

LXVIII.—*The Action of Alkalis on Cinnamic Acid Dibromide and its Esters.*

By JOHN J. SUDBOROUGH and KENWORTHY J. THOMPSON.

THE reaction between cinnamic acid dibromide ($\alpha\beta$ -dibromo- β -phenylpropionic acid) or its esters and alkalis has been studied by a number of investigators, and is the basis of the usual methods for the preparation of the α -bromocinnamic acids.

Glaser (*Annalen*, 1867, 143, 325) obtained two monobromocinnamic acids by the action of alcoholic potash on a hot solution of $\alpha\beta$ -dibromo- β -phenylpropionic acid. The product, when neutralised with hydrochloric acid, was poured into water and evaporated to dryness; the solid residue was extracted with water and a small amount of tarry matter left undissolved. The two acids were then separated from the solution of their potassium salts by fractional precipitation with hydrochloric acid. The acid which was first precipitated, melted at 130—131°, whilst its isomeride melted at 120°; they were termed α -bromocinnamic and β -bromocinnamic acids respectively, although the bromine in both acids was represented as occupying the α -position with respect to the carboxylic group. The two acids are now usually known respectively as α -bromo- and α -bromo*allo*-cinnamic acids.

Barish (*J. pr. Chem.*, 1879, [ii], 20, 177) prepared these isomerides by the same method, and observed, in addition to the two acids, the formation of a small amount of oil, which was shown to be a bromocinnamene. The two acids were separated by Glaser's method, and it was found that the amount of the less fusible α -bromo-acid was always far less than that of the α -bromo*allo*-acid.

The production of the bromocinnamene was supposed to be due to the decomposition of one or both of the α -bromo-acids, as the solution became strongly alkaline when evaporated, and the formation of the

oil was largely prevented by keeping the liquid faintly acid. Since the yield of the less fusible acid was always far below that of its isomeride, it was concluded that the oil was produced from the substance of higher melting point. The bromocinnamene formed was isomeric with the α -bromocinnamene obtained from cinnamene dibromide, but identical with the bromocinnamene obtained by Glaser (*Annalen*, 1870, 154, 18, 168), and by Fittig and Binder (*ibid.*, 1879, 195, 142); the compound was therefore assumed to be a β -bromocinnamene, $\text{CBrPh}\cdot\text{CH}_2$, and hence the acid melting at 131° would be a β -bromocinnamic acid, $\text{CBrPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, whilst its more fusible isomeride would have the formula $\text{CHPh}\cdot\text{CBr}\cdot\text{CO}_2\text{H}$. The difference in melting points of the two acids and the inequality in reactivity of the halogen atoms in the different compounds were adduced in support of such formulæ for the two bromocinnamenes and the two bromo-acids.

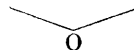
Plöchl (*Ber.*, 1882, 15, 1945), by comparing these isomerides with the chlorocinnamic acids, one of which he obtained from chloroacetic acid by Perkin's synthesis, arrived at the conclusion that the acid of higher melting point is the true α -bromocinnamic acid, whilst its isomeride is the β -bromocinnamic acid, $\text{CBrPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$.

Stockmeir (*Beilstein*, 3rd ed., 2, 1411) recommends practically the same method as that employed by Glaser, whereas Kinnicutt (*Amer. Chem. J.*, 1882, 4, 26) states that very poor yields of the two acids are obtained by the action of alkali on cinnamic acid dibromide, and recommends the employment of the corresponding ethyl ester, when a 90 per cent. yield of the mixed bromocinnamic acids is obtained. Kinnicutt separated the two acids by fractional crystallisation from water, in which the β -acid (m. p. 120°) is more readily soluble.

Michael and Brown, after preparing the two β -bromocinnamic acids by the addition of hydrogen bromide to phenylpropionic acid (*Ber.*, 1886, 19, 1378), concluded that both the acids obtained from cinnamic acid dibromide are α -bromo-acids.

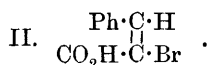
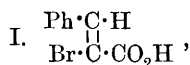
Erlenmeyer (*Ber.*, 1886, 19, 1936) has suggested that possibly certain of the acids are bimolecular, but this conclusion has been rendered untenable by the molecular weight determinations of the esters of these acids by Michael and Browne (*Ber.*, 1887, 20, 550).

Anschütz and Selden (*ibid.*, 1388) have suggested that the acid melting at 131° is the true α -acid, and that the so-called β -acid melting at 120° is structurally isomeric, having the formula $\text{CHPh}\cdot\text{CBr}\cdot\text{C}\cdot\text{OH}$.



The discovery of *allo*- and *iso*-cinnamic acids by Liebermann, and the introduction of the idea of stereochemistry among ethylene derivatives, led to the adoption of stereochemical formulæ for the two α -bromo-acids.

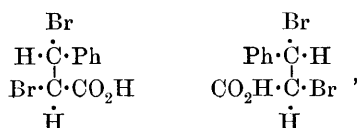
E. Erlenmeyer (*Ber.*, 1890, 23, 2130) showed that both acids, when oxidised with permanganate, yielded benzaldehyde, and should therefore both contain the bromine atom in the α -position. He also proved that the more fusible acid is α -bromo*isocinnamic* acid, since on reduction it yields Liebermann's *isocinnamic* acid, together with a certain amount of cinnamic acid. Liebermann (*Ber.*, 1895, 28, 134) obtained cinnamic acid by the reduction of the α -acid melting at 131° , and hence concluded that it was α -bromocinnamic acid. The formulæ for the two acids are thus:



Formula I is generally assigned to α -bromocinnamic acid melting at 131° , whereas α -bromo*allo*-(or *iso*)-*cinnamic acid is represented by II. Most of the characteristic reactions and physical data are in harmony with these formulæ, for example, the *allo*-acid reacts readily with sulphuric acid to form a hydrindone derivative (Roser and Hasehoff, *Ber.*, 1887, 20, 1577), whereas sulphuric acid does not readily decompose the α -bromo-acid. The rates of esterification of the two acids (Sudborough and Lloyd, *Trans.*, 1898, 73, 91) are also in agreement with the views suggested by these configurations.

A strong argument brought against these formulæ by Michael is the fact that the α -bromo-acid is transformed into phenylpropionic acid much more readily than the α -*allo*-acid.

