XLIX.—*On the Action of Sodium Alcoholates on Fumaric Ethers.*

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It is well known that in aceto-acetic ether, in malonic ether, and in the nitroparaffins, atoms of hydrogen, which are directly united with a particular atom of carbon, may be replaced by atoms of strongly positive metals. This property seems to depend on the presence of electronegative atoms or radicals, which are combined with the carbon-atom in question. It is also a well-known fact that a relatively electronegative character is imparted to a hydrocarbon group, if one or more double or triple bonds between carbon-atoms occur in the molecule; the general behaviour of many benzene derivatives, and the replaceability of an atom of hydrogen by sodium in acetylene and its homologues may be cited as examples in point.

It seemed not improbable that similar relations might be found to exist in the ethers of the unsaturated acids; that, for example, in the case of fumaric ether, the combined influence of the double bond, and the proximity of the carboxyl groups might so weaken the force with which the hydrogen atoms of the $-\text{CH}=\text{CH}-$ group are bound, that one or both of them might be replaced by sodium. It would then be possible by the action of haloid ethers on the sodium-compound to effect a direct synthesis of the homologues of fumaric acid.

Professor Wislicenus, in whose laboratory and under whose direction the following research was conducted, had already investigated the action of the alkali-metals on ethyl fumarate. Sodium exerted little or no action at the ordinary temperature; potassium acted vigorously, but the product was of such a complicated nature as to offer little prospect of a satisfactory elucidation of the reaction. More recently, on the other hand, by the action of sodium ethylate in alcoholic solution and subsequent addition of methyl iodide, according to the method practised in the University Laboratory at Würzburg in the aceto-acetic ether syntheses, Wislicenus had obtained a dibasic acid, the composition of which, according to the analyses of the barium and the silver salt, corresponded with the formula $\text{C}_6\text{H}_{10}\text{O}_5$. A saturated

addition product had evidently been formed, probably, as it seemed, a dimethylmalic acid of the formula $\text{CH}_3.\text{C}(\text{OH})(\text{CO}_2\text{H}).\text{CH}(\text{CO}_2\text{H}).\text{CH}_3$. In this experiment sodium ethylate, ethyl fumarate, and methyl iodide had been employed in the proportions of their molecular weights, and monomethylfumaric acid was expected as the probable product of the reaction. The simultaneous substitution of two atoms of hydrogen by methyl-groups seemed easily explained on the ground of the symmetrical structure of the fumaric ether.

The presence of a large quantity of unaltered fumaric ether in the product of the reaction confirmed the supposition. Besides this the solubility of the barium salt indicated that the acid was a hydroxy acid. According to this hypothesis, the element of a molecule of water had been added by a secondary reaction during the saponification, and a saturated acid formed. It was, however, possible that the methyl-radical did not enter at all into the constitution of the acid, but that the elements of a molecule of ethylic alcohol had been added to the fumaric acid, and an ethyl-malic acid formed.

The reaction might then be expressed as follows :—

or

In either case only the basic ethoxyl-groups would of course be replaced by hydroxyl by the saponification. The following experiments were undertaken, at the suggestion of Professor Wislicenus, in order to determine the constitution of the acid and the mode of its formation.

Preparation of the Fumaric Acid.

The fumaric acid was prepared in the usual manner from malic acid. The malic acid was heated slowly in a current of air to 150° ,

and finally to 180° , as long as water and maleic acid distilled over. The solid residue was powdered, washed with small quantities of cold water, and dried at 100° . The yield in three different experiments, 250 grams of malic acid being used each time, was 169 grams, 154 grams, and 170 grams of fumaric acid.

Preparation of Ethyl Fumarate.

The ethylic ether was prepared from the acid in three different ways, namely: by passing hydrochloric acid gas into a mixture of alcohol and acid; by heating the acid with sulphuric acid and alcohol; and by the action of silver fumarate on ethyl iodide.

