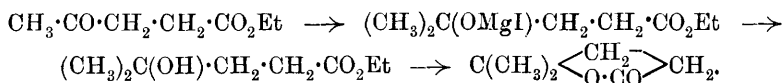


CLXX.—*A New Synthesis of isoCaprolactone and Certain Derivatives.*

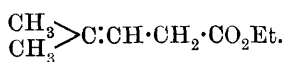
By DAVID TREVOR JONES and GEORGE TATTERSALL.

IN a recent paper (*Compt. rend.*, 1902, 135, 629), Grignard described the application of his magnesium reaction to the formation of the lactone of γ -hydroxy- γ -ethylvaleric acid from ethyl lævulate and magnesium ethyl iodide. Wishing to prepare a quantity of the corresponding methyl compound, *isocaprolactone*, for some synthetical experiments, the authors found that this lactone might be readily obtained in a yield of 30 per cent. by a similar process from ethyl lævulate and magnesium methyl iodide in accordance with the following scheme :

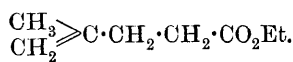


All attempts to prepare γ -bromo*isocaproic* acid from *isocaprolactone* by treatment with strong aqueous hydrobromic acid under varied conditions gave only negative results ; treatment with alcoholic hydrobromic acid has, however been shown to yield ethyl γ -bromo*isocaproate* (Desfontaines, *Compt. rend.*, 1902, 134, 295).

When treated successively with phosphorus pentabromide and alcohol, *isocaprolactone* is converted into ethyl γ -bromo*isocaproate*, $\text{CMe}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, and this, on digesting with diethylaniline, is decomposed with the elimination of hydrogen bromide and the formation of an unsaturated ester, for the constitution of which there are two possibilities :



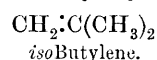
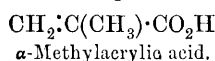
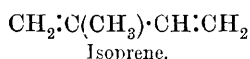
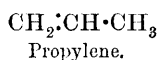
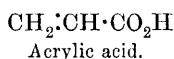
Ethyl pyroterebate.

Ethyl γ -methylallylacetate.

In the former case, boiling with concentrated caustic soda would not only hydrolyse the ester, but, at the same time, bring about a

transference of the double linking from the $\beta\gamma$ - to the $\alpha\beta$ -position (Fittig, *Annalen*, 1894, 283, 47, 269) so that Δ^{α} -isohexenoic acid, $\text{Me}_2\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, would be produced. In the latter case, simple hydrolysis would take place and γ -methylallylacetic acid, an acid which has not been previously described, would be obtained. Δ^{α} -isohexenoic acid has been obtained by Braun (*Monatsh.*, 1898, 17, 213) and by Franke and Kohn (*loc. cit.*, 1901, 20, 883), and these authorities agree in describing this acid as distilling without decomposition even under the ordinary pressure.

The acid obtained in the present investigation exhibited quite different properties, since it decomposed or polymerised considerably even on distillation under reduced pressure. There can, therefore, be little doubt that it is γ -methylallylacetic acid. The property of polymerising shown by the acid, $\text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is rather remarkable when it is remembered that its lower homologue, allylacetic acid, $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, distils unchanged under the ordinary pressure. There exist, however, several cases analogous to this in which a compound containing the group $\text{CH}_2\cdot\text{CH}\cdot\text{C}$ is stable and does not polymerise under conditions which cause polymerisation of similar substances containing the group $\text{CH}_2\cdot\text{C}\begin{smallmatrix} \diagup \text{C} \\ \diagdown \text{C} \end{smallmatrix}$. The following short table illustrates this point; the compounds in the first column do not polymerise, whereas those in the second readily do so.



EXPERIMENTAL.

Preparation of isoCaprolactone.

In preparing the lactone, ethyl lævulate (36 grams) mixed with about four times its volume of dry ether was slowly added to a well-cooled ethereal solution of magnesium methyl iodide (prepared from 7 grams of magnesium and 40 grams of methyl iodide). After about an hour, the resulting magnesium compound was decomposed by cautiously adding water and dilute sulphuric acid. The ethereal layer was then separated and the acid solution extracted twice with small quantities of ether. The mixed ethereal extracts were washed with a little sodium hydrogen sulphite solution to remove iodine and afterwards dried over calcium chloride and evaporated. On distilling

the residual yellow oil under reduced pressure (100 mm.), most of it passed over between 85° and 140°, and on repeated fractionation a quantity of oil was obtained distilling at 140—150°/100 mm., which on examination was found to consist of a mixture of *isocapro*lactone with much unchanged ethyl *læv*ulate.

