BROMO-DERIVATIVES OF PARA-METHOXYCINNAMIC ACID.

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INTRODUCTION.

In previous papers[1] attention has been drawn to a number of interesting observations connected with the chemistry of halogen derivatives of cinnamic acid, more particularly of the α- and β-bromocinnamic acids. As the result of the steam-distillation of about 150 kilos of the moist rhizomes of *Kampheria galanga*, L., about 1500 grams of ethyl *p*-methoxycinnamate were at our disposal, and we decided to undertake a study of the bromo-derivatives of this ester and of the corresponding acid in order to ascertain whether the generalisations drawn from an examination of the bromo-derivatives of the unsubstituted acid hold good also when a *para*-methoxy-substituent is present.

The generalisations drawn in the case of the derivatives of the unsubstituted cinnamic acid may be grouped as follows:—

1. Good yields of α-bromo- and α-bromo*allo*cinnamic acids may be obtained by the action of alcoholic potash on cinnamic acid dibromide, αβ-dibromo-β-phenylpropionic acid.

2. Using the dibromide and working at room temperature the relative proportions of α-bromo- and α-bromo*allo*-acids are 1 : 7.

3. This ratio is increased to about 1 : 3 when alcoholic sodium hydroxide is used, and to 1 : 3 or 1 : 2·5 with aqueous potassium hydroxide at low temperatures.

4. Small amounts of β-bromo*allo*cinnamic acid are formed during the reaction. The amount is about one-seventh of the weight of the α-bromo-acid.

5. A by-product is ω-bromo-cinnamene, $C_6H_5{\cdot}CH{:}CHBr$, and the amount of this is increased when the reaction takes place at high temperatures, when aqueous solutions or weak alkalis are used. The bromocinnamene is produced directly from the dibromide and not from the α-bromo-acids.

6. The proportions of the two bromo-acids are completely altered when an ester dibromide is substituted for the acid dibromide; thus with ethyl αβ-dibromo-β-phenylpropionate and alcoholic potash (2 mols.) the relative proportions are 1 : 0·75.

7. The proportions are much the same when methyl, *iso*butyl and phenyl esters are used.

8. No trace of the β-bromo*allo*-acid appears to be formed when the ethyl ester is used.

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[1] Sudborough and Thompson, *J. Chem. Soc.*, 1903, 83, 666, 1153; Sudborough and Williams, *This Journal*, 1922, 5, 107. P. Ramaswami Ayyar and Sudborough, *ibid.*, 1923, 6, 82.

3. The oil from the calamus roots distilled in Bangalore is devoid of low-boiling constituents and differs from the commercial oils, more especially as regards density and solubility in alcohol and in these respects resembles the oil from Java.

4. The waste ginger from the West Coast gives exceptionally high yields of oil, but the distillation is slow.

5. Mysore cardamom fruits—pericarps and seeds—of good quality gave a 6 per cent. yield of high grade oil.

6. Although camphor wood gives up its oil much more readily when disintegrated than when in the form of chips, this method of treatment is not recommended as during disintegration appreciable amounts of camphor are lost.

The roots of the Bangalore tree gave a very high percentage of oil, viz., 7·9 and of this one-fourth was camphor.

The proportion of safrole in the oils, from the roots and the stump was small.

7. *Zanthoxylum Rhetsa* contains the volatile oil in the carpels only and not in the seeds. The yield is 5·8 per cent. of the weight of the dry carpels.

8. The yields of oil from the fruits of certain species of *Umbelliferae* grown in India, e.g., coriander and fennel are low when compared with the yield from European fruits. Whether this is due to climatic causes, to insufficient manuring or to variations in the plants is not certain.

9. The East Indian dill oil when freed from dill-apiol closely resembles the European oil.

10. The East Indian coriander oil has a higher percentage of esters and an odour superior to that of the European oil.

In conclusion we wish to thank Messrs. B. Gopalaswamy Reddy, Sridhara Menon, M. Rangaswamy, P. B. Panicker and M. B. Bhagwat for assistance in carrying out the experiments.

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9. When an organic base such as dimethylaniline is used in place of a mineral alkali the results are quite different, e.g., cinnamic acid dibromide, when boiled with an alcoholic or benzene solution of dimethylaniline, yields mainly cinnamic acid and ω-bromocinnamene. In a similar manner methyl αβ-dibromo-β-phenylpropionate yields mainly methyl cinnamate.

The base in these cases removes bromine and not hydrogen bromide from the dibromide, and is itself transformed into *p*-bromodimethylaniline.

10. The α-bromo- and α-bromo*allo*-acids are readily separated by means of their barium salts, as the salt derived from the former is practically insoluble in water and that of the latter readily soluble.

11. The α-bromo*allo*-acid may be transformed into its stereoisomeride by exposure to sunlight or by heating it at 204° for ten minutes.

12. Mixtures of the two β-bromocinnamic acids are formed by the addition of hydrogen bromide to phenylpropiolic acid when aqueous solutions of the former are employed. The proportions are roughly 1 part by weight of β-bromo-acid melting at 134 – 135° and 2 parts by weight of β-bromo*allo*-acid melting at 159 – 160°, and the proportions are not materially affected by temperature or light. The solvent, however, plays an extremely important part in the reaction. With glacial acetic acid as solvent the proportion of β-bromo-acid to its stereoisomeride is 1 : 0·55 and when benzene or carbon disulphide is used the main product is the structural isomeride, α-bromocinnamic acid.

13. The addition of hydrogen bromide to ethyl phenylpropiolate is similar to the addition to the free acid. In ethereal or alcoholic solution the product is a mixture of the esters of the two β-bromo-acids, but in dry benzene solution 72 per cent. of the product consists of ethyl α-bromocinnamate.

14. The α-bromo-acid loses hydrogen bromide more readily than the α-bromo*allo*-acid, so that in the preparation of phenylpropiolic acid it is better to use the α-bromo-acid rather than its *allo*-isomeride or a mixture of the two. Both β-bromo-acids lose hydrogen bromide more readily than the structurally isomeric α-acids and with potassium hydroxide solutions at the ordinary temperature the β-bromo-acid reacts about forty times more rapidly than the β-bromo-*allo*-acid.

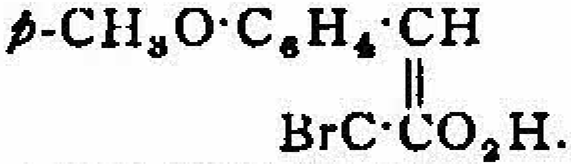
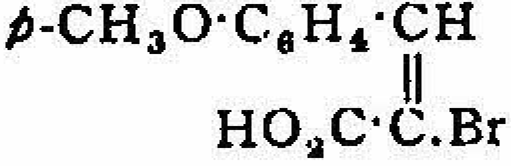
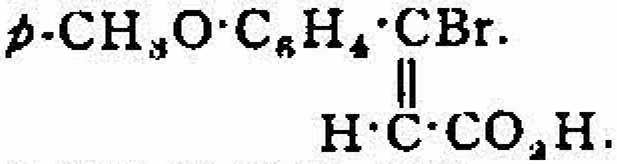
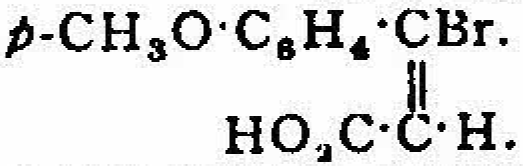
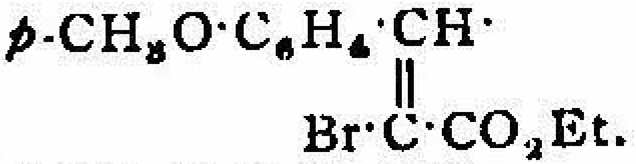
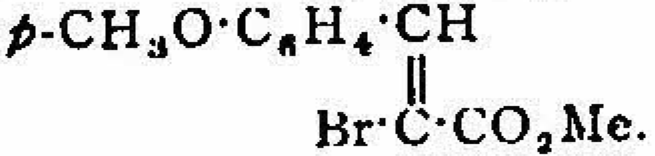
15. Sunlight transforms the β-bromo*allo*-acid into the β-bromo-acid.

16. Although there is an appreciable difference in the solubilities of the barium salts of the two acids they cannot be completely separated by means of these salts.

EXPERIMENTAL.

Table I gives a list of the compounds dealt with in the course of the work together with their formulæ and melting or boiling points.

TABLE I.

