

XIX. *On the Action of Isobutyric Anhydride on the Aromatic Aldehydes.*

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WHEN an aromatic aldehyde is heated with normal butyric anhydride and a butyrate, an angelic acid is obtained containing the hydrocarbon radicle of the aldehyde employed. Thus benzoic aldehyde yields phenylangelic acid and cuminic aldehyde cumenylangelic acid. It was therefore thought desirable to make further experiments in this direction, using isobutyric anhydride in place of the normal compound. These experiments led to the following results.

A mixture of cuminic aldehyde, isobutyric anhydride and sodium isobutyrate was heated in sealed tubes to about 150° for twenty-four hours. The resulting product when cool was amber-coloured and viscid, and on opening the tubes, frothed up very much, large quantities of carbonic anhydride escaping. It was mixed with water and boiled in a retort until the distillate was nearly free from oily matter. After cooling, the aqueous portion, consisting of sodium isobutyrate, was poured off from the thick oily product with which it was associated. The latter was then boiled with an excess of a solu-

* As stannic ethide always deposits a copious white precipitate after being kept for several years in stoppered bottles, it probably undergoes a very slow oxidation.

tion of sodium carbonate, and the insoluble oil removed. The boiling alkaline solution, on being acidified, deposited a thick oily acid, becoming a sticky mass on cooling. This was collected and dissolved in petroleum spirit, and after standing for several days, the solution deposited a quantity of oblique crystals. These were separated from the mother-liquors, pressed and recrystallised several times from the same solvent. They fused at 80° . On analysis they gave the following numbers:—

I. ·2342 of substance gave—

·6412 of CO_2 = 74·85 p. c. of carbon.

·1718 of H_2O = 8·15 p. c. of hydrogen.

II. ·2337 of substance gave—

·6396 of CO_2 = 74·62 p. c. of carbon.

·1770 of H_2O = 8·43 p. c. of hydrogen.

No. II was crystallised about six times.

After recrystallising specimens of the above eight or ten times from petroleum spirit, two sorts of crystals were deposited, one being the original product, the other large well-defined crystals of some other body. These were separated mechanically, and the latter recrystallised several times. On analysis, they gave the following numbers. Its fusing point was 91° :—

III. ·2158 of substance gave—

·6054 of CO_2 = 76·5 p. c. of carbon.

·1554 of H_2O = 8·00 p. c. of hydrogen.

A quantity of the acid first analysed, and fusing at 80° , was heated until it commenced to boil, an acid was volatilised having the odour of isobutyric acid. The residue was purified by conversion into the sodium salt and precipitation by hydrochloric acid. It was then crystallised, and gave on analysis the following numbers. It fused at 91° :—

IV. ·2176 of substance gave—

·6110 of CO_2 = 76·56 p. c. of carbon.

·1518 of H_2O = 7·75 p. c. of hydrogen.

The products used in analyses III and IV were evidently cumenylcrotonic acid, which required 76·5 per cent. of carbon and 7·87 of hydrogen, and fuses at 90 — 91° . That used in analyses I and II is apparently a compound of cumenylcrotonic acid with isobutyric acid, a substance of the composition $4(\text{C}_{13}\text{H}_{16}\text{O}_2)\text{C}_4\text{H}_8\text{O}_2$ would require 74·3 per cent. of carbon and 7·9 per cent. of hydrogen.

On making similar experiments with benzoic aldehyde, phenylcrotonic acid was used.

The isobutyric anhydride used in these operations was prepared with considerable care; nevertheless it was thought that the formation of the crotonic acids might be due to the presence of propionic anhydride. A quantity of isobutyric acid was therefore carefully and repeatedly fractioned, and fresh anhydride prepared from it. This was also fractioned. On using this, it was found that it yielded with cuminic and benzoic aldehydes a much smaller quantity of the crotonic acids, so that the formation of these compounds would appear to be due to propionic anhydride in the isobutyric anhydride. Under all circumstances, however, small quantities of uncrySTALLISABLE acids are produced, but up to the present time these have not been obtained in a fit state for analysis.

I have mentioned, in describing the foregoing experiments, that large quantities of carbonic anhydride escaped when the sealed tubes were opened. It was thought desirable to determine roughly the amount of this, and also to examine the oily fluids which pass over when the contents of these tubes are distilled with water.

