LX.—*Syntheses with the Aid of Monochloromethyl Ether. Part IV. The Condensation of Ethyl Benzyl Sodiomalonnate and Monochloromethyl Ether.*

By JOHN LIONEL SIMONSEN.

THE conversion of substituted ethyl benzylacetates into derivatives of hydrindene takes place with comparative ease. Thus, Mitchell and Thorpe (T., 1910, **97**, 2263) have shown that ethyl *o*-cyano-benzylmalonnate (I), when warmed with a trace of sodium ethoxide in alcoholic solution, is converted quantitatively into ethyl 1-imino-

hydrindene-2-carboxylate (II), which, on treatment with hydrochloric acid, yields ethyl 1-hydrindone-2-carboxylate (III).

It appeared to the author to be a matter of some interest to investigate the properties of *ethyl benzylmethoxymethylmalonate* (IV), since it seemed possible that this ester might on hydrolysis lose methyl alcohol, with the formation of hydrindene-2-carboxylic acid (V).

The required ester was readily obtained in an excellent yield by the condensation of ethyl benzylsodiummalonate and monochloromethyl ether. On hydrolysis with alcoholic potassium hydroxide, it gave *benzylmethoxymethylmalonic acid*, which decomposed at 160–162°, with the formation of *β-phenyl-α-methoxymethylpropionic acid*. All attempts to convert the methoxy-acid into the hydrindenecarboxylic acid were unsuccessful. When heated with concentrated hydrochloric acid, *α-benzylacrylic acid* was obtained, and the same acid was formed when ethyl benzylmethoxymethylmalonate or benzylmethoxymethylmalonic acid were heated with mineral acids.

It is clear from the above that ethyl benzylmethoxymethylmalonate shows properties similar to those of the methoxymethyl esters described in Part III of this series (T., 1915, 107, 783), and shows no tendency to undergo ring-formation on hydrolysis. It had been intended to extend these experiments to derivatives of ethyl benzylmalonate with negative groups in the aromatic nucleus, but as there is little prospect of the author being able to continue the work in the near future, it has appeared desirable to publish the results obtained in their present, somewhat incomplete, form.

EXPERIMENTAL.

Ethyl Benzylmethoxymethylmalonate (IV).

Ethyl benzylmalonate (25 grams) was gradually added to finely divided sodium (2.3 grams) suspended in dry ether (200 c.c.), when the sodium rapidly dissolved and a clear solution of the sodium

compound of ethyl benzylmalonate was obtained. Monochloromethyl ether (8 grams) dissolved in twice its volume of dry ether was cautiously added, when a vigorous reaction took place, which was controlled by cooling in ice-water. Next day water was added to dissolve the colloidal sodium chloride, the ether separated, dried, and evaporated. The residual oil was distilled under diminished pressure, when practically the whole passed over at 194—200°/18 mm. On redistillation, the oil boiled constantly at 194—195°/19 mm. (yield, 23 grams):

0.0988 gave 0.2358 CO_2 and 0.0676 H_2O . $\text{C}=65.1$; $\text{H}=7.6$.

$\text{C}_{16}\text{H}_{22}\text{O}_5$ requires $\text{C}=65.3$; $\text{H}=7.5$ per cent.

This ester was obtained as a very viscid oil, which, on keeping for some weeks, crystallised in massive plates melting at about 49—50°. Owing to its ready solubility in all the ordinary organic solvents, it was not found possible to recrystallise it.

Hydrolysis of Ethyl Benzylmethoxymethylmalonate. I. With Potassium Hydroxide. Benzylmethoxymethylmalonic Acid.

In performing this hydrolysis, the ester (5 grams) was mixed with methyl-alcoholic potassium hydroxide solution (2.5 grams of KOH) and allowed to remain in the cold overnight, when a sparingly soluble *potassium* salt (A) separated in fine needles. This was washed with a little methyl alcohol, and the filtrate heated on the water-bath for one hour, when a further quantity of the potassium salt separated, which was added to A.*

The potassium salt was dissolved in water and the solution faintly acidified with hydrochloric acid, when an acid separated as a viscid oil, which rapidly crystallised, and was recrystallised from a mixture of ether and light petroleum:

0.0886 gave 0.1952 CO_2 and 0.0495 H_2O . $\text{C}=60.1$; $\text{H}=6.2$.