No.	Name of substance	Formula	Melting point
1	*p*-Methoxyphenylacetylene tetrabromide.	*p*-$CH_3O\cdot C_6H_4\cdot CBr_2\cdot CHBr_2$	85–86°
2	*s*-Tri-*p*-anisylbenzene	*s*-$C_6H_3\ (C_6H_4\cdot OCH_3)_3$	169–170°
3	*s*-Tri-*p*-hydroxytriphenylbenzene.	*s*-$C_6H_3\ (C_6H_4\cdot OH)_3$	300–303° with decomposition.
4	*p*-Bromophenylhydrazone of methyl anisyl ketone.	*p*-$CH_3O\cdot C_6H_4\cdot CMe : N\cdot NH\cdot C_6H_4Br.$	131–132° to a brown liquid.
5	*p*-Methoxy-*α*,*β*-dibromostyrene.	*p*-$CH_3O\cdot C_6H_4\cdot CBr : CHBr$	90–91°
6	*p*-Methoxyphenylpropiolic acid	*p*-$CH_3O\cdot C_6H_4\cdot C \vdots C\cdot CO_2H$	135–140° with decomposition.
7	*p*-Methoxy-*α*-bromocinnamic acid.	 $\begin{array}{c} p\text{-}CH_3O\cdot C_6H_4\cdot CH \\ \Vert \\ BrC\cdot CO_2H. \end{array}$	184–185°
8	*p*-Methoxy-*α*-bromo*allo*-cinnamic acid.	 $\begin{array}{c} p\text{-}CH_3O\cdot C_6H_4\cdot CH \\ \Vert \\ HO_2C\cdot C.Br \end{array}$	102–103°
9	*p*-Methoxy-*α*-bromocinnamic acid.	……	123°
10	*p*-Methoxy-*β*-bromocinnamic acid.	 $\begin{array}{c} p\text{-}CH_3O\cdot C_6H_4\cdot CBr. \\ \Vert \\ H\cdot C\cdot CO_2H. \end{array}$	139–140°
11	*p*-Methoxy-*β*-bromo*allo*-cinnamic acid.	 $\begin{array}{c} p\text{-}CH_3O\cdot C_6H_4\cdot CBr. \\ \Vert \\ HO_2C\cdot C\cdot H. \end{array}$	145°
12	*p*-Methoxy-*ααβ*-tribromo-*β*-phenylpropionic acid.	*p*-$CH_3O\cdot C_6H_4\cdot CHBr\cdot CBr_2\cdot CO_2H$	142–145°
13	*p*-Methoxy-*ααβ*-2-tetrabromo-*β*-phenylpropionic acid.	*p*-$CH_3O\cdot C_6H_3Br\cdot CHBr\cdot CBr_2\cdot CO_2H$ Derived from No. 7.	117–118°
14	Ethyl *p*-methoxy-*α*-bromocinnamate.	 $\begin{array}{c} p\text{-}CH_3O\cdot C_6H_4\cdot CH\cdot \\ \Vert \\ Br\cdot C\cdot CO_2Et. \end{array}$	168–170°[1] 5 mm.
15	Methyl *p*-methoxy-*α*-bromocinnamate.	 $\begin{array}{c} p\text{-}CH_3O\cdot C_6H_4\cdot CH \\ \Vert \\ Br\cdot C\cdot CO_2Me. \end{array}$	49–50°
16	Ethyl *p*-methoxy-*ααβ*-tribromo-*β*-phenylpropionate.	*p*-$CH_3O\cdot C_6H_4\cdot CHBr\cdot CBr_2\cdot$ CO_2 Et.	106–108°

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[1] Boiling point.

The melting and boiling points given in this paper are all corrected.

ETHYL-*p*-METHOXYCINNAMATE AND *p*-METHOXYCINNAMIC ACID AND THEIR DIBROMIDES.

The fresh rhizomes of *Kampheria galanga* yield 2·4 to 3·2 per cent. of oil calculated on the dry rhizomes, and the oil, when kept, deposits an appreciable quantity of a solid, which Romburgh[1] has shown to be the ethyl ester of *p*-methoxycinnamic acid. Additional amounts of the ester can be obtained from the oil left after the crystals are removed, by distillation under a pressure of 10 mm. and collecting the last fraction. The total ester is purified by distillation, when it passes over at 245–255° under a pressure of 120 mm., and finally by crystallisation from light petroleum, when it is obtained as large transparent, glistening prisms melting at 49–50°. The yield of ester is practically 30 per cent. of the total oil.

The free acid is readily obtained by hydrolysing the ester with aqueous sodium hydroxide or alcoholic potash. An almost theoretical amount is obtained by boiling the ester with a 5 per cent. aqueous solution of sodium hydroxide for 45 minutes and acidifying with hydrochloric acid. It is completely hydrolysed by boiling with a slight excess of 10 per cent. alcoholic potash for about 20 minutes or by dissolving in cold alcohol (5 parts), mixing with slight excess of alcoholic potash and keeping at room temperature (20–25°) for five hours. The acid crystallises from 80 per cent. alcohol in slender needles melting at 170° to an opalescent liquid which becomes translucent at 185°[2].

αβ-*Dibromo-β-p-methoxyphenylpropionic acid and its esters.*

The acid dibromide is readily prepared by the following process: A slight excess of a 10 per cent. solution of bromine in chloroform is added at 0° to a solution of the methoxy-acid dissolved in about eighteen times its weight of dry chloroform. The chloroform and excess of bromine are removed under reduced pressure and the product crystallised from chloroform when it is obtained as slender needles melting and decomposing at 149°[3].

When prepared by the action of bromine vapour upon the dry solid[4] the addition of bromine takes place comparatively slowly, as only 80 per cent. of the bromine had combined after 84 hours and addition was complete after 132 hours.

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[1] *Proc. K. Akad. Wetensch. Amsterdam*, 1900, 3, 38; 1902, 4, 618.
[2] Romburgh, *loc. cit.*
[3] Eigel, *Ber.*, 1887, 20, 2536.
[4] *Cf.* Sudborough and Thompson, *J. Chem. Soc.*, 1903, 83, 669.

The dibromide of the methyl ester has been prepared by Eigel and melts at 118°. The dibromide of the ethyl ester, ethyl $\alpha\beta$-dibromo-β-*p*-methoxyphenylpropionate has been prepared by both Reychler[1] and Bunge[2]; the former gives the melting point as 114° and the latter as 111·5°. In the preparation of this compound it is advisable to work at 0° and to add the bromine solution slowly to the solution of the ester. If these precautions are not taken hydrogen bromide is evolved and apparently substitution takes place in the benzene nucleus. Good yields are obtained by the following process: A solution of 17 grams of bromine in 106 grams of dry chloroform is added gradually to 20 grams of the ethyl ester dissolved in 120 grams of dry ether and placed in a freezing mixture. After an hour the solvents are removed under reduced pressure and the white crystalline residue crystallised from chloroform. It melts at 111–112° and the melting point is not raised by repeated crystallisation.

As *p*-methoxycinnamic acid and its ethyl ester in solution appeared to combine with bromine much more readily than cinnamic acid and its ester, an attempt was made to determine the velocity constants of the reactions with the two esters in carbon tetrachloride solution in diffused daylight. It was not found possible to obtain accurate velocity constants owing to the readiness with which the addition to the methoxycinnamate took place, but the following numbers illustrate the great difference between the two reactions. Working at 4° in diffused daylight with dry carbon tetrachloride solutions, after 8 minutes it was found that 95 per cent. of the methoxy-ester had combined, whereas only 3·4 per cent of the unsubstituted ester had united with bromine. It is thus clear that the presence of the *para*-methoxy-group greatly facilitates the addition of bromine to the olefine linking in the cinnamic ester molecule.

ACTION OF BASES ON THE ETHYL ESTER DIBROMIDE.

(*a*) *Alcoholic potash.*—In order to ascertain the manner in which alcoholic potash reacts with the ethyl ester dibromide, a series of experiments was undertaken to estimate the total amount of alkali satisfied and the amount of potassium bromide formed after definite intervals of time. For this purpose 10 grams of the ester dibromide was dissolved in alcohol, mixed with a solution of alcoholic potash at 25° in the proportions of one molecule of dibromide for three molecules of potassium hydroxide and the whole made up to 250 cc. and kept at 25°. After a definite interval 25 cc. were removed, the free alkali titrated with a standard solution of nitric acid using

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[1] *Bull. Soc. chim.*, 1897, [iii], 17, 511.

[2] *J. Russ. Phys. Chem. Soc.*, 1909, 41, 460.

phenolphthalein as indicator and the potassium bromide subsequently determined by the volumetric process using ferric alum as indicator. The results obtained are recorded in Table II.

TABLE II.

Alcoholic potash (0·33N.) and Ethyl αβ-*dibromo*-β-p-*methoxyphenylpropionate: Temperature 25°.*

Time in minutes	Equivalents of potash satisfied	Equivalents of hydrogen bromide formed
5	0·95	0·95
60	1·40	1·00
120	1·50	do.
180	1·70	do.
240	1·85	do.
300	2·00	do.

These results clearly prove that the alkali is first used in removing hydrogen bromide and then in hydrolysing the monobromo-ester so formed to the free acid. It therefore becomes possible to prepare either the *p*-methoxymonobromocinnamic acid or its ester by the action of alcoholic potash on the ester dibromide.

Preparation of monobromo-ester.—An alcoholic solution of the ester dibromide (20 grams) is mixed with rather more than 1 gram molecule of potassium hydroxide in the form of 20 per cent. solution and the whole left at room-temperature for 1 hour. The alcohol is then removed by distillation and the residue extracted with ether, dried with anhydrous sodium sulphate and the ether removed. The yield of ester so obtained is 97 per cent. of the theoretical. It is a yellow oil and when distilled 90 per cent. passes over at 168–170° under a pressure of 5 mm.

Analysis :—

0·1272 gave 0·0826 of silver bromide. Br=27·63; calculated for $C_{12}H_{13}O_3$ Br, Br=28·07 per cent.

Preparation of monobromo-acids.—The monobromo-acids are readily formed by adding slightly more than two molecules of potash, in the form of 20 per cent. alcoholic solution, to a solution of 40 grams of the ester dibromide in 220 grams of alcohol and allowing the mixture to remain for 5 hours at 25°. After removal of the alcohol, solution of the potassium salts in water and precipitation with hydrochloric acid, a 95 per cent. yield of monobromo-acids is obtained melting at 160–165°. This mixture is readily resolved into two isomeric acids by conversion into barium salts, in the same manner as the separation of α-bromo- and α-bromo*allo*cinnamic acid.[1] The acid from the insoluble barium salt corresponds with 85 per cent. of the crude acids and after crystallisation from 80 per cent. alcohol forms colourless long needles melting at 184–185°. The acid from the soluble barium salt corresponds with 15 per cent. of the mixture, melts in the crude state at 98–100° and after crystallisation from a mixture of chloroform and light petroleum (50–70°) forms yellow prismatic needles, melting at 102–103°.

