

V.—*Stereochemistry of Unsaturated Carbon Compounds.*
Part I. Etherification of Substituted Acrylic Acids.

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IN a series of communications presented to the German Chemical Society (*Ber.*, 1894, 27, 510, 1580, and 3146), Victor Meyer and one of us were enabled to show that, as regards the ease with which they are etherified, diortho-substituted benzoic acids differ completely from

their isomerides. Acids of the type $\begin{array}{c} \text{COOH} \\ | \\ \text{X} \diagup \quad \diagdown \text{X} \end{array}$, where X = Cl, Br, NO₂,

COOH, &c., are entirely unacted on when their methyl alcoholic solutions are saturated with dry hydrogen chloride, either in the cold or at the boiling point of the alcohol. Acids in which X = CH₃, OH, F, &c., that is in which the weights of the substituting groups are small, yield minute quantities of their methylic salts when their boiling solutions are treated with hydrogen chloride for some time (V. Meyer, *Ber.*, 1895, 28, 1259). V. Meyer has since shown that the method of etherification suggested by E. Fischer and Speier (*Ber.*, 1895, 28, 3252), in

which the acid is boiled with a 3 per cent. solution of hydrogen chloride, yields similar results, and is preferable to the method first adopted, as many acids, which are but sparingly soluble or practically insoluble in cold methylic alcohol, dissolve readily on warming. It was stated by Victor Meyer and one of us that this abnormal behaviour of diortho-substituted benzoic acids is to be attributed to stereochemical causes, and Wegscheider (*Monatsh.*, 1895, **16**, 75) has since suggested that, if etherification be preceded by the formation of an additive compound of the acid and alcohol, the groups or atoms in the ortho-positions may be in such proximity to the carboxylic group as to hinder or completely prevent the formation of the additive compound. This view is supported by the fact that the radicle weight or volume plays an important part in the retardation or prevention of etherification (Meyer, *Ber.*, 1895, **28**, 1259). Recent investigations by Kellas (*Zeit. phys. Chem.*, 1897, **24**, 221) prove that the retardation is not merely due to the weight of the group in the ortho-position, as among ortho-substituted benzoic acids the nitro-group ($\text{NO}_2 = 46$) has a greater retarding influence than either bromine or iodine ($\text{Br} = 80$, $\text{I} = 127$).

Menschutkin has also been able to draw generalisations regarding the etherification of saturated acids of the aliphatic series from his researches on primary, secondary, and tertiary fatty acids* (*Annalen*, 1879, **195**, 334, and 1879, **197**, 193).

Formic acid.....	61.7 p. cent.	Isobutyric acid	29.0 p. cent.
Acetic acid	44.4 „	Methylacetic acid	21.5 „
Propionic acid...	41.2 „	Trimethylacetic acid	8.3 „
Butyric acid ...	33.3 „	Dimethylethylacetic acid	3.5 „

From these results, it is evident that an acid with the grouping

$\begin{matrix} \text{R} \\ \text{R}_1 \\ \text{R}_n \end{matrix} \text{C} \cdot \text{COOH}$ is much more difficult to convert into its ethereal salt

than acids of the types $\text{RCH}_2 \cdot \text{COOH}$ and $\text{RR}_1\text{CH} \cdot \text{COOH}$, where R, R_1 , and R_n represent alkyl groups. The broader generalisation, that

acids of the type $\begin{matrix} \text{X} \\ \text{X}_1 \\ \text{X}_n \end{matrix} \text{C} \cdot \text{COOH}$, where X not only represents alkyl

groups but also Cl, Br, NO_2 , &c., are difficult to etherify, does not, however, hold good, since trichloroacetic acid is more readily etherified than acetic acid itself. A reason for this anomalous behaviour of trihalogenised acetic acid has been put forward by Feilmann and one of us (*Proc.*, 1897, 241).

* These numbers represent the initial velocity or the amount of acid (in percentage of the quantity originally present) converted into ethereal salt when molecular quantities of the acid and isobutylic alcohol are heated at 155° for 1 hour.

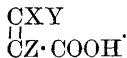
Although generalisations of the above nature have been made with reference to substituted benzoic acids, and also to the fatty acids, no systematic study of unsaturated acids appears to have been made; we therefore determined to prepare a number of the latter and to study the amounts of ethereal salt formed under different conditions, in order to find whether any general rules could be drawn from the results. A further incentive to this study was the suggestion made by one of us (*Chem. News*, 1895, '72, 187) with reference to the constitution of camphoric acid. In that note, attention was drawn to the fact that Bredt's constitutional formula accounts for the characteristic behaviour of camphoric acid on etherification with ethylic alcohol and hydrogen chloride, if the assumption be made that an acid with the grouping



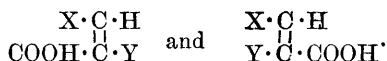
is difficult to etherify. At the time this suggestion was



put forward, no facts were known which justified the assumption, and it was partly with the object of determining whether further investigations might supply satisfactory evidence on this point that the present research was started. Acids of the type mentioned are by no means common, whereas many acids are known of somewhat similar constitution, namely, unsaturated acids of the type



We selected the latter class of acids as being the most suitable, and also because it seemed interesting to determine whether there was any great difference in the amounts of ethereal salt formed by the stereoisomeric acids



During the course of this investigation, a communication by Anschütz (*Ber.*, 1897, 30, 2652) appeared which bears on the same subject, with the exception that he investigated only dicarboxylic acids, whereas we have restricted ourselves to the study of monobasic acids. In the summary at the end of this paper, we discuss Anschütz's results and compare them with our own.