If the above configurations are correct, then cinnamic acid must be represented as $\begin{array}{c} \text{Ph} \cdot \dot{\text{C}} \cdot \text{H} \\ | \\ \text{H} \cdot \dot{\text{C}} \cdot \text{CO}_2\text{H} \end{array}$ and its dibromide must be the racemic compound,



and by elimination of hydrogen bromide, α -bromo*allocinnamic* acid (m. p. 120°) alone should result. All authorities are agreed that a mixture of the two α -bromo-acids is obtained by the action of potassium hydroxide solution on the dibromide.

We have undertaken the study of different alkalis on the dibromide under varying conditions in order to determine (*a*) whether it is possible to obtain, under any given conditions, only the α -bromo-

* Michael's recent work would indicate that the halogenated *allo*-acids are, in reality, derivatives of *isocinnamic* acid; in view of Liebermann's criticisms (*Ber.*, 1903, 36, 176), the old notation is retained.

allo-acid, and (b) the conditions favourable to the formation of the *α*-bromo-acid.

Some three years ago, it was noticed by one of us that the yield of *α*-bromo-acid is largely increased when ethyl cinnamate dibromide is employed, and we have therefore continued the study of the action of alkalis on the different esters of the dibromide. During the progress of the work, a short note by Michael has appeared (*Ber.*, 1901, 34, 3666) in which attention is drawn to the influence of the ethyl group in the elimination of hydrogen bromide from cinnamic acid dibromide and its ester.

The experimental work which has been carried out with these objects in view may be classified under the following heads:

I. Preparation of cinnamic acid dibromide (*αβ*-dibromo-*β*-phenylpropionic acid) and its esters.

II. Separation of *α*-bromo- and *α*-bromo*allo*-cinnamic acids.

III. Action of alkalis on cinnamic acid dibromide and its esters under varying conditions.

IV. Investigation of the bromocinnamene.

V. Transformations of *α*-bromo*allo*cinnamic acid into *α*-bromocinnamic acid.

I. Preparation of α:β-Dibromo-β-phenylpropionic Acid and its Esters.

The method usually recommended for the preparation of this acid is the addition of the requisite amount of bromine to a carbon disulphide solution of cinnamic acid, and we find that for the preparation of small amounts of the dibromide this gives a very good yield; but although the dibromide is obtained pure when the crystals which separate from the solution are removed and washed with a little cold carbon disulphide, the process is somewhat inconvenient for the preparation of large quantities of the dibromide, as cinnamic acid is not readily soluble in the moderately cold solvent, and we have, therefore, adopted the following method for the preparation on a large scale.

From one to two hundred grams of finely powdered cinnamic acid are placed on a large clock glass in a desiccator over sulphuric acid, and a very slight excess of bromine, previously dried with sulphuric acid, is introduced in a small dish and the whole left for three days. When the weight of the acid has increased to the required extent, the product is crystallised from warm alcohol, as it always has a red colour. We have never observed the evolution of hydrogen bromide during the reaction and have obtained, after one crystallisation from alcohol,

almost theoretical yields of the pure acid melting and decomposing at 197°.*

Michael states that small amounts of *allocinnamic acid dibromide* are obtained by the action of bromine on cinnamic acid, but using the method just indicated we have never been able to isolate any of this compound. In some cases, we obtained a small amount of oil by washing the crude dibromide with warm carbon disulphide. The solution, when cold, deposited a small amount of the ordinary dibromide, and when ultimately evaporated gave an oily residue amounting to less than 1 gram from 100 grams of cinnamic acid, from which no definite crystals could be obtained. The conditions of bromination were such that the production of any large amount of the *allo*-compound could not be expected.

Methyl Cinnamate Dibromide (Methyl Dibromo- β -phenylpropionate).—Methyl cinnamate, which was prepared by Fischer and Speyer's method (*Ber.*, 1895, 28, 3252), using a 4 per cent. solution of hydrogen chloride in methyl alcohol, was subsequently brominated in carbon bisulphide solution, and the dibromide, when purified by crystallisation from methyl alcohol, melted at 117°.

As the results obtained by the action of alcoholic potash on this ester were very different from those produced by the action of the same alkali on the acid dibromide, it was thought probable that the ester might not be a pure substance, but a mixture of two isomerides, and would therefore not correspond with the acid dibromide decomposing at 197°. This assumption did not appear at all probable, since the isomeric methyl dibromo- β -phenylpropionate is already known and melts at 52—53° (*Liebermann, Ber.*, 1891, 24, 1107).

In order to be sure that the ester employed was the one corresponding with the acid decomposing at 197°, we have esterified cinnamic acid dibromide by the Fischer-Speyer method, 20 grams of cinnamic acid dibromide being boiled for 9 hours with 100 grams of methyl alcohol containing 4.5 grams of hydrogen chloride. On cooling, colourless, prismatic crystals separated, the weight of which was 11 grams. The melting point (116—117°) indicated that the substance was identical with the ester obtained by the addition of bromine to methyl cinnamate. A small amount of hydrogen chloride was passed into the liquid, from which the crystals had been

* The melting points given in this communication were all determined by short normal thermometers, the whole of the thread of which was immersed in the bath. The temperature at which this acid melts and decomposes varies considerably with the method of heating. When slowly heated, it melts at 197°, but when quickly heated the thermometer may register a temperature as high as 207° before decomposition occurs.

removed, and it was boiled for a further period of 8 hours, when an additional 5.3 grams of the same ester were obtained.

In a second experiment, 30 grams of cinnamic acid dibromide and 60 c.c. of methyl alcohol under the foregoing conditions yielded 27 grams of the ester. The product thus obtained reacted with alcoholic potash in exactly the same manner as the ester produced by the addition of bromine to methyl cinnamate.

Ethyl Cinnamate Dibromide (Ethyl Dibromo- β -phenylpropionate).—This ester has also been prepared by two distinct methods:

(a) Addition of bromine to a carbon disulphide solution of ethyl cinnamate.

(b) Alkylation of cinnamic acid dibromide by the aid of dry silver oxide and ethyl iodide.

The yield obtained by this second method was only 60 per cent. of the theoretical when the reaction was carried out in the cold, as secondary reactions occurred leading to the formation of an oil. This oil, when subjected to fractional distillation under reduced pressure, has been found to consist of ethyl cinnamate dibromide (m. p. 75–76°) and ω -bromocinnamene.

As prepared by both methods, the ester crystallised from carbon disulphide in large, colourless prisms melting at 75–76°. Treatment with alcoholic potash gave results similar to those obtained with the methyl ester.