(*b*) *Dimethylaniline.*—A series of experiments was made by mixing the ester dibromide with an alcoholic (92 per cent.) solution of dimethylaniline and estimating the amount of hydrogen bromide formed after given intervals of time. The ester formed was also estimated and analysed and the base used was recovered and examined in order to ascertain if *p*-bromodimethylaniline had been formed. The results obtained are given in Table III.

TABLE III.

Action of Dimethylaniline on the Ester Dibromide.

No. of experiment	Dibromide in grams	Alcohol in grams	Base in grams	Temperature	Time in minutes	Equivalents of hydrogen bromide formed	Weight of ester in grams	Bromine-content of ester
107	2·815	11	1·90	25	5	1·00	2·1	28·2 per cent.
106*a*	0·344	18	0·25	25	15	1·01	...	...
106*b*	0·234	15	0·20	Boiling	25	1·24	...	...
108	2·570	11	1·80	,,	120	1·27	1·6	21·8
104	0·500	10	0·35	,,	180	1·28	...	...

In both experiments 107 and 108 the weight of base recovered was practically the same as the amount taken, the recovered base from the former contained only 0·4 per cent. of bromine and the latter 2·8 per cent.

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[1] Sudborough and Thompson *loc. cit.*

The results show that after five minutes at room-temperature the base removes one molecule of hydrogen bromide yielding a practically pure monobromo-ester. The theoretical bromine-content is 28·1 per cent. compared with 28·2 per cent. found. When the alcoholic solution is boiled, an increased amount of hydrogen bromide is eliminated and the resulting ester contains less bromine. The presence of bromine in the recovered base proves the formation of monobromodimethylaniline and hence presumably the formation of a certain amount of *p*-methoxycinnamic ester from its dibromide. The ester obtained is thus evidently a mixture containing ethyl *p*-methoxy-α-bromocinnamate, ethyl *p*-methoxycinnamate and ethyl *p*-methoxyphenylpropiolate, and the approximate quantities of the three calculated from the above data are ethyl *p*-methoxybromocinnamate=77, ethyl *p*-methoxyphenylpropiolate = 16 and ethyl *p*-methoxycinnamate=8 per cent.

A quantity of monobromo-ester prepared as in experiment 107 was hydrolysed with cold alcoholic potash and the acids so obtained examined. The alcoholic liquid deposited an appreciable amount of a sparingly soluble potassium salt and when decomposed, this gave an acid melting at 170–175°. The potassium salts obtained from the mother liquor were converted into barium salts and from the insoluble barium salt a further quantity of the acid melting at 173–178° was obtained; the soluble salt gave an acid melting at 93–98° and after crystallising from light petroleum this was obtained as yellow needles melting at 101°. The yields of the two acids were respectively 80·7 and 9·3 per cent. of the theoretical and it is thus clear that the ester obtained by the action of a cold alcoholic solution of dimethylaniline on the ester dibromide is a mixture of two monobromo-esters in practically the same proportions as when cold alcoholic potash is used. In this respect the methoxy-ester dibromide differs markedly from ethyl cinnamate dibromide.

Preparation of p-*methoxyphenylpropiolic acid.*—Reychler[1] prepared this acid by the following process:—Ethyl *p*-methoxycinnamate dibromide is boiled for nine hours with excess of alcoholic potash, the product is collected and again heated with alcoholic potash.

The method is tedious and the yield is poor. We have been able to obtain a 96 per cent. yield by boiling the α-bromo-acid melting at 184–185° with two equivalents of potash (plus 5 per cent. excess) in alcoholic solution (6 per cent.) for three hours, removing the alcohol, dissolving the residue in water and precipitating with hydrochloric

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[1] *Bull. Soc. chim.*, 1897, [iii], 17, 511.

acid. The crude acid melted at 134–137° and after crystallisation from chloroform at 135–140°[1] with decomposition.

Action of Bases on the Methyl Ester Dibromide.

By the action of alcoholic potash on the methyl ester dibromide Eigel[2] states that two acids are formed. The one dissolves in hot water and melts at 158–168° and the second is soluble in hot alcohol and melts at 127–132°.

As these results appear somewhat remarkable when compared with those obtained with the ethyl ester dibromide, we decided to examine the behaviour of the methyl ester dibromide with alcoholic potash.

Methyl *p*-methoxycinnamate was prepared from the acid by the Fischer-Speyer method and was brominated in chloroform solution. The dibromide crystallises from light petroleum in small prisms melting at 118–119°.

An 80 per cent. yield of the methyl ester was readily obtained by boiling for 10 minutes 10 grams of the ethyl ester in 60 grams of methyl alcohol in which 0·04 gram of sodium had been previously dissolved.

Preliminary experiments made at 26° with a 1 per cent. alcoholic solution of potassium hydroxide showed that after 5 minutes, 1·5 molecules of alkali were satisfied and 1·0 molecule of hydrogen bromide eliminated; after 3 hours 1·97 molecules were satisfied and 1 molecule of hydrogen bromide eliminated.

The methyl ester (5·6 grams) was dissolved in alcohol and left in contact for 4·5 hours with slightly more than two molecules of potash in the form of 1·355N. alcoholic solution. The excess of alkali was neutralised, the alcohol removed by evaporation and from the potassium salts an acid melting at 150–160° was isolated. This was separated into insoluble and soluble barium salts and, by this means, a 59·4 per cent. yield of the monobromo-acid melting at 184° and a 37·6 per cent. yield of the yellow monobromo-acid melting at 101–102° were obtained making a total of 97·0 per cent. of the theoretical.

It thus appears that the dibromides of the methyl and ethyl esters yield the same two monobromo-acids under the influence of alcoholic

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[1] *Bull. Soc. chim.*, 1897 [iii], 17, 511, cf. also Valentini, *Gazzetta*, 1886, 16, 424.

[2] *Ber.*, 1887, 20, 2537.

potash, but that the proportions of acids are different in the two cases. With ethyl ester the proportion of high melting to low melting acid is 85 : 15 and with the methyl ester roughly 60 : 40.

In order to make quite sure that alcoholysis did not take place at the same time as the elimination of hydrogen bromide, methyl alcoholic potassium hydroxide was substituted for ordinary alcoholic potash. A preliminary experiment at 28° using a one per cent. solution of potash in methyl alcohol showed that 1 equivalent of hydrogen bromide was removed after five minutes, but that 1·5 equivalents of potassium hydroxide were used after 1·5 hours and 2 equivalents after six hours.

When an 8 per cent. methyl alcoholic solution is used and the two acids formed are separated by means of their barium salts, the relative proportion of the two acids were found to be:—

Experiment 220*a*: Acid melting at 184°, 57·6 per cent. Acid melting at 101°, 38·3 per cent.

Experiment 220*b*: Acid melting at 184°, 54·0 per cent. Acid melting at 101°, 40·0 per cent.

ACTION OF WATER ON *p*-METHOXYCINNAMIC ACID DIBROMIDE.

In attempting to eliminate hydrogen bromide from the acid dibromide, evolution of carbon dioxide was noticed and the formation of *p*-methoxybromostyrene proved. This is similar to the action of alkalis on ααβ-tribromo-β-phenylpropionic acid[1] and it was therefore decided to ascertain if the decomposition into carbon dioxide and *p*-methoxy-ω-bromostyrene takes place when the acid dibromide is boiled with water.

Experiment 200.—5·052 grams of the acid dibromide (Br=47·1 : theory requires 47·3 per cent.) were boiled for 15 minutes with 70 cc. of water in a reflux apparatus. The product was extracted twice with ether and the hydrogen bromide estimated in the aqueous layer. The ethereal solution was freed from acids by shaking with sodium carbonate solution and both acid and neutral products isolated. It was found that 1·02 molecules of hydrogen bromide had been eliminated and an 85 per cent. yield of *p*-methoxybromostyrene was obtained. The acid obtained weighed 0·276 grams, was free from bromine and after crystallisation from 90 per cent. alcohol melted at 170° to an opalescent liquid which became transparent at 186°. That this acid

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[1] *This Journal*, 1923, 6, 76.

is *p*-methoxycinnamic acid was proved by (*a*) mixed melting point determination and (*b*) conversion into its methyl ester which melted at 87–89°.

In a similar experiment (No. 209) 6·1 per cent. of acid melting at 167° was obtained together with an 87 per cent. yield of neutral product. The bromine-content of the crude neutral solid melting at 44–46°, viz., 39·5 per cent. indicates that the compound is not pure *p*-methoxybromostyrene, as this requires 37·6 per cent. of bromine.

It appears highly probable that two reactions take place, viz.,

(*a*) $X\cdot CHBr\cdot CHBr\cdot CO_2H \longrightarrow HBr + CO_2 + X\cdot CH{:}CHBr$ about 90 per cent.

(*b*) $X\cdot CHBr\cdot CHBr\cdot CO_2H \longrightarrow Br_2 + X\cdot CH{:}CH\cdot CO_2H$ under 10 per cent.