β -Butenylbenzene.

Twenty grams of benzoyl hydride, thirty of isobutyric anhydride, and fifteen of sodium isobutyrate were heated together in a retort, the neck of which was raised, a condensing tube being attached to it, and to this an apparatus for the absorption of carbonic anhydride. When the temperature of the mixture had reached about 140° , carbonic anhydride began to form, and when it had reached 150° , the gas was evolved very rapidly, the temperature then gradually rose, until in the course of two or three hours, it reached about 180° . The amount of carbonic anhydride given off in this experiment amounted to 4.58 grams. In a second experiment it was 4.75 grams.

The product left in the retort was distilled with water until oily matter ceased to come over. The oily part of the distillate was then washed with alkali to remove isobutyric acid, and when separated from the alkaline fluid, distilled with solid potassium hydrate, and then several times with sodium. The potassium hydrate and also the sodium at first caused a brown substance to form in the oily product. When this was no longer produced, the oil was fractioned, that part boiling between 184° — 187° being kept separate. This constituted the principal part of the distillate. On analysis, however, it was found to contain a little oxygen, probably due to a trace of benzylic alcohol formed by the action of the caustic alkali upon benzoic aldehyde in the crude product. It was therefore shaken with a solution of potassium permanganate and potassium hydrate, and then after being dried and distilled over sodium, it gave the following numbers:—

·1716 of substance gave—

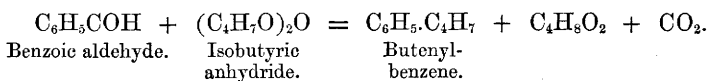
·5695 of CO₂, and

·1395 of H₂O.

| | Theory for C ₁₀ H ₁₂ . | Experiment. |
|----------------|--|-------------|
| Carbon | 90·9 | 90·5 |
| Hydrogen | 9·09 | 9·03 |

This hydrocarbon has therefore the composition of butenylbenzene, but curiously it is not identical with that obtained from phenylangelic acid (*Jour. Chem. Soc.*, 1877, **2**, 667). I therefore propose to call it *β-butenylbenzene*. Its boiling point is 184—186°, or nearly two degrees lower than that of the butenylbenzene already described. When oxidised with chromic mixture, it yields benzoic and acetic acids.

The formation may be expressed thus:—



Dibromide of β-Butenylbenzene.

On adding a standard solution of bromine in glacial acetic acid to a weighed quantity of this hydrocarbon, the colour of the bromine rapidly disappears, until about the theoretical quantity of bromine has been added to produce a dibromide. On adding water, a heavy oil separates. This, after being collected, washed with dilute alkali, and dried, appears as a colourless transparent and thick oil. It evidently has the formula C₁₀H₁₂Br₂.

This substance differs from the dibromide of *α*-butenylbenzene in being liquid; in fact, it cannot be made to solidify even when cooled to −20°, and well agitated with a glass rod, a few crystals of the *α*-dibromide being likewise added to it.

Bromo-β-Butenylbenzene.

The above dibromide when gently heated with an excess of alcoholic potassium hydrate, rapidly decomposes, potassium bromide separating in quantity. On adding water, a heavy oil separates. This is bromo-*β*-butenylbenzene, C₁₀H₁₁Br.

It is a transparent fluid more mobile than the dibromide.

Dibromide of Bromo-β-Butenylbenzene.

On dissolving bromo-*β*-butenylbenzene in a sufficient quantity of a ten per cent. solution of bromine in glacial acetic acid to form a dibromide, the liquid gradually becomes lighter in colour, and in the

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course of an hour or two, begins to deposit crystals. After standing for about twelve hours, most of the bromine has disappeared, and the liquid is filled with crystals. These were collected, washed with glacial acetic acid, and then recrystallised from that solvent. In this manner the new body was obtained beautifully white, and like freshly sublimed benzoic acid.

The following numbers were obtained on analysis :—

·2205 of substance gave—

·2615 of CO_2 , and

·0604 of H_2O .