In a recent communication (*Ber.*, 1901, 34, 3660), Michael states that when ethyl cinnamate is brominated under suitable conditions the product may contain as much as 54 per cent. of ethyl *allo*-cinnamate dibromide melting at 28–30°.

As in most of our earlier experiments the yield of the dibromide melting at 75–76° was good, we determined to repeat the brominations, working as far as possible under the specified conditions, namely, low temperature, slight excess of bromine, absence of light, and in carbon tetrachloride solution. Even under these conditions, we have not been able to confirm Michael's results. The product obtained in each case, after removing the solvent in a desiccator over caustic soda at the ordinary temperature and under reduced pressure, consisted of a mass of large, prismatic crystals. In no case was the amount of oil appreciable, and the crude residue, which invariably melted at 66–74°, could therefore contain only the merest trace of the *allo*-dibromide, and when recrystallised from alcohol yielded the pure ester melting at 75–76°.

Expt. 1.—Eight grams of ethyl cinnamate were added to a solution of slightly more than the theoretical amount of bromine in well-cooled dry carbon disulphide. The mixture was allowed to

remain surrounded by ice for 24 hours and the solvent then removed under reduced pressure, the whole experiment being performed in the dark. The melting point of the slightly discoloured crude product was 69–72°; its weight was 15.1 grams.

Expt. 2.—Under similar conditions to Expt. 1, but with a larger excess of bromine, only a trace of oil was formed, whilst 13.3 grams of pure product melting at 75–76° were obtained after crystallisation from carbon disulphide.

Expt. 3.—In this case, carbon tetrachloride was used as solvent and only a slight excess of bromine was employed. The crystalline product, which was only slightly discoloured, weighed 15.4 grams and melted at 67–73°.

Expt. 4.—Similar to Expt. 3. The crude product, which weighed 14.9 grams, melted at 65–74°, and after recrystallising from carbon disulphide yielded 12.2 grams melting at 75–76°. The mother liquor, after evaporation, deposited large crystals of the ester melting at 75–76°, mixed with only a trace of oil.

Expt. 5.—A repetition of Expt. 1 gave 15.15 grams of ester melting at 67–75°. After recrystallisation, 12.6 grams of pure ester were obtained, and the solvent, on evaporation, left crystals of the ester mixed with very small amount of oil.

Expt. 6.—Ethyl cinnamate (8 grams) was placed in a stoppered bottle and 20 c.c. of carbon disulphide added, 7.7 grams of dry bromine were enclosed in a sealed bulb and placed in the bottle. The bottle was packed in a tin containing sawdust to prevent light affecting the reaction. The mixture was allowed to stand surrounded by ice for 2 hours, the bulb then broken by shaking, the bottle kept for 16 hours surrounded by ice, and the solvent finally removed as before. The weight of crude product melting at 67–73° was 14.5 grams, and on recrystallising from alcohol, 12.2 grams of ester melting at 75–76° were obtained. The mother liquor, on addition of water, gave an oily product which slowly solidified; this substance weighed 0.4 gram and melted at 35–60°.

Expt. 7.—Similar to Expt. 6, but the bottle was kept at 0° for 36 hours. Weight of product melting at 68–74° was 14.2 grams, and 12 grams of the pure recrystallised ester were obtained. The addition of water to the mother liquor precipitated an oil which subsequently solidified; the solution of this product in cold light petroleum (b. p. 30–60°) yielded on evaporation 0.2 gram of oil, which became solid and melted at 27–40°.

Expt. 8.—Similar to Expt. 7, but with carbon tetrachloride as solvent, the ester being sealed in the bulb. The crude product, which melted at 66–74° and weighed 13.6 grams, when recrystallised from alcohol gave 12 grams of ester melting at 75–76°. The oil

obtained from the mother liquor, when extracted with ligroin and carbon disulphide, gave 0.2 gram of a substance which solidified and melted at 30—40°.

We are not able to explain the difference between these results and those of Michael, as we followed as far as possible the conditions indicated by him and used carbon tetrachloride or carbon disulphide which had been thoroughly dried and freshly distilled.

In some of our experiments, the ester was added to the bromine solution, whereas in Michael's experiments the bromine was always added to the solution of the ester.

II. *Separation of α -Bromo- and α -Bromoallo-cinnamic Acids.*

The methods employed by Kinnicutt and Glaser and described in the earlier part of this paper are tedious and of little value for the quantitative separation of the two acids. Preliminary experiments were therefore made in order to find some simple and rapid quantitative method of separation. The process which first suggested itself was the separation by the aid of the barium salts, as, according to Glaser, barium α -bromocinnamate is very sparingly soluble and barium α -bromoallo-cinnamate readily soluble in water.

Two grams of each were mixed, dissolved in ammonium hydroxide solution, and excess of fairly concentrated barium chloride solution was then added. The precipitated barium salt was collected, washed with barium chloride solution, and then decomposed with dilute hydrochloric acid; the liberated acid, when dry, was found to melt at 131° and the weight obtained was 1.97 grams. The filtrate containing the soluble barium salt was also acidified, and when dry the acid thus precipitated melted at 120° and weighed 1.85 grams. These results prove that the two acids may be completely separated by this method, but that a slight loss of both acids occurs. The amount of this is under two per cent. in the case of the α -acid, whilst in that of the α -allo-acid the loss is under eight per cent.

The mixtures of the two acids obtained by treating cinnamic acid dibromide with alkalis were invariably separated by the above method.

III. *Action of Alkalis on $\alpha\beta$ -Dibromo- β -phenylpropionic Acid and its Esters.*

The object to which our attention has been mainly directed in the course of this part of the work has been the determination of the manner in which the reaction between cinnamic acid dibromide and alkali is affected by (a) light, (b) increase in temperature, (c) vibrations

due to prolonged shaking, (d) the employment of the methyl, ethyl, isobutyl, and phenyl esters in place of the acid dibromide, (e) employment of different alkalis.

The general method adopted was as follows: the acid dibromide (10 grams) or an equivalent amount of an ester (10.45 grams of the methyl, 10.91 grams of the ethyl, or 11.83 grams of the isobutyl ester) was mixed with the calculated quantity of the alkali in aqueous or alcoholic solution; in all cases, two molecules of alkali were employed for each molecule of acid dibromide or ester. The mixture was kept under the special conditions enumerated in each experiment, the alcohol was removed by evaporation on the water-bath unless otherwise stated, and the dry mixture of alkali salts obtained was stirred with a little water. In no case did the whole of the residue dissolve, as nearly all the salts of α -bromocinnamic acid are only sparingly soluble in water. An excess of barium chloride solution was added and the two acids separated by the method described above.

