XXIV.—On α -Ethylvalerolactone, α -Ethyl β -Methylvalerolactone, and on a Remarkable Decomposition of β -Ethyl-aceto-succinic Ether.

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α -Ethylvalerolactone.

FITTIG and Krafft (*Annalen*, **208**, 71) prepared a heptolactone of unknown constitution from teracrylic acid, and examined its properties. At Professor Fittig's suggestion the following work was undertaken to prepare a heptolactone of known constitution so as to compare it with the above-mentioned compound.

To a cooled solution of 10.2 g. of sodium in about 100 g. alcohol, 58 g. acetoacetic ether were added, and 87 g. α -bromobutyric ether then gradually introduced. The mixture was heated on the water-bath until it became neutral, the reaction being complete in about two days. The alcohol was then distilled off and the ether washed with water, dried with calcium chloride, and distilled. The boiling point of β -ethyl-aceto-succinic ether is given by Thorne (*Chem. Soc., J.*, **39**,

336) as 267° , but I did not get a constant boiling point. Portions were collected after two fractionations below 260° , from 250 — 260° , from 260 — 265° , and above 265° .

About 12 g. of the portion between 250° and 260° was boiled with twice its weight of hydrochloric acid, 1 part concentrated acid to 2 of water, for about two days, until the oily layer had disappeared. The resulting product, consisting mostly of α -ethyl- β -acetopropionic acid, was then extracted with ether and the latter distilled off.

The residue crystallised in part at the temperature of a mixture of ice and salt. It was therefore left in a desiccator in the ice-chamber for two or three days, after water had been added, and evaporated off to remove the last traces of ether and alcohol. The crystals were collected on a filter, washed with a little cold water, and dried between filter-paper. They were difficultly soluble in cold water, but much more easily in hot, and good crystals were obtained from the aqueous solution.

About 3.5 g. of the filtrate was dissolved in about 200 c.c. of water and treated with 175 g. of 4 per cent. sodium-amalgam. The liquid was cooled at first, but was finally warmed on the water-bath. The reaction was complete in about three days, when the liquid was poured from the mercury, and any impurities extracted with ether. The solution was then acidified with sulphuric acid and boiled for half an hour in a flask with reversed condenser. When cool it was made alkaline with potassium carbonate and extracted with ether. The residue from the ether was dried with potassium carbonate and distilled. The greater part came over between 218° and 220° . The lactone was redistilled, and was found to boil constantly at 219.5° (thermometer entirely in the vapour). It did not solidify in a mixture of snow and salt.

On analysis 0.2556 g. lactone gave 0.6120 CO_2 and 0.2180 H_2O .

C per cent. = 65.30.	Calc. for $\text{C}_7\text{H}_{12}\text{O}_2$	C per cent. = 65.62.
H ,, = 9.47.	,, ,, H ,, = 9.37.	

The sp. gr. of the lactone at 16° was 0.992.

Some of the lactone was dissolved in the smallest possible quantity of ice-cold water. The liquid was quite clear, but became turbid at about 17° , and remained so up to about 95° , when the lactone was redissolved; on cooling the solution became turbid at about 90° and clear again at from 15 — 20° . It was quite neutral.

This lactone, therefore, exhibited the peculiar properties possessed by those previously obtained, but it differed from the heptolactone obtained by Fittig and Krafft, which solidified at 0° , its melting point being about 11° (*Annalen*, 208, 88).

The formation of the compound is expressed thus:—

Barium α -ethyloxyvalerate, $(\text{CH}_3.\text{CH.OH}.\text{CH}_2.\text{CH.C}_2\text{H}_5.\text{CO}_2)_2\text{Ba}$, was prepared by boiling the lactone with barium hydrate about $2\frac{1}{2}$ hours until the former disappeared. The excess of barium was precipitated with carbon dioxide, and the carbonate removed by filtration. The filtrate was evaporated to a syrupy mass, redissolved in water filtered from deposited barium carbonate, and again evaporated to dryness, but more barium carbonate was precipitated. The residue was therefore dissolved in absolute alcohol, filtered, and left in a desiccator over sulphuric acid. A gummy mass was thus obtained which, after a time, assumed a porcelain-like appearance.

A portion was dried till constant at 60° . At 100° it lost weight rapidly with formation of barium carbonate.