The following is a list of the acids we have investigated.

Cinnamic acid, allocinnamic acid, atropic acid, ortho-, meta-, and para-nitrocinnamic acids.

α -Bromocinnamic acid and α -bromallocinnamic acid.

The two isomeric β -bromocinnamic acids.

The two isomeric $\alpha\beta$ -dibromocinnamic acids.

Dichloro- and di-iodo-cinnamic acids.

α -Cyanocinnamic acid, orthonitro- α -cyano- and metanitro- α -cyano-cinnamic acid.

α -Phenylcinnamic acid and α -phenylallocinnamic acid.

α -Phenylorthonitrocinnamic acid, α -phenylorthonitro-allocinnamic acid and the corresponding meta- and para-compounds.

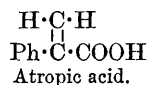
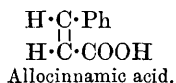
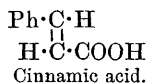
Triphenylacrylic acid.

$\alpha\beta$ -Di-iodoacrylic acid.

The results obtained are given in tabular form at pp. 91—92.

In some of our earlier experiments, we attempted to etherify the acids by saturating their methyl alcoholic solutions with hydrogen chloride in the cold and allowing the mixture to stand for some time, but we found that this method was not adapted to our purpose, as certain acids, especially nitrated acids, were almost insoluble in cold methylic alcohol and, therefore, yielded little or no ethereal salt by this treatment. In all the later experiments, namely, those described in this paper, we used the Fischer-Speier method. A considerable amount of a 3 per cent. solution of hydrogen chloride in pure methylic alcohol (3 grams HCl in 100 grams of solution) was prepared, and half a gram of the acid was boiled with 10 c.c. of this solution for an hour on the water bath, in a small flask fitted with a reflux condenser. For this purpose, the condenser described by Feilmann and one of us (*J. Soc. Chem. Ind.*, 1897, 16, 979) is admirably adapted, as it does away with the possibility of moisture permeating the cork and thus vitiating the result. At the end of the specified time, water was added and the whole extracted twice with ether, any unaltered acid was removed by the aid of dilute sodium carbonate, and the ethereal solution, after drying with calcium chloride, was slowly distilled from a tared flask. The amount of ethereal salt formed was weighed after the flask had been standing over sulphuric acid for several hours. In all cases where the ethereal salts were solid, the residue was crystallised from methylic alcohol and the melting point taken. Oily ethereal salts were hydrolysed, and the melting points of the acids thus obtained were determined. The melting points of recovered acids, in cases where etherification did not take place, or took place to but a slight extent, were also taken.

Cinnamic Acid, Allocinnamic Acid, and Atropic Acid.



These three isomeric phenylacrylic acids were first investigated. The cinnamic acid obtained from Kahlbaum melted at 133°. The results, Nos. 1—8, obtained are given in the Table (p. 91).

The ethereal salt, after recrystallisation from methylic alcohol, melted at 34° (Anschütz and Kinnicutt, *Ber.*, 1879, 11, 1220, give $33\cdot4^{\circ}$), and the regenerated acid obtained by hydrolysis melted at 133° (Kraut, *Annalen*, 1865, 133, 193, gives 133°).

Allocinnamic Acid.—Prof. C. Liebermann, of Charlottenberg, was kind enough to provide us with about 2 grams of this acid, and we desire to express our thanks to him for his kindness. The acid melted at 68° (Liebermann, 68°). The results, Nos. 9—14, are given in the Table, p. 91.

The oily ethereal salt, after hydrolysis with warm potash, yielded an acid melting at 66 — 67° . It is thus evident that Fischer's method of etherification yields the salt of allocinnamic acid and not of cinnamic acid.

Atropic Acid.—This acid, which we obtained from Schucharat, melted at 106° . The results, No. 15—22, are given in the Table.

The oily product, after hydrolysis with potash, gave an acid melting at 105° .

Ortho-, Meta-, and Para-nitrocinnamic Acids from Kahlbaum.

Orthonitrocinnamic Acid.—See Table, Nos. 23 and 24.

The ethereal salt, after crystallisation from methylic alcohol, melted at 73° (Beilstein and Kuhlberg, *Annalen*, 1872, 163, 126, give 72 — 73°).

Metanitrocinnamic Acid.—See Table, Nos. 25 and 26.