(a and b) Influence of Light and Temperature.

The following series of experiments prove that neither the nature of the reaction nor the relative amounts of the two acids produced are affected to any appreciable extent by the presence or absence of sunlight or by an increase in temperature amounting to 100° .

Expt. 1.—Ten grams of cinnamic acid dibromide were mixed at -10° with the calculated amount of alcoholic potash (10 per cent. solution) and kept at -10° to -5° for 2 days, the whole experiment being conducted in the dark. At the end of that time, the cinnamic acid dibromide had wholly disappeared, but a precipitate had been formed. The alcohol was allowed to evaporate at the ordinary temperature and the residue separated in the usual manner. The weights of α bromo- and α -bromo α llo-acids, melting at $128-130^{\circ}$ and $110-117^{\circ}$ respectively, were 0.75 and 5.85 grams.

The acids obtained directly from the barium salts were usually not quite pure, the α -acid in all cases melted at $126-130^{\circ}$ instead of $130-131^{\circ}$, and the α - α llo-acid usually at 115° instead of 120° . Each acid was obtained in a pure state after one crystallisation from a mixture of benzene and light petroleum or chloroform and light petroleum.

Expt. 2.—The conditions were the same as in Expt. 1, with the exception that the mixture, cooled to -5° , was placed in fairly bright sunlight and occasionally shaken, the reaction being complete after about 28 hours. The weights of α -bromo- and α -bromo α llo-acids were 0.76 and 5.8 grams respectively.

Expt. 3.—Ten grams of the acid were mixed with the calculated amount of alcoholic potash, care being taken to avoid rise of tempera-

ture; the mixture was subsequently kept at the ordinary temperature for 3 hours, the whole of the experiment being carried out in the dark. The alcohol was evaporated on the water-bath; 0.83 gram of α -bromo-acid and 5.8 grams of α -bromoallo-acid were obtained.

Expt. 4.—The conditions were the same as in *Expt. 3*, with the exception that the experiment was carried out in the light, the mixture being shaken for 3 hours; 0.76 gram of α -bromo-acid and 6.05 grams of α -bromoallo-acid were obtained.

Expt. 5.—Ten grams of the acid dibromide were mixed with the calculated amount of alcoholic potash and boiled for 20 minutes in ordinary daylight; 0.8 gram of α -bromo-acid and 5.2 grams of α -bromoallo-acid were obtained.

Expt. 6.—The methyl ester (10.45 grams) was boiled for 6 minutes with the calculated amount of alcoholic potash; 3.85 grams of α -bromo-acid and 2.7 grams of α -bromoallo-acid were obtained.

Expt. 7.—As in *Expt. 6*, except that the mixture was shaken at the ordinary temperature for 3 hours; 4.15 grams of α -bromo-acid and 2.64 grams of α -bromoallo-acid were obtained.

It has already been stated that methyl cinnamate dibromide was also prepared by the direct esterification of the acid dibromide by the Fischer-Speyer method. The results obtained when this preparation was employed were similar to those of *Expts. 6* and *7*, in which the ester formed by the union of bromine and methyl cinnamate was used.

Expt. 8.—10.45 grams of the ester dibromide, obtained by esterification of the acid dibromide, were treated as in *Expt. 6*. The yield was 4 grams of the α -bromo-acid and 2.7 grams of its isomeride.

(c) *Influence of Rapid Vibration.*

It was thought possible that the vibrations and shock produced by shaking the medium in which the reaction was taking place might influence the yields of the two acids.

Expts. 9–11, which were carried out by the aid of a Dunstan-Dymond shaker, when compared with the previous experiments, appear to negative this assumption. The relative amounts of the two acids are not altered, either by violent agitation during the reaction or by prolonged shaking after the reaction is complete.

Expt. 9.—10.45 grams of the methyl ester were added to the calculated amount of alcoholic potash at the ordinary temperature and the mixture shaken for 6 hours; 4.25 grams of the α -bromo-acid and 2.8 grams of the α -bromoallo-acid were obtained.

Expt. 10.—Similar to *Expt. 9*, except that the shaking was continued for 20 hours. The yields were 4.20 and 2.78 grams of the α -bromo-acid and its isomeride respectively.

Expt. 11.—Similar to *Expt. 9*, except that the alcoholic potash was added in two stages; 10·45 grams of the ester were mixed with one equivalent of alcoholic potash and shaken for 1 hour; a second equivalent of alkali was then introduced, and the shaking continued for another hour.

The yields were the same as in *Expt. 9*.

(d) *Replacement of Cinnamic Acid Dibromide by its Esters.*

The experiments already describe indicate that the relative amounts of α -bromo- and α -bromo α lo-acids produced are greatly altered by employing an ester in place of the free acid dibromide.

Comparative experiments have been carried out by using cinnamic acid dibromide and its methyl, ethyl, *isobutyl*, and phenyl esters.

In each case, 10 grams of the acid dibromide or an equivalent quantity of ester were boiled for 5—6 minutes with the calculated amount of alcoholic potash. The results were as follows:

Expt.	α -Bromo- acid.	α -Bromo- <i>allo</i> -acid.	Expt.	α -Bromo- acid.	α -Bromo- <i>allo</i> -acid.
12 Cinnamic acid dibromide...	0·84	5·5	17 Ethylester di- bromide.....	3·7	2·65
13 Cinnamic acid dibromide...	0·81	5·4	18 <i>isoButyl</i> ester dibromide ...	3·6	2·75
14 Methyl ester dibromide...	3·8	2·6	19 <i>isoButyl</i> ester dibromide ...	3·7	2·9
15 Methyl ester dibromide...	3·85	2·7	23 Phenyl ester dibromide ...	3·8	2·04
16 Ethylester di- bromide.....	3·8	2·64			

Preparation of isoButyl Cinnamate and its Dibromide.

As these compounds have not been previously described, we give a brief account of their preparation.

A slight excess of *isobutyl* alcohol was added to freshly prepared cinnamyl chloride; the reaction, when started by warming, progressed rapidly until all the chloride had disappeared. After warming on the water-bath for a few minutes, the ester was distilled under reduced pressure. As thus obtained, *isobutyl cinnamate* is an almost colourless liquid with an ethereal odour; it boils at 164—165° under 16—17 mm. pressure.

