LXXIX.—*Action of Sodic Alcoholates on Ethereal Fumarates and Maleates.*

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IN a former communication to this Journal (Trans., 1881, 344), it was shown, that by the action of sodic alcoholates in alcoholic solution on the ethereal salts of fumaric acid, the elements of 1 mol. of alcohol are added to the ether; and that by saponification of the products of the action, an etheric acid is obtained, bearing the same relation to malic acid which the etheric acids of the formula

do to the acids of the lactic series. Thus by the action of sodic ethylate in ethylic alcohol on ethylic fumarate, and by the action of sodic isobutylate in butylic alcohol on isobutylic fumarate, ethoxy-succinic and isobutoxysuccinic acids are respectively obtained. The most probable explanation of the reaction seems to be, that by the addition of 1 mol. of sodic alcoholate to the fumaric ether, a sodium-derivative of the ethereal salt of the new acid is first formed, and that this intermediate product is decomposed by the free alcohol, sodium being replaced by hydrogen, and sodic alcoholate reproduced. The action in fact seems to be analogous to that which takes place when malic acid is produced by heating sodic fumarate with an aqueous solution of sodic hydrate. Whilst, however, the latter change is effected only after prolonged heating, the former takes place rapidly and with considerable evolution of heat.

In the present investigation, further experiments have been made with the view of elucidating the nature of the chemical change in question; the action has also been applied to the ethereal salts of maleic acid with the object of contributing to our still imperfect

knowledge of the nature of the isomerism of fumaric and maleic acids.

The experiments described furnish some new facts regarding the nature of the reactions concerned in the production of these bibasic etheric acids, and show that the addition products obtained from fumaric and maleic ethers are dentical, or if not identical, that their isomerism is of the same kind as that of substances which differ only in crystallographic and optical properties.

In order to obtain evidence that the first stage in the reaction between sodic alcoholates and fumaric ethers is the formation of a sodium-derivative, attempts were made in various ways to cause alcoholic iodides to act on the supposed sodium compound, in the expectation that the higher homologues of etheric succinic acids would be formed. Experiments in this direction, however, have been so far unsuccessful, owing to the instability of the sodium compounds in the presence of alcohol, and to the formation of bye-products, when alcohol is excluded. Thus dry sodic ethylate was added in simple molecular proportion to ethylic fumarate, and the product of the reaction, a thick semi-solid mass, digested with methylic iodide, and then saponified. A lead salt was obtained from the product of the saponification, yielding by decomposition with sulphuretted hydrogen an acid which did not crystallise, but remained on drying in the form of a thick dark-coloured syrup. This substance contained no ethoxy-succinic acid, for its ammonium salt did not give the characteristic precipitate of calcic ethoxysuccinate on addition of calcic chloride. A silver salt, obtained approximately pure by the fractional precipitation of the ammonium salt, was analysed by combustion, and gave numbers which, though they led to no simple formula, indicated that a synthesis had taken place. In other experiments, in which a solution of ethylic fumarate in dry ether was used with the object of moderating the action of the alcoholate, attempts to obtain the products in a pure state were not more successful. The action of the alcoholates in the dry state was therefore not further investigated.

As the action of the methylate seemed to be attended with the production of less bye-product than that of the ethylate or isobutylate, the reaction between sodic methylate in alcoholic solution and ethylic fumarate was next examined.

Action of Sodic Methylate on Ethylic Fumarate.

In the first experiment described below, the ethylic fumarate used was made by heating the alcoholic solution of fumaric acid with sulphuric acid, but this method, it was afterwards found, is unsuitable for obtaining pure ethylic fumarate. By subjecting the ether pre-

pared by this method to fractional distillation, a considerable quantity of a substance was obtained from the higher fractions, which solidified on cooling in the form of crystalline scales of pearly lustre, and proved on analysis to be the hydric ethylic fumarate described by Laubenheimer :—

0·2437 gram of the substance gave 0·1268 gram H_2O and 0·4446 gram CO_2 .

	Calculated for $\text{C}_6\text{H}_8\text{O}_4$.	Found.
Carbon	50·00	49·76
Hydrogen	5·55	5·78
Oxygen	44·45	—
	<hr/> 100·00	

Ethylic fumarate was added to a solution of sodic methylate, formed by dissolving sodium in ten times its weight of methylic alcohol, the sodium used being in excess of the proportion of 1 atom of sodium to 1 mol. of ethereal salt. A considerable amount of heat was evolved by the action, but by adding the ether slowly and cooling, much less coloration was produced than in the reaction between sodic ethylate and ethylic fumarate. A heavy white precipitate was quickly thrown down, some more methylic alcohol was added, and after the mixture had stood for an hour, water was added, which dissolved the precipitate without causing the separation of oil. The alcohol was distilled off, and the residue heated with addition of potassic hydrate until the solution remained permanently alkaline. Neither on acidifying with hydrochloric acid, nor on boiling a test portion of the neutralised solution with baric chloride was any precipitate produced, showing that no fumaric acid was left unacted on. On boiling the neutral solution, however, with calcic chloride, a heavy crystalline precipitate gradually formed resembling calcic ethoxysuccinate in appearance and mode of precipitation. The salt was dried at 100° , and on combustion was found to be calcic methoxysuccinate :—

- I. 0·2271 gram gave 0·0739 gram H_2O and 0·2364 gram CO_2 ; the residue weighed 0·0966 gram and yielded 0·1636 gram CaSO_4 , and it contained therefore 0·0292 gram CO_2 .
- II. 0·2326 gram gave 0·0729 gram H_2O , 0·2369 gram CO_2 , and a residue weighing 0·1050 gram, yielding 0·1247 gram CaCO_3 , and containing therefore 0·0352 gram CO_2 .
- III. 0·3324 gram gave 0·1016 gram H_2O , 0·3278 gram CO_2 , and 0·1630 gram of residue, yielding 0·1780 gram CaCO_3 , and containing therefore 0·0633 gram CO_2 .

	Calculated for $C_5H_6CaO_5$.	Found.		
		I.	II.	III.
Carbon.....	32.26	31.90	31.90	32.09
Hydrogen	3.22	3.62	3.48	3.40
Calcium	21.51	21.19	21.44	21.42
Oxygen	43.01	—	—	—
	<hr/> 100.00			

A weighed quantity of the calcic salt was treated with rather less than the volume of decinormal solution of sulphuric acid required by calculation for its decomposition; the mixture was evaporated on the steam-bath, and the acid separated from the calcic sulphate by means of absolute alcohol. On evaporating the alcoholic solution, a syrup was left, which solidified to an opaque crystalline mass. The acid, after being powdered and pressed between filter-paper, was dissolved in ether, and filtered; on evaporating the ether, the residue was dissolved in water, and the solution filtered again. The water was then evaporated, and the residual syrup allowed to crystallise in a vacuum over sulphuric acid. The acid was found to melt at 101—103°, and the following results were obtained by combustion:—

0.2342 gram gave 0.1179 gram H_2O and 0.3482 gram CO_2 .