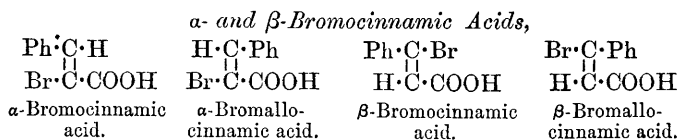
This ethereal salt does not appear to have been described before. It crystallises from methylic alcohol in pale yellow prisms melting at 123 — 124° . It is only sparingly soluble in methylic or ethylic alcohol, and in ether or carbon bisulphide, but dissolves readily in chloroform or benzene.

0.500 gave 28.8 c.c. of moist nitrogen at 17° and 757 mm. N = 6.65.

Theory requires 6.76 per cent.

Paranitrocinnamic Acid.—See Table, Nos. 27 and 28.

As the ethereal salt is almost insoluble in ether, the amount formed could not be determined by the usual method. The process we adopted was as follows: water was added at the end of the hour, the precipitate collected, treated with dilute sodium carbonate solution in order to remove any unaltered acid, and then washed, dried at 100° , and weighed. After recrystallisation from alcohol, in which it is only slightly soluble, it melted at 160° (Kopp, *Jahresbericht*, 1861, 410, gives 161°).



The two *α*-acids were obtained by the method described by Scockmeyer (*Diss.*, 1883), namely, by the action of alcoholic potash on cinnamic acid dibromide, and were separated by fractionally precipitating the solutions of their potassium salts with hydrochloric acid. The *α*-bromocinnamic acid, purified by crystallisation of its sparingly soluble ammonium salt, melted at 131°.

0.200 gave 0.1656 AgBr. Br = 35.21.

$\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CBr} \cdot \text{COOH}$ requires Br = 35.24 per cent.

The results obtained with *α*-bromocinnamic acids, Nos. 29 and 30, are given in the Table (p. 91).

The *α*-bromallocinnamic acid, after purification by recrystallisation from water, was obtained in glistening plates melting at 120°.

0.200 gave 0.1662 AgBr. Br = 35.36. Theory requires 35.24 per cent.

The results obtained with *α*-bromallocinnamic acid, Nos. 31—34, are given in the Table.

As we thought the somewhat high numbers in 31—32 might be due to the presence of a small quantity of the isomeric acid melting at 131°, we took the acid recovered from the above experiments, and determined the amount of ethereal salt formed from this; the results, Nos. 33 and 34, agree with those given above.

The oily ethereal salts, when hydrolysed with cold aqueous potash, yielded an acid melting at 119°. From the fact that it crystallised from water in plates, that it dissolved with the greatest readiness in ammonia, and also from its melting point, the acid thus obtained was undoubtedly the *α*-allo-acid. From this, it is apparent that *α*-bromallocinnamic acid is converted into its true ethereal salt, and not into the isomeric *α*-bromocinnamate, when etherified by Fischer's method; whereas, when its alcoholic solution is saturated with hydrogen chloride, molecular rearrangement occurs, and the salt of *α*-bromocinnamic acid is obtained.

The isomeric *β*-brom-acids were obtained by the method described by Michael and Brown (*Ber.*, 1886, 19, 1379, and 1887, 20, 552), and we are able to confirm their work in every respect; the two acids were separated by crystallisation, first from alcohol and then from chloroform, as these chemists recommend.

The β -bromocinnamic acid melting at $134\text{--}135^\circ$ crystallises from its chloroform solution on spontaneous evaporation in well-developed cubical crystals.

0.200 gave 0.1645 AgBr. Br = 35.0. Theory requires 35.24 per cent.

The results obtained with this acid, Nos. 35—42, are given in the Table, p. 91.

The oily ethereal salt, on hydrolysis, gave an acid which melted at $133\text{--}134^\circ$, after recrystallisation from carbon bisulphide.

β -Bromallocinnamic acid (see Erlenmeyer, *Annalen*, 1895, 287, 1), melting at 159° , is readily obtained pure after one recrystallisation from a small quantity of alcohol.

0.2044 gave 0.1701 AgBr. Br = 35.42. Theory requires 35.24 per cent.

The results, Nos. 43—48, are given in the Table.

The *methylic* salt crystallises from alcohol in thick, colourless prisms melting at 58° . It is moderately soluble in ethylic alcohol or benzene, and dissolves with great readiness in ether, chloroform or carbon bisulphide.

0.2423 gave 0.1887 AgBr. Br = 33.06.

0.2582 „ 0.2019 AgBr. Br = 33.28.

Theory requires 33.19 per cent.

The ease with which the two β -brom-acids can be obtained pure by following Michael and Brown's directions renders inexplicable such statements as those of Liebermann and Scholz (*Ber.*, 1892, 25, 552) and of Erlenmeyer (*ibid.*, 1886, 19, 1936) that the acid melting at $133\text{--}134^\circ$ does not exist.