On analysis 0.2860 g. barium salt dried at 60° gave 0.1554 BaSO_4 .

Ba per cent. = 31.95. Calc. for $(\text{C}_7\text{H}_{13}\text{O}_3)_2\text{Ba}$ = 32.08.

It was found that the salt obtained by slow evaporation of the alcoholic solution did not dissolve, either in alcohol or water, to a perfectly clear solution, so that the salt is not very stable even at ordinary temperatures.

The *silver salt* was prepared by adding silver nitrate to a concentrated solution of the barium salt. A dense cheesy-white precipitate was thus formed which was easily soluble in both hot and cold water, but much more so in the former. The liquid blackens on boiling, and slowly in the cold. Some of the precipitate was filtered with the pump, pressed between filter-paper, and then dissolved in a little hot water and filtered while hot. The filtrate on cooling deposited part of the salt, more being obtained by passing a current of air over the gently warmed solution in the hot water-bath.

The salt was analysed, when 0.1165 g. gave 0.0495 g. Ag
and 0.0988 " 0.0425 "

Ag per cent. (1) 42.49. Calc. for $\text{C}_7\text{H}_{13}\text{O}_3\text{Ag}$ = 42.69.
" " (2) 43.02.

On acidifying the barium or silver salt at 0° , and to a smaller extent at ordinary temperatures, and shaking with ether, a piece of moistened blue litmus-paper dipped in the ether became red, but when the acidified solution was previously boiled the ethereal solution was perfectly neutral.

Again, on precipitating the barium or silver salt with an acid and filtering at once, the addition of potassium carbonate caused the separation of some lactone which was extracted with ether.

Thus at ordinary temperatures a mixture of lactone and oxy-acid is formed, the latter being too unstable to obtain free from lactone.

Decomposition by Heat of β -Ethyl-aceto-succinic Ether.

On preparing larger quantities of the crystalline acid, which will be called *ketolactonic acid*, the portion of β -ethyl-aceto-succinic ether coming over between 260° and 265° was found to yield proportionately a much larger quantity of crystals than that between 250° and 260° , while the distillate above 265° yielded still more. It thus appeared as if the decomposition had taken place during the distillation and not during the saponification. A portion of the liquid coming over above 265° was therefore slowly distilled until about a third had gone over. The distillate was fractionated, when it was found that a considerable portion of it came over below 100° . This distillate was light, limpid, and burned with a clear blue flame, whereas the ether is almost incombustible. It also gave the iodoform reaction with iodine and caustic soda, and was therefore alcohol. It appeared to be formed thus:—

On saponification, the remaining C_2H_5 -group was apparently simply replaced by hydrogen, thus:—

The ketolactonic acid was found to have the formula $\text{C}_8\text{H}_{10}\text{O}_4$, as above.

The aqueous solution, which was strongly acid, deposited well-formed crystals which were washed with cold water, dried between filter-paper, and then in the air-bath at 60° . The melting point was found to be 181° , but, on repeated fusion and solidification, the melting point was lowered slightly, the acid apparently decomposing to some extent.

Analysis of the acid dried at 100° :—

I. 0.1640 g. acid gave 0.3409 CO_2 and 0.0940 H_2O .

II. 0.2669 „ „ 0.5516 „ 0.1419 „

C per cent. (1) 56.69 (2) 56.37. Calc. for $\text{C}_8\text{H}_{10}\text{O}_4$ C per cent. 56.47.

H „ 6.37 5.90. „ „ H „ 5.89.

Barium Ketolactonate, $(C_8H_9O_4)_2Ba + 2H_2O$.

A quantity of the acid was dissolved in water and excess of barium carbonate added. The excess of carbonate was filtered off, and the filtrate evaporated to dryness. The residue was dissolved in water, filtered, evaporated to a small bulk, and allowed to crystallise.

The well-formed crystals were pressed between filter-paper, left in the desiccator a short time, and analysed.

0.2814 g. barium salt dried till constant at 100° , lost 0.0154 g. H_2O
 " " " 130° , " 0.0199 "
 " " " 130° , gave 0.1278 g. $BaSO_4$.

A second analysis, which will be referred to later, gave the following numbers:—

0.2027 g. lost at 100° 0.0099 g. H_2O , and at 130° 0.013, and gave 0.0925 g. $BaSO_4$.