The bromine formed according to (*b*) can react with the monobromo-product formed in (*a*), $X\cdot CH{:}CHBr + Br_2 \longrightarrow X\cdot CHBr\cdot CHBr_2 \longrightarrow HBr + XCBr : CHBr$, and the dibromide thus formed decomposes into hydrogen bromide and *p*-methoxy-αβ-dibromostyrene, which will account for the relatively high percentage of bromine in the neutral product.

ACTION OF BASES ON *p*-METHOXYCINNAMIC ACID DIBROMIDE.

Alcoholic potash.—Eigel[1] observed the formation of appreciable amounts of *p*-methoxy-ω-bromostyrene when the acid dibromide reacted with a warm aqueous solution of potassium hydroxide. We have carried out a series of experiments on the action of alcoholic potash on *p*-methoxycinnamic acid dibromide with the object of studying the effects of (*a*) temperature, (*b*) concentration of the alkali and (*c*) concentration of the alcohol, on the yields of products.

A preliminary experiment made with the object of studying the rate of elimination of hydrogen bromide showed that at 25° and using 0·1 N. solution of alcoholic potash one equivalent of hydrogen bromide was eliminated during the first ten minutes, and an examination of the products proved the presence of appreciable amounts of *p*-methoxy-ω-bromostyrene and small amounts of an acid melting at 108–115° crude or at 123° after recrystallisation from 70 per cent. alcohol, benzene or petroleum ether (b. p. 70–80°) and is thus quite distinct from either of the two acids formed by the action of alcoholic potash on the ester

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[1] *Ber.*, 1887, 20, 2536.

dibromides. From dilute alcohol it crystallises in extremely well-developed prisms[1] containing 0·5 H_2O. 0·735 when kept in a vacuum desiccator for 50 hours lost 0·028 or 3·8 per cent. 0·5 H_2O requires 3·4 per cent. The crystals under this treatment crumble to a fine powder which melts at 123°. From benzene the anhydrous acid is obtained in the form of hexagonal prisms. It yields a soluble barium salt and appears to be isomeric with the two monobromo-acids obtained from the ester dibromides and melting respectively at 184° and 102°.

Table IV gives the results of the experiments made with the acid dibromide.

TABLE IV.

Action of alcoholic potash on p-methoxycinnamic acid dibromide.

Experiment No.	Concentration of alcohol by weight	Concentration of alcoholic potash	Temperature in degrees centigrade	Alcohol evaporated mm.	Percentage yield of neutral product	Percentage yield of bromo-acid
39	92	0·5 N	25–35	685	75	20
40	92	0·5 N	25	685	68	25
41	92	0·5 N	0 to − 5	685	65	30
84	95	1·0 N	−5 to − 10	40	53	40
164	95	1·0 N	0 to − 2	40	55	37
44	92	3·5 N	0	685	55	35
206	92	3·5 N	−5 to − 10	685	57	36
219	95	0·16 N	0 to − 2	do.	62	32
219*a*	95	0·16 N	do.	do.	64	30
213	95	0·5 N	do.	do.	62	33
213*a*	95	0·5 N	do.	do.	62	34
165	95	1·0 N	do.	do.	56	34
222	95	1·0 N	do.	do.	62	34
215	95	3·5 N	do.	do.	57	36
215*a*	95	3·5 N	do.	do.	58	35
206	92	3·5 N	− 5	do.	57	36
215	95	3·5 N	0	do.	57	36
215*a*	95	3·5 N	0	do.	58	35
207	98·5	3·5 N	− 5	do.	56	39

The general method of procedure adopted in these experiments was as follows:—5 grams of the acid dibromide were dissolved in 50cc. of alcohol, the solution cooled to the temperature stated and slightly more than two equivalents of potassium hydroxide dissolved in alcohol run in from a burette drop by drop. The mixture was shaken during the addition and then kept at the given temperature for 15 minutes. The slight excess of alkali was neutralised with dilute hydrochloric

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[1] According to Professor P. Sampat Aiyangar of the Central College these belong to the monoclinic system and show four prisms, two clinopinacoids and two basal planes and exhibit basal cleavage.

acid, the alcohol removed either on the water bath in an open dish or under reduced pressure, and the residue made alkaline and extracted with ether to remove the neutral products. The alkaline liquid was acidified with hydrochloric acid and on standing a crystalline precipitate of the monobromo-acid was obtained. By extracting the clear solution obtained after removal of the crystals a small amount of an oily acid mixture was obtained. The weight of this was usually about 10 per cent. of that of the crystalline acid.

From these experiments it is clear that the tendency of the dibromide to lose carbon dioxide and hydrogen bromide and thus yield an ω-bromostyrene is much greater when the *p*-methoxy-group is present than in the unsubstituted cinnamic acid dibromide.

In all cases examined the yield of *p*-methoxy-ω-bromostyrene is more than 50 per cent. of the theoretical quantity calculated from the equation:

$$CH_3O{\cdot}C_6H_4{\cdot}CHBr{\cdot}CHBr{\cdot}CO_2H \longrightarrow CO_2 + HBr + CH_3O{\cdot}C_6H_4{\cdot}CH{:}CHBr.$$

The yield of monobromo-acid formed according to the equation: $CH_3O{\cdot}C_6H_4{\cdot}CHBr{\cdot}CHBr{\cdot}CO_2H \longrightarrow HBr+CH_3O{\cdot}C_6H_4{\cdot}CH{:}CBr{\cdot}CO_2H$ is always under 40 per cent. of the theoretical.

The yield of monobromo-acid is affected to only a very slight extent by change in concentration of the alcohol or of the added alkali. On the whole it is advisable to use a fairly concentrated solution of alcoholic potash and not too dilute alcohol. Temperature is the most important factor, at 25° the yield of monobromo-acid is only 20 per cent., but at 0° to − 5° can rise to 30 or 40 per cent. according to conditions.

Several experiments were made to see if the yield of acid could be improved, but without success. When the powdered acid dibromide was added to a normal solution of potassium hydroxide at − 5° to − 10° and the alcohol removed at 40° the yield of monobromo-acid was only 11 per cent. and that of the neutral product rose to 82 per cent. Experiments made with chloroform solutions of the acid dibromide and normal alcoholic potash at − 5° to − 10° gave a 20 per cent. yield of monobromo-acid, and a 75 per cent. yield of the cinnamene.

Dimethylaniline.—When the acid dibromide was mixed with 2 molecules of dimethylaniline dissolved in alcohol, a slight rise of temperature took place, a vigorous effervescence was observed, and the acid gradually dissolved. It was found that 1 molecule of hydrogen bromide was eliminated and a 60 per cent. yield of *p*-methoxy-ω-bromostyrene and a 40 per cent. yield of monobromo-acid melting at 103–110°. (Br = 29·8 per cent.) were obtained. The acid, when crystallised, melted at 123°, gave 30·7 per cent. of bromine and was found to be identical with the acid obtained by the action of alcoholic potash on the acid dibromide. In one experiment the carbon dioxide formed during the reaction was estimated and agreed with the 60 per cent. yield of the bromocinnamene.

The base was also recovered. The crude base yielded a very small amount of a solid melting at about 183° and containing nitrogen but free from bromine, and then contained only 0·3 per cent. of bromine and when distilled gave as the main product dimethylaniline.

Configurations of the three bromo-acids melting at 185°, 102° *and* 123°.—

As already pointed out, three well-defined acids corresponding with the formula $CH_3O{\cdot}C_8H_5Br{\cdot}CO_2H$, have been isolated from the products of the action of alcoholic potash on *p*-methoxycinnamic acid dibromide or its esters.[1] Theoretically only two stereoisomeric α-bromo-acids are possible. No one of the three acids can be a β-acid as they are too resistant to the action of cold alkalis, and also the two β-bromo-acids have been prepared by other methods and are quite distinct from the three acids prepared by the elimination of hydrogen bromide from the acid dibromide and its esters.

The conversion of the acid melting at 102° into the isomeride melting at 185° under the influence of (*a*) sunlight, (*b*) bromine and (*c*) sulphuric acid (88 per cent.) indicates that in all probability the two acids are stereoisomeric α-bromo-acids and that the former is the *allo*-acid corresponding with α-bromo*allo*cinnamic acid melting at 120°.

Experiments have been carried out to show that all three acids under the influence of potassium hydroxide yield *p*-methoxyphenylpropiolic acid.

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[1] The bromine-content and the neutralisation equivalent of each of these three acids have been determined and agree with the formula $CH_3O{\cdot}C_8H_5Br{\cdot}CO_2H$. Br=31·13 per cent. and equivalent=257.

Acid melting at 185°—
0·1378 gave 0·0997 of silver bromide. Br=30·79
0·1276 gram required 24·75 cc. of 0·0202 N. alkali.
Equivalent=255·2.
Acid melting at 102–103°—
0·2018 gave 0·1472 of silver bromide. Br = 31·04
0·1326 gram required 25·35 cc. of 0·0202 N. alkali.
Equivalent=258·9.
Acid melting at 123°—
0·1634 gave 0·1170 of silver bromide. Br = 30·48
0·1642 gram required 32·1 cc. of 0·0202 N. alkali.
Equivalent=253·1.

This has already been proved for the acid melting at 185°, as it is the best method for the preparation of the propiolic acid (cf. p. 196) The acid melting at 123° when boiled for three hours with alcoholic potash (2 molecules) gives a 70 per cent. yield of the crude acetylenic acid melting and decomposing at 129 – 134°. After crystallisation from chloroform the pure acid melting at 135 – 140° with decomposition and having neutralisation equivalent 177 (theory 176), is obtained.