$\text{C}_{12}\text{H}_{14}\text{O}_5$ requires $\text{C}=60.5$; $\text{H}=5.9$ per cent.

Benzylmethoxymethylmalonic acid crystallised in stellate needles decomposing at 160—162°. It was readily soluble in ether, chloroform, or benzene, but only sparingly so in water or light petroleum. It yielded a sparingly soluble, amorphous *barium* salt; the *calcium* salt was obtained as a sparingly soluble, caseous, white precipitate, which appeared to be microcrystalline:

* The filtrate from the potassium salt was saturated with carbon dioxide, the alcohol removed on the water-bath, and the aqueous solution acidified, when an oil separated which partly solidified. The solid was collected and found to consist of benzylmethoxymethylmalonic acid. The oily acid was obtained in too small a quantity for investigation.

0.7088 lost 0.2121 H_2O at 120° . $\text{H}_2\text{O}=29.9$.

0.3123 gave 0.1068 CaSO_4 . $\text{Ca}=10.0$.

$\text{C}_{12}\text{H}_{12}\text{O}_5, 6\frac{1}{2}\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=29.9$; $\text{Ca}=10.2$ per cent.

0.1029 Gram neutralised 0.0735 gram of barium hydroxide, whereas a dibasic acid, $\text{C}_{12}\text{H}_{14}\text{O}_5$, should neutralise 0.074 gram.

As has been mentioned above, benzylmethoxymethylmalonic acid melted with decomposition, this being due to loss of carbon dioxide with the formation of the monobasic acid, *β -phenyl- α -methoxymethylpropionic acid*. This acid has, so far, only been obtained as a viscid oil. In one experiment, the dibasic acid (0.775 gram) was heated at 165° until all evolution of carbon dioxide had ceased, when a loss in weight of 0.142 gram was observed, whereas this weight of a dibasic acid should lose 0.139 gram in passing to a monobasic acid. A further proof of the formation of the monobasic acid was furnished by the analysis of the *silver* salt, which separated from a faintly alkaline solution as a granular, white powder:

0.1991 gave 0.0727 Ag. $\text{Ag}=36.5$.

$\text{C}_{11}\text{H}_{13}\text{O}_3\text{Ag}$ requires $\text{Ag}=35.9$ per cent.

When benzylmethoxymethylmalonic acid was boiled for some hours with hydrochloric acid (50 per cent.), it was converted into *α -benzylacrylic acid* (see below), and this was found to be the simplest method for the preparation of this acid.

II. With Hydrochloric Acid. *α -Benzylacrylic Acid*,

Ethyl benzylmethoxymethylmalonate was hydrolysed by hydrochloric acid only with great difficulty. The ester (20 grams) was mixed with hydrochloric acid (100 grams), acetic acid (25 grams), and water (50 c.c.), and the mixture heated under reflux for thirty-six hours. The oil was dissolved in ether, and the acid removed from the ethereal solution by washing with sodium carbonate solution, from which, on acidification, 2.5 grams of an oily acid* were obtained. The ether was evaporated, and the residual oil mixed with methyl-alcoholic potassium hydroxide solution (7 grams of KOH), when, on keeping, the sparingly soluble potassium salt of benzylmethoxymethylmalonic acid separated. The filtrate from this salt was saturated with carbon dioxide, the alcohol removed by evaporation, and the aqueous solution rendered just acid with hydrochloric acid, when an oil separated which rapidly solidified.

* The oily acid partly solidified and, after draining on porous porcelain, the crystals were found to consist of *α -benzylacrylic acid*.

The solid was purified by repeated crystallisation from dilute methyl alcohol:

0.1586 gave 0.43 CO_2 and 0.0876 H_2O . $\text{C}=73.8$; $\text{H}=6.1$.

$\text{C}_{10}\text{H}_{10}\text{O}_2$ requires $\text{C}=74.1$; $\text{H}=6.1$ per cent.

α -Benzylacrylic acid separated in glistening prisms, which melted at $68-69^\circ$. It was readily soluble in all the ordinary organic solvents, but only very sparingly so in water.

On titration, 0.1109 gram neutralised 0.0589 gram of barium hydroxide, whereas a monobasic acid, $\text{C}_{10}\text{H}_{10}\text{O}_2$, should neutralise 0.0587 gram.