The first of these methods, which is the one most frequently employed for the preparation of the ether, is coupled with certain disadvantages. Owing to the slight solubility of fumaric acid in alcohol in the cold, it is necessary to conduct the operation over the water-bath, and at this temperature much chlorosuccinic ether is formed. The decomposition of the latter is effected only after often repeated distillation, and entails a loss of ether due to saponification by the evolved hydrochloric acid gas.

The following may serve as an example of the second method of preparation: To 149 grams of fumaric acid were added 450 grams of absolute alcohol, and 15 grams of concentrated sulphuric acid, and the mixture was heated for four hours over the water-bath. On cooling, water was added, and the oily layer was separated, washed with water, and dried with calcium chloride. The wash-water was shaken up with ether, and the fumaric ether thus extracted added to the main portion. After distilling twice, the portion between 213° and 220° , which was used for part of the experiments described below, amounted to 123 grams. The actual boiling point of ethyl fumarate is 218° (*Jahresb.*, 1872, 515; *Ber.*, 1879, 2282). In the preparation of the ether from the silver salt, the following method was pursued: Silver fumarate precipitated with silver nitrate from the solution of ammonium fumarate was dried at 80° , 81 grams of the dried salt were added gradually to 100 grams of ethyl iodide in a retort fitted with inverted condenser, the retort being gently heated until action set in. When the violent action had ceased, ether was added, and the mixture heated over the water-bath. The liquid was then filtered off, the silver iodide washed with ether, and the residue after distilling off the ether fractionated. The portion boiling at $214\text{--}216^{\circ}$ (not corrected) amounted to 17 grams, and was found by the following analysis to be pure.

0.2320 gram of the substance yielded on combustion 0.1471 gram of water, and 0.4725 gram of carbonic anhydride.

	Calculated for $C_8H_{12}O_4$.	Found.
Carbon	55.81	55.54
Hydrogen	6.98	7.05
Oxygen	37.21	—
	<hr/> 100.00	

Action of Sodium Ethylate and Methyl Iodide on Ethyl Fumarate.

This operation was conducted according to the method used in the Würzburg Laboratory in the preparation of the organic disubstituted aceto-acetic ethers, which, as it has been frequently described (*Annalen*, 192, 153), it is unnecessary to treat in detail. In the first experiment the ingredients were used in the proportion of 2 mols. of methyl iodide to 2 atoms of sodium, and 1 mol. of ethyl fumarate. On adding the first half of the sodium ethylate, a yellow precipitate is formed with evolution of heat, and also on addition of the methyl iodide, considerable heating takes place. The mixture was heated over the water-bath for half an hour, after which it was neutral to test paper; the alcohol was then distilled off, and water added to the residue. No oil separated; by shaking with ether, a small quantity was extracted from the aqueous solution, which, however, on saponification and decomposition of a lead salt procured from it, yielded only hydriodic and fumaric acids. The aqueous solution from which this oil was extracted was then examined. On evaporating, besides sodium iodide and a smeary substance, an organic sodium salt separated out. As the latter could not be procured pure, the calcium salt was precipitated with calcium chloride. The difficultly soluble crystalline precipitate was filtered off, pressed between filter-paper, and then dissolved in a large quantity of water. The solution yielded on evaporation a crystalline powder, which, after being washed with alcohol and dried *in vacuo*, gave on analysis the following numbers:—

0.1860 gram of the substance yielded 0.0751 gram H_2O , 0.2469 gram CO_2 , and 0.0523 gram CaO .