The acid melting at 102° treated in a similar manner for 26 hours gives a 96 per cent. yield of the crude propiolic acid melting at 125–132° with decomposition and after one crystallisation at 133–138° with a neutralisation value = 175 (theory = 176).

Attempts have been made to prepare dibromides from each of the three acids, but only the acid melting at 123° has given a well-defined crystalline dibromide; the acid melting at 102° is transformed into the acid melting at 185° and the latter, when left in contact with bromine vapour or solution for many hours, yields a resin which cannot be crystallised.

A definite product can be obtained by treating the sodium salt of the acid melting at 185° with bromine vapour,[1] but this contains 4 and not 3 atoms of bromine and presumably contains a bromine substituent in the benzene nucleus.

Attempts to determine the *cis* or *trans* configurations of the three acids by conversion into a bromotruxone[2] by means of sulphuric acid or phosphoric anhydride were unsuccessful.

The possibility that the acid melting at 123° is *p*-$CH_3O{\cdot}C_6H_4{\cdot}CH(OEt){\cdot}CHBr{\cdot}CO_2H_3$ is precluded by its bromine content, its forming a dibromide, and its giving *p*-methoxyphenylpropiolic acid with hot alcoholic potash. On oxidation with potassium permanganate in neutral solution anisaldehyde was obtained the yield being 12 per cent. of the theoretical.

Tetrabromo-p-methoxyphenylpropionic acid, $CH_3O{\cdot}C_6H_3Br{\cdot}CHBr{\cdot}CBr_2{\cdot}CO_2H$, is formed when the sodium salt of the acid melting at 185° is left in contact with bromine vapour until the increase in weight has reached its maximum, viz., for 82 hours. This increase corresponds with slightly more than four atoms of bromine per

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[1] Cf. Agamirian, *Arch. Sci. phys. nat.*, 1918, **45**, 191.

[2] Leuckart, *Ber.*, 1882, **15**, 16; Liebermann, 1898, **31**, 2096; Manthey, 1899, **32**, 2475.

[3] Cf. A. Angeli, *Atti. R. Accad. Lincei*, 1924, (V), **33**, 109–116 and also A. Werner, *Ber.*, 1906, **39**, 27.

molecule of sodium salt. The final product is not entirely soluble in dry ether, but the residue appears to be sodium bromide as it dissolves in water and yields no precipitate with nitric acid. The ethereal solution yields an acid melting at 117° and after crystallisation from ether forms ill-defined crystals melting at 117–118° (0·1580 gave 0·2416 of silver bromide. Br = 65·1. $CH_3O{\cdot}C_6H_3Br{\cdot}CHBr{\cdot}CBr_2{\cdot}CO_2H$ requires Br = 64·5 per cent.).

Dibromide of the acid melting at 123°.—When this acid is left in contact with a solution of bromine in chloroform for 40 hours in diffused daylight at 25° or in the dark for 60 hours at 10° followed by 20 hours at 25°, practically the theoretical quantity of bromine is added, and the crude product melts at 139–142°. After two crystallisations from a mixture of chloroform and light petroleum, it forms small prisms melting at 145° after softening at 142°. (0·1502 gave 0·2046 of silver bromide. Br = 58·0. $CH_3O{\cdot}C_6H_4{\cdot}CHBr{\cdot}CBr_2{\cdot}CO_2H$ requires Br = 57·6 per cent.).

Action of concentrated sulphuric acid on the three acids.—The finely powdered acids were introduced into about 36 times their weight of concentrated sulphuric acid and the mixture kept at 25° or at 0–5° and then at 5–20° for 0·5–16 hours. The mass was then poured on to ice, the mixture extracted with ether, the ethereal solution shaken with sodium carbonate solution to remove acids and both the ethereal and the alkaline solutions examined. In no case did the ethereal solution yield any neutral product, indicating the absence of a truxone or indone. The chief product was always an acid. From the 185° acid a product swelling up at 100–150° and melting with decomposition at about 160° was obtained. This contained bromine and had an equivalent of 295.

With acid of 88 per cent. concentration the acid melting at 102° is transformed at 20–25° into the stereoisomeride melting at 185°, but with more concentrated acid (95 per cent.) it yields an acid which swells up at 200° and melts with decomposition at 215–223°. This contains 27·7 per cent. of bromine and has a neutralisation equivalent of 289. A bromomethoxydihydroxyphenylpropionic acid requires Br = 27·5 per cent. and an equivalent 291.

The monobromo-ethyl ester obtained by removal of hydrogen bromide from ethyl *p*-methoxycinnamate dibromide and distilling the product also yields a *dibromide* after 50 hours in contact with a 10 per cent. solution of bromine in chloroform. This crystallises from chloroform in small needles melting at 106–108°. (0·1760 gave 0·2211 of silver bromide. Br = 53·5 and $CH_3O{\cdot}C_6H_4{\cdot}CHBr{\cdot}CBr_2{\cdot}CO_2C_2H_5$ requires Br = 53·9 per cent.).

The ethyl ester of the acid melting at 123° obtained by the usual method of esterification is an oil. It reacted with a chloroform solution of bromine evolving hydrogen bromide and giving an oily product, but a dibromide could not be isolated.

Velocity of reaction between the three α-bromo-acids and aqueous potassium hydroxide at 73·2° :—The reaction bottles were placed in a copper vessel surrounded by the vapour of boiling carbon tetrachloride and were thus kept at a constant temperature of 73·2°. The alkali used in all cases was 0·1030 N sodium hydroxide and always in the proportion of three molecules of alkali to one of the monobromo-acid. 18·3cc. of the alkali were run into a 30cc. stoppered bottle which was left in the bath for several hours in order to attain the constant temperature. 0·1612 gram of bromo-acid was introduced, the contents of the bottle shaken and at the end of the time specified the bottle was removed, cooled as quickly as possible and the contents transferred to a flask. The unused alkali was titrated against standard nitric acid using phenolphthalein as indicator and after adding excess of nitric acid the hydrogen bromide was estimated by means of standard silver nitrate (0·1 N) and standard ammonium thiocyanate (0·05 N), using a burette reading to 0·01 cc.

In the majority of cases the values obtained by alkali titration corresponded with those calculated from the amount of hydrogen bromide eliminated. The latter values are given in Table V.

Attempts were made to study the reaction velocities at 30°, but the reactions were too slow, as even with the acid melting at 185° only 5 per cent. was decomposed after 432 hours. At 100° on the other hand, there was a tendency for the elimination of carbon dioxide and the formation of *p*-methoxyphenylacetylene, and with the 185° acid after 20 hours 10 per cent. of the acid had decomposed in this manner.

TABLE V.

Rate of elimination of hydrogen bromide from the three α-bromo-p-methoxycinnamic acids.

A. *Acid melting at 185°.*

Time in hours	x	$b-x$	$b-\frac{x}{2}$	$k = \frac{2{\cdot}302}{b \times t} \log_{10} \frac{b-\frac{x}{2}}{b-x}$
4·75	1·80	10·75	11·65	0·00135
11·00	3·02	9·53	11·04	0·00106
19·50	4·90	7·65	10·10	0·00113
50·30	8·20	4·35	8·45	0·00105
B. *Acid melting at 103°.*				
4·75	0·66	11·89	12·22	0·000456
18·00	1·10	11·45	12·00	0·000208
48·00	2·45	10·10	11·32	0·000189
119·00	4·90	7·65	10·10	0·000186
235·00	9·16	3·39	7·97	0·000290
C. *Acid melting at 123°.*				
2·00	2·60	9·95	11·25	0·00489
4·75	4·90	7·65	10·10	0·00466
8·00	6·74	5·81	9·18	0·00456
11·50	7·90	4·65	8·60	0·00426
17·75	8·80	3·75	8·15	0·00349
25·00	9·50	3·05	7·80	0·00299

The values for *k* in this table are not absolute velocity constants, but are directly comparable with each other. *x* is the number of cc. of 0·05 N ammonium thiocyanate required and *b* the number which would be required if all the hydrogen bromide were eliminated. This was in all cases 12·55. Hence, *b-x* represents the concentration of undecomposed acid and, since one molecule of alkali is used in forming the sodium salt, *2b-x* is the concentration of alkali.

THE ADDITION OF HYDROGEN BROMIDE TO *p*-METHOXYPHENYLPROPIOLIC ACID.

(*a*) *Aqueous suspension.*—It was anticipated that a mixture of two stereoisomeric *p*-methoxy-β-bromo-acids would be formed by the addition of hydrogen bromide to the *p*-methoxyphenylpropiolic acid:

$$MeO{\cdot}C_6H_4{\cdot}C\vdots C{\cdot}CO_2H + HBr \longrightarrow MeO{\cdot}C_6H_4{\cdot}CBr : CH{\cdot}CO_2H.$$

Experiments soon showed (see Table VI) that the products vary with the temperature of the reaction and also with the nature of the solvent. At 0° with aqueous hydrobromic acid of sp. gr. 1·78–1·80 hydrogen bromide was added, and an acid product free from neutral compounds and containing 30·5–31·2 per cent. of bromine was obtained. The percentage of bromine in a monobromo-acid is 31·1. The yield was never theoretical and varied between 72 and 84 per cent. of the theoretical. In addition, 5–10 per cent. of a neutral oil was obtained by extracting the aqueous liquid with ether but so far it has not been found to account for the remaining 12 to 18 per cent. of the propiolic acid. The absence of any neutral product in the acid mixture obtained at 0° was shown by the fact that with dilute aqueous sodium carbonate a test sample gave a clear solution; this, however, became turbid when kept for a short time owing to the decomposition of the bromo-acids and the formation of neutral products. The acid product was not homogeneous as its melting-point was not sharp and on crystallisation from acetone or benzene two distinct types of crystals could be observed. The readiness with which the acid mixture loses hydrogen bromide and also carbon dioxide points to the presence of β-bromo-acids.