Calc. for $(C_8H_9O_4)_2Ba + 2H_2O$.		Found.	
$1\frac{1}{2}H_2O =$	5.28	(1) 5.47	(2) 4.89
$2H_2O =$	7.04	7.07	6.41
Ba =	26.81	26.72	26.83

The salt began to decompose above 130° , and the crystals lost water slowly in the desiccator.

When the salt is evaporated nearly to dryness on the water-bath and treated with alcohol, it is obtained as a white anhydrous powder.

On analysis 0.2519 g. salt dried at 100° gave 0.1249 g. $BaSO_4$.

Ba per cent. = 29.15. Calc. for $(C_8H_9O_4)_2Ba = 28.84$.

The silver salt was obtained by heating a solution of the barium salt with silver nitrate. When deposited from a dilute solution it is distinctly crystalline. It is slightly soluble in water and insoluble in alcohol. The dry salt is scarcely coloured by the light, but the aqueous solution blackens slowly.

On analysis 0.1455 g. silver salt gave on ignition 0.0569 g. Ag.

0.3163 " " combustion 0.4019 g. CO_2 ,
 0.0947 H_2O , and 0.1243 Ag.

C per cent. (1) —	(2) 34.65	Calc. for $C_8H_9O_4Ag$	34.65
H " —	3.33	" "	3.25
Ag " 38.90	39.29	" "	38.99

Action of Barium Hydrate on Ketolactonic acid.

On adding barium hydrate to a solution of the acid, the liquid remains clear in the cold, even after long standing, but when it is

heated to nearly 100° a sudden and copious precipitation of barium carbonate takes place.

Some of the acid was treated with excess of barium hydrate and left in the cold for two days, the liquid remaining perfectly clear. The excess of barium was precipitated with carbon dioxide, and the carbonate removed by filtration. The filtrate when warmed deposited barium carbonate rapidly, but the salt was precipitated on addition of alcohol to the aqueous solution. A portion of the filtrate was treated in this way, but the precipitated salt was gelatinous and difficult to filter, and the residue contained a large quantity of barium carbonate. In this condition it was difficultly soluble in water, and the large amount required for solution prevented its reprecipitation by alcohol. The remainder was allowed to stand in an exhausted desiccator, but it deposited barium carbonate slowly. It was therefore filtered and treated with silver nitrate, when a white granular precipitate was obtained, which was less soluble than silver ketolactonate. It was filtered, dried between filter-paper, and placed in the desiccator. It decomposed even at 60°, and the aqueous solution blackened on heating.

The analyses, though not very accurate, showed that this was the salt of a dibasic acid derived from ketolactonic acid.

- I. 0.0865 gram silver salt gave 0.0459 Ag.
 II. 0.0809 " " 0.0428 "
 III. 0.1191 " " 0.0996 CO₂ and 0.0299 H₂O.

	Calc. for C ₈ H ₁₀ O ₅ Ag ₂ .		Found.	
C per cent.	= 23.88	(1) —	(2) —	(3) 22.81
H "	= 2.49	—	—	2.79
Ag "	= 53.73	53.06	52.90	—

There was not enough substance for a thorough investigation of the acid, but the filtrates from the silver salt were acidified, exhausted with ether, and the latter evaporated. The acid thus formed was mostly liquid, but contained a few crystals, which, when dried between filter-paper and in the desiccator, were found to melt at 181°, and appeared therefore to be ketolactonic acid.

Some of the crystalline acid was boiled for half an hour with barium hydrate. When the temperature approached 100° a sudden precipitation of barium carbonate took place, the action being apparently complete in a very short time. After removal of the excess of barium in the usual way, and evaporation of the filtered solution, the salt was obtained as a gummy mass. It was dissolved in absolute alcohol and left in the desiccator. The salt resembled barium γ -oxy-ethyl valerate in appearance, and could not be crystallised.

0.1470 barium salt dried at 100° gave 0.0815 BaSO_4 .

0.2200 " " " 0.1217 "

Ba per cent. (1) 32.45. Calc. for $(\text{C}_7\text{H}_{11}\text{O}_3)_2\text{Ba} = 32.39$.

" " (2) 32.53.