	Calculated for $C_6H_8CaO_3$.	Found.
Carbon	36.00	36.21
Hydrogen	4.00	4.48
Calcium	20.00	20.09
Oxygen	40.00	—
	<hr/> 100.00	

From the small quantity of oil obtained by extraction, and the occurrence of the above-mentioned sodium salt in the aqueous solution, it was concluded that the ether, which was probably formed, had been

saponified by the excess of sodium ethylate. In the next experiment, therefore, only half as much sodium and methyl iodide were used as is required by the proportions already mentioned. The mixture showed a neutral reaction after being heated for only 20 minutes. On addition of water, much oil remained undissolved, which was separated from the aqueous solution, and treated as is described below. The aqueous solution by extracting with ether yielded an oil, which, after drying with potassium carbonate, boiled above 225° , but as it showed signs of decomposition at this temperature, it was distilled under diminished pressure. On fractioning, the chief portion boiled between 195° and 200° under a pressure of 250 mm., and on analysis proved to be the diethylic ether of the acid of formula $C_6H_{10}O_5$, already referred to, although the calculated composition of this body does not differ so much from that of ethyl fumarate that the purity of the substance can be proved by analysis.

- I. 0.2282 gram of the substance gave 0.1713 gram H_2O and 0.4587 gram CO_2 .
 II. 0.2402 gram of the substance gave 0.1786 gram H_2O and 0.4814 gram CO_2 .

Calculated for $C_{10}H_{18}O_5$.		Found.	
		I.	II.
Carbon	55.04	54.82	54.66
Hydrogen	8.26	8.34	8.26
Oxygen	36.70	—	—
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100.00			

The main portion of the oil, which was separated from the aqueous solution, was directly saponified with potassium hydrate, and the solution then neutralised with acetic acid. On addition of neutral, and afterwards of basic lead acetate, only small precipitates were formed, which were filtered off. By adding lead nitrate to the filtrate, after it had been slightly acidulated with nitric acid and then neutralised with ammonia, a heavy crystalline precipitate was formed more quickly on stirring. This lead salt was decomposed with sulphuretted hydrogen, and yielded on evaporation of the aqueous filtrate, and subsequent drying of the residue *in vacuo*, a colourless syrup, which after some days solidified to transparent crystals. The melting point of the acid crystallised from ethereal solution and dried *in vacuo*, was 86° . The analysis gave the following numbers:—

- I. 0.3042 gram of the substance gave 0.1705 gram H_2O and 0.4933 gram CO_2 .
 II. 0.2588 gram of the substance gave 0.1453 gram H_2O and 0.4217 gram CO_2 .

Calculated for $C_6H_{10}O_5$.		Found.	
		I.	II.
Carbon	44.45	44.23	44.44
Hydrogen	6.17	6.23	6.24
Oxygen	49.38	—	—
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100.00			

Action of Sodium Ethylate and Ethyl Iodide on Ethyl Fumarate.

In order to determine whether the acid obtained as above was a dimethylmalic acid, or a product formed by the simple addition of the elements of a molecule of ethylic alcohol, the action of ethyl iodide on a mixture of ethyl fumarate and sodium ethylate was investigated. According to the constitution of the acid there would be formed either a dimethylmalic acid, or the same acid as when methyl iodide is employed. The proportion of ingredients used and the process were the same as in the last experiment. By addition of water to the product of the reaction, an oil and an aqueous solution were obtained. Before saponifying the former, an attempt was made to purify it by distillation, but decomposition took place, and no acid except some fumaric acid could be procured from it. On the other hand, from the aqueous solution containing much sodium iodide, a calcium salt was procured in the form of a crystalline precipitate, which was pressed in filter-paper, washed with alcohol, dissolved again in hydrochloric acid, and by neutralising and boiling again precipitated. It resembled in every respect the calcium salt obtained from the previous experiment, and the analysis of the salt dried *in vacuo* proves that the same acid is formed, no matter whether methyl or ethyl iodide be used.

- I. 0.1906 gram of the substance gave 0.0717 gram H_2O , 0.2506 gram CO_2 , and 0.0546 gram CaO and $CaCO_3$; after treatment with ammonium carbonate, 0.0968 gram $CaCO_3$.
- II. 0.1880 gram of the substance gave 0.0706 gram H_2O , 0.2498 gram CO_2 , and 0.0543 gram CaO and $CaCO_3$; after treatment with ammonium carbonate, 0.0957 gram $CaCO_3$.