The dibromide was prepared by adding a very slight excess of bromine in carbon disulphide to a solution of the ester in the same

solvent; after 2 hours, the solution was left to evaporate spontaneously, and the residue purified by crystallisation from light petroleum.

isoButyl cinnamate dibromide crystallises from light petroleum (b. p. 30—60°) in aggregates of silky needles melting at 59—60°; it is also readily soluble in chloroform, carbon disulphide, and warm ligroin. 0.2532 gave 0.2646 AgBr; Br = 44.5. $C_{13}H_{16}O_2Br_2$ requires 44.0 per cent.

The results obtained with phenyl cinnamate dibromide, melting at 127°, are somewhat different, and some of the experiments are therefore given in detail.

Expt. 20.—12.45 grams of the ester dibromide (equivalent to 10 grams of cinnamic acid dibromide), when boiled for 5 minutes with alcoholic potash (2 mols.), gave 3.1 grams of α -bromo-acid melting at 128—130°, and 1.75 grams of α -bromo*allo*-acid melting at 115—118°.

Expt. 21.—12.45 grams, when treated similarly, gave 3.3 grams of α -bromo-acid and 1.55 grams of the *allo*-isomeride.

As the yields of the two acids were much less than the theoretical, and a considerable amount of an oily by-product was also observed, further experiments were carried out.

Expt. 22.—12.45 grams of the ester dibromide were boiled for 5 minutes with alcoholic potash (2 mols.), and after removing the alcohol the residue was dissolved with water and extracted with ether. From the aqueous solution, 3.35 grams of α -bromo-acid and 1.65 grams of α -bromo*allo*-acid were obtained. The ethereal extract, after being washed three times with dilute caustic soda solution to remove phenol, was dried and the solvent distilled off. The oily residue weighed 2.3 grams and boiled with decomposition at about 270°; with concentrated aqueous caustic potash, it gave, after some time, a clear solution, from which a mixture of α -bromo- and α -bromo*allo*-acids was obtained by acidifying.

Expt. 23.—15.6 grams of the ester dibromide were added to cooled alcoholic potash (2 mols.) and the mixture shaken for 2 days at the ordinary temperature, when the alcohol was allowed to evaporate and the residue then treated as in *Expt. 22*.

3.85 grams of α -bromo-acid and 0.90 gram of α -bromo*allo*-acid were obtained, together with 4.35 grams of an oil which distilled over at 153—155° under 11—12 mm. pressure. The oil was left in contact with strong aqueous caustic potash for a day, when the hydrolysis was complete; the alkaline solution of potassium salts was treated in the usual manner with barium chloride, 0.90 gram of α -bromo-acid and 1.65 grams of α -bromo*allo*-acid being obtained.

The oil distilling at 153—155° under 11—12 mm. pressure must have been a mixture of the phenyl esters of α -bromo- and α -bromo*allo*-cinnamic acids. This proves conclusively that in the case of the phenyl

dibromide the elimination of hydrogen bromide precedes the hydrolysis.

The fact that the oil consists mainly of the ester of the *allo*-acid would indicate that this ester is not so readily hydrolysed by alkalis as the ester of the isomeric α -bromo-acid. This is interesting, as it has already been shown (Sudborough and Lloyd, *Trans.*, 1898, 73, 91) that the α -bromo*allo*-acid is not so readily esterified as the isomeric α -bromo-compound.

From the results given in the preceding table, it is obvious that the substitution of an ester for the free acid dibromide tends, in all cases, to increase greatly the amount of α -bromocinnamic acid formed. When alcoholic potash is employed, the amount of α -bromo-acid obtained from 10 grams of cinnamic acid dibromide is always less than 1 gram, but when an ester is used with the same alkali, the amount is more than quadrupled, and reaches nearly 4 grams.

As stated in the introduction, the normal compound, which should be formed by the elimination of hydrogen bromide from cinnamic acid dibromide, is α -bromo*allo*-(or *iso*)-cinnamic acid, that is, the acid which on reduction yields *allo*-(or *iso*)-cinnamic acid. This has been shown by Erlenmeyer (*Annalen*, 1895, 287, 21) to be the acid melting at 120°, which is usually called α -bromo*allocinnamic* acid. The results obtained when the acid dibromide is employed may be regarded as being in harmony with this theoretical deduction; the main product is α -bromo*allocinnamic* acid, and only a small amount of the α -bromo-cinnamic acid is obtained. The formation of this may be attributed to the fact that the *allo*-acid is unstable (see later experiments, p. 685), and either at the moment of its formation or afterwards becomes partially converted into the more stable α -bromo-acid.

When the esters are employed, the chief product is the α -bromo-acid, together with smaller amounts of the α -bromo*allo*-acid. This undoubtedly points to the fact that the alkali does not first completely hydrolyse the ester and then eliminate hydrogen bromide, it being far more probable that the withdrawal of hydrogen bromide occurs before the hydrolysis. In the case of the phenyl ester, the withdrawal of hydrogen bromide before complete hydrolysis is proved by the foregoing experiments.

The fact that the chief product is α -bromo-acid can be accounted for by assuming that the esters of the *allo*-acid are even less stable than the free acid, and therefore are more readily transformed into the esters of the α -bromo-acid.

Michael (*loc. cit.*) has recently come to the conclusion that the ethyl cinnamate dibromide melting at 75–76° is the true dibromide of ethyl *allocinnamate*, and not that of ethyl cinnamate. This view is supported, to a certain extent, by his experiments on the addition of

bromine to ethyl cinnamate, but for some unknown reason our own experiments have not yielded similar results.

If we assume that the esters employed are not the dibromides of the esters of cinnamic acid, but of *allocinnamic* acid, then the chief product formed by the action of alkali should be the α -bromo-acid. The production of the relatively large amount of the α -bromo*allo*-acid presents a difficulty, as this is the less stable isomeride, and is not likely to be produced by the molecular rearrangement of the α -bromo-acid. The fact that the esters we have employed undoubtedly correspond with the ordinary cinnamic acid dibromide decomposing at 197° , since this substance, when esterified, yields these compounds, is a further argument against the conclusion that these esters are derivatives of *allocinnamic* acid. Moreover, if the esters are derivatives of *allo*-cinnamic acid, then the acid dibromide itself is also an *allo*-compound, and it becomes a little difficult to reconcile this conclusion with the fact that the main product produced by the action of alkali is α -bromo-*allocinnamic* acid.