	Calculated for $C_5H_8O_5$.	Found.
Carbon	40.54	40.55
Hydrogen	5.41	5.59
Oxygen	54.05	—
	<hr/> 100.00	

Attempts to determine the nature of the white precipitate which was formed on adding the fumarate to the methylate were unsuccessful. It contained about 19 per cent. of sodium, and was probably a mixture of salts, the production of which was due to the presence of the monethylic fumarate already referred to. When dried in a vacuum, and heated with ethylic iodide in a closed tube at 100°, no sodium iodide was formed.

Throughout the rest of the investigation pure ethylic fumarate, prepared by the action of ethylic iodide on argentic fumarate, was used, but as the material thus procured is somewhat costly, the experiments were performed on a smaller scale than would have been otherwise desirable.

Preliminary experiments having shown that on adding pure ethylic fumarate to a solution of sodic methylate prepared from the anhydrous alcohol, a crystalline substance is thrown down which after-

wards dissolves again in the liquid, two or three drops of sodic methylate solution, prepared by dissolving sodium in ten times its weight of methylic alcohol, were added to 3 grams of ethylic fumarate diluted with 2 grams of methylic alcohol; the whole solidified at once to a crystalline mass with considerable evolution of heat and some coloration of the product. Water was at once added, and the crystals filtered off and thoroughly freed from adherent liquid by filter-paper; they were then dissolved in hot ether, and the solution separated by filtration from a slight residue. The crystals obtained by evaporation of the ether were dried in a vacuum. The substance fused at 102° , left no residue when heated on platinum foil, and was soluble in water and in methylic alcohol from which it crystallised in long needles. These properties are the same as those of methylic fumarate (*Ber.*, **12**, 2282), and the substance was identified by the following analysis:—

0.2384 gram gave 0.1229 gram H_2O and 0.4376 gram CO_2 .

	Calculated for $C_6H_8O_4$.	Found.
Carbon	50.00	50.06
Hydrogen	5.56	5.73
Oxygen	44.44	—
	<hr/> 100.00	

The weight of methylic fumarate thus obtained from 3 grams ethylic fumarate was 1.2 grams; after a time, however, some more of the substance came out from the solution from which the main portion had been separated. This solution was saponified with sodic hydrate, acidified with hydrochloric acid, and allowed to stand, when very little fumaric acid separated, but on boiling the neutral solution with calcic chloride a considerable quantity of calcic methoxysuccinate was obtained.

Another experiment was made exactly as that just described, and with the same quantities of material, but the mixture of ethereal salt and alcoholate was allowed to stand a few minutes. The crystalline semi-solid product became partially liquid, only 0.3 gram of methylic fumarate was obtained, whilst an oil separated on evaporating off the methylic alcohol from the filtrate; this oil yielded an abundant precipitate of calcic methoxysuccinate on saponification, and only traces of fumaric acid.

In a third experiment, 10 grams of ethylic fumarate were added gradually to sodic methylate solution containing 5 grams of sodium. The methylic fumarate which was formed on each addition of the ethylic salt dissolved almost immediately to a clear solution, which was poured into cold dilute sulphuric acid. The acid solution was

shaken up with ether several times; after removing the ether, neither fumaric acid, methoxysuccinic acid, nor other organic acid could be detected in the remaining liquid. The ethereal extract was dried with calcic chloride, and on distillation yielded an oil which boiled about 220° , but not without considerable loss from decomposition. The oil weighed about 8 grams, and did not contain fumarate. The quantity was too small to fractionate, but a combustion gave results approximating to the numbers required for methylic methoxysuccinate. This substance contains 6.82 per cent. of hydrogen and 47.73 per cent. of carbon; the numbers obtained by analysis were 7.05 and 46.24. The oil, which was insoluble in water, was readily saponified by sodic hydrate; the solution was acidified with hydrochloric acid, but no fumaric acid separated, whilst on neutralising and boiling with calcic chloride, the characteristic calcic methoxysuccinate was obtained.

In a fourth experiment, 10 grams of ethylic fumarate in 5 grams of methylic alcohol, and a quantity of sodic methylate containing about 0.3 gram sodium were used, the weight of sodium being thus less than a quarter of that required by calculation for 1 atom of sodium to 1 mol. of ethereal salt. The same phenomena were observed as before, but the methylic fumarate did not entirely dissolve even on heating on the water-bath; methylic alcohol was therefore added until all was dissolved, and the heating was continued, using a reflux condenser. For some time, the presence of methylic fumarate could be detected on evaporating some of the alcohol from a small test portion in a watch-glass, but after heating for about two hours, the crystalline methylic fumarate could no longer be observed; a slight amorphous precipitate had been formed, due probably to saponification. The whole product was poured into water, which it rendered only faintly alkaline. From this solution, the methylic methoxysuccinate was extracted with ether as before. The residual aqueous solution contained only traces of fumaric acid, and yielded 1 gram of dry calcic methoxysuccinate; the oil obtained from the ethereal extract after being heated to 115° , weighed 8 grams, and when saponified with potassic hydrate, gave 6.6 grams of calcium salt. When the solution was acidified before precipitation, no fumaric acid separated, but a crystalline salt was formed, readily soluble in excess of hydrochloric acid; this was found to be the acid potassium salt of methoxysuccinic acid: an analysis of this salt will be found below. Methoxysuccinic acid of melting point $101-103^{\circ}$ was obtained from the calcic salt as already described.