Dichloro-, Dibromo-, and Di-iodo-cinnamic Acids,

Dichlorocinnamic Acid, $\begin{array}{c} \text{Ph} \cdot \text{C} \cdot \text{Cl} \\ | \\ \text{Cl} \cdot \text{C} \cdot \text{COOH} \end{array}$ or $\begin{array}{c} \text{Ph} \cdot \text{C} \cdot \text{Cl} \\ | \\ \text{COOH} \cdot \text{C} \cdot \text{Cl} \end{array}$.—This acid

was prepared by saturating a chloroform solution of phenylpropionic acid with chlorine. After recrystallisation from light petroleum, it melted at 120° (Nissen, *Ber.*, 1892, 25, 2665, gives $120\text{--}121^\circ$). The results, Nos. 49 and 50, are given in the Table.

The ethereal salt was obtained in the form of an oil.

Dibromocinnamic Acids.—Two isomeric dibrom-acids were obtained by adding bromine to phenylpropionic acid in chloroform solution (Roser and Haselhoff, *Annalen*, 1888, 247, 139); they were separated by dissolving them in a small quantity of chloroform, and adding light

petroleum until a permanent turbidity was produced. The acid melting at 139° crystallised first, and was purified by recrystallisation from boiling light petroleum (b. p. 60—80°). The isomeric acid melting at 100° was obtained pure only after repeated solution in chloroform and precipitation by light petroleum.

The results with the acid melting at 139° (Nos. 51 and 52), and with the acid melting at 100° (Nos. 53 and 54), are given in the Table. The acid recovered from the former melted at 139°.

Di-iodocinnamic Acid, $\text{CIPh}:\text{CI}\cdot\text{COOH}$, obtained by the method given by Liebermann and Sachse (*Ber.* 1891, **24**, 4113), after several recrystallisations from chloroform, melted at 167°. (L. and S. give 171°). The recovered acid melted at 170°. The results, Nos. 55 and 56, are given in the Table (p. 92).

α-Cyanocinnamic Acids.

α-Cyanocinnamic acid, $\text{Ph}\cdot\overset{\text{H}}{\underset{\text{NC}\cdot\text{C}\cdot\text{COOH}}{\text{C}}}$ or $\text{H}\cdot\overset{\text{H}}{\underset{\text{CN}\cdot\text{C}\cdot\text{COOH}}{\text{C}}}\cdot\text{Ph}$, obtained by Carrick's method (*J. pr. Chem.*, 1892, **45**, 401), after recrystallisation from alcohol, melted at 180° (Carrick, 180°). See Table, Nos. 57 and 58.

The *methylic* salt thus obtained crystallised from its alcoholic solution in small, colourless prisms melting at 89°. It is readily soluble in chloroform or ether, and moderately in alcohol, benzene, and carbon bisulphide.

0.5 gave 31.8 c.c. moist nitrogen at 13° and 752 mm. $\text{N} = 7.43$.

$\text{CHPh}:\text{C}(\text{CN})\cdot\text{COOMe}$ requires 7.48 per cent.

α-Cyano-orthonitrocinnamic Acid.—The ethylic salt of this acid was obtained by the action of sodium ethoxide on a mixture of ethylic cyanacetate and orthonitrobenzaldehyde (Riedel, *J. pr. Chem.*, 1896, **54**, 541), and was hydrolysed by the requisite quantity of normal sodium hydroxide at about 60°. The acid thus obtained melted at 223° (Riedel, 223°). The results obtained are given in Nos. 59 and 60 of the Table.

The recovered acid melted at 220°. The *methylic* salt crystallised from alcohol in small, discoloured needles melting at 142°.

α-Cyanometanitrocinnamic acid was obtained in a similar manner. We find that the ethylic salt melts at 134°, and that the melting point is not altered by repeated crystallisation from alcohol. (Riedel gives 127—128°).

0.4 gave 39.4 c.c. moist nitrogen at 16° and 761 mm. $\text{N} = 11.5$.

$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{C}(\text{CN})\cdot\text{COOEt}$ requires $\text{N} = 11.38$ per cent.

The results, Nos. 61 and 62, obtained with this acid are given in the Table.

The recovered acid melted at 170—171° (Riedel, 172°). The methylic salt, after recrystallisation from alcohol, was obtained in fine, silky needles melting at 135—136°, and readily soluble in the usual solvents.

0.3 gave 30.8 c.c. moist nitrogen at 16° and 762 mm. $N = 12.0$.

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{C}(\text{CN}) \cdot \text{COOMe}$ requires $N = 12.07$ per cent.

α-Phenylcinnamic Acids,



These acids were prepared and separated by Bakunin's method (*Gazz.*, 1897, 27, ii, 48). The yield of allo-acid was extremely small.

The α -phenylcinnamic acid, melting at 172°, gave the results Nos. 63 and 64 of the Table.

The ethereal salt, after recrystallisation from alcohol, melted at 77° (Bakunin, 77°).

The α -phenylallocinnamic acid, after crystallisation from water, was obtained in colourless prisms melting at 136°.

0.5 gram, after 1 hour with 3 per cent. solution, gave 0.2137 gram ethereal salt.

The methylic salt thus obtained was semi-solid, whereas Bakunin, who obtained the same compound by the action of methylic iodide on the silver salt of the acid, describes it as an oil. The solid we obtained apparently contained a considerable amount of the solid ethereal salt of the isomeric α -phenylcinnamic acid, as the acid recovered from this first etherification yielded an oil when treated a second time with the 3 per cent. hydrogen chloride solution. The results are given in Nos. 65 and 66 of the Table. The recovered acid melted at 137—138°.

α-Phenylorthonitrocinnamic Acids.—A mixture of the two isomeric acids was obtained by the action of acetic anhydride and sodium phenylacetate on orthonitrobenzaldehyde (Bakunin, *Gazz.*, 1895, 25, i,

137). The α -phenylorthonitrocinnamic acid, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{H}$
 $\quad \quad \quad |$
 $\quad \quad \quad \text{Ph} \cdot \text{C} \cdot \text{COOH}$, was readily obtained pure by Bakunin's method. It melted at 195—196°, and on etherification gave the results Nos. 67 and 68 of the Table. The ethereal salt, after recrystallisation from alcohol, melted at 75° (Bakunin, 75—76°).

A mixture of the above acid with the isomeric allo-acid was obtained by Bakunin's method; it melted at 155° , whereas the pure allo-acid melts at $146-147^{\circ}$. We adopted the following method for its purification. The mixture of acids was boiled for 1 hour with a 5 per cent. solution of hydrogen chloride in methylic alcohol, 20 c.c. of this solution being used for each gram of the mixed acids; after etherification, the solution was poured into water, extracted with ether, and the ethereal solution washed with sodium carbonate solution; on the addition of hydrochloric acid to this alkaline solution, the α -phenylortho-nitroallo-cinnamic acid, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{H}$
 $\text{COOH} \cdot \text{C} \cdot \text{Ph}$, was thrown down, and after recrystallisation from dilute acetic acid melted at 146° .

Whether the results, Nos. 69 and 70 in the Table, are somewhat too high owing to the presence of a small quantity of the isomeric acid, we cannot at present say with any degree of certainty, as the yield of allo-acid is extremely poor and we had but a gram or so at our disposal.

α -Phenylmetanitrocinnamic Acids.—The two acids were obtained by Bakunin's method (*loc. cit.*). The α -phenylmetanitrocinnamic acid melted at 181° and gave the results Nos. 71 and 72 in the Table (p. 92). The ethereal salt, after recrystallisation from alcohol, melted at 72° .

α -Phenylmetanitroallocinnamic acid melted at 196° . The results, Nos. 73 and 74, obtained with this acid are given in the Table.

α -Phenylparanitrocinnamic acid melting at 214° gave the results Nos. 75 and 76 of the Table. The ethereal salt crystallised from alcohol in yellow needles melting at $141-142^{\circ}$ (Bakunin, $141-142^{\circ}$).

α -Phenylparanitroallocinnamic acid melted at 144° (Bakunin, 142°). For results, see Nos. 77 and 78 of Table. The recovered acid melted at 144° .

Triphenylacrylic acid, $\text{CPh}_2 \cdot \text{CPh} \cdot \text{COOH}$, was prepared from the acid amide (Heyl and Meyer, *Ber.*, 1896, 29, 2786) by a method very similar to that adopted by Heyl and Meyer, except that we used the amide, in a fine state of division, suspended in dilute sulphuric acid, and kept the mixture well stirred by an automatic stirrer while the nitrite solution was being run in; the acid thus obtained melted at 213° . The results of etherification, Nos. 79 and 80, are given in the Table. The unaltered acid melted at $213-214^{\circ}$.

Heyl and Meyer (*loc. cit.*) have already shown that this acid is only slowly etherified when hydrogen chloride is passed for several hours through its solution in boiling methyl alcohol.

$\alpha\beta$ -Di-iodacrylic acid, $\text{CHI} \cdot \text{CI} \cdot \text{COOH}$.—This acid was prepared by the addition of iodine to propiolic acid, as described by Bruck (*Ber.*, 1891, 24, 4120); after recrystallisation from chloroform, it melted at about 76° , but after recrystallisation from water at 104° (Bruck, 104°).

Table of Results.

No. of experiments.	Name of acid.	Amount of acid.	Strength of methyl alcoholic solution of HCl.	Amount of HCl solution.	Time.	Amount of ethereal salt formed.	Per cent. of acid converted into ethereal salt.
		gram.	per cent.	c. c.	mins.	gr.	
1	Cinnamic.	0.5	3	10	60	0.5425	99.12
2	Do.	0.5	3	10	60	0.5447	99.54
3	Do.	0.5	3	10	10	0.4958	90.60
4	Do.	0.5	3	10	10	0.4982	91.02
5	Do.	0.5	1	10	60	0.5433	99.28
6	Do.	0.5	1	10	60	0.5459	99.74
7	Do.	0.5	1	10	30	0.4996	91.28
8	Do.	0.5	1	10	30	0.5033	91.96
9	Allocinnamic.	0.5	3	10	60	0.5282	96.52
10	Do.	0.5	3	10	60	0.5304	96.92
11	Do.	0.5	3	10	10	0.4269	78.00
12	Do.	0.5	3	10	10	0.4261	77.86
13	Do.	0.5	1	10	60	0.4820	88.06
14	Do.	0.5	1	10	30	0.4692	85.73
15	Atropic.	0.5	3	10	60	0.5102	93.22
16	Do.	0.5	3	10	60	0.5112	93.40
17	Do.	0.5	3	10	10	0.3420	62.50
18	Do.	0.5	3	10	10	0.3421	62.52
19	Do.	0.5	1	10	60	0.4442	81.16
20	Do.	0.5	1	10	60	0.4408	80.54
21	Do.	0.5	1	10	30	0.2989	54.62
22	Do.	0.5	1	10	30	0.3023	55.23
23	Orthonitrocinnamic.	0.5	3	10	60	0.3176	59.22
24	Do.	0.5	3	10	60	0.3195	59.58
25	Metanitrocinnamic.	0.5	3	10	60	0.5227	97.48
26	Do.	0.5	3	10	60	0.5203	97.02
27	Paranitrocinnamic.	0.5	3	10	60	0.5223	97.40
28	Do.	0.5	3	10	60	0.5218	97.30
29	α -Bromocinnamic.	0.5	3	10	60	0.4091	77.06
30	Do.	0.5	3	10	60	0.4038	76.06
31	α -Bromallocinnamic.	0.5	3	10	60	0.1312	24.72
32	Do.	0.5	3	10	60	0.1302	24.52
33	Do.	0.5	3	10	60	0.1332	25.09
34	Do.	0.5	3	10	60	0.1312	24.72
35	β -Bromocinnamic, m. p. 134—135°.	0.5	3	10	60	0.5291	99.68
36	Do.	0.5	3	10	60	0.5308	100.00
37	Do.	0.5	3	10	60	0.5256	99.02
38	Do.	0.5	3	10	60	0.5281	99.48
39	Do.	0.5	1	10	60	0.4666	87.90
40	Do.	0.5	1	10	60	0.4698	88.50
41	Do.	0.5	1	10	30	0.4222	79.54
42	Do.	0.5	1	10	30	0.4231	79.70
43	β -Bromallocinnamic, m. p. 159°.	0.5	3	10	60	0.5241	98.74
44	Do.	0.5	3	10	60	0.5260	99.08
45	Do.	0.5	1	10	60	0.4648	87.56
46	Do.	0.5	1	10	60	0.4630	87.22
47	Do.	0.5	1	10	30	0.4165	78.46
48	Do.	0.5	1	10	30	0.4154	78.26

Table of Results—(continued).

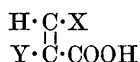
No. of experiments,	Name of acid.	Amount of acid.	Strength of methyl alcoholic solution of HCl.	Amount of HCl solution.	Time.	Amount of ethereal salt formula.	Per cent. of acid converted into ethereal salt.
		gram.	per cent.	c.c.	mins.	gr.	
49	Dichlorocinnamic.	0.5	3	10	60	0.1645	30.90
50	Do.	0.5	3	10	60	0.1615	30.34
51	Dibromocinnamic, m. p. 139°.	0.5	3	10	60	0.0414	7.92
52	Do.	0.5	3	10	60	0.0428	8.19
53	Dibromocinnamic, m. p. 100°.	0.5	3	10	60	0.0700	13.38
54	Do.	0.5	3	10	60	0.0687	13.13
55	Di-iodocinnamic.	0.5	3	10	60	0.0109	2.10
56	Do.	0.5	3	10	60	0.0102	1.96
57	α -Cyanocinnamic.	0.5	3	10	60	0.3466	64.14
58	Do.	0.5	3	10	60	0.3472	64.24
59	α -Cyano-orthonitrocinnamic.	0.5	3	10	60	0.2677	50.32
60	Do.	0.5	3	10	60	0.2702	50.78
61	α -Cyanometanitrocinnamic.	0.5	3	10	60	0.3203	60.20
62	Do.	0.5	3	10	60	0.3176	59.70
63	α -Phenylcinnamic.	0.5	3	10	60	0.3981	74.94
64	Do.	0.5	3	10	60	0.4013	75.54
65	α -Phenylallocinnamic.	0.5	3	10	60	0.0631	11.88
66	Do.	0.5	3	10	60	0.0596	11.22
67	α -Phenylorthonitrocinnamic.	0.5	3	10	60	0.3974	75.55
68	Do.	0.5	3	10	60	0.3982	75.70
69	α -Phenylorthonitroallocinnamic.	0.5	3	10	60	0.0813	15.45
70	α -Phenylorthonitroallocinnamic.	0.5	3	10	60	0.0795	15.11
71	α -Phenylmetanitrocinnamic.	0.5	3	10	60	0.3829	72.79
72	Do.	0.5	3	10	60	0.3849	73.17
73	α -Phenylmetanitroallocinnamic.	0.5	3	10	60	0.0744	14.14
74	Do.	0.5	3	10	60	0.0710	13.53
75	α -Phenylparanitrocinnamic.	0.5	3	10	60	0.3746	71.21
76	Do.	0.5	3	10	60	0.3804	72.32
77	α -Phenylparanitroallocinnamic.	0.5	3	10	60	0.0684	12.99
78	Do.	0.5	3	10	60	0.0657	12.48
79	Triphenylacrylic.	0.5	3	10	60	0.0112	2.14
80	Do.	0.5	3	10	60	0.0124	2.37
81	$\alpha\beta$ -Di-iodacrylic.	0.5	3	10	60	0.0387	7.42
82	Do.	0.5	3	10	60	0.0352	6.75