A small amount of oil, 5–10 per cent., was always found in the aqueous filtrate after the solid had been removed and washed. This oil was subsequently proved to be methyl *p*-anisyl ketone.

When, during the addition of the hydrogen bromide, the temperature was allowed to rise to 25–35°, the solid product obtained by pouring the mixture into water was found to yield an insoluble solid residue when treated with dilute aqueous sodium carbonate. The solid was therefore removed by filtration and washing and was afterwards extracted with a ten per cent. aqueous solution of sodium carbonate at the ordinary temperature, and the sodium carbonate solution immediately acidified. The neutral solid on further examination was shown to possess the properties of a tri-*p*-anisylbenzene. The small amounts of acids formed in these experiments were extracted from the acidified liquid by means of ether. The mixture of aqueous liquid and oil obtained by filtering the original solid was extracted with ether and after removal of the ether an oily liquid was obtained. Treatment with sodium carbonate solution showed that this oil was practically insoluble in sodium carbonate solution and contained about 99·5 per cent. of methyl *p*-anisyl ketone and only 0·04 per cent. of bromo-acids.

The results obtained in a series of experiments under different conditions are given in Table VI.

TABLE

Addition of hydrogen bromide to p-methoxyphenylpropiolic

No. of experiment	Specific gravity of hydrobromic acid at 0°	Temperature of addition in degrees centigrade	Time in hours	Grams of acetylenic acid taken	Solid precipitate[1]		
					Grams	Melting point in degrees centigrade	Per centage of bromine
238	1·80	0	4·25	3·770	4·446	108–119	27·0
228	1·78	0–3	8·0	2·403	2·490	118–130	29·9
241	1·80	0	16·5	2·914	3·302	109–116	30·9
248	1·78	0	,,	4·996	5·228	110–123	30·5
255	1·74	0–23	14·0	2·187	1·350	105–112	...
325	,,	0–20	14·5	4·370	2·638	85–130	...
306*a*	1·56 at 20°	0	14·0	0·730	0·755	115–131	14·1
306*b*	,,	25	,,	0·715	0·567	123–140	29·8[2]
302	1·65	0	19·0	14·00	14·50	127–133	14·9
303	1·78	0	17·0	Ppt. from Exp. 302	16·70	125–132	31·0
221	...	0–20	14·0	0·985	0·635	90–140	...
227	——[3]	0–22	20·0	3·110	3·584	120–132	31·2
275	——[4]	25–35	16·0	1·206	0·202	113–160	...
277	——[4]	25–28	16·5	4·586	0·712	142–164	...

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[1] At the end of the given period the mass was poured into water and filtered with the
funnel constitutes the solid precipitate. To determine the percentage of neutral product in
carbonate solution and the residue after removal of the ether weighed. The filtrate from the
with ether and the residue after removal of the ether constitutes the oil mentioned in

[2] From the composition of the mixture the percentage of bromine should be 28·0.

[3] Dry hydrogen bromide was passed into hydrobromic acid (sp. gr. 1·47) at 0° for

[4] Dry hydrogen bromide was passed into a suspension of the acetylenic acid in hydro-

VI.

acid in aqueous suspension in the dark.

Percentage composition of solid precipitate		Grams of oil from filtrate[1]	Percentage composition of the oil		Percentage yield of monobromo-acids
Acid	Neutral		Acid	Neutral	
Practically 100	...	0·351	53	47	74
,,	...	0·297	52	48	73
,,	...	0·292	14	86	79
,,	...	0·337	...	...	More than 72
40	60	0·608	...	Practically 100	17
51	45	1·200	2	98	21
Practically 100	...	0·046 solid	Practically 100	...	34
90	9	0·152	...	Practically 100	49
Practically 100	...	0·138 solid	Practically 100	...	34
,,	...	2·172	83	16	84
18	82	0·575	...	...	More than 10
Practically 100	...	0·146	...	...	More than 80
10	90	0·830	...	Practically 100	1
13	87	3·210	...	,,	1

aid of suction and washed until practically free from hydrobromic acid. The residue on the the dry precipitate, a portion was dissolved in ether and rapidly shaken with aqueous sodium precipitate consisted of an aqueous liquid together with an oil, the whole was extracted column 11.

35 minutes.
bromic acid (sp. gr. 1·47) at 25° for 60 minutes.

p-Methoxy-β-bromocinnamic acid, $CH_3O{\cdot}C_6H_4{\cdot}CBr{:}CH{\cdot}CO_2H$.—Considerable difficulty was experienced in separating the mixture of bromo-acids obtained by the addition of hydrogen bromide to the propiolic acid in aqueous suspension. Methods based on differences in solubilities of the barium salts in water, the potassium salts in alcohol and the sodium salts in common salt solutions proved unsuccessful. A method of fractional crystallisation of the mixed acids from acetone was found to give one of the acids in a pure state in the form of large yellow prisms melting at 139–140° and stable at 160°. The following method of procedure has been found to give good results. 15 grams of the mixture of acids is dissolved in 60 cc. of dry acetone and the solution placed in a desiccator and allowed to evaporate slowly. When evaporated to about two-thirds of its original volume, crystals begin to appear and when the volume is 20 cc., a crop of 2·5 grams of the acid is obtained and two more batches (2·9 grams) of crystals are obtained from the mother liquors. The crystals are well-developed yellow prisms and form at the bottom of the vessel. At the same time a considerable amount of the solute is deposited as a crust on the upper part of the vessel, and as this is a mixture it is kept quite separate from the yellow crystals, and is finally dissolved in dry acetone and further crops of yellow crystals obtained totalling 2·30 grams. The yellow prisms melt at 134–138° and after one recrystallisation from acetone melt without decomposition at 139–140°, and the melting point is not raised by further crystallisations from acetone or benzene. The total yield is 7·7 grams from 15·2 grams of mixed acids.

The acid crystallises in yellow prisms belonging to the triclinic system,[1] and dissolves readily in all organic solvents. (0·2132 gave 0·1563 silver bromide, Br = 31·2; $C_{10}H_9O_3$ Br requires 31·1 per cent.) 0·1866 gram dissolved in 15cc. of neutral alcohol and cooled to 0° required 15·95 cc. of 0·0462N. alkali for neutralisation. Equivalent = 253·2; $CH_3O{\cdot}C_6H_4{\cdot}CBr : CH{\cdot}CO_2H$ requires 257.

Although the β-acid dissolved in sodium carbonate yields a perfectly clear solution, turbidity is soon noticed unless the temperature is maintained at about 0°. This reaction with sodium carbonate solution has been followed in detail.

0·1266 gram of finely powdered β-bromo-acid was left in contact with 10 cc. of saturated sodium carbonate solution for 22 hours at 25°. On extraction with ether 0·059 gram of a neutral oil was obtained corresponding with 91 per cent. of the theoretical yield of *p*-methoxyphenylacetylene, and the sodium carbonate solution when acidified

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[1] According to Professor P. Sampat Aiyangar of the Central College, the crystals are triclinic with cleavage parallel to the pinacoid. The faces developed are two macro- and two brachy-pinacoids, two brachy-domes and two basal planes.

with nitric acid gave no precipitate, but contained 31·4 per cent. of the weight of the original acid in the form of hydrogen bromide. (Theory 31·5 per cent.).

The neutral oil solidified when cooled to 0° and then melted at 23° and readily combined with bromine yielding a product which crystallised from a mixture of chloroform and light petroleum in colourless needles melting at 85–86° and containing 70·3 per cent. of bromine. (Theory for $CH_3O\cdot C_6H_4\cdot CBr_2\cdot CHBr_2 = 70{\cdot}8$ per cent.).

Although the β-bromo-acid is readily decomposed by sodium carbonate at 25°, the following experiment shows that the decomposition is practically nil at 0°.

0·197 gram of the β-bromo-acid (m.p. 139–140°) was dissolved in 20 cc. of ether and the solution cooled to 0° to 2°. It was then vigorously shaken twice with 10 cc. of a 5 per cent. solution of sodium carbonate also cooled. The combined alkaline liquids were immediately acidified with cold nitric acid and the liberated bromo-acid collected. In this manner 0·158 gram of the original acid was recovered and a further 0·034 gram by extraction with ether, making a total of 0·192 gram. At the same time no trace of hydrogen bromide could be detected in the aqueous liquid and the original ethereal solution gave no residue on evaporation.

*p-Methoxy-β-bromo*allo*cinnamic acid.* — This acid mixed with appreciable amounts of the isomeride melting at 139–140° is present in the residues obtained by evaporating the mother liquors from which the latter has crystallised. The simplest method of separation is to decompose the β-acid into hydrogen bromide, carbon dioxide and *p*-methoxyphenylacetylene by leaving the mixed acids in contact with concentrated sodium carbonate solution for 22 hours at room-temperature (25°), extracting the neutral product with ether, acidifying the sodium carbonate solution and crystallising the precipitated β-bromo-*allo*acid from chloroform. From 7·4 grams of mixed acids 4·72 grams of acid is precipitated melting at 127–131° and after crystallisation from chloroform 3·9 grams of acid melting at about 142° are obtained. The neutral product weighs 1·262 grams and is proved to be *p*-methoxyphenylacetylene by conversion into its tetrabromide melting at 85–86°. The weight corresponds with 2·46 grams of β-acid, so that the original 15·2 grams of mixed acids contained 67 per cent. of β-bromo-acid melting at 139–140° and 31 per cent. of β-bromo*allo*-acid melting at 146°.