(e) *Influence of Different Alkalis on the Reaction.*

Our earlier experiments were all carried out with alcoholic potash. In order to determine whether the nature of the alkali was an important factor in determining the yields of the two acids, we have made experiments with the following alkalis: caustic potash in alcoholic or aqueous solution, caustic soda in alcoholic solution, alcoholic sodium or potassium ethoxide, aqueous sodium carbonate, aqueous or alcoholic ammonia, aqueous baryta, and alcoholic dimethylaniline.

The esters reacted so slowly with aqueous solutions of the different alkalis, and also with alcoholic sodium ethoxide or dimethylaniline, that the products could not be investigated.

The experiments were carried out on the plan previously described, and the results obtained are given in the following table:

	Alkali.	Weight of α -bromo- acid.	Weight of α -bromo- <i>allo</i> -acid.	Method.
Cinnamic acid dibromide		0.95	4.96	} Boiling for 5 minutes
" "		0.84	5.5	
" "		0.81	5.4	
" "	Alcoholic potash	0.80	5.69	Boiling for 4 hours
" "		0.76	6.10	Shaking for 2 hours
" "		0.76	6.05	
" "		0.76	5.8	At -5° in sunlight
" "		0.75	5.85	At -5° in the dark

	Alkali.	Weight of α -bromo- acid.	Weight of α -bromo- <i>allo</i> -acid.	Method.
Cinnamic acid dibromide	Alcoholic soda	1.61	4.85	Boiling for 5 minutes
“ “		1.51	4.92	“ “
“ “		1.62	4.93	Shaking for 2 hours
“ “	Sodium ethoxide	0.91	5.89	Shaking for 3 hours
“ “		0.84	6.01	“ “
“ “	Potassium ethoxide	0.45	6.10	Boiling for 5 minutes
“ “		0.50	5.87	“ “
“ “	Aqueous potash	1.16	2.78	{ Shaking, no cooling during addition. Shaking, low tem- perature.
“ “		1.54	4.46	
“ “		1.8	4.5	
“ “	Aqueous baryta.....	Bromocinnamene, with a small amount of the acids		
“ “	Aqueous sodium car- bonate.....	Bromocinnamene only		
“ “	Aqueous ammonia ...	“ “		
“ “	Alcoholic ammonia ...	Acid dibromide unaltered		
	Alkali.	Weight of α -bromo- acid.	Weight of α -bromo- <i>allo</i> -acid.	Method.
Methyl ester dibromide	Alcoholic potash	3.8	2.6	Boiling for 5 minutes
“ “		3.85	2.7	“ “
“ “		4.25	2.8	Shaking for 3 hours
“ “		4.15	2.64	“ “
“ “	Alcoholic soda	3.93	2.3	Boiling for 5 minutes
“ “		3.8	2.4	“ “
“ “		4.25	2.6	Shaking for 3 hours
Ethyl ester dibromide	Alcoholic potash	3.78	2.64	Boiling for 5 minutes
“ “		3.72	2.65	“ “
“ “		3.8	2.68	Boiling for 4 hours
“ “		3.7	2.8	“ “
“ “		4.16	2.9	Shaking for 3 hours
“ “	Alcoholic soda	3.53	2.55	Boiling for 5 minutes
“ “		3.45	2.54	“ “
“ “		4.10	2.89	Shaking for 3 hours

The results obtained with dimethylaniline are somewhat curious, the products being cinnamic acid, ω -bromocinnamene, and only a trace of a bromo-acid.

Expt. 24.—Ten grams of cinnamic acid dibromide were boiled for 45 minutes with a slight excess of an alcoholic solution of dimethylaniline (2 mols.). The alcohol was removed by evaporation and the residue acidified with hydrochloric acid. The precipitated acids were collected and washed, when an oil passed into the filtrate; this substance was bromocinnamene, which, after drying, weighed 1.6 grams; the acid on the filter-paper proved to be cinnamic acid, the yield being 3.07 grams.

Expt. 25.—Ten grams of the acid dibromide were boiled for 2 hours with an alcoholic solution of dimethylaniline and treated as in *Expt. 24.* 2.2 grams of cinnamic acid were obtained together with a large amount of oil.

Expt. 26.—19.48 grams of acid dibromide were treated as in *Expt. 25*, but the boiling was continued for $1\frac{1}{2}$ hours. 2.8 grams of cinnamic acid were obtained together with 6.8 grams of bromocinnamene.

Expt. 27.—Ten grams of acid dibromide were added to alcoholic dimethylaniline, the mixture shaken for 6 hours, and the alcohol removed. The reaction was not complete, some unaltered acid dibromide still remained, but in this case also a large amount of oil was formed.

The oil obtained in each experiment proved to be ω -bromocinnamene; it distilled at $215\text{--}220^\circ$ under the ordinary pressure, and on bromination gave a dibromide melting at $35\text{--}36^\circ$.

Cinnamic Acid Dibromide and Aqueous Ammonia.

Expt. 28.—Ten grams of the dibromide were gradually added to the calculated amount of aqueous ammonia, the temperature being kept down by means of cold water. After a short time, the formation of oil was indicated by the odour. The mixture was left for a week in a corked flask, but the acid did not appear to have undergone appreciable alteration. The mixture was therefore warmed on the water-bath for a few minutes, an oil was immediately formed, this was extracted with ether, and after drying the extract, the ether was distilled off, when 3.7 grams of an oil were left; this product, which proved to be ω -bromocinnamene, distilled almost entirely at $215\text{--}217^\circ$, and gave the dibromide melting at $35\text{--}36^\circ$. The filtrate, on acidifying, gave 0.02 gram of an acid which had no definite melting point.

Expt. 29.—Ten grams of the dibromide were gradually added to the calculated amount of aqueous ammonia, and the mixture left for three weeks. Some solid remained mixed with oil. On extraction

with ether, 2.0 grams of bromocinnamene were obtained with 2.7 grams of unaltered cinnamic acid dibromide decomposing at 194—196°.

Cinnamic Acid Dibromide and Alcoholic Ammonia.

Expt. 30.—Ten grams of acid dibromide were added to the calculated amount of alcoholic ammonia and the mixture left for a week. As the dibromide did not appear appreciably altered, the mixture was boiled for 5 minutes and the alcohol then evaporated on the water-bath. A white solid was left showing no trace of oil. The acid obtained from this by the addition of hydrochloric acid weighed 9.6 grams, and proved to be unaltered dibromide.