In order to separate these substances, the oil was hydrolysed with alcoholic potash; water was then added and the solution evaporated until free from alcohol. The concentrated liquid was acidified with excess of hydrochloric acid and heated for 15 minutes on the water-bath in order to convert the γ -hydroxy*isocaproic* acid into the lactone. After extracting several times with ether, the ethereal extract was washed with sodium carbonate to remove the *læv*ulic acid, dried over calcium chloride and evaporated. The resulting crude oil yielded on distillation pure *isocapro*lactone boiling at 205—207°.

0.1674 gave 0.3864 CO₂ and 0.1323 H₂O. C = 62.9; H = 8.7.

0.1860 „ 0.4285 CO₂ „ 0.1492 H₂O. C = 62.8; H = 8.9.

C₆H₁₀O₂ requires C = 63.1; H = 8.7 per cent.

Ethyl γ -Bromoisocaproate, (CH₃)₂CBr·CH₂·CH₂·CO₂Et.—*isocapro*lactone (4 grams) was treated with phosphorus pentabromide (18 grams) at the ordinary temperature and the mixture left for 24 hours, when most of the pentabromide had disappeared. The mixture was then poured in a thin stream into excess of absolute alcohol, the flask being carefully cooled during the operation. After 12 hours, the product was mixed with water and extracted three times with ether; the ethereal extract was then washed with water and dilute sodium carbonate solution, dried over calcium chloride, evaporated, and the yellow residue was freed from ether by being kept for several days over sulphuric acid in a vacuum desiccator.

As the bromo-ester decomposed considerably even when distilled under greatly reduced pressure, an analysis of the undistilled oil was made, the result of which shows that the oil consists essentially of ethyl γ -*bromoisocaproate*.

0.1998 gave 0.1541 AgBr. Br = 32.8.

C₇H₁₃O₂Br requires Br = 35.9 per cent.

Ethyl γ -Methylallylacetate, CH₂:C(CH₃)·CH₂·CH₂·CO₂Et.—The foregoing bromo-ester was now mixed with twice its volume of freshly distilled diethylaniline and the mixture, after being heated at 150—160° for 10 minutes, cooled and poured into dilute hydrochloric acid; the acid solution was extracted with ether and the extract washed successively with hydrochloric acid and aqueous sodium carbonate, dried over calcium chloride and evaporated. The residual oil distilled at 98—100° under 57 mm. and at 85° under 20 mm. pressure.

0.1210 gave 0.2905 CO₂ and 0.1050 H₂O. C = 65.5 ; H = 9.6.

0.1485 ,, 0.3597 CO₂ ,, 0.1307 H₂O. C = 66.1 ; H = 9.8.

C₈H₁₄O₂ requires C = 67.5 ; H = 9.8 per cent.

The low value obtained for the carbon was found to be due to the presence of a trace of bromine which could not be entirely removed by treatment with diethylaniline.

Ethyl γ -methylallylacetate is a mobile, fragrant liquid, which in chloroform solution readily decolorises bromine.

γ -Methylallylacetic Acid, CH₂:C(CH₃)·CH₂·CH₂·CO₂H.—In order to obtain this acid, the ester just described was hydrolysed by boiling with 10 per cent. aqueous caustic soda (1 mol. ester to 10 mols. NaOH) for 12 hours, in accordance with the instructions given by Fittig for the conversion of a $\beta\gamma$ -unsaturated acid into the $\alpha\beta$ -isomeride (*Annalen*, 1894, 283, 51, 269). The product was acidified with dilute sulphuric acid and extracted with ether, and, after evaporating, the pungent oil was distilled in steam; the distillate was extracted with ether, the ethereal solution dried over calcium chloride, and evaporated. As the residue was found to decompose on distilling even under reduced pressure—a resinous substance remaining in the flask—no direct analysis of the acid was made, and a second experiment was carried out as follows:—The acid extracted with ether from the steam distillate was dissolved in ammonia and the silver salt obtained by precipitating with silver nitrate. The white, curdy precipitate was washed and dried under reduced pressure over sulphuric acid, the desiccator being kept in the dark because the salt is rapidly discoloured by light.

0.1897 gave 0.0930 Ag. Ag = 48.9.

C₆H₉O₂Ag requires Ag = 48.8 per cent.

We hope to prepare large quantities of this and some other similarly constituted acids and subject them to a more detailed examination.

In conclusion, the authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant with the aid of which these experiments were carried out.

THE VICTORIA UNIVERSITY,
MANCHESTER.