A sample of the original mixed acids was analysed by treatment with sodium carbonate solution at 25° and the neutral oil obtained indicated the presence of 61 per cent. of the acid melting at 139–140° and the recovered acid showed the presence of 34 per cent. of the β-bromo*allo*-acid in the original mixture.

The β-bromo*allo*-acid dissolves readily in most organic solvents, crystallises best from chloroform and forms colourless needles melting at 146°. (0·1796 gave 0·1332 silver bromide, Br = 31·6. Theory requires 31·1 per cent.).

0·2132 required 16·6 cc. of 0·0502 N alkali for neutralisation. Equivalent = 256; $CH_3O{\cdot}C_6H_4{\cdot}CBr : CH{\cdot}CO_2H$ requires 257.

The acid is much more resistant to the action of sodium carbonate than the isomeric β-bromo-acid, as shown by the following experiment:—

0·346 gram of the acid melting at 145–146° was dissolved in 30 cc. of saturated sodium carbonate solution and left for 24 hours at 22–26°. The solution remained clear and no trace of turbidity could be observed. No neutral oil could be isolated by extracting the sodium carbonate solution with ether and the recovered acid weighed 0·328 gram and melted at 141–143°. Only a trace of hydrogen bromide could be detected corresponding with the decomposition of under 1 per cent. of the bromo-acid.

Configurations of the β-acids.—The acid melting at 139–140° has been termed the β-bromo-acid and the isomeric acid melting at 145–146° the β-bromo*allo*-acid.

This is largely based on analogy with the unsubstituted β-bromo-cinnamic acids. There it has been found that the *allo*-acid has the higher melting point, forms a readily soluble barium salt, loses hydrogen bromide less readily than its stereoisomeride and in sunlight tends to pass over into the β-bromo-acid.

When these tests are applied to the two methoxy-β-bromo-acids they clearly show that the acid melting at 145–146° is the *allo*-acid, i.e., the derivative of *allo*cinnamic acid. The following experiments on the action of light are of interest in this connection:—

A solution of the barium salt of the higher melting acid was prepared by dissolving 0·02 gram of the acid in 5 cc. of 0·017 N. ammonia, neutralising with a drop of very dilute hydrochloric acid and adding 1 cc. of a 15 per cent. solution of barium chloride. When such a solution was kept in the dark, it remained perfectly clear and no hydrogen bromide was eliminated. When however the same solution was exposed to sunlight a small amount of precipitate was deposited after 3 hours and after 6 hours the liquid had become distinctly turbid and smelt strongly of *p*-methoxyphenylacetylene, the presence of which was proved by extracting with ether and conversion into the tetrabromide melting at 80–83°. The explanation of this phenomenon is that the barium salt of the higher melting acid becomes transformed into the salt of the stereoisomeric acid under the influence of light and that the latter salt decomposes into hydrogen bromide, carbon dioxide and *p*-methoxyphenylacetylene in exactly the same manner as the sodium salt (cf. p. 210).

Methyl p-*anisyl ketone.*—The oil present in the aqueous filtrate obtained by adding water to the crude product from the addition of hydrogen bromide to *p*-methoxyphenylpropiolic acid in aqueous suspension and subsequent filtration, was found to solidify when kept. It had a pleasing odour, melted at 33–35° and reacted with phenylhydrazine, but it was not found possible to isolate a stable phenylhydrazone. The crude product melted at 117–119°, but decomposed when kept for a short time.

It yields a *p*-bromophenylhydrazone which crystallises from 60 per cent. alcohol in colourless needles melting at 131–132° to a dark liquid. (0·1542 gave 0·0886 of silver bromide, Br=24·4: theory for $CH_3O{\cdot}C_6H_4{\cdot}CMe{:}N{\cdot}NH{\cdot}C_6H_4Br$ is 25·1 per cent. Br.).

The confirmation of the view that the original neutral product is identical with Reychler's[1] *p*-anisylmethyl ketone was afforded by its conversion into the phosphate melting at 83°, as compared with the melting point 86° given by Klages and Lickroth.[2]

Tri-p-*anisylbenzene.*—$C_6H_3(C_6H_4{\cdot}OCH_3)_3$.—As already pointed (p. 207) out, the solid product obtained by addition of hydrogen bromide to an aqueous suspension of the propiolic acid at 25°, subsequently pouring into water and filtering, is not entirely acidic, but contains a neutral solid. The amount of this solid was estimated in one experiment (No. 306 *b*) by the following process:—0·411 gram of the dry precipitate was dissolved in 25 cc. of ice cold ether and shaken twice with 10 cc. of a 5 per cent. sodium carbonate solution also cooled to 0°. The weight of the neutral solid product melting at 162–165° was 0·032 gram corresponding with 8 per cent. of the original solid taken. By acidifying the sodium carbonate extracts while still cold 0·374 gram, or 91 per cent. of the original solid was recovered. The percentage of bromine in this acid, viz., 30·9, corresponds with that required for a methoxybromocinnamic acid (31·1 per cent.).

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[1] *Bull. Soc. chim.*, 1897 [iii], 17, 511.
[2] *Ber.*, 1899, 32, 1559.

The neutral solid crystallises from a mixture of chloroform and light petroleum (b.p. 60–80°) in minute yellow needles melting at 169–170°, and is easily soluble in chloroform, somewhat sparingly soluble in ether and very sparingly soluble in alcohol. It dissolves in cold concentrated sulphuric acid giving a solution with a greenish yellow fluorescence, but this disappears on dilution with water.

Analyses :—

i. 0·2264 gave 0·6740 of carbon dioxide and 0·1326 of water.
ii. 0·2160 ,, 0·6498 ,, ,, 0·1324 ,,
iii. 0·1604 gave 0·2770 of silver iodide.

	Found			Calculated for	
	i	ii	iii	$C_6H_3(C_6H_4{\cdot}OCH_3)_3$	
C	81·2	82·0	—	81·8	per cent.
H	6·5	6·8	—	6·1	,,
Methoxyl	—	—	22·8	23·5	,,

The molecular weight was determined in pure camphor by Rast's method[1] and the values 377 and 385 were obtained as compared with the theoretical value 396 for $C_6H_3(C_6H_4{\cdot}OCH_3)_3$.

The chloroform solution of the compound reacts readily with twice its weight of bromine, yielding hydrogen bromide and a solid which crystallises from carbon disulphide in slender needles softening at 238° and melting at 242° with decomposition (0·2120 gave 0·2444 of silver bromide. Br=49·1, $C_{27}H_{19}Br_5O_3$ requires 50·6 per cent. Br).

When three times the weight of bromine is used, a *hexabromo-derivative*, which crystallises from carbon disulphide in small needles melting and decomposing at 286–290° is obtained (0·1724 gave 0·2194 of silver bromide. Br=54·2. $C_{27}H_{18}Br_6O_3$ requires 55·2 per cent. Br).

The original yellow solid appears to be a tri-*p*-anisylbenzene formed by the polymerisation of the anisylacetylene or the condensation of methyl anisyl ketone. Opposed to the view that it is *s*-tri-*p*-anisylbenzene is the fact that Schneider and his collaborators[2] claim to have obtained this compound by the action of sulphoacetic acid on anisole. This compound melts at 142° and is quite distinct from the compound obtained by us. We have repeated Schneider's experiments but obtained a crystalline solid melting at 156–157°.

[1] *Ber.*, 1922, 55, 1051.
[2] *Ber.*, 1921, 54, 2298.

The product formed by the hydrolysis of the methoxyl to hydroxy-groups, crystallises from ether or chloroform in ill-defined crystals melting at 300–303° with decomposition.

(*b*) *In benzene suspension.*—As the methoxyphenylpropiolic acid is not very readily soluble in benzene, dry hydrogen bromide was passed into a suspension of 5 grams of the propiolic acid in 60 cc. of dry benzene for 1·25 hours at 25–26°. The liquid became brown, but all the solid did not dissolve, the insoluble portion being removed by filtration and washed with 10 cc. of benzene. In this manner 3·62 grams of product melting at 166–173° was obtained, and from the benzene solution 3·49 grams of acids melting at 126–129°, or a total of 7·11 grams of acids corresponding with a 97 per cent. yield of monobromo-acids. The acids were practically free from neutral products as they dissolved to clear solutions in sodium carbonate and the β-bromo-acid melting at 139–140° was not present, such solutions not becoming turbid when kept. By extracting with ether the sodium carbonate solution of the residue obtained by evaporating the benzene solution, 0·042 gram of a neutral product was obtained and this gave the reactions of methyl *p*-anisyl ketone.

The presence of the α-bromo-acid melting at 184° in both the benzene-insoluble as also in the benzene-soluble acids could easily be proved and hence attempts were made to separate this acid by means of the insolubility of its barium salt. It was subsequently found that the other acid present in appreciable quantity is the β-bromo*allo*-acid melting at 146° and as the barium salt of this acid is somewhat sparingly soluble in water or barium chloride solution the separation of the two acids requires some care. The following conditions were found to yield a clear separation.

1·5 grams of the mixture is dissolved in a slight excess of dilute ammonia, the excess neutralised with hydrochloric acid and the whole made up to 250 cc. and mixed with 50 cc. of saturated barium chloride solution. The precipitated barium salt is washed with barium chloride solution and the acids precipitated from both the soluble and insoluble barium salts.