Expt. 31.—Ten grams of acid dibromide, when treated as in *Expt. 30*, with the difference that the mixture was left for three weeks instead of warming, gave 9.4 grams of unaltered dibromide decomposing at 194—196°.

Cinnamic Acid Dibromide and Aqueous Sodium Carbonate.

Expt. 32.—Ten grams of the acid dibromide were added slowly to the calculated amount of sodium carbonate solution, the mixture being left for a week, and then warmed for a few minutes, when an oil was produced; this product was extracted with ether, and from the ethereal solution, 3.6 grams of bromocinnamene were obtained.

From the filtrate, 0.02 gram of an acid was precipitated; this product melted indefinitely from 150° upwards.

Expt. 33.—Ten grams of acid dibromide were added to the calculated amount of sodium carbonate solution, and the mixture left for 3 weeks. The oil formed was then extracted with ether, and 3.8 grams of bromocinnamene were obtained; 0.4 gram of unaltered dibromide was recovered from the filtrate.

As the presence of excess of sodium carbonate might favour the formation of bromocinnamene, an experiment was carried out in which the acid dibromide was always in excess. The results obtained were similar to those of previous experiments.

Expt. 34.—The calculated amount of sodium carbonate solution was added drop by drop from a burette to 10 grams of the acid dibromide, and the mixture left for three weeks; 4.1 grams of bromocinnamene were obtained.

Cinnamic Acid Dibromide and Aqueous Baryta.

Expt. 35.—Five grams of acid dibromide were shaken for 5 hours with the calculated amount of aqueous baryta. Some bromocinnamene was formed, and unaltered acid dibromide remained.

Expt. 36.—Five grams of acid dibromide were shaken for 24 hours with the calculated amount of baryta; bromocinnamene was formed together with 0.23 gram of α -bromocinnamic acid and 0.77 gram of an acid melting at 170—184° with decomposition, this substance being probably unaltered cinnamic acid dibromide.

IV. *Bromocinnamene.*

Barish was the first to note the formation of a bromocinnamene by the action of alcoholic potash on cinnamic acid dibromide. The quantity thus obtained is usually small, but by altering the conditions the amount may be largely increased. The production of only a minute quantity of the bromocinnamene can be readily detected by the characteristic odour. We have noticed its formation from the acid dibromide under the following conditions: action of (i) alcoholic or aqueous caustic potash; (ii) alcoholic potash at high temperatures; (iii) aqueous ammonia, baryta, or sodium carbonate, especially at higher temperatures; (iv) alcoholic dimethylaniline. The substance is also produced during the esterification of the dibromide by the aid of dry silver oxide and ethyl iodide, and also by the action of dimethylaniline on α -bromo- and α -bromo*allo*-cinnamic acids.

The factors which tend to increase the amount of bromocinnamene are (a) employment of the acid dibromide and not its esters; (b) relatively high temperature; (c) employment of aqueous, rather than alcoholic, solutions of alkalis; (d) employment of a feeble, rather than a strong alkali.

Contrary to Kinnicutt's statement, we have found that good yields of the two α -bromocinnamic acids may be obtained by the action of alcoholic, and even of aqueous caustic potash on cinnamic acid dibromide, provided that the temperature is not allowed to rise.

The bromocinnamene obtained in all these experiments is identical with the compound obtained by boiling cinnamic acid dibromide with water, and is β - or ω -bromocinnamene (α -bromo- β -phenylethylene) (Fittig and Binder, *Annalen*, 1879, 195, 141; Nef, *Annalen*, 1899, 308, 267). It is most readily characterised by transformation into its dibromide, which crystallises from light petroleum in needles melting at 37—38°. In Beilstein's *Handbuch* (2nd edition), this compound is termed $\alpha : \beta : \beta$ -tribromoethylbenzene, but the proper correction has been made in the Supplement, and also in Richter's *Lexicon*. The oils obtained under the foregoing conditions gave practically quantitative yields of this solid dibromide, thus proving that none of them contained appreciable amounts of the isomeric α -bromocinnamene.

Barish attributed the formation of the bromocinnamene to the elimination of carbon dioxide from one or both of the α -bromo-acids.

A number of experiments made by us tend to render this view untenable. We have boiled cinnamic acid dibromide and its ethyl ester for 5 minutes, and for 4 hours with the calculated amount of alcoholic potash, and the yield of α -bromo- and α -bromo*allo*-acids has not been affected by the prolonged heating.

	Time.	α -Bromo-acid.	α -Bromo <i>allo</i> -acid.
10 grams cinnamic acid dibromide	5 minutes	0.80 gram	5.69 grams
10 grams cinnamic acid dibromide	4 hours	0.84 „	5.5 „
10.91 grams ethyl ester ...	5 minutes	3.78 grams	2.64 „
10.91 grams ethyl ester ...	4 hours	3.8 „	2.68 „

Similarly, when the pure α -bromo- or α -bromo*allo*-acid is boiled with alcoholic potash (1 mol.) for several hours, no trace of decomposition occurs, and even when an excess of alkali is employed the product produced from the α -bromo-acid is phenylpropionic acid, whereas the *allo*-acid is practically unaffected.

It would thus appear that the bromocinnamene is not a secondary decomposition product obtained by the elimination of carbon dioxide from one of the α -bromo-acids, but is a primary decomposition product. Experiments have proved that those alkalis, aqueous baryta, aqueous sodium carbonate, and aqueous caustic potash, for example, which readily yield ω -bromocinnamene from the dibromide, are practically without action on the α -bromo-acids; in all these cases, the solution of the acids were shaken for several days with the alkali, and practically the calculated amount of unaltered acid (either α -bromo- or α -bromo*allo*-) was recovered, and no odour of the bromocinnamene was noticed. When the α -bromo-acids were boiled with alcoholic dimethylaniline (2 mols.), nearly the calculated amount of unaltered acid was obtained. A minute trace, however, of oil was formed in each case—less than 0.1 gram from 5 grams of acid—and this was proved to be ω -bromocinnamene by conversion into its dibromide melting at 37–38°. This may be taken as a further proof of the position of the bromine atom in the bromocinnamene.

It is highly probable that the elimination of hydrogen bromide and the withdrawal of carbon dioxide, required for the production of bromocinnamene from cinnamic acid dibromide, occur simultaneously. The experiments described above indicate that the elimination of hydrogen bromide does not precede the loss of carbon dioxide.