Calculated for $C_6H_8CaO_5$.		Found.	
		I.	II.
Carbon	36.00	35.92	36.33
Hydrogen	4.00	4.18	4.17
Calcium	20.00	20.31	20.36
Oxygen	40.00	—	—
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100.00			

Action of Sodium Ethylate on Ethyl Fumarate.

It appeared from the above experiments that the alcohol iodide had taken no part in the formation of the acid, except in so far as it might serve for the decomposition of the sodium compound, which, it was to be presumed, was first formed. Accordingly in the next experiment sodium ethylate, in alcoholic solution as before, was made to act by itself on ethyl fumarate, and in the proportion of 1 atom of sodium to 1 molecule of the ether. To avoid rise of temperature, the ether was gradually added to the sodium ethylate solution, and then after some hours, without heating, simply water was added, in which the product dissolved, without any considerable evolution of heat or any separation of oil, to a reddish-brown neutral liquid. This was heated over the water-bath, and sodium hydrate added, until the solution remained permanently alkaline. After neutralising with acetic acid and distilling off the alcohol, on addition of neutral lead acetate a lead salt was procured, which yielded only fumaric acid. When the solution, freed in this way from fumaric acid, was neutralised with nitric acid, and lead nitrate added, a crystalline insoluble lead salt was obtained. This yielded on decomposition with sulphuretted hydrogen an acid syrup, which solidified on standing to a crystalline mass. The melting point (86°) of the acid, crystallised from ether and dried *in vacuo*, and also its composition, as determined by the following analysis, agreed exactly with those of the acid already described.

0.2127 gram of the substance gave 0.1201 gram H_2O and 0.3467 gram CO_2 .

Calculated for $C_6H_{10}O_5$.		Found.
Carbon	44.45	44.45
Hydrogen	6.17	6.27
Oxygen	49.38	—

It was afterwards found that the ethyl fumarate which had been employed in the experiments in which the acid was obtained in the free state, was contaminated with a substance containing chlorine, probably with ethyl chlorosuccinate. It is evident that this ether, by double decomposition with sodium ethylate, would yield an ethyl malic acid. The ethyl fumarate used in the other experiments was prepared by the sulphuric acid method, and it is scarcely possible that it could contain an addition-product corresponding to the ethyl chlorosuccinate. The reaction with sodium ethylate was, nevertheless, repeated on pure ethyl fumarate prepared from the silver salt, the analysis of which has already been given. The same acid, melting at 86° , was obtained, as is seen from the following analysis:—

0.2345 gram of the substance gave 0.1310 gram H_2O and 0.3813 gram CO_2 .

	Calculated for $C_6H_{10}O_5$.	Found.
Carbon	44.45	44.35
Hydrogen	6.17	6.21
Oxygen	49.38	
	<hr/> 100.00	

From 5 grams of ethyl fumarate, 2 grams of the new acid were obtained.

It appears from this experiment that the acid in question is produced by the addition of the elements of a molecule of ethyl alcohol to fumaric acid, but this, as already mentioned, could take place in two different ways. According as the oxygen on the splitting up of the sodium ethylate remains in combination with the ethyl-group or with the sodium, there will result, as a final product, when the atom of sodium is replaced by hydrogen, either ethyl ether malic acid, or ethylmalic acid proper. To determine which of these two had been formed, the substance was heated with fuming hydriodic acid. The reduction products of the first must be ethyl iodide and succinic acid, that of the second ethyl-succinic acid. 0.7 gram of the acid was heated to 120° for three hours in a closed tube with fuming hydriodic acid. On distilling off the latter a few drops of oil first passed over, which, judging from its smell, consisted of ethyl iodide. From the crystalline residue, which was mixed with much free iodine, 0.15 gram of a pure product was obtained, which agreed exactly in its properties with succinic acid. Inhalation of its vapour produced the characteristic irritation, the acid neutralised with ammonia, gave with ferric chloride a brown, and with baric chloride, on addition of alcohol, a white precipitate.