The results obtained with this acid, Nos. 81 and 82, are given in the Table. The recovered acid melted at 103—104°.

Discussion of Results.

From the results of the experiments described in the preceding pages, we consider ourselves justified in drawing the following conclusions.

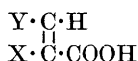
1. Unsaturated acids which, in addition to an α -substituting group, also contain a radicle in the *cis*-position relatively to the carboxylic group, that is, acids of the type



are difficult to etherify when boiled for an hour with a 3 per cent. solution of hydrogen chloride in methylic alcohol. The same property is also characteristic of acids in which the third hydrogen atom of acrylic acid is replaced by a substituting group



2. Di-substituted acrylic acids in which one group is in the α -position and the other in the *trans*-position relatively to the carboxylic group, are readily etherified under the conditions given above.



This remarkable difference in behaviour supplies us with a simple method of determining the configurations of stereoisomeric acids, $\text{CHX}:\text{CY} \cdot \text{COOH}$, where X and Y may be alike or dissimilar. We require merely to boil half a gram of each acid with 10 c.c. of a 3 per cent. solution of hydrogen chloride in methylic acid, and determine which acid yields the larger percentage of ethereal salt. This acid will be the one with the substituting group in the *trans*-position, and the acid which yields little or no ethereal salt will have the substituting group in the *cis*-position.

We also think it probable that this difference on etherification may be made use of in the separation of such stereoisomeric acids, in very much the same manner as Martz (*Ber.*, 1894, 27, 3147) and Jannasch and Weiler (*ibid.*, 3447) have been able to separate diortho-substituted benzoic acids from their isomerides. The separation in the acrylic series will not be so complete as in the benzoic, as, according to our results, the difference on etherification is not so marked as in the benzoic series. We have found that the method can be used with advantage in the separation of α -phenylallocinnamic acid from α -phenylcinnamic acid, and it can undoubtedly be used with equal

advantage in the separation of the corresponding nitro-acids. The method adopted by Bakunin (*loc. cit.*) for the purification of these acids is lengthy and tedious, and can probably be considerably curtailed by the process of etherification. We may point out that our results confirm in a remarkable manner the constitutions of the α -phenylcinnamic acids arrived at by Bakunin from entirely different considerations.

3. Substituted acrylic acids in which the substituting groups are only in the β -position are readily etherified under the conditions given above. As examples of this generalisation, we have the two β -bromocinnamic acids, both of which yield over 90 per cent. of ethereal salt. We are at present engaged in preparing $\beta\beta$ -di-iodoacrylic acid, and hope shortly to be able to state that this obeys the same law.

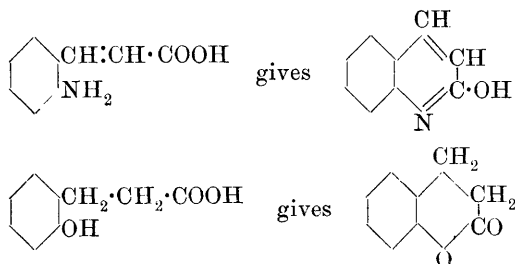
4. The results we have obtained with mono-substituted acrylic acids are somewhat too meagre for us to draw general conclusions with any degree of certainty; those, however, which we have so far obtained by using more dilute solutions of hydrogen chloride, namely, a 1 per cent., in methylic alcohol, seem to indicate that an α -substituted acrylic acid is more difficult to etherify than the isomeric β -compound. In support of this, we have the fact that atropic acid (α -phenylacrylic acid) is more difficult to etherify than either of the β -phenylacrylic acids (cinnamic and allocinnamic acid). This conclusion is further supported by Anschütz's results (*Ber.*, 1897, 30, 2652). Anschütz finds that mesaconic acid, $\begin{array}{c} \text{Me}\cdot\text{C}\cdot\text{COOH} \\ | \\ \text{COOH}\cdot\text{C}\cdot\text{H} \end{array}$, when boiled for a short time with a 0.5 per cent. solution of hydrogen chloride, yields the monomethylic salt, $\begin{array}{c} \text{Me}\cdot\text{C}\cdot\text{COOH} \\ | \\ \text{COOMe}\cdot\text{C}\cdot\text{H} \end{array}$.