If carbon dioxide were eliminated before the hydrogen bromide, cinnamene dibromide would be first formed, and this, by the loss of hydrogen bromide, might then yield ω -bromocinnamene. That this

does not occur is proved by the fact that cinnamene dibromide, on treatment with alkali, yields α -bromocinnamene, $\text{CPhBr}\cdot\text{CH}_2$, or, according to Nef (*Annalen*, 1899, 308, 273), a mixture of α - and ω -bromocinnamenes. In our experiments, we have not been able to find any trace of the α -compound.

V. *Transformation of α -Bromoallocinnamic Acid into α -Bromocinnamic Acid.*

This transformation has been accomplished by three methods, namely, (a) action of sunlight on the dry acid; (b) action of sunlight on an aqueous solution of the barium salt; (c) action of heat on the free acid.

Action of Light on the Acid.—One gram of the α -*allo*-acid, in the form of glistening, flat plates, was exposed between watch-glasses to ordinary diffused daylight on August 28th, 1900. It was noticed that the crystals gradually lost their lustre and became opaque on the surface. On November 1st, the melting point had sunk to 96° , and by December 10th, to about 90° . The mixture of acids was then transformed into barium salts, which were separated in the usual manner, 0.22 gram of α -bromocinnamic acid melting at 131° being thus obtained.

Action of Light on Barium α -Bromoallocinnamate in Aqueous Solution.—As the barium salt of α -bromocinnamic acid is almost insoluble in water, it was thought possible that the barium salt of the *allo*-acid might be quantitatively transformed into the isomeric barium salt by exposure of its aqueous solution to sunlight. The following experiments indicate that this is, to a large extent, true.

One gram of α -bromoallocinnamic acid was dissolved in a slight excess of dilute ammonia, and excess of barium chloride solution added, the total volume of liquid being about 10 c.c. The solution was exposed to fairly bright sunlight in a south-west window on September 9th, 1901. Well-defined crystals of barium α -bromocinnamate began to separate after two days. The solution was examined on October 25th, and the acids separated in the usual manner. 0.29 gram of α -bromocinnamic acid melting at 131° and 0.7 of unaltered *allo*-acid melting at 119 – 120° were obtained.

Two grams of the α -*allo*-acid were dissolved in slight excess of baryta solution, and the excess of baryta precipitated as carbonate by leaving the solution in an atmosphere of carbon dioxide. The clear solution was then placed in a corked flask and exposed to sunlight in a south window on June 4th, 1902. After two days, crystals appeared; the solution was left until September 29th, when the crystals were removed and yielded 1.98 grams of α -bromocinnamic acid melting at 130 – 131° .

The clear filtrate from the crystals, when acidified, gave no trace of unaltered *allo*-acid.

Effect of heating α -Bromoallocinnamic Acid.—Michael states (*Ber.*, 1901, 34, 3648) that the *α -allo*-acid is completely transformed into the isomeric *α -bromo*-acid when a mixture of the two acids is kept in the liquid state for 1 minute. Some of our earlier experiments indicated that the transformation does not take place nearly so readily as suggested by Michael, and we have made a more careful study of this transformation.

The following table gives a list of the experiments made in order to determine (*a*) the temperature and (*b*) the time required for practically complete transformation. The method of procedure was as follows: 5 grams of pure *α -bromoallocinnamic acid* were placed in a test-tube provided with a loosely-fitting cork which carried a thermometer. The test-tube was then plunged into a sulphuric acid bath heated to the required temperature, and the time measured from the moment when the thermometer placed in the molten acid indicated the fixed temperature. The mixture of acids was separated in the usual manner by the aid of their barium salts.

Temperature.	Time in minutes.	Weight of <i>α-bromoallo-</i> acid.	Weight of <i>α-bromo-</i> acid.
132—133°	10	4.76	0.05
132—133	30	4.61	0.23
143—144	12	4.70	0.12
143—144	30	4.50	0.35
155	10	4.59	0.22
155	30	4.08	0.72
165	10	4.38	0.46
175	10	3.96	0.85
185	10	3.65	1.18
196	10	1.86	2.85
203—204	10	0.73	4.11

It is obvious from these results that the transformation is not complete even when the *allo*-acid is heated at 203—204° for 10 minutes. Michael's statement that a complete transformation is effected by keeping the *α -allo*-acid in a molten state for 1 minute must be incorrect. We have examined some of the numbers obtained in the transformation of the *α -allo*-acid in order to see whether the change may be included amongst the ordinary unimolecular reactions. The numbers in the following table indicate that the reaction is unimolecular:

Temp.	Time in minutes.	Weight of α -bromo α llo-acid taken.	Weight of α -bromo-acid formed.	$1/\log a/a - x$.
155°	10	5	0.26	0.00232
155	30	5	0.76	0.00238
155	45	5	1.05	0.00227
155	60	5	1.41	0.00239
155	60	5	1.39	0.00236

The amount of bromo-acid given in the table is the actual weight of acid obtained *plus* the portion retained in solution. The experiments proved that the amount remaining in solution was practically 0.04 gram for the amount of liquid employed in each experiment.

Conclusion.

The more important results obtained in the course of this investigation may be summarised as follows :

1. Only minute amounts of an *allo*-compound are obtained by the addition of bromine to ethyl cinnamate.

2. Good yields of α -bromo- and α -bromo α llocinnamic acids may be obtained by the action of alcoholic potash on cinnamic acid dibromide or its esters. When the acid dibromide is employed, it is advisable to work at the ordinary temperature and to keep the mixture cool.

3. The relative amounts of the two acids vary considerably when an ester is employed in place of the acid dibromide. The use of the ester increases the amount of α -bromo-acid, and all the esters investigated, the methyl, ethyl, *isobutyl*, and phenyl esters, behave in exactly the same way.

4. The relative amounts of the two acids are also affected to a less extent by the nature of the alkali and of the solvent (either alcohol or water).

5. A by-product often obtained is ω -bromocinnamene. This is produced (*a*) when the temperature is raised, (*b*) when aqueous solutions or feeble alkalis are employed.

6. The bromocinnamene is produced directly from the cinnamic acid dibromide and not from the α -bromo-acids.

7. The α -bromo- and α -bromo α llo-acids are most readily separated by means of their barium salts.

8. The α -bromo α llo-acid may be transformed into the isomeric acid by sunlight or by heat, but the transformation by the latter method does not occur as readily as is stated by Michael.

CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH.