisulphide and once from ligroin, it melted at 76°, but the melting point was, none the less, unsharp. Accord-

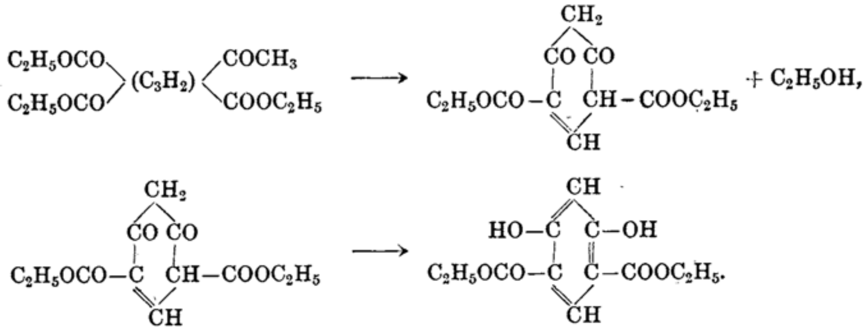
---

(1) Claisen, *Ann.*, **297** (1897), 48.
(2) Cf. Feist, *Ber.*, **59** (1926), 2958.

ing to Feist this compound melts at 73°, and, as he states, it seems difficult to purify it.

2. *Condensation of methyl ethoxymethylene-acetoacetate with ethyl sodio-acetoacetate.*(1) γ-Methyl α-ethyl α,γ-diacetylglutaconate was isolated. The substance, recrystallised three times from carbon bisulphide and once from ligroin, melted at 85°, and after it was recrystallised further twice from carbon bisulphide and once from ligroin, it melted sharply at 90°. According to Feist the melting point of this substance is 87°.

3. *Condensation of diethyl ethoxymethylene-malonate with ethyl sodio-acetoacetate.* An oily fraction, on standing, changed into a crystalline mass. This was recrystallised from carbon bisulphide. Anal. Found: $C=56.83$; $H=5.53\%$. Calc. for $C_6H_7O_3$: $C=56.67$; $H=5.55\%$. Melting point: 77°. Molecular weight: about 220. If $C_{12}H_{14}O_6$ be the molecular formula of the substance, it is less C_2H_6O or C_2H_5OH than a triethyl acetyl-carboxy-glutaconate $C_{14}H_{20}O_7$, one of the expected products of this condensation. It is, therefore, most natural to suppose the formation of a triethyl acetyl-carboxy-glutaconate, the product of the first or the second kind, and to consider the substance $C_{12}H_{14}O_6$ a derivative of resorcine produced by the following reactions:



Besides the above substance, diethyl α, γ-diacetyl-glutaconate was isolated. Anal. Found: $C=57.67, 57.59$; $H=6.69, 6.70\%$. Calc. for $C_{13}H_{18}O_6$: $C=57.78$; $H=6.67\%$. Melting point: 93°. The melting point observed by Claisen is 96°.

Further tetraethyl α,γ-dicarboxyglutaconate was isolated. Anal. Found: $C=54.68$; $H=6.74\%$. Calc. for $C_{15}H_{22}O_8$: $C=54.51$; $H=6.72\%$.

4. *Condensation of ethyl ethoxymethylene-acetoacetate with diethyl sodio-malonate.* From the fraction which was expected to be consisted of diethyl diacetylglutaconate an oil giving the following analytical results

---

(1) Cf. Feist, loc. cit.

was obtained. Anal. Found: C=57.57; H=6.39%. This seems to have been impure diethyl diacetyl-glutaconate.

The same resorcine derivative as obtained in condensation 3 was isolated. Anal. Found: C=56.75; H=5.63%. This indicates the formation of a triethyl acetyl-carboxy-glutaconate; but, as the isolated substance $C_{12}H_{14}O_6$ is not the direct product, it is impossible to determine whether this triethyl acetyl-carboxy-glutaconate is the first kind or the second, and whether it is identical with the triethyl acetyl-carboxy-glutaconate of condensation 3.

Further tetraethyl dicarboxyglutaconate was isolated. Anal. Found: C=54.42; H=6.73%.

5. *Condensation of diethyl ethoxymethylene-malonate with sodio-acetyl-acetone.* An oily compound giving an analytical result corresponding to diethyl α,α-diacetyl-propylene-γ,γ-dicarboxylate or to diethyl γ, γ-diacetyl-propylene-α,α-dicarboxylate was isolated. Anal. Found: C=57.61, 57.13; H=6.63, 6.66%. Calc. for $C_{13}H_{18}O_6$: C=57.78; H=6.67%.

Tetraethyl dicarboxyglutaconate was isolated. Anal. Found: C=54.76; H=6.76%.

6. *Condensation of ethoxymethylene-acetylacetone with diethyl sodio-malonate.* An oil corresponding in analysis to diethyl α,α-diacetyl-propylene-γ,γ-dicarboxylate or to diethyl γ,γ-diacetyl-propylene-α,α-dicarboxylate was isolated. It could not be determined whether this was identical with the substance obtained in condensation 5 or not. Anal. Found: C=57.61, 57.43; H=6.66, 6.66%.

Tetraethyl dicarboxyglutaconate was isolated. Anal. Found: C=54.22; H=6.66%.

7. *Condensation of ethyl ethoxymethylene-acetoacetate with sodio-acetyl-acetone.* Diethyl α,γ-diacetylglutaconate was isolated. Anal. Found: C=57.80; H=6.66%.

8. *Condensation of ethoxymethylene-acetylacetone with ethyl sodio-acetoacetate.* Diethyl α, γ-diacetylglutaconate was isolated. Anal. Found: C=57.76; H=6.55%. Melting point: about 92°.

The same condensation as condensation 4, that is the condensation of ethyl ethoxymethylene-acetoacetate with diethyl sodio-malonate, was carried out in alcohol. Diethyl α, γ-diacetylglutaconate (C=57.80; H=6.63%), the product of the fourth kind, and tetraethyl α, γ-dicarboxyglutaconate (C=54.37; H=6.69%), the product of the third kind, were isolated. This experiment shows that there is no fundamental difference between the condensations in alcohol and those in ether.

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

Chemical Institute, Faculty of Science,
Tokyo Imperial University.