By this process it was found possible to isolate from the original 3·62 grams insoluble in benzene, 3·53 grams of acid from the insoluble barium salt and similarly 0·762 gram of a similar acid from the 3·49 grams soluble in benzene. The melting points of the acid so obtained was 175–182° and the yield 60 per cent. of the total acids formed by the addition of hydrogen bromide to the methoxyphenylpropiolic acid. From the soluble barium salts the weights of acids were:—0·067 gram from the benzene-insoluble and 2·61 grams from the benzene-soluble acids, or a total of 2·68 grams corresponding with 38 per cent.

of the original bromo-acids. This acid from the soluble barium salts melted between 134° and 142°; a bromine estimation, viz., 31·5 per cent. showed it to be free from any unchanged methoxyphenylpropiolic acid. When crystallised from chloroform it gave colourless needles (2·264 grams) melting at 142–145° and identical with the β-bromo*allo*-acid already described.

p-*methoxy*-αβ-*dibromostyrene*, $CH_3O\cdot C_6H_4\cdot CBr : CHBr$.—By the action of bromine, either in the light or dark, on chloroform solutions of the two stereoisomeric β-bromo-acids the same neutral product is produced and practically no acids. After shaking with sodium carbonate solution and crystallising from chloroform the product forms small colourless prisms melting at 90–91°. 0·1632 gave 0·2125 silver bromide; $Br = 55{\cdot}4$, and $C_9H_8OBr_2$ requires $Br = 54{\cdot}8$ per cent.

The product thus appears to be *p*-methoxy-αβ-dibromostyrene formed from the unstable additive product of the β-bromo-acids and bromine.[1]

$$CH_3O\cdot C_6H_4\cdot CBr_2\cdot CHBr\cdot CO_2H \longrightarrow$$
$$HBr + CO_2 + CH_3O\cdot C_6H_4\cdot CBr{:}CHBr.$$

Attempt to prepare p-*methoxy*allo*cinnamic acid*.—The *p*-methoxy-β-bromo*allo*cinnamic acid melting at 145° was heated with twice its weight of zinc filings and eight times its weight of absolute alcohol for three hours on the water bath. One molecule of hydrogen bromide was eliminated from the acid, and the resulting product was found to be almost pure *p*-methoxycinnamic acid melting at 169–170°. Hence, the case is different from the reduction of β-bromo*allo*cinnamic acid to *allo*cinnamic acid.

SUMMARY.

1. A 30 per cent. yield of ethyl *p*-methoxycinnamate can be obtained from the oil from the rhizomes of *Kaempheria galanga* and the ester is readily hydrolysed to the corresponding acid.

2. By the action of alcoholic potash on the ester dibromide (m.p. 111° to 112°) it is possible to isolate two stereoisomeric *p*-methoxy-α-bromocinnamic acids, melting respectively at 185° and 102°. These acids are readily separated by means of their barium salts as the salt of the higher melting acid is practically insoluble in water or barium chloride solutions. The proportions of the two acids

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[1] Compare decomposition of αββ-tribromo-β-phenylpropionic acid. *This Journal*, 1923, 6, 71.

are as 85 : 15, but when the methyl ester dibromide is used the proportion is 60 : 38.

3. By the action of alcoholic potash on the acid dibromide (m.p. 149°) much neutral product, *p*-methoxy-ω-bromostyrene (m.p. 54·5°), is formed together with a certain amount of a bromo-acid melting at 123° and isomeric with the two α-bromo-acids. The yield of this acid is about 40 per cent. of the theoretical at –5° to –10° and falls to 20 to 25 per cent. at 25°.

4. All three acids lose hydrogen bromide slowly at 30° and when heated with aqueous potassium hydroxide at 73·2° they lose hydrogen bromide in the following order of diminishing velocity, 123°, 185°, 102°, and in all three cases the main product is *p*-methoxyphenylpropiolic acid.

5. The acid melting at 185° appears to be the *p*-methoxy-α-bromocinnamic acid corresponding with the α-bromocinnamic acid melting at 131°; the acid melting at 102° is the *allo*-isomeride corresponding with the α-bromo*allo*cinnamic acid melting at 120°, as it is readily transformed into the acid melting at 185° by (*a*) exposure to sunlight for three hours, (*b*) the action of a chloroform solution of bromine and (*c*) treatment with 88 per cent. sulphuric acid.

6. When the ester dibromide is boiled with an alcoholic solution of dimethylaniline the chief product is a mixture of ethyl *p*-methoxy-α-bromocinnamates together with some ethyl *p*-methoxyphenylpropiolate and a little ethyl *p*-methoxycinnamate. When the acid dibromide is treated in the same manner the main product is *p*-methoxy-ω-bromostyrene together with the monobromo-acid melting at 123°.

Organic bases thus react in much the same manner as alcoholic potash and do not tend to eliminate bromine in place of hydrogen bromide.

7. The acid dibromide boiled with water yields *p*-methoxy-ω-bromostyrene together with a little *p*-methoxycinnamic acid.

8. The acid melting at 123° forms a definite dibromide, presumably $CH_3O{\cdot}C_6H_4{\cdot}CHBr{\cdot}CBr_2{\cdot}CO_2H$, melting at 145° after softening at 142°. With bromine vapour or with a chloroform solution of bromine the acid melting at 185° yields resinous products which cannot be crystallised and the sodium salt of this acid in contact with bromine vapour yields a tetrabromo-acid, presumably

$$CH_3O{\cdot}C_6H_3Br{\cdot}CHBr{\cdot}CBr_2{\cdot}CO_2H$$

melting at 117–118°. So far it has not been found possible to assign a definite configuration to the acid melting at 123°.

9. Good yields of the acetylenic acid, *p*-methoxyphenylpropiolic acid can readily be obtained by the action of alcoholic potash on the ethyl ester dibromide, isolating the acid melting at 185° and heating this for three hours with alcoholic potash.

10. Two stereoisomeric *p*-methoxy-β-bromocinnamic acids can be prepared by the addition of hydrogen bromide to an aqueous suspension of the acetylenic acid at 0°. The β-bromo*allo*-acid melts at 145° and is comparatively stable towards sodium carbonate at room temperature, whereas the β-bromo-acid melts at 139° and is completely decomposed when left in contact with sodium carbonate solution for 24 hours at 25°, yielding *p*-methoxyphenylacetylene (m.p. 28·5°), carbon dioxide and hydrogen bromide.

The two acids can be separated by slow crystallisation from acetone when about 50 per cent. of the total β-bromo-acid separates as well-developed yellow prisms. From the crust which contains the β-bromo*allo*-acid together with the remainder of the β-bromo-acid, the latter is removed by decomposition with sodium carbonate at 25° and the residual acid crystallised from chloroform. The proportions are roughly 2 parts of the β-acid to 1 of the β-bromo*allo*-acid.

11. Neither acid yields a definite dibromide with a chloroform solution of bromine at room-temperature. The chief products are carbon dioxide, hydrogen bromide and a neutral product melting at 90–91° and presumably *p*-methoxy-αβ-dibromostyrene.

12. If during the addition of hydrogen bromide to the acetylenic acid the temperature is maintained at 25°, the yield of β-bromo-acids is diminished and neutral products are formed. The chief neutral product is methyl *p*-anisyl ketone melting at 38–39° and another is a yellow solid melting at 169–170° and having the composition of tri-*p*-anisylbenzene, $C_6H_3\,(C_6H_4\cdot OCH_3)_3$.

13. By the addition of hydrogen bromide to *p*-methoxyphenylpropiolic acid in benzene suspension the products are the α-bromo-acid melting at 185° and the β-bromo *allo*-acid melting at 145° and the reaction is thus analogous to that between hydrogen bromide and the unsubstituted phenylpropiolic acid in benzene suspension.

14. The introduction of the *p*-methoxy-group into the cinnamic acid molecule has increased its reactivity in several directions.[1]

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[1] Angeli (*Atti. R. Accad. Lincei*, 1924, [v], 33, 109) has drawn attention to the fact that a methoxy substituent activates a halogen atom attached to a carbon atom in the *ortho* or *para* position. Thus *o*- or *p*-$CH_3O\cdot C_6H_4\cdot CH_2\,Br$ when boiled with alcohol yield $CH_3O\cdot C_6H_4\cdot CH_2\cdot OC_2H_5$ and similarly it is stated that the *ortho*- and *para*-methoxycinnamic acid dibromides when boiled with alcohol yield an α-bromo-β-ethoxy-4-methoxy-β-phenylpropionic acid $CH_3O\cdot C_6H_4\cdot CH(OC_2H_5)\cdot CHBr\cdot CO_2H$, but no experimental details are given.

(*a*) The acid and its ester combine with bromine much more readily than the unsubstituted acid and ester.

(*b*) The acid dibromide loses carbon dioxide and hydrogen bromide much more readily than cinnamic acid dibromide, so that it is impossible to obtain theoretical yields of bromo-acids by the action of alcoholic potash on the acid dibromide, much *p*-methoxy-ω-bromostyrene is always formed.

(*c*) So far it has not been found possible to isolate the tribromo-acid, $CH_3O{\cdot}C_6H_4{\cdot}CBr_2{\cdot}CHBr{\cdot}CO_2H$, as it decomposes so readily into carbon dioxide, hydrogen bromide and *p*-methoxy-αβ-dibromostyrene.

(*d*) The ester dibromide is more reactive towards alcoholic potash than ethyl cinnamate dibromide.

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