The reaction may be expressed thus—

The silver salt was easily soluble in water, and very unstable, and was not obtained pure. On acidifying it with hydrochloric acid and exhausting with ether, a liquid acid was obtained, but the quantity was too small to allow of investigation.

Ethylsuccinic Acid.

Thorne obtained two acids by the saponification of β -ethylacetosuccinic ether, viz., α -ethyl- β -acetopropionic acid and ethylsuccinic acid.

So far I had obtained the first of these, and also the new ketolactonic acid. Since there was always a certain amount of acid unacted on by sodium-amalgam, it seemed probable that this was ethylsuccinic acid. This residual acid was therefore treated with barium carbonate, and filtered. After evaporation part of the residue was soluble, part insoluble, in alcohol. The insoluble salt was purified by repeatedly dissolving in water, evaporating to a small bulk, and precipitating with alcohol. After repeating this process six times, the salt was obtained almost colourless, but the acid when set free did not crystallise. The barium salt was again prepared, and the purification repeated as far as the small amount of substance permitted.

The percentage of barium (43.37, calc. for $\text{C}_6\text{H}_8\text{O}_4\text{Ba} = 48.75$) was much higher than in either of the other salts, and Thorne describes the salt as being extremely difficult to obtain in a state of purity, so that it was probably impure barium ethylsuccinate.

On α -Ethyl- β -methylvalerolactone.

Methylacetoacetic ether was first prepared by the action of sodium ethylate and methyl iodide on acetoacetic ether, and was employed in place of acetoacetic ether in the preparation of the lactone, just as in the previous case. The yield, however, was very poor, and the lactone contained some of the lower homologue, the action of the sodium ethylate and methyl iodide being apparently incomplete.

A quantity of β -ethylacetosuccinic ether was therefore prepared as before, and a portion was treated, after drying with calcium chloride, but without distillation, with sodium ethylate and methyl iodide, so

as to obtain β -ethylacetomethylsuccinic ether. The latter was then distilled, when it was found that alcohol was again split off, and after saponification a crystalline acid was again obtained. The lactone was prepared as before, but boiled between 219° and 226° , so that the action of sodium ethylate and methyl iodide was again incomplete. The failure of this reaction was also noticed by Mr. Gottstein in this laboratory.

The crystalline acid melted at 181° , and was found on analysis to be ketolactonic acid. The analysis of the hydrated salt $(C_8H_9O_4)_2Ba + 2H_2O$ has been already given.

Of the anhydrous salt 0.1803 g. gave 0.0883 g. $BaSO_4$.
Ba per cent. 28.79. Calc. for $(C_8H_9O_4)_2Ba = 28.84$.

The remainder of the β -ethylacetosuccinic ether was distilled, and the portions coming over between 257° and 270° treated with sodium ethylate and methyl iodide. This time $1\frac{1}{2}$ times the calculated quantities of sodium and methyl iodide were used, and the ether was dried with potassium carbonate, calcium chloride being partially dissolved by these ethers. The greater part distilled between 260° and 275° . On saponification no crystals were obtained, even from the portion boiling above 275° .

The lactone was obtained as before. The greater part distilled between 224° and 228° , but even after repeated fractionation a constant boiling point was not obtained, though the greater portion of the substance came over between 226° and 227° , and this was therefore analysed.

0.2311 gram lactone gave 0.5677 gram CO_2 and 0.2019 H_2O .

0.1135 ,, ,, 0.2799 ,, 0.1016 ,,

C per cent. (1) 67.00 (2) 67.26. Calc. for $C_8H_{14}O_2$ C per cent. 67.60.

H ,, 9.71 9.94. ,, ,, H ,, 9.86.

The lactone was therefore moderately pure.

An analysis of the portion distilling between 224° and 225° was also made.

0.2124 gram lactone gave 0.5184 CO_2 and 0.1855 H_2O .

C per cent. = 66.56. Calc. for $C_8H_{14}O_2 = 67.60$ and for $C_7H_{12}O_2 = 65.62$.

H ,, = 9.70. ,, ,, = 9.86 ,, ,, = 9.37.

Since the lactones boil without the slightest decomposition, the residues which remained in the bulbs after the highest fractionations were used to prepare the barium salt.

Barium α -ethyl- β -methylvalerate prepared as above was obtained as a gummy mass exactly resembling the lower homologue. On analysis—

0.2143 gram barium salt dried at 60° gave 0.1094 gram BaSO_4 .