It will be seen from these experiments that the first change which takes place when sodic methylate acts on ethylic fumarate in presence of methylic alcohol, is the production of methylic fumarate by double

decomposition with evolution of heat; further, that the sodic methylate is able to produce much more than its equivalent molecular proportion of methylic fumarate, from which it appears that the sodium ethylate, which is produced by the double decomposition, is reconverted in the presence of an excess of methylic alcohol into sodic methylate, which acts on a fresh quantity of ethylic fumarate, until the greater part, if not the whole, of the latter is converted into methylic fumarate. The methylic fumarate, if left in contact with the methylic alcohol, is dissolved, and under the action of the sodic methylate, even in the cold, rapidly takes up the elements of 1 mol. of methylic alcohol, forming methylic methoxysuccinate. If the latter action be assisted by heat, a small quantity of sodic methylate will gradually convert a comparatively large quantity of fumarate into methoxysuccinate, little saponification taking place, and very little fumaric acid being left unacted on. It appears, therefore, that in this change also, as in the production of the methylic fumarate, the action of the sodic methylate is continuous. If a larger quantity of sodic methylate be used, as in the third experiment described, almost the whole of the ethylic fumarate is converted into methyl methoxysuccinate, even without the application of heat. The chemical reactions which take place may be expressed by the following equations:—

The experiments, it is true, afford no proof of the formation of a sodium compound at any time during the reaction, but the addition of the elements of 1 mol. of alcohol to the ether is explicable only on the assumption of the actual or potential existence of such a compound in the solution. Ethylic fumarate was heated in closed tubes at 100° with ethylic alcohol, but no addition product could be found.

We must conclude, therefore, either that the unstable sodium compound is actually formed and rapidly decomposed, or that nascent alcohol, so to speak, formed by the interaction of molecules of sodic methylate and methylic alcohol, is able to effect the addition though free alcohol cannot. The sodium compound formed may possibly be the derivative of an acid hydrol, represented by the formula—

which, by decomposition in the presence of alcohol, yields a saturated compound, but according to this supposition we should expect to get, as a final product, a sodic methylic salt, and not a normal ethereal salt, as is the case.

The interchange of alcoholic radicles between an ethereal salt and an alcohol effected in the manner described above, does not appear to have been observed hitherto. Salomon has described several chemical changes of a somewhat similar nature (*Ber.*, 8, 1506), as for instance, when potassic methylete acts on ethereal salts of thiocarbonic acids and on ethylic oxalate, but in all these cases the interchange is accompanied by partial saponification of the normal ether. Thus, when potassic methylete and methylic oxalate were made to react, potassic methylic oxalate was found to have been formed. The reaction may be represented by supposing (see Miller's *Elements of Chem.*, III, Sec. I, 923) that one of the COOC_2H_5 groups combines with the methylete, forming $\text{C}(\text{OCH}_3)(\text{OC}_2\text{H}_5)(\text{OK})$, which then probably reacts with the other COOC_2H_5 group, forming potassic methylic oxalate and ethylic ether. In order, however, to apply that method of representation to the present case, we must suppose that the potassoxyl group splits off entirely from the acid radicle, forming potassic ethylete according to the equation—

a change which seems rather anomalous. It is more probable that the interchange is effected simply by double decomposition, as has been already suggested, and this supposition is rendered the more probable considering the high *etherification velocity* of methylic, as compared with ethylic alcohol, whilst the heat of formation of sodic methylete differs but slightly from that of sodic ethylete (*Compt. rend.*, 101, 318). The conversion of ethylic into methylic fumarate is by no means an isolated instance of the kind of reaction under discussion. I have been for some time engaged with the investigation of the interchange of alcoholic radicles between the ethereal salts of other acids and alcohols, induced by the presence of various reagents, and being desirous of reserving the field of research, I append some of the results already obtained. It has been found that other substances besides the sodic derivatives of the carbinols are able to induce the change. The addition of potassic carbonate or baric hydrate to a mixture of ethylic fumarate and methylic

alcohol produces an immediate precipitate of the methylic salt; sodic carbonate, anhydrous borax, and calcic chloride, induce the change more slowly. When potassic carbonate is added to a mixture of ethylic oxalate and methylic alcohol, methylic oxalate is produced simultaneously with potassic methylic oxalate. Ethylic cinnamate is similarly converted into methylic cinnamate.

Properties of Methoxysuccinic Acid and its Salts.

Methoxysuccinic acid is readily soluble in alcohol, water and ether, and on evaporation of the solvent, it remains as a thick syrup which quickly solidifies to a soft, opaque, white, crystalline mass. The crystallisation proceeds from points on the surface of the syrup, forming circular patches, which with their fine radiating lines and concentric rings have somewhat the appearance, when seen in a thin layer on glass, of the section of a dicotyledonous stem. It melts at $101-103^{\circ}$, and when heated in an ignition tube it evaporates, probably forming an anhydride, and leaves only a slight residue. Baric chloride gives no precipitate with a solution of ammoniac methoxysuccinate even on boiling, but calcic chloride gives a characteristic crystalline precipitate, which, unless the solution is very concentrated, forms only on boiling, and is then very sparingly soluble in water. The lead salt, in appearance and mode of precipitation, is extremely like plumbic ethoxysuccinate. When plumbic nitrate is added to a solution of ammoniac methoxysuccinate, no precipitate is formed for some time; but on shaking or rubbing the sides of the vessel containing the solution with a glass rod, plumbic methoxysuccinate separates in the form of a dense crystalline precipitate. Besides the calcic salt, of which analyses have been already given, the following salts have been also examined.

Hydric Potassic Methoxysuccinate.—A portion of the acid dissolved in water was neutralised with potassic carbonate, and then to the solution another equal portion of acid was added. In a few hours the bottom of the vessel was covered with a crust of minute sparingly soluble crystals, which were dried on filter-paper and analysed. The crystals were heated to 175° without losing weight; the salt is, therefore, anhydrous.

0.4895 gram gave 0.2270 gram K_2SO_4 .

	Calculated for	Found.
	$C_6H_7KO_5$.	
Potassium	21.01	20.82

Zincic Methoxysuccinate.—The aqueous solution of the acid was heated with zincic carbonate in excess, filtered, and allowed to eva-

porate spontaneously in the air. Under these conditions, the solution evaporates until it forms a thick syrup, in which hard rounded crystalline nodules gradually form composed of flat plates massed together. If the solution is evaporated on the water-bath, a viscid gum is left, which does not crystallise, but on being rubbed with a glass rod, solidifies to a white crystalline powder, sparingly soluble in water. The exact determination of the water of crystallisation is attended with difficulty, as the salt is extremely efflorescent, losing 10 to 15 per cent. of its weight when exposed to the air for a few hours; whilst the last portions of water are given off only at a temperature a little below that at which the substance undergoes decomposition. From the analyses quoted below, it appears to crystallise with 4 mols. H_2O , with 3 of which it parts at a temperature somewhat above 100° , whilst it does not become anhydrous until about 210° ; at about 220° it begins to decompose. Certain irregularities regarding the temperatures at which the water is given off, were observed and could not be accounted for. Thus, in Analyses I, III, IV, and V, the salt was found, when heated to 135° , to contain 1 mol. H_2O , very little loss of weight occurring between 100 and 135° , whilst in II the water lost at 100° amounted to considerably more than 3 mols., the total loss at 210° being, however, 4 mols., as in the other cases. The zinc was precipitated as carbonate, the filtrate being in each case tested with ammonium sulphide to ensure that the precipitation was complete.

- I. 0.8286 gram, dried in filter-paper, lost at 135° 0.1561 gram.
- II. 0.4842 gram, dried in filter-paper, lost at 210° 0.1212 gram, and gave 0.1401 gram ZnO .
- III. 0.7674 gram, dried in filter-paper, lost at 135° 0.1400 gram; at 210° suffered an additional loss of 0.0482 gram, and gave 0.2192 gram ZnO .
- IV. 0.3297 gram, dried at 135° , gave by combustion in oxygen 0.1096 gram H_2O , 0.3169 gram CO_2 , and 0.1151 gram ZnO .
- V. 0.3468 gram, dried at 135° , lost at 210° 0.0265 gram, and the residue gave by combustion in oxygen 0.0831 gram H_2O , 0.3004 gram CO_2 , and 0.1118 gram ZnO .

Calculated on $\text{C}_5\text{H}_6\text{ZnO}_5 + 4\text{H}_2\text{O}$.		Found.		
		I.	II.	III.
$3\text{H}_2\text{O}$	19.08	18.84	—	18.24
$4\text{H}_2\text{O}$	25.44	—	25.03	—
Zinc	22.97	—	23.22	—

Calculated on $C_5H_6ZnO_5 + H_2O$.		Found.		
		III.	IV.	V.
H_2O	7.86	7.68	—	7.64
Carbon....	26.20	—	26.21	—
Hydrogen .	3.49	—	3.69	—
Zinc	28.39	28.04	28.00	—
Oxygen ...	41.92	—	—	—
<hr/>				
100.00				

	Calculated on $C_5H_6ZnO_5$.	Found. V.
Carbon	28.44	28.14
Hydrogen	2.84	3.17
Zinc	30.81	30.82
Oxygen	37.91	—

It may be explained that Analyses IV and V were made on the same portion of substance which served for the estimation of water under I; also that the estimations of loss of water between 135° and 210° and of zinc given under III, are calculated on the substance dried at 135° , as it was found more easy to obtain the salt of constant composition when dried at that temperature than when dried on filter-paper. The salt loses water so readily, that it must be quickly dried with filter-paper, and it is difficult to remove adherent moisture without running the risk of efflorescence taking place. The estimations in II and III were made on portions of salt prepared separately. Considering the extremely efflorescent character of the salt, it is surprising that a portion of the water of crystallisation should be retained to such a high temperature as 210° . It must be admitted that the direct estimation of loss of water between 135° and 210° is not very trustworthy, as the substance begins to undergo decomposition at about 220° . On the other hand, the combustions, which were performed slowly in an abundant current of oxygen so as to avoid loss of zinc, and the direct estimations of zinc by precipitation, afford sufficient evidence that a molecule of water is retained when the salt is dried at 135° .

Action of Sodium Ethylate on Ethylic Fumarate.

The results of the investigation of this reaction and the properties of ethoxysuccinic acid have been already described in a previous communication. It was found that when the ingredients used were in the proportion of one atom of sodium to one molecule of ether, although some saponification took place, a large portion of the ethylic

fumarate was converted into ethylic ethoxysuccinate. Professor Wislicenus has informed me that he has observed in this reaction the same peculiarity of which mention has been already made in the case of the action of sodic methylate, namely, that a small quantity of the alcoholate will effect the addition of the alcohol to a comparatively large quantity of ethereal salt. Some more observations have been made with the view of further elucidating the nature of the reaction. When sodium is used in large excess, nearly the whole of the ethylic fumarate is converted, even without the aid of heat, into a sodium-derivative of ethoxysuccinic acid, which is gradually precipitated on standing. In two experiments, in which this compound was collected and washed with alcohol, 5.5 grams and 10 grams of dry substance were obtained respectively from 5 grams and 10 grams of ethylic fumarate. The compound is soluble in water with slight evolution of heat, producing an alkaline solution, which, on being heated, becomes neutral. No fumaric acid is precipitated on acidifying the solution with strong acid, but on boiling with calcic chloride, an abundant precipitate of calcic ethoxysuccinate is obtained. These reactions seem to indicate that a sodium-derivative, possibly sodic ethylic ethoxysodosuccinate, is formed, which is decomposed by water, with the formation of sodic ethoxysuccinate according to the equation—

Determinations of sodium in two separate preparations of the dry compound gave 19.22 and 18.87 per cent., the number required for sodic ethylic ethoxysodosuccinate being 19.66. Sodic ethoxysuccinate contains 22.33 per cent. of sodium; the numbers obtained from estimations of sodium in the substance prepared by treating the supposed sodium-derivative with water and drying the residue at 120°, were 19.41 and 19.78. I purpose making a further study of the nature of these compounds, as soon as I have material available for the purpose. By heating the sodium-derivative, if such it is, with alcoholic iodides, the homologues of the alkyloxysuccinic acids should be formed.

Ethoxysuccinic acid is an extremely stable substance. Whilst hydroxysuccinic acid—malic acid—when heated, parts readily with the elements of water, the etheric acid may be distilled without alcohol being split off. When heated to 150°, the acid loses weight, but very little decomposition takes place, the melting point of the residue being only 2° lower than that of the original acid. When distilled, an anhydride is probably produced; but it is evident from the fol-

lowing analysis of the product of distillation, that no further decomposition takes place, and that the acid is again reproduced on standing.

0.2433 gram gave 0.1267 gram H_2O and 0.4005 gram CO_2 .

	Calculated for $C_6H_{10}O_5$.	Found.
Carbon	44.45	44.89
Hydrogen	6.17	5.79
Oxygen	49.38	—
	<hr/> 100.00	

Descriptions and analyses of the calcium, barium, and silver salts have been already given (Trans., 1881, *loc. cit.*). The lead salt being characteristic, was also analysed for the purpose of comparing the acid with the corresponding compound obtained from maleic acid. On adding plumbic nitrate to a neutral solution of ammoniac ethoxysuccinate, the solution remains clear for some minutes; but on stirring it a dense crystalline precipitate of the anhydrous lead salt gradually forms. On heating the salt, previously dried in filter-paper, to 100° , no loss of weight occurred, and the following results were obtained by ignition and subsequent extraction with acetic acid:—

0.5295 gram salt yielded 0.2668 gram PbO and 0.0515 gram Pb .

	Calculated for $C_6H_8PbO_5$.	Found.
Lead	56.40	56.50

Action of Sodic Methylate on Ethylic Maleate.

Maleic anhydride was prepared by the method devised by Perkin (Trans., 1881, 561), namely, by the action of acetyl chloride on malic acid, the yield obtained being much the same as that quoted by Perkin. Thus 100 grams and 150 grams of maleic acid yielded respectively 46 grams and 70 grams of maleic anhydride. Ethylic maleate was prepared by acting on the silver salt with ethylic iodide according to Anschütz's method (*Ber.*, 12, 2280), the presence of free iodine being carefully avoided. A little of the ether was saponified and fumaric acid carefully tested for, but none was found. 10 grams ethylic maleate were added to 3 grams sodium dissolved in 30 grams methylic alcohol. The mixture became warm and slightly coloured, and a bulky precipitate was produced. On heating for some time, using a reflux condenser, saponification apparently took place, as much more precipitate was formed. The saponification in this case was probably due to the presence of water, as the alcohol had not been

carefully rectified. Water was then added—no oil separating—and the strongly alkaline solution was heated for some time. The methylic alcohol was boiled off, and fumaric acid tested for by acidifying a small portion with sulphuric acid; none was found. The neutralised solution gave no precipitate with baric chloride, but on adding calcic chloride and boiling, a calcium salt separated, which in appearance exactly resembled the calcic salt obtained in the corresponding reaction with ethylic fumarate, and on analysis was proved to have the same composition.

0.3528 gram gave 0.1080 gram H_2O , 0.3421 gram CO_2 , and 0.1755 gram residue, yielding 0.1888 gram CaCO_3 , and containing, therefore, 0.0698 gram CO_2 .

	Calculated for $\text{C}_5\text{H}_6\text{CaO}_6$.	Found.
Carbon	32.26	31.84
Hydrogen	3.22	3.40
Calcium.....	21.51	21.41
Oxygen	43.01	—
	<hr/> 100.00	

The acid was procured as before by decomposing the calcic salt with a little less than the calculated quantity of sulphuric acid, and extracting with alcohol. It formed a syrup which, on standing, solidified exactly like the methoxysuccinic acid obtained from fumaric acid, but it was slightly coloured, and was not obtained pure by successive solution in water and ether, the melting point, $95-100^\circ$, being less definite and some degrees lower than that of the methoxysuccinic acid prepared from the fumarate. Further efforts were not made to obtain it in the pure state from ethylic maleate, as it was afterwards found that a solution of maleic anhydride in alcohol could be substituted for the normal ether, and the acid was preferably prepared from this material.

Action of Sodid Ethylate on Ethylic Maleate.

The sodium used was somewhat in excess of that required by calculation for 2 atoms of sodium to 1 mol. of ethereal salt. In one experiment, the mixture was heated on the water-bath for a quarter of an hour, in another it was allowed to stand for some time without heating, but in neither case was any product obtained in a state fit for analysis. The phenomena attending the reaction were different from those observed in the case of ethylic fumarate and sodic ethylate. When the ethylic maleate was added to the solution of the ethylate, the mixture became quickly of a reddish-brown colour, heat

was evolved, and in the course of half an hour the liquid assumed a syrupy consistency, slight turbidity, but no precipitation being produced; even on heating there was only a slight precipitation. On heating the saponified product with calcic chloride as before, no precipitate formed until the solution was much concentrated, and the calcium salt bore no resemblance to calcic ethoxysuccinate, being readily soluble in water, and not so distinctly crystalline. Baric chloride produced but a slight precipitate; lead acetate and nitrate produced precipitates which were not at all like the characteristic crystalline lead ethoxysuccinate. Attempts to procure an acid in the pure state by decomposition of the lead salt and by extraction of the acidified solution with ether were equally unsuccessful; in both cases a dark-coloured uncrystallisable syrup inclosing some acicular crystals was obtained. The latter, as they were sparingly soluble in cold water, readily soluble in hot water, and sublimed without melting, were probably fumaric acid. If the reaction were moderated by cooling, and a smaller proportion of sodium used, a more satisfactory result would probably be obtained. I propose repeating the experiment with these modifications, as the reaction seems to differ in important respects from that which occurs with ethylic fumarate.

Action of Sodid Methyrate on Hydric Methylic Maleate.

In order to avoid the preparation of the maleic ether, which is a troublesome as well as an expensive operation, the reaction under discussion was applied to a solution of maleic anhydride in methylic alcohol, in the hope that the acid ethereal salt, which would presumably be formed, might be capable of the same additive change as the normal ether. This was found to be the case.

Maleic anhydride was dissolved in its own weight of methylic alcohol, and the solution, after being boiled for some time with a reflux condenser and cooled, was added very gradually to the solution of sodium methyrate, which was also kept cool; the proportion of materials used was somewhat in excess of 2 atoms of sodium to 1 mol. of anhydride, and the sodium was dissolved in twelve times its weight of methylic alcohol. When solutions prepared in this manner are mixed as above, evolution of heat and slight coloration of the liquid indicate that chemical action has taken place, but as long as the vessel is kept in cold water no precipitation occurs. When the mixture is no longer kept cool, it soon begins to become turbid, and a bulky white, partially crystalline precipitate gradually forms. Even after heating the mixture, it gives at first, when water is added, a strongly alkaline reaction, but on further heating the aqueous solution it becomes neutral. When the precipitate above referred to is filtered off from

the alcoholic liquor, freed from adherent sodium methylate by pressing between filter-paper and washing with a little methylic alcohol (if much alcohol is used the substance dissolves), and dissolved in water, it gives a strongly alkaline solution which becomes quickly neutral on boiling; this, on addition of calcic chloride, yields an abundant precipitate of calcic methoxysuccinate. It appears from these observations that the chemical changes which take place are probably as follows:—

When the maleic anhydride is heated with methylic alcohol, hydric methylic maleate is formed. On the addition of this ethereal salt to the sodic methylate, sodic methylic maleate, which is soluble in methylic alcohol, is produced, and when the temperature rises this compound adds on to itself the elements of 1 mol. of sodium methylate, forming sodic methylic methoxysodosuccinate; the latter substance, being less soluble in the alcohol, is precipitated, and when water is added to it sodium is exchanged for hydrogen with the production of sodic hydrate, which quickly effects complete saponification and leaves sodic methoxysuccinate.