The formula $\text{C}_{10}\text{H}_{11}\text{Br} \cdot \text{Br}_2$ requires—

| | | Experiment. |
|----------------|-------|-------------|
| Carbon | 32·34 | 32·34 |
| Hydrogen | 2·96 | 3·04 |

This substance is therefore the dibromide of bromo- β -butenylbenzene. It melts at $63\cdot5^\circ$, and when strongly heated decomposes, hydrobromic acid being evolved, and a colourless oily body distilling over. It is not very easily soluble in cold, but readily in boiling alcohol. Both ether and petroleum spirit dissolve it freely in the cold. It is not very easily soluble in boiling glacial acetic acid, and very slightly soluble in the cold acid.

When boiled with alcoholic potassium hydrate, it rapidly decomposes, with formation of potassium bromide and a heavy brominated oil. With an alcoholic solution of silver nitrate, it rapidly decomposes when heated, with formation of silver bromide.

Fuming nitric acid dissolves it, with formation of red fumes. On adding water to the product of the reaction, a thick yellow oil separates. Cold concentrated sulphuric acid does not dissolve it.

The formation of dibromide of bromo- β -butenylbenzene confirms the formula given for bromo- β -butenylbenzene.

Dibromide of α -butenylbenzene yields with alcoholic potassium hydrate, potassium bromide and an oily bromobutenylbenzene. This when treated with bromine yields only an oily derivative; all endeavours to obtain it in a crystalline condition have failed.*

* α -Butenylbenzene is somewhat difficult to obtain in quantity, the hydriodophenylangelic acid, when treated with alkaline solutions, being to a large extent reconverted into phenylangelic acid. As the dibromide of α -butenylbenzene had not been analysed, a portion was submitted to combustion, and gave the following numbers :—

·1097 of substance gave—

·1641 of CO_2 , and

·0416 of H_2O .

The formula $\text{C}_{10}\text{H}_{12}\text{Br}_2$ requires—

| | | Experiment. |
|----------------|-------|-------------|
| Carbon | 41·09 | 40·79 |
| Hydrogen | 4·1 | 4·17 |

On boiling a mixture of fifteen parts of isobutyric anhydride, ten of cuminic aldehyde, and five of sodium isobutyrate, large quantities of carbonic anhydride are produced, and the resulting product when distilled with water, yields a large quantity of an oil. This was washed with alkali, and then distilled with solid potassium hydrate, and finally several times with sodium; when fractioned, the principal part came over between 234° and 235° . On analysis, it gave the following numbers:—

·5037 of CO_2 , and
·1430 of H_2O .

•5070 of CO_2 , and
•1456 of H_2O .

| | | Experiment. | |
|--------------------|-------|-------------|-------|
| | | I. | II. |
| Carbon | 89.65 | 89.31 | 89.26 |
| Hydrogen | 10.35 | 10.33 | 10.44 |

$$\text{C}_6\text{H}_4(\text{C}_3\text{H}_7)\text{COH} + (\text{C}_4\text{H}_7\text{O})_2\text{O} = \text{C}_6\text{H}_4 \left\{ \frac{\text{C}_3\text{H}_7}{\text{C}_4\text{H}_7} + \text{C}_4\text{H}_8\text{O}_2 + \text{CO}_2 \right.$$

Cuminic aldehyde. Isobutyric anhydride. Isopropylbutenylbenzene.

Butenylcinnamene.

Ten grams of cinnamic aldehyde, fifteen grams of isobutyric anhydride, and seven and a-half grams of sodium isobutyrate were heated in a retort for about two hours. Carbonic anhydride was given off, and amounted to 2.5 grams. The product was mixed with water and distilled until no more oil came over with the water. The oil was separated and mixed with aqueous ammonia to remove isobutyric acid. It was then washed with water, collected and dried. When rectified, very little came over under 240° , but nearly all between

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this and 260° . On distilling it with sodium, the principal fraction passed over between 248° and 250° . This was analysed, but the numbers were a little low. It was then left in contact with sodium for two days and frequently agitated. A certain amount of a brownish product formed. After this it was again distilled, and the portion boiling between 245° and 248° analysed. This last treatment with sodium apparently caused some of the hydrocarbon to polymerise, as the last portion had a very high boiling point.

The following numbers were obtained:—

I. ·1492 of substance gave—

·4957 of CO_2 , and

·1222 of H_2O .

II. ·1610 of substance gave—

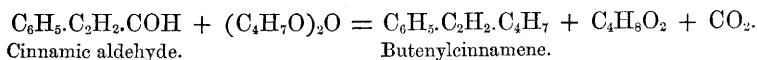
·5363 of CO_2 , and

·1313 of H_2O .