The acid melted at 180° , and on analysis gave the following results:—

0.1053 gram of the substance gave 0.0499 gram H_2O and 0.1572 gram CO_2 .

	Calculated for $C_4H_6O_4$.	Found.
Carbon	40.68	40.71
Hydrogen	5.08	5.27
Oxygen	54.24	—
	<hr/> 100.00	

The acid in question is therefore an ethyl ether malic acid of the

$$\begin{array}{l} \text{CH(OC}_2\text{H}_5\text{)COOH} \\ \text{formula } \left| \begin{array}{l} \text{CH}_2\text{.COOH} \end{array} \right. \end{array}$$
, isomeric with the monethyl malate ob-

tained by Demondesir in preparing diethyl malate (*Jahresb.*, 1851, 514). It is readily soluble in water and in ether, and by evaporation of the solvent is obtained as a thick syrup, which crystallises on standing in crystals apparently rhombic. With basic lead acetate it is not precipitated; in neutral and in weakly acid solution, however, it is precipitated by lead nitrate; neutral acetate also causes precipitation, but less quickly. Besides the already mentioned anhydrous insoluble calcium salt, the silver and barium salts were also analysed. The silver salt was prepared by precipitating with silver nitrate from the aqueous solution of the ammonium salt (in combustion I), and from that of the barium salt (in combustion II). It forms a flocculent, on standing somewhat granular precipitate, little soluble in water, and, when dry and protected from light, tolerably stable.

The analysis of the salt, dried *in vacuo*, gave the following numbers:—

- I. 0.2468 gram gave 0.0498 gram H_2O , 0.1752 gram CO_2 , and 0.1414 gram Ag.
 II. 0.2690 gram gave 0.0543 gram H_2O , 0.1915 gram CO_2 , and 0.1536 gram Ag.

	Calculated for $\text{C}_6\text{H}_8\text{Ag}_2\text{O}_5$.	Found.	
		I.	II.
Carbon	19.15	19.36	19.42
Hydrogen	2.13	2.24	2.24
Silver	57.45	57.29	57.10
Oxygen	21.27	—	—
	<hr/> 100.00		

The barium salt, obtained by neutralising the aqueous solution of the acid with barium hydrate, and evaporation over sulphuric acid, forms a powder consisting of microscopic prisms, readily soluble in water. The salt contains apparently a molecule of water of crystallisation, which is given off partly by standing over sulphuric acid, but completely only by heating to 160° . As the salt is also extremely hygroscopic, no satisfactory determination of the water of crystallisation could be obtained.

- I. 0.2773 gram of the salt, dried over sulphuric acid, lost, when heated to 160° , 0.0139 gram H_2O ; 0.2557 gram of the salt, dried at 160° , gave on combustion 0.0642 gram H_2O , 0.1843 gram CO_2 ; and from the residue 0.2004 gram BaSO_4 , corresponding to 0.0378 gram CO_2 and 0.1178 gram Ba.

- II. 0.2665 gram of the substance (dried at 160°) gave 0.0660 gram H_2O , 0.1985 gram CO_2 , and 0.1767 gram BaCO_3 , corresponding to 0.0395 gram CO_2 , and 0.12288 gram Ba.
- III. 0.3629 gram of the substance (dried at 160°) gave 0.0892 gram H_2O , 0.2695 gram CO_2 , and 0.2412 gram BaCO_3 , corresponding to 0.0539 gram CO_2 , and 0.16774 gram Ba.