The differences between cinnamic and allocinnamic acids point to the conclusion that a β -substituted acrylic acid, in which the substituting radicle is in the *cis*-position relatively to the carboxylic group, is more difficult to etherify than the isomeric *trans*-compound. We give these generalisations with the greatest reserve, as further investigations with other acids, for example, crotonic acids, are necessary to prove whether they are correct.

5. The radicle weights or volumes of the substituting groups in the α - and *cis*-positions appear to be an important factor in determining the actual amount of ethereal salt formed in each case. A survey of the results obtained with dichloro-, dibromo-, and di-iodo-cinnamic acids brings out this generalisation with great clearness. The dichloro-acid yields more ethereal salt than either of the two dibromo-acids, and these again yield more than the di-iodo-acid. This conclusion is entirely in accordance with V. Meyer's work on diortho-substituted benzoic acids, and with that of Kellas (*Z. physik. Chem.*, 1897, 24,

221) on mono-substituted benzoic acids, and also with our own on substituted benzamides (Trans., 1895, 233).

6. The presence of a nitro-group in the ortho-position in certain cinnamic acids, for example, in orthonitrocinnamic acid itself, and also in α -cyano-orthonitrocinnamic acid, appears to have a retarding influence on the formation of the ethereal salt. This is in complete harmony with a suggestion made by Victor Meyer and one of us several years ago, but which received no support from actual experiment conducted at that time (*Ber.*, 1895, 28, 1267). It is a well known fact that ortho-substituted cinnamic and hydrocinnamic acids readily undergo condensation, yielding ring compounds. For example,

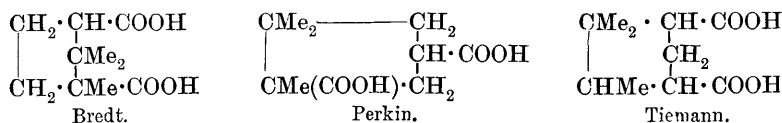


The fact that the isomeric meta- and para-compounds undergo no similar condensations is supposed to be due to the fact that, in these acids, the substituting groups are not sufficiently near to the carboxylic group to allow of the elimination of H_2O , HBr , &c. The results we have obtained may be due to the fact that the nitro-group is in closer proximity to the carboxylic group in the ortho-acids than in the meta- and para-acids, and this may account for the retardation. If so, we should expect to meet the same phenomenon in all ortho-substituted cinnamic acids, and also in diortho-substituted cinnamic acids. This is a point which we consider deserves a little more attention, and we purpose studying a number of these acids.

7. The results we have obtained by the etherification of allocinnamic acid and α -bromallocinnamic acid indicate that Fischer's method of etherification yields the ethereal acids of the allo-acids, and not those of the more stable isomeric acids. This is an extremely interesting point, since other authorities state that these allo-acids, when their alcoholic solutions are saturated with hydrogen chloride and allowed to stand, yield the ethereal salts of the more stable acids.

8. In the introduction to this paper, we stated that one of the reasons for undertaking the investigation was to account for the characteristic behaviour of camphoric acid on etherification by the aid of the stereochemistry of the acid molecule. As the result of our

investigation, we are able to state that in *unsaturated* acids a carboxylic group which has substituting groups in the α - and *cis*-positions with respect to itself is difficult to etherify. It is true that in Bredt's formula for camphoric acid, and also in the newer formula suggested by W. H. Perkin, jun. (Proc., 1897, 218), one of the carboxylic groups is thus situated, it has substituting groups in the α - and also in the *cis*-position. The other carboxylic group in camphoric acid is not so situated; it has a substituting group in the *cis*-position, but none in the α -position. We consider, then, that our results render the behaviour of camphoric acid on etherification explicable if we adopt either Bredt's or Perkin's formula. The same remarks, however, do not apply to Tiemann's formula (*Ber.*, 1895, 28, 1079) :



The great difference is that camphoric acid is a ring compound, whereas our researches have been limited to aliphatic unsaturated acids.

9. The results we have obtained are in complete harmony with the configurations of unsaturated acids according to the van't Hoff-Wislicenus theory, and we consider that they establish with certainty the conclusion previously arrived at, namely, that in what are usually termed *cis*-substituted monocarboxylic acids the substituting group is in closer proximity to the carboxylic group than when it is in the *trans*-position.

In conclusion, we may state that, having obtained such interesting results with monocarboxylic acids, we at once turned our attention to dibasic acids. From a private communication from Professor Anschütz, we learn that he has already taken up the study of a number of such acids in the direction indicated in the *Berichte*, and we have therefore not investigated any of these acids ourselves.

The question whether generalisations similar to those we have obtained for unsaturated acids may not also hold, to some extent, for saturated acids immediately presented itself to us, and the fact that such acids as dibromosuccinic acid, dibromhydrocinnamic acid and its nitro-derivatives, are difficult to etherify indicates that interesting results may probably be obtained in this direction.

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