

CCXLVI.—*The Probable Cause of the Elimination of a Carbethoxyl Group as Ethyl Carbonate by the Action of Sodium Ethoxide.*

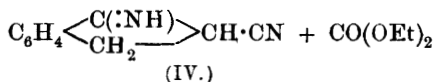
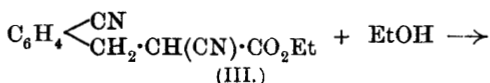
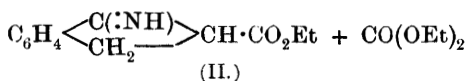
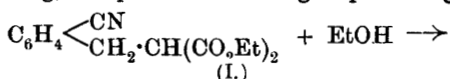
By FERDINAND BERNARD THOLE and JOCELYN FIELD THORPE.

SEVERAL instances have now been recorded in which the passage of an open-chain  $\delta$ -cyanoethyl salt into an imino-derivative of *cyclopentane* through the agency of cold alcoholic sodium ethoxide is accompanied by the elimination of a carbethoxy-group as ethyl carbonate. It is sufficient for our purpose to select two examples of this type of reaction from the recent experiments of Mitchell and Thorpe (*Trans.*, 1910, **97**, 2261) on the formation of imino-derivatives of  $\alpha$ -hydrindone. It was then shown that ethyl *o*-cyano-benzylmalonate (I) was transformed into ethyl 1-iminohydrindene-2-carboxylate (II), and that ethyl  $\alpha$ -*o*-dicyano- $\beta$ -phenylpropionate (III) was converted into 1-imino-2-cyanohydrindene (IV).

It was suggested that these and other reactions of the same kind

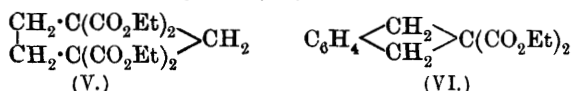
\* Dried at 100°.

might be due to spatial conditions, and that, in the five-membered ring, the presence of two groups of large molecular volume attached

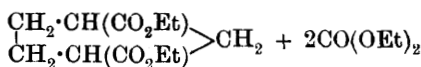
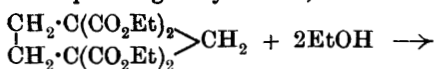


to any one carbon atom might not be a condition of stability, and consequently, when the compound was treated by a suitable reagent, one of these groups was eliminated.

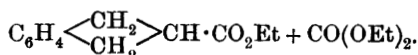
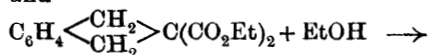
An examination of the facts shows that several derivatives of the five-carbon ring are known which have more than one carboxyl group attached to any one carbon atom, such as, for example, ethyl *cyclopentane-1:1:3:3-tetracarboxylate* (V) and ethyl *hydrindene-2:2-dicarboxylate* (VI):



If our hypothesis is correct, these compounds should pass, on treatment with sodium ethoxide, into ethyl carbonate and the corresponding ethyl esters, thus:



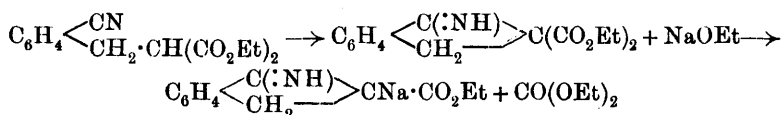
and



We have therefore prepared these compounds, the former by Pospischill's method (*Ber.*, 1898, **31**, 1950) from the disodium derivative of ethyl butanetetracarboxylate by the action of methylene iodide, and the latter by v. Baeyer and Perkin's method (*Ber.*, 1884, **17**, 122) from *o*-xylylene dibromide and ethyl sodiomalonate.

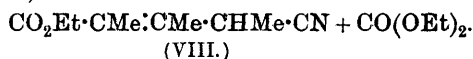
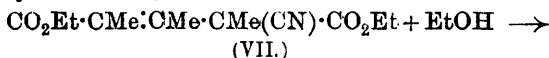
We find that both these esters are quite unacted on by cold alcoholic sodium ethoxide. It is evident, therefore, that the

influences causing the elimination of the carbethoxyl group prior to the formation of the five-ring imino-compounds cannot be ascribed to spatial conditions or to the over-weighting of any one carbon atom of the ring. A careful review of the facts showed, moreover, that the displacement of the carbethoxy-group by sodium in the manner illustrated by the equation :