That this acid was not identical with the isomeric *α -methylcinnamic acid* melting at 74° was shown by the fact that a mixture of the two melted at 40° . Further, these two acids are readily distinguished in that *α -benzylacrylic acid* yields a readily soluble barium salt, whereas the barium salt of *α -methylcinnamic acid* is only sparingly soluble.

In alkaline solution, *α -benzylacrylic acid* is unstable towards potassium permanganate; when dissolved in chloroform, it readily absorbs bromine, with considerable evolution of heat. In one experiment, the acid (0.5 gram) was dissolved in chloroform (3 c.c.) and treated with the calculated quantity of bromine in chloroform solution. On keeping, the *bromo-acid* separated, and was purified by crystallisation either from chloroform or dilute acetic acid:

0.1196 gave 0.14 AgBr . $\text{Br}=49.8$.

$\text{C}_{10}\text{H}_{10}\text{O}_2\text{Br}_2$ requires $\text{Br}=49.7$ per cent.

$\alpha\beta'$ -Dibromo- β -phenylisobutyric acid, $\text{CH}_2\text{Ph}\cdot\text{CBr}(\text{CH}_2\text{Br})\cdot\text{CO}_2\text{H}$, crystallised in fine needles melting at $145-146^\circ$. When reduced with sodium amalgam, it yielded *β -phenylisobutyric acid*, which was identified by conversion into the characteristic amide melting at 107° , and this melting point was not altered by admixture with a specimen of the amide from another source (Found: $\text{N}=8.6$. Calc.: $\text{N}=8.5$ per cent.).

β' -Bromo- β -phenylisobutyric Acid.—This acid was formed when *α -benzylacrylic acid* was mixed with an acetic acid solution of hydrogen bromide (saturated at 0°) and heated in a sealed tube at 100° for two hours. On pouring into water, a heavy oil separated, which was dissolved in ether, the ethereal solution washed to remove acetic acid, dried, and evaporated, when a viscous oil was obtained. After remaining for some days in a vacuum desiccator, it was analysed, and was evidently nearly pure:

0.1455 gave 0.1037 AgBr . $\text{Br}=30.3$.

$\text{C}_{10}\text{H}_{11}\text{O}_2\text{Br}$ requires $\text{Br}=32.9$ per cent.

The bromo-acid dissolved readily in potassium hydroxide solution or ammonia, but, on warming, the solution clouded, owing probably to the separation of the hydrocarbon; the acid was, however, much more stable than its isomeride (see below).

When dissolved in concentrated aqueous ammonia and allowed to remain for some days in the cold, it was converted quantitatively into β' -amino- β -phenylisobutyric acid. For analysis, it was re-crystallised from chloroform:

0.1587 gave 11.6 c.c. N_2 at 32° and 760 mm. $N=7.8$.

$C_{10}H_{13}O_2N$ requires $N=7.8$ per cent.

This acid separated from chloroform in glistening leaflets melting at 128° . It was readily soluble in water or alcohol, more sparingly so in the ordinary organic solvents.

β -Bromo- β -phenylisobutyric Acid, $CHBrPh \cdot CHMe \cdot CO_2H$.—For purposes of comparison, this bromo-acid, which does not appear to have been described previously, was prepared from α -methylcinnamic acid by the action of an acetic acid solution of hydrogen bromide in the manner described above. On pouring the mixture into water, a solid separated, which crystallised from formic acid in glistening prisms melting at 168 — 170° :

0.1347 gave 0.1037 AgBr. $Br=32.7$.

$C_{10}H_{11}O_2Br$ requires $Br=32.9$ per cent.

Like other β -bromo-acids, this acid reacted very readily with alkalis. When dissolved in cold sodium carbonate solution, the solution rapidly clouded, with the separation of an oil, and the same behaviour was observed with ammonia, so that it was not found possible to prepare the amino-acid.

In one experiment, the oil formed by the action of dilute sodium carbonate solution was separated, dissolved in chloroform, and treated with a chloroform solution of bromine, when, on allowing the solvent to evaporate, needles were obtained which melted at 65 — 66° , and evidently consisted of the dibromide derived from allylbenzene, which had resulted from the action of the alkali on the bromo-acid (Found: $Br=57.9$. Calc.: $Br=57.5$ per cent.).

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