The formula $\text{C}_{12}\text{H}_{14}$ requires—

| | | Experiment. | |
|--------------------|-------|-------------|-------|
| | | I. | II. |
| Carbon | 91·13 | 90·61 | 90·84 |
| Hydrogen | 8·87 | 9·1 | 9·06 |

The formation of this hydrocarbon may be represented thus:—



Butenylcinnamene is a highly refracting liquid lighter than water. Its odour is somewhat pleasant and aromatic. It is very remarkable for the rapidity with which it oxidises. If a small quantity be left exposed to the air in a watch-glass for about twelve hours, it will become as thick as Canada balsam. With concentrated sulphuric acid it becomes orange-red in colour; heat is also given out, and a thick oily product forms, which is apparently a polymeride of the hydrocarbon. Fuming nitric acid acts upon it with explosive violence, boiling dilute nitric acid gradually changes it into a yellow oil. Chromic mixture rapidly oxidises it.

Butenylcinnamene combines with bromine. It also appears to form a compound with picric acid which crystallises in needles.

Ortho-butenylphenol.

On heating the sodium-derivatives of salicyl hydride with an excess of isobutyric anhydride, large quantities of carbonic anhydride were evolved, and a thick oily product obtained. This was first treated with water to remove sodium isobutyrate, and then boiled with alcoholic potassium hydrate to saponify the isobutyric derivative of the new substance which had been formed. Water was added and the

alcohol boiled off. On acidifying the alkaline solution, an oil separated which was collected and distilled. The first parts which came over contained isobutyric acid and salicyl hydride; all that boiled below 200° was rejected. The rest was shaken with cold aqueous potassium hydrate and then with ether to remove neutral products. The clear alkaline solution was heated and acidified with hydrochloric acid; and the oil which separated was washed with dilute ammonia to remove traces of isobutyric acid and salicyl hydride, and then distilled with water. It came over very slowly and sank as an oil in the receiver. After being collected and dried, it was distilled; a little came over between 220 — 223° , but most at 223 — 225° , and the residue principally between 225 — 230° , after which the temperature went up quickly. On cooling, the residue in the retort solidified, owing to the presence of propionic coumarin, formed from a small quantity of propionic anhydride in the isobutyric anhydride used.

A second experiment was made, using salicyl hydride instead of the sodium-derivatives.

Thirty grams of salicyl hydride, twenty-two grams of sodium isobutyrate, and forty-five grams of isobutyric anhydride were heated together for about four hours. The amount of carbonic anhydride evolved weighed 4.3 grams. The sodium isobutyrate was separated from the product by means of water, and the oil washed with dilute potassium hydrate, enough being used to make the liquid pretty strongly alkaline, but avoiding too large an excess. The undissolved oil, consisting mainly of the isobutyric derivatives of the new product, was separated, a little ether being used to facilitate this operation. The ether was boiled off and the oil saponified with alcoholic potassium hydrate; water was then added, the alcohol boiled off, and hydrochloric acid added in excess. The new product (which separated as a thick oil) was collected, washed with dilute ammonia, dried and distilled, all being collected that came over under 250° (a good deal of residue was left in the retort). The distillate was then fractioned and the portion coming over between 220 — 230° kept separate; this was again distilled, and the portions between 223 — 225° collected. This process is superior to the first one, but the yield of the pure new product is but small in either case.

It gave on analysis the following numbers:—

·1457 of substance gave—

·4310 of CO_2 , and
·1064 of H_2O .

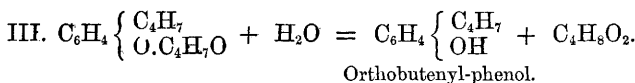
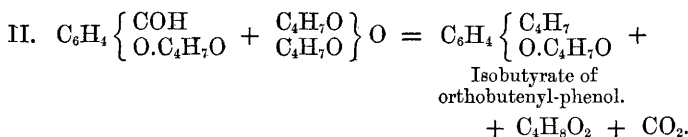
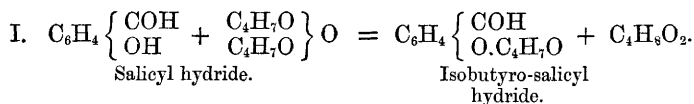
The formula $\text{C}_{10}\text{H}_{12}\text{O}$ requires—

| | |
|----------------|-------|
| Carbon | 81.08 |
| Hydrogen | 8.10 |

Experiment.

| |
|-------|
| 80.67 |
| 8.11 |

I propose to call this substance *orthobutenyl-phenol*. Its formation may be expressed thus—



It will be remembered that normal butyric acid and salicyl hydride, &c., yield butyric coumarin.