0.1942 " " " 0.0988 " "

Ba per cent. (1) 30.02. Calc. for $(\text{C}_6\text{H}_{15}\text{O}_3)_2\text{Ba} = 30.11$.
(2) 29.91.

The barium salt was therefore perfectly pure.

The silver salt resembled that obtained from α -ethylvalerolactone, but was somewhat less soluble in water and rather more stable.

The formation of the lactone is thus expressed:—

The residual acid, after treatment with sodium-amalgam, was treated just as in the previous case. After repeated purification of the barium salt, the acid was set free, and was found to crystallise. After pressing between filter-paper, the crystals melted between 158° and 160° .

The barium salt was prepared from the crystals, and after drying at 70° —

0.1080 gram yielded 0.0839 BaSO_4 . Ba per cent. = 45.68.

Calc. for $\text{C}_7\text{H}_{10}\text{O}_4\text{Ba} = 46.44$.

There was not enough substance to allow of further purification, but the analysis shows that ethylmethylsuccinic acid is formed in small quantities by the saponification of β -ethylacetomethylsuccinic ether with hydrochloric acid.

Note on the Anhydride prepared by Thorne (Chem. Soc. J., 39, 336).

Thorne states that by distillation of α -ethyl- β -acetopropionic acid, an anhydride is formed, and he examined the properties of this compound to some extent. Having a mixture of the two homologous substituted propionic acids mentioned in this paper, which was otherwise useless, I repeated Thorne's experiments, obtaining a similar anhydride, or rather mixture of anhydrides, which boiled at about the same temperature as the corresponding lactones. Thorne states that the anhydride is insoluble in water, but I found, on the contrary, that the mixed anhydrides were slightly soluble, and distinctly more so at about 0° and 100° than at intermediate temperatures, thus resembling the saturated lactones in this peculiar property.

Constitution of Ketolactonic Acid.

It has been seen that this acid is formed from the compound

$$\begin{array}{c} \text{COOC}_2\text{H}_5 \\ | \\ \text{CH.CO.CH}_3 \\ | \\ \text{CH.C}_2\text{H}_5 \\ | \\ \text{COOC}_2\text{H}_5 \end{array}, \text{ and not from its homologue, } \begin{array}{c} \text{COOC}_2\text{H}_5 \\ | \\ \text{C(CH}_3\text{).CO.CH}_3 \\ | \\ \text{CH.C}_2\text{H}_5 \\ | \\ \text{COOC}_2\text{H}_5 \end{array}, \text{ and that}$$

in the former case alcohol is split off.

One of the (O.C₂H₅) groups and an additional H-atom must then be removed from the first compound to form the alcohol. As regards the hydrogen-atom, the only difference between the two ethers is that an H-atom in the one is replaced by CH₃ in the other; but in the latter case no crystalline acid is formed. It is therefore at least probable that this hydrogen-atom is the one removed. It is also almost certain that it is the (OC₂H₅) group farthest from this H-atom which is split off, because if so an unsaturated lactone group would be formed thus—

and the acid appears in its behaviour with the carbonate and hydrate of barium to contain such a group.

Moreover the splitting off of alcohol in this way would resemble the formation of an unsaturated anhydride noticed by Thorne on distillation of α -ethyl- β -acetopropionic acid, which anhydride (or at least its next homologue) resembles the lactones markedly in its solubility in water.

Ketolactonic acid would then be obtained from its ether by simple saponification.

The barium salts, or for the sake of clearness the acids derived from ketolactonic ether, would then be—

(1.) Ketolactonic acid yielding a barium salt when treated with barium carbonate—

(2.) Probably β -ethylacetosuccinic acid, obtained by the action of barium hydrate in the cold, that is by simple addition of H₂O—

(3.) Probably α -ethyl- β -acetopropionic acid by the action of barium hydrate at 100° , that is by removal of CO_2 from the last acid—

Since ketolactonic acid is decomposed by boiling with barium hydrate, it is easy to understand why Thorne did not obtain it, since he saponified the ether by boiling with caustic potash, so that the acid would be decomposed as soon as formed.

Before closing this paper I wish to return my sincere thanks to Professor Fittig for his ever ready advice and assistance in carrying out this investigation.