Calculated for $\text{C}_6\text{H}_8\text{BaO}_5 + \text{H}_2\text{O}$.		Found.
		I.
Carbon	22.86	22.51
Hydrogen	2.54	2.65
Barium	43.49	43.77
Oxygen	25.40	—
Water.....	5.71	5.01
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100.00		

Calculated for $\text{C}_6\text{H}_8\text{BaO}_5$.		Found.	
		II.	III.
Carbon	24.24	24.35	24.30
Hydrogen.....	2.69	2.75	2.73
Barium	46.13	46.11	46.22
Oxygen.....	26.94	—	—
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100.00			

Action of Sodium Isobutylate on Isobutyl Fumarate.

That ethyl fumarate should form addition compounds with great ease on treatment with bromine or hydrobromic acid is not surprising. R. Anschütz (*Ber.*, 1879, 2282) has in fact found that this ether takes up bromine as easily as any known compound of maleic acid. It is, however, rather remarkable that a substance of this nature should effect the splitting up of sodium ethylate. It seemed, therefore, desirable to ascertain if the reaction were general, and for this purpose the action of sodium isobutylate was investigated. This homologue was chosen in preference to sodium methylate, partly because it is more readily decomposed than the latter, partly because the isobutyl fumarate, which must be used in the reaction instead of the ethyl ether, has not as yet been prepared.

By the action of hydrochloric acid on fumaric acid and isobutylic alcohol, the isobutyl fumarate was not procured free of chlorine compound. Fumaric acid in contact with isobutylic alcohol, which is saturated with hydrochloric acid gas, is but sparingly dissolved in the cold; at 100° etherification is quickly effected. The oil, separating on addition of water, dried with potassium carbonate, boiled after dis-

tilling off the excess of alcohol at 265—270°. It contained, however, even after prolonged heating to 220°, while a stream of dry air was passed through it, a large quantity of a chlorine compound. The ether was therefore prepared from silver fumarate and isobutyl iodide in the same way as the ethyl fumarate already described.

The action is not so violent as when ethyl iodide is employed. An evolution of gas seemed to take place, consisting probably of isobutylene, which would account for the small yield of ether obtained. From 40 grams of fumaric acid only 20 grams of the ether were obtained. Isobutyl fumarate is an oily liquid, which, under a pressure of 160 mm. boils at 170°; it was not, however, obtained pure. It contained some fumaric acid, from which it was found impossible to free it by redistillation.

The following analyses may be adduced, although on account of this impurity, the numbers agree only approximately with the calculated percentages:—

I. 0.1488 gram of the substance gave 0.1146 gram H_2O and 0.3369 gram CO_2 .

II. 0.2178 gram gave 0.1683 gram H_2O and 0.4932 gram CO_2 .

Calculated for $\text{C}_{12}\text{H}_{20}\text{O}_4$.		Found.	
		I.	II.
Carbon	63.16	61.75	61.76
Hydrogen	8.77	8.56	8.59
Oxygen	28.07	—	—
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100.00			

The action of sodium isobutylate on the isobutyl fumarate was conducted as follows:—Sodium isobutylate not being very soluble in isobutyl alcohol, in order to avoid too great dilution, less of the latter was added than was required for complete solution. The isobutyl fumarate was added to the partly dissolved sodium isobutylate in the proportion of one molecule of the former to two atoms of sodium. The mixture gradually dissolved to a reddish-brown liquid; the reaction, however, proceeded much more slowly than in the experiments already described. After standing some hours, the product was heated for an hour over the water-bath, and after addition of water saponified with excess of potassium hydrate solution. The aqueous solution having been separated from the isobutylic alcohol, was acidulated with nitric acid, a small precipitate of fumaric acid was filtered off, and from the filtrate, neutralised with ammonia, a lead salt was precipitated by means of lead nitrate. The acid, obtained by decomposition of the lead salt with sulphuretted hydrogen, formed a thick syrup, solidifying *in vacuo* to a deliquescent crystalline mass, which, however, after repeated crystallisation from aqueous and ethereal solution remained

still deeply coloured. On account of its small quantity, it was impossible to obtain the acid in a state pure enough for analysis. The analyses of the calcium and silver salts, however, given below, show that it has the composition of an isobutyl malic acid corresponding to