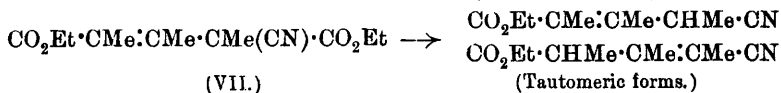
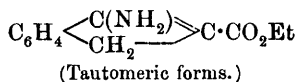
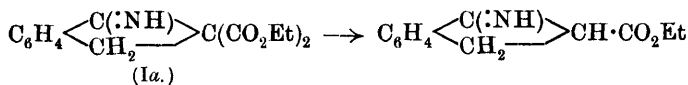


could not be the determining cause of this reaction, because, *inter alia*, ethyl 1-iminohydrindene-2-carboxylate (II) and analogously constituted compounds do not react with sodium ethoxide to form sodium derivatives. Finally, we decided to compare the various classes of compounds in which this reaction had been noticed, and ultimately arrived at an explanation, which forms the subject of the present communication.

During some experiments on the constitution of glutaconic acid (Trans., 1905, **87**, 1681) it was found that ethyl  $\alpha$ -cyano- $\alpha\beta\gamma$ -trimethylglutaconate (VII) when treated with sodium ethoxide was converted into ethyl  $\alpha$ -cyano- $\alpha\beta\gamma$ -trimethylcrotonate (VIII) and ethyl carbonate, thus:



A comparison of ethyl  $\alpha$ -cyano- $\alpha\beta\gamma$ -trimethylglutaconate (VII) with the normal ring-compound from ethyl *o*-cyanobenzylmalonate (Ia) shows that these substances have one important point in common, namely, that it is necessary for each of them to part with the carbethoxyl group before the hydrogen atom necessary to permit the substance to react in its tautomeric form can be acquired, thus:



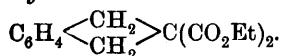
This view at once suggests a close relationship between compounds having the complex  $\text{HC} \cdot \text{C} : \text{C}$  and those, such as the imino-compounds, which have the complex  $\text{HC} \cdot \text{C} : \text{NH}$ , and leads to the

general conclusion that when the terminal hydrogen atoms in systems of this type are all replaced, the tendency for the compound to acquire that hydrogen atom which is necessary to enable it to react in its tautomeric form is such that any group capable of replacement by hydrogen is at once eliminated in the presence of a suitable reagent.

In the next communication several instances are recorded in which this reaction has been employed for the preparation of substituted glutaconic acids. These examples clearly prove that when the mobile hydrogen atoms in derivatives of glutaconic acid are replaced, the tendency for the compound to acquire the mobile atom causes it to eliminate one carboxyl group as ethyl carbonate when it is treated with alcoholic sodium ethoxide.

#### EXPERIMENTAL.

*Ethyl Hydrindene-2:2-dicarboxylate,*



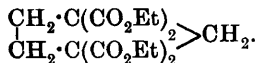
This substance was originally prepared by v. Baeyer and Perkin (*Ber.*, 1884, 17, 122) by the condensation of *o*-xylylene dibromide and the sodium compound of ethyl malonate. It was, however, hydrolysed to the acid without further purification. The method of preparation used by us was the same as that employed by these chemists, but we find that the ester boils at 186°/19 mm., and that it sets to a crystalline mass on cooling. When recrystallised from a small quantity of alcohol it is obtained in long needles, which melt at 38°:

0.2030 gave 0.5092 CO<sub>2</sub> and 0.1272 H<sub>2</sub>O. C=68.81; H=6.92.

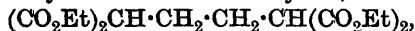
C<sub>15</sub>H<sub>18</sub>O<sub>4</sub> requires C=68.7; H=6.9 per cent.

The ester is quite unaltered by sodium ethoxide.

*Ethyl cyclopentane-1:1:3:3-tetracarboxylate,*



This substance was prepared by Pospischill's method (*Ber.*, 1898, 31, 1950) from ethyl butanetetracarboxylate,



which was obtained both by the condensation of ethylene dibromide and ethyl sodiomalonate and by the condensation of ethyl *cyclo*-propane-1:1-dicarboxylate, which is also formed in this action, with a further quantity of the sodium compound of ethyl malonate. The desired ester was obtained by condensing ethyl butanetetracarboxylate with methylene iodide. We find that it can be distilled

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under 15 mm. pressure when small quantities are employed, and boils at 225—227°:

0·2013 gave 0·4201  $\text{CO}_2$  and 0·1342  $\text{H}_2\text{O}$ .  $\text{C}=56\cdot93$ ;  $\text{H}=7\cdot41$ .

$\text{C}_{17}\text{H}_{26}\text{O}_8$  requires  $\text{C}=57\cdot0$ ;  $\text{H}=7\cdot3$  per cent.

The ester was treated with two atomic proportions of sodium dissolved in alcohol, but was recovered unchanged.

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