Orthobutenyl-phenol is a colourless oil boiling at about 223—225°, having a smoky and cedar-like odour; its sp. gr. at 150° is 1·0171. It dissolves in a solution of potassium hydrate, but requires an excess. Ammonia dissolves it only to a small extent.

With nitric acid it forms a yellow resinous product; chromic mixture acts on it with violence. It decolorises bromine-water quickly, yielding a thick oily substance. Picric acid dissolves in it with an orange-red colour. With concentrated sulphuric acid it forms a cerise-coloured solution; this, however, soon becomes turbid from the separation of a gummy product, soluble in boiling water.

A mixture of orthobutenyl-phenol and anisic aldehyde, treated with three or four times its volume of concentrated sulphuric acid, forms a rich purple fluid; on the addition of water a resinous product separates, most of the colour disappearing. This product dissolves in alcohol, with an orange-red colour, destroyed by ammonia. With salicyl hydride and sulphuric acid, this phenol likewise forms a purple solution, but rather redder than in the previous case. On addition of water, a dark-coloured product separates; this is slightly soluble in water with a red colour; it is also partially soluble in aqueous potassium hydrate, its colour becoming very weak, but on addition of acid it is again restored.

Orthobutenyl-phenol, when mixed with chloroform and an excess of strong aqueous potash, becomes slightly warm and pink in colour; this changes to purple when heat is applied, and a strong reaction sets in, the liquid boiling vigorously by itself. The colour then changes to greenish-red, and finally to orange. On adding water and boiling off the excess of chloroform which has been employed, a yellowish-red

solution is obtained and some resinous matter deposited. On filtering the solution and adding hydrochloric acid, an oil separates, which is probably butenyl-salicyl hydride. When distilled it is a nearly colourless oil. It does not appear to combine very freely with bisulphites.

Parabutenyl Phenol.

Paroxybenzoic aldehyde treated with isobutyric anhydride and sodium isobutyrate behaves in the same manner to salicylic aldehyde; the mixture gives off carbonic anhydride and a new phenol is obtained. The yield however is very small, a great deal of neutral products being formed. This phenol boils at about $230-235^{\circ}$; it is an oil, but when cooled in a freezing mixture, solidifies to a crystalline mass. I did not obtain it sufficiently pure for analysis, but there can be no doubt about its identity, as when heated with alcoholic potassium hydrate and methylic iodide it produces an oil having the characteristics of β -butenylanisöl.

β -Para-Butenylanisöl.

Twenty grams of anisic aldehyde, thirty grams of isobutyric anhydride, and fifteen grams of sodium isobutyrate were heated in a retort, the mixture boiled at about 180° , and carbonic anhydride came over in abundance during the first half hour. The heating was continued for three or four hours. The amount of carbonic anhydride evolved amounted to 3.9 grams.

The product was distilled with water and the oily part of the distillate collected and washed with ammonia; after being again separated it was dried over carbonate of potassium. On being cooled by a mixture of ice and hydrochloric acid, it solidified to a beautiful crystalline mass. This was very strongly pressed between calico in a powerful screw-press cooled below 0° . The solid product then obtained fused at about $+7^{\circ}$, and formed the chief part of the product. For further purification it was dissolved in about its own bulk of alcohol and again frozen, being well stirred at first. The solid mass was again pressed, and then appeared as a pure white waxy substance; this was powdered and exposed to the cold air* until any adhering alcohol had evaporated; it was then fused and distilled with sodium.

This substance gave on analysis the following numbers:—

1.284 of substance gave—

0.3830 of CO_2 , and

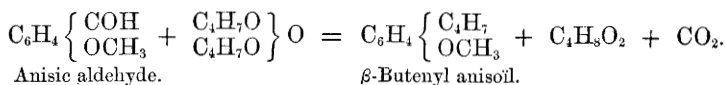
0.1008 of H_2O .

* Of course these operations can only be conducted in winter time, when the temperature of the air is below 0° .