The hydric methylic maleate, formed as above, is a syrupy liquid which does not crystallise on standing; if exposed to the air it deposits crystals of maleic acid. In order to test the supposed solubility of sodic methylic maleate in methylic alcohol, the solution of the acid ethereal salt in methylic alcohol was shaken up with ignited sodic carbonate and filtered; the filtrate, on evaporating the alcohol over sulphuric acid, deposited sodic methylic maleate as an indistinctly crystalline powder.

0.5847 gram of the salt yielded 0.2017 gram Na_2CO_3 .

	Calculated for $\text{C}_5\text{H}_5\text{NaO}_4$.	Found.
Sodium	15.13	14.97

An estimation of sodium in the supposed sodic methylic methoxysodosuccinate, obtained as already indicated, gave no satisfactory result, 23.54 per cent. being found instead of 22.33 per cent., as required by theory. The substance is excessively deliquescent, and partial saponification probably occurs during the process of washing with alcohol and drying. Some of the substance was dissolved in water, evaporated to dryness, and dried at 100° ; an estimation of the sodium showed that it had been thus converted into sodic methoxysuccinate.

0.4657 gram gave 0.2576 gram Na_2CO_3 .

	Calculated for $\text{C}_5\text{H}_5\text{Na}_2\text{O}_5$.	Found.
Sodium	23.96	24.00

In the main experiment made with the view of procuring the acid, no attempt was made to separate the sodium compound. After

heating the mixture for some time, water was simply added to the whole product of the reaction, and, after saponification, the calcium salt was thrown down, from which the acid was got as before. Both these substances were exactly like the corresponding compounds obtained from ethylic fumarate, but repeated analyses of the acid gave results for the carbon about 1 per cent. under the percentage required by theory for methoxysuccinic acid, and the melting point was 93—98°, whilst that of the corresponding acid from the fumarate had been found to be 101—103°. On the supposition that the acid was contaminated with maleic acid, a fresh quantity was prepared, particular care being taken to avoid the precipitation of calcium maleate. The solution from which the salt was to be precipitated was made up to half a litre, and the precipitate, after being filtered off, was redissolved with the aid of hydrochloric acid, and reprecipitated from a solution of the same bulk as before. 10 grams of maleic anhydride produced, in spite of the large loss unavoidably incurred by reprecipitation and thorough washing, 18·5 grams of pure calcium salt, being about 49 per cent. of the theoretical maximum yield. The following results were obtained by combustion of the salt dried at 100°:—

- I. 0·2560 gram gave 0·0798 gram H_2O , 0·2515 gram CO_2 , and 0·1236 gram residue, yielding 0·1363 gram CaCO_3 , and containing, therefore, 0·0473 gram CO_2 .
 II. 0·2937 gram gave 0·0883 gram H_2O , 0·2779 gram CO_2 , and 0·1566 gram residue, yielding 0·1597 gram CaCO_3 , and containing, therefore, 0·0672 gram CO_2 .

	Calculated for $\text{C}_5\text{H}_6\text{CaO}_5$.	Found.	
		I.	II.
Carbon	32·26	31·83	32·05
Hydrogen.... ..	3·22	3·46	3·34
Calcium	21·51	21·30	21·75
Oxygen.....	43·01	—	—
	<hr/> 100·00		

The acid was prepared from the salt as before, and was found to melt at 102—104°; its composition, as appears from the analysis below, agrees with that of methoxysuccinic acid.

0·2305 gram gave 0·1187 gram H_2O and 0·3439 gram CO_2 .

	Calculated for $\text{C}_5\text{H}_6\text{O}$	Found.
Carbon	40·54	40·69
Hydrogen	5·41	5·72
Oxygen	54·05	—

It is unnecessary to enumerate the properties of this acid, as they were found to be the same in all respects as those of the methoxysuccinic acid obtained from fumaric ether. Its melting point, like that of the latter, was not perfectly definite, and it was found to be about 1° higher; but this slight divergence was no doubt due to traces of impurity, as the acid in both cases had to be procured by solidification of the syrup, no solvent being found from which it would crystallise.

The calcic salt, of which analyses are given above, and the plumbic salt, resemble in appearance and mode of precipitation the calcic and plumbic methoxysuccinates obtained from ethylic fumarate; the baric salt also is soluble. For purposes of more exact comparison, the acid potassium, and zinc salts, were prepared.

Hydric Potassic Methoxysuccinate.—This substance was prepared as before; it was found to be anhydrous and to be unaltered at a temperature of 175° , as was the case with the salt obtained from ethylic fumarate. The results given below were obtained by combustion.

0.3225 gram gave 0.1156 gram H_2O , 0.3437 gram CO_2 , and 0.1183 gram K_2CO_3 .

	Calculated for $C_5H_7KO_5$.	Found.
Carbon.....	32.24	32.25
Hydrogen	3.76	3.98
Potassium	21.01	20.76
Oxygen	42.99	—
	<hr/> 100.00	

Zincic Methoxysuccinate.—This salt was prepared in the same manner as before. It will be seen from the estimations of water of crystallisation and of zinc which are given below, that the salt has the same constitution as the corresponding substance obtained from ethylic fumarate. It loses 3 mols. H_2O at 100° , or at a temperature slightly higher; at 135° it still retains 1 mol., with which it parts at a temperature only a little below that at which decomposition begins. The difficulty in getting correct estimations of the water of crystallisation was the same as that previously encountered (p. 864).