By neutralising the aqueous solution of the acid with calcium hydrate solution and boiling, an insoluble crystalline calcium salt was obtained, which, when dried *in vacuo*, gave on analysis the following results :—

- I. 0.1886 gram of the substance gave 0.0919 gram H_2O , 0.2775 gram CO_2 ; in the residue 0.0582 gram CaO and CaCO_3 , which gave 0.1116 gram CaSO_4 , giving by calculation 0.0122 gram CO_2 and 0.03282 gram Ca .
- II. 0.1609 gram gave 0.0774 gram H_2O , 0.2331 gram CO_2 ; in the residue 0.0522 gram CaO and CaCO_3 , which gave 0.0949 gram CaSO_4 , giving by calculation 0.0131 gram CO_2 and 0.02791 gram Ca .

		Found.	
Calculated for $\text{C}_8\text{H}_{12}\text{CaO}_5$.		I.	II.
Carbon	42.11	41.89	41.73
Hydrogen	5.26	5.41	5.34
Calcium	17.54	17.40	17.35
Oxygen	35.09	—	—
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100.00			

The silver salt was obtained as an insoluble flocculent precipitate by adding silver nitrate to the aqueous solution of the acid, neutralised with ammonia. On analysis the carbon was found $\frac{7}{10}$ per cent. too low, and the silver correspondingly high, this discrepancy with the theoretical numbers being probably due to the presence of fumaric acid.

To get rid of this impurity, a solution of the soluble barium salt was prepared by neutralising an aqueous solution of the acid with barium hydrate, the barium fumarate which separated out on evaporation was filtered off, and from the filtrate the silver salt was obtained by fractionated precipitation with silver nitrate. The analysis of the last precipitated fraction gave the following results :—

- I. 0.2022 gram of the substance gave 0.0525 gram H_2O , 0.1738 gram CO_2 , and 0.1083 gram Ag .
- II. 0.2555 gram gave 0.0659 gram H_2O , 0.2185 gram CO_2 , and 0.1371 gram Ag .

		Found.	
		I.	II.
Calculated for $C_8H_{12}Ag_2O_5$.			
Carbon	23·76	23·44	23·32
Hydrogen	2·97	2·88	2·87
Silver	53·47	53·56	53·66
Oxygen	19·80	—	—
		100·00	

The formation of these acid ethers by the action of sodium alcoholates on fumaric ethers is analogous to that of malic acid from fumaric acid (*Annalen*, 192, 80) effected by F. Loyde, by heating the latter with sodium hydrate solution. While, however, for the latter reaction heating for 100 hours is required, ethyl fumarate reacts with sodium ethylate at the ordinary temperature with evolution of heat. The ease with which the reaction takes place is no doubt partly due to the fact that the ether is a liquid. Sodium fumarate when heated over the water-bath with alcoholic sodium ethylate, yields no ethyl malic acid.

An attempt to isolate the sodium compound did not succeed; the formation, however, of a sodium ethyl malic acid as an intermediate product is very probable.

An experiment, in which chloracetic ether was added to the product of the reaction of alcoholic sodium ethylate on ethyl fumarate, showed that the reaction took place in the same sense as when an alcohol iodide was added.

When sodium ethylate, free of alcohol, is added to ethyl fumarate, an addition-product is apparently formed, from which, by addition of alcohol iodide, the synthesis of homologous acids might possibly be effected. The presence of alcohol seems to be the cause of the replacement of the atom of sodium by hydrogen. The course of the reaction in the experiments described is to be represented no doubt by the following equations:—

The research will be prosecuted in the direction indicated above, and the corresponding reactions with maleic acid will be included within the scope of the investigation.

In conclusion the writer begs to express his indebtedness to Professor Wislicenus for advice and help received during the progress of this research.