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| | Theory for $C_{11}H_{14}O$. | Experiment. |
|----------------|------------------------------|-------------|
| Carbon | 81.48 | 81.35 |
| Hydrogen | 8.64 | 8.72 |

This substance I propose to call β -*para-butenylanisoil*; its formation may be expressed thus:—

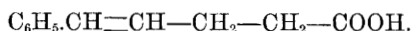
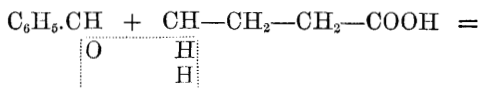


In most of its properties this substance resembles the *para*-butenylanisoil obtained from phenyl angelic acid (*Jour. Chem. Soc.*, 1877, **2**, 671). Its odour and taste are similar, and it is a solid crystalline body. Its fusing point, however, is only 8.5 or 9° , whereas the other is 17° . Its boiling point is 236 — 237° , or about six degrees lower than the above, so that there can be no doubt about its being isomeric. A number of preparations of this substance have been made, and in all these physical properties have been constant.

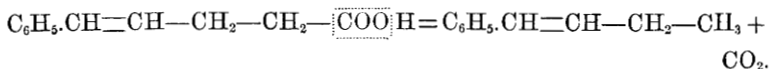
When oxidised with chromic mixture it yields anisic and acetic acids.

From the foregoing results we now know of two butenylbenzenes, two isopropyl butenylbenzenes, and two *para*-butenylanisoils, obtained by somewhat analogous processes, one class being formed by the decomposition of the replaced angelic acid is prepared from the aromatic aldehydes by normal butyric acid, the other being produced from the aromatic aldehydes by the action of the isobutyric acid. The question to be considered is why are they isomeric?

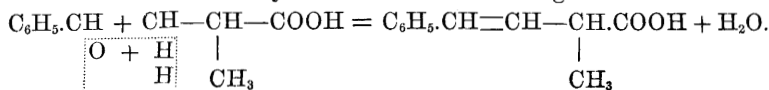
We will consider the two butenylbenzenes. In the formation of the one I described some time since, it will be remembered that it was prepared from phenylangelic acid by abstraction of carbonic anhydride. First I would draw attention to the formation of this acid from benzoic aldehyde, and for simplicity sake we will assume that it is formed from this and butyric acid, instead of butyric anhydride.



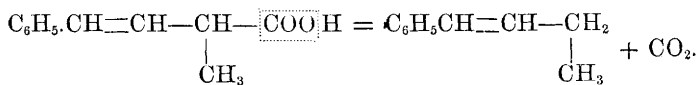
On separating CO_2 from this acid we get—



Now if we take isobutyric acid what should we get?—



This acid, however, does not appear to be sufficiently stable to exist, and immediately splits up into carbonic anhydride and the hydrocarbon,



Now according to this equation, the hydrocarbons obtained by butyric or isobutyric acid ought to be identical.

Baeyer, on treating furfural with isobutyric anhydride, obtained a furfurbutylene, and he evidently considered it to be formed in a manner analogous to the above, as he assumes that it is constituted thus—

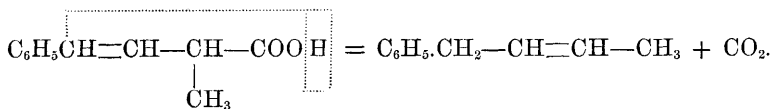


β -Butenylbenzene when oxidised yields benzoic and acetic acids, the formation of the latter showing that it probably contains CH_3 . What can its constitution be? It is not



as Aronheim obtained this substance by acting on benzylic chloride and iodide of allyl with sodium, and found it to have a boiling point of $176-178^\circ$ (*Deut. Chem. Ges. Ber.*, **5**, 1068).

It may be possible that the acid which is assumed to be formed when isobutyric anhydride acts upon benzoic aldehyde, on splitting up, does not give up the hydrogen of the COOH group to the carbon group with which it is in juxtaposition, but to one of the others thus—



This would appear not improbable, as there is only one other arrangement $-\text{CH}=\text{C}<\begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}$ for the group C_4H_7 than those in the three formulæ above given.

Of course any reasoning which is found to be true in the case of β -butenylbenzene, will be equally true in the case of all the other bodies described in this paper.