- I. 0.3323 gram dried in filter-paper lost 0.0626 gram at 135° .
- II. 0.8812 " " " 0.1739 "
- III. 0.2697 gram dried at 135° lost 0.0212 gram at 220° .
- IV. 0.3083 gram dried at 135° lost 0.0258 gram at 220° , and gave 0.1085 gram ZnO .
- V. 0.5502 gram dried at 135° gave 0.1955 gram ZnO .
- VI. 0.7073 " " " 0.2447 "
- VII. 0.7812 " " " 0.2728 "

		Found.	
		I.	II.
Calculated for $C_5H_6ZnO_5 + 4H_2O$.			
$3H_2O$	19.08	18.84	19.73

		Found.				
		III.	IV.	V.	VI.	VII.
Calculated for $C_5H_6ZnO_5 + H_2O$.						
H_2O	7.86	7.86	8.37	—	—	—
Zinc	28.39	—	28.24	28.51	27.76	28.02

In spite of the close resemblance between the zincic methoxysuccinates obtained from the two separate sources, certain differences in the behaviour of the salts were observed, which seem to indicate that they are not identical. It will be seen that the salt obtained from ethylic fumarate is anhydrous at 210° , whilst that from ethylic maleate has to be heated 10° higher before it parts with all its water of crystallisation. Besides the estimations which are quoted above, experiments were made by heating portions of the two substances in watch-glasses placed close together in the same oven. The results as regards the exact temperatures at which the water is eliminated, and at which decomposition sets in, were not quite concordant, but in each case the salt from ethylic maleate had to be heated to a higher temperature than that from ethylic fumarate, before the changes in question occurred. Other differences also were observed, which could scarcely be attributed to traces of impurity in the substance. Thus the solution of the salt from ethylic fumarate, when left to evaporate spontaneously, assumes the form of a viscid syrup or gum before it crystallises, and the crystals, examined under the microscope, have the form of six-sided plates, whilst the solution of the salt from ethylic maleate, under similar conditions, though it becomes somewhat syrupy, crystallises without becoming of such a viscid consistence, and the individual crystals are for the most part prisms often arranged in a radiate fashion. In some cases this salt separated partly in crystals, partly in the form of a fine powder, before the solution attained the consistence of a syrup at all. The crystals obtained in both cases were too small for measurement.

Action of Sodid Ethylate on Hydric Ethylic Maleate.

In order to confirm the identity of the etheric acids obtained from fumaric and maleic acids, it seemed desirable to prepare ethoxysuccinic acid from maleic acid by the method just described for the preparation of the methoxy-acid, more particularly so as the action of sodic ethylate on normal ethylic maleate had failed to yield the acid in question.

The experiment was conducted as already described; the ingredients were used in the same proportion as in the preparation of methoxysuccinic acid, absolute ethylic being substituted for methylic alcohol. The ethylate seems to act more rapidly than the methylate. If the ethereal salt is added to the alcoholate, precipitation of a sodium-derivative takes place at once; if, however, the alcoholate is added in small quantities at a time to the ether, the solution remains clear until the mixture is nearly completed, a few minutes after which the whole becomes a semi-solid mass. From the product of the action, a sparingly soluble calcic salt was obtained, and from this the acid was prepared by decomposition with sulphuric acid and extraction with alcohol. 28 grams of maleic anhydride yielded 32 grams of calcium salt. The properties of this salt and of the acid were the same as those of the corresponding compounds obtained from fumaric acid, the only difference observed being that the melting point of the acid ($84-86^\circ$) was not quite so well defined as that of the acid prepared from fumaric acid which melts at 86° . Analyses of both the salt and the acid indicated the presence of some impurity, estimations of carbon in repeated combustions being lower than could be accounted for by the usual errors of analysis. The salt was therefore reprecipitated; estimations of calcium, as quoted below (I, II, and III), agreed closely with the calculated percentages, but the acid prepared from this salt still gave unsatisfactory results for carbon. It was again converted into the calcic salt, by combustion of which the results given below (IV) were obtained:—

- I. 0.2777 gram gave 0.1400 gram CaCO_3 .
 II. 0.3286 ,, 0.1663 ,,
 III. 0.3164 ,, 0.1592 ,,
 IV. 0.2677 ,, 0.0998 gram H_2O , 0.2949 gram CO_2 , and
 0.1336 gram residue, yielding 0.1349 gram CaCO_3 , contain-
 ing therefore 0.0581 gram CO_2 .

	Calculated for $\text{C}_6\text{H}_8\text{CaO}_5$.	Found.			
		I.	II.	III.	IV.
Carbon	36.00	—	—	—	35.96
Hydrogen ..	4.00	—	—	—	4.14
Calcium	20.00	20.17	20.24	20.13	20.16
Oxygen	40.00	—	—	—	—

The acid prepared from the pure calcium salt showed the same melting point as before, namely, $84-86^\circ$, and still yielded low results for carbon, as will be seen from the following combustions:—

- I. 0.2290 gram gave 0.1312 gram H_2O and 0.3682 gram CO_2 .
 II. 0.2006 ,, 0.1143 ,, ,, 0.3229 ,,
 III. 0.2048 ,, 0.1144 ,, ,, 0.3297 ,,

	Calculated for $C_6H_{10}O_5$.	Found.		
		I.	II.	III.
Carbon.....	44.45	43.85	43.90	43.91
Hydrogen	6.17	6.37	6.33	6.20
Oxygen	49.38	—	—	—
<hr/>				
100.00				

In preparing ethoxysuccinic acid from ethylic fumarate, it was procured by decomposition of the lead salt with sulphuretted hydrogen. This method would probably have yielded a purer product in the present case, but as the various data concerning the acid itself, as well as its salts which are enumerated below, leave no doubt of its identity with the acid prepared from ethylic fumarate, it was thought unnecessary to undertake the further purification of the substance.

Ethoxysuccinic acid, prepared from hydric ethylic maleate, is very soluble in water, alcohol, and ether, and on evaporating the solvent, it is left in the form of a syrup, which on standing over sulphuric acid solidifies slowly to a transparent anhydrous crystalline mass. It melts at $84-86^\circ$, and after being heated to 150° and allowed to solidify again, the melting point is little altered. When calcic chloride is added to a soluble ethoxysuccinate, unless the solution is very concentrated, no precipitation takes place until the liquid is boiled, when the calcic salt separates in the form of a sparingly soluble crystalline powder. The baric salt is readily soluble in water. The lead salt is less readily precipitated by plumbic acetate than by plumbic nitrate; on addition of the latter reagent to a solution of ammoniac ethoxysuccinate, precipitation does not take place until the solution is well shaken or stirred; the anhydrous salt then separates as a dense crystalline powder. As the baric and plumbic salts are characteristic, they were subjected to analysis.

Baric Ethoxysuccinate.—This salt was prepared by neutralising an aqueous solution of the acid with baric hydrate, and allowing the liquid to evaporate spontaneously. As an analysis of the salt gave a rather low result for carbon, it was redissolved, and the solution allowed to evaporate until a portion of the salt had separated. The liquid was filtered, and the residue left by the spontaneous evaporation of the filtrate was used for the analysis, the particulars of which are given below. The salt prepared in this manner is a crystalline powder of a silky lustre, consisting of microscopic prisms which contain apparently one molecular proportion of water. An exact determination of the water of crystallisation is attended with difficulty, as it is given off partly on drying over sulphuric acid, but completely only when the substance is heated to about 160° . The salt being

hygroscopic, it cannot be weighed in the air-dried condition. The number calculated for 1 mol. H_2O is 5.71 per cent.; the percentage found was 6.45. The salt, dried at 160°C ., gave by combustion the following results:—

- I. 0.2842 gram gave 0.0729 gram H_2O , 0.2072 gram CO_2 , and 0.1886 gram BaCO_3 .
 II. 0.3206 gram gave 0.0813 gram H_2O , 0.2390 gram CO_2 , and 0.2121 gram BaCO_3 .

	Calculated for $\text{C}_6\text{H}_8\text{BaO}_5$.	Found.	
		I.	II.
Carbon	24.24	23.92	24.36
Hydrogen	2.69	2.85	2.82
Barium	46.13	46.15	46.01
Oxygen	26.94	—	—
	<hr/> 100.00		

Plumbic Ethoxysuccinate.—This salt was prepared by adding plumbic nitrate to a neutral solution of the ammoniac salt. It was dried in filter-paper, and did not lose weight on heating to 100° . By ignition and subsequent extraction with acetic acid, the following analytical results were obtained:—

1.1630 grams gave 0.2900 gram PbO and 0.3872 gram Pb .

	Calculated for $\text{C}_6\text{H}_8\text{PbO}_5$.	Found.
Lead	56.40	56.43

The various properties of ethoxysuccinic acid and its salts, which have been described, agree with those of the corresponding substance obtained from fumaric ether (Trans., 1881, 352).

Besides the cases of fumaric and maleic ethers, which have been discussed in this communication, we are acquainted with various instances of the conversion of an unsaturated into a saturated compound by the addition of the elements of a molecule of alcohol. A. Rinne (*Ber.*, 6, 389) observed that in the preparation of allylic cyanide a compound of this substance with alcohol was formed, which A. Pinner (*Ber.*, 12, 2053) has shown to be ethoxybutyronitrile. Since the publication of my first communication, Claisen and Crisner (*Annalen*, 218, 141) have found that by the saponification of ethylic benzalmalonate with alcoholic potash, potassic ethoxybenzylmalonate is formed, and K. Grosner has recently (*Inaug. Diss.*, Würzburg, 1885) applied the reaction to the ethers of the pyrocitric acids, and obtained from them ethoxypropanedicarboxylic acids. Probably the ethereal salts of many other monobasic and bibasic unsaturated acids

will be found capable of the same reaction. It may be mentioned that attempts to obtain etheric acids by heating the potassic salts of fumaric and maleic acids with sodic alcoholates were unsuccessful.

From the descriptions of the alkyloxysuccinic acids and their salts, prepared from fumaric and maleic ethers, it will be seen that the only compounds obtained from the two sources in which any difference of properties has been observed are the zinc salts of the methoxysuccinic acids. These differences may possibly be due to the presence of impurities in one or both of the substances, but they are more probably attributable to actual difference of constitution. It may be concluded that the additive compounds in question are either absolutely identical, or if not identical, then their relation to each other is of the same kind as the relation of certain of the malic and tartaric acids to one another. We may also conclude that this identity or close resemblance is a result of the constitutional relations of maleic and fumaric acids, and is not to be attributed to the conversion of the former into the latter substance during the progress of the reaction, as the chemical change takes place at ordinary temperatures and in alkaline solution.

The result obtained from the experiments is such as might be expected, reasoning from analogy. Accepting provisionally Fittig's formulæ, $\text{CH}\cdot\text{COOH}$ and $\text{CH}_2\cdot\text{COOH}$ for fumaric and maleic acid as

best representing the chemical reactions of which these substances are capable, it is evident that the compounds obtained from them by the addition of the elements of a molecule of alcohol should be chemically identical. On the other hand, it is by no means improbable that the acids so obtained might differ in optical and crystallographic characters, and that slight differences might be found in their salts, such as seem to exist in the methoxysuccinates of zinc. This is rendered the more probable in view of the interesting discovery of Kekulé and Anschütz (*Ber.*, **14**, 717) that fumaric and maleic acids when oxidised yield respectively racemic and mesotartaric acids, and in view of the hypothesis advanced by these authors, that fumaric acid probably consists of dextro- and lævo-maleic acids.

Considering the parallelism which has been found to exist between the reactions of fumaric and maleic acids on the one hand, and mesaconic and citraconic acids respectively on the other, the results obtained by K. Grosner, already alluded to, are remarkable and interesting. He finds that ethylic citraconate and ethylic mesaconate, unlike ethylic maleate and fumarate, yield essentially different ethoxypropanedicarboxylic acids, and that ethylic mesaconate and itaconate yield the same acid.

I purpose subjecting the salts of the etheric succinic acids, prepared from fumaric and maleic acids, to a more thorough examination, with the object more particularly of determining whether the additive products from fumaric acid are capable of being resolved into two optically active substances, as may probably be the case should the hypothesis of Kekulé and Anschütz be correct. I propose also to bring the etheric acid, prepared direct from malic acid and by other methods, within the scope of the investigation, as it will be a matter of interest to compare the alkyloxysuccinic acids from different sources with the different malic acids which Anschütz (*Ber.*, **18**, 1949) has now under investigation. I am desirous also of reserving for further study the various sodium-derivatives, which appear to be formed by the action of sodium alcoholates on fumaric and maleic ethers.

The results obtained in the preceding investigation may be summed up as follows:—

1. Sodic methylate dissolved in methylic alcohol acts *continuously* on ethylic fumarate, producing methylic fumarate, and ultimately methylic methoxysuccinate, an intermediate compound, methylic sodomethoxysuccinate, probably being formed. By saponification, methoxysuccinic acid is produced.

2. By the action of an alcoholic solution of sodium ethylate on ethylic fumarate, the latter is converted into ethylic ethoxysuccinate, or into a compound which is probably sodic ethylic ethoxysodosuccinate, according to the conditions of the experiment. Both compounds yield by saponification ethoxysuccinic acid.

3. By the action of sodium methylate on ethylic maleate or on hydric methylic maleate, methoxysuccinic acid is obtained; in the latter case a compound, probably sodic methoxysodosuccinate, being formed, which on treatment with water yields sodic methoxysuccinate.

4. By the action of sodic ethylate on hydric ethylic maleate, ethoxysuccinic acid is obtained.

5. The corresponding etheric acids formed from fumaric and maleic acids by the addition of the elements of a molecule of alcohol are identical, or, if not identical, their relation to each other is that of isomerides which differ only in crystallographic and optical characters.