THE ACTION OF BASES ON αaβ- AND αββ-TRIBROMO-β-PHENYLPROPIONIC ACIDS AND THEIR ESTERS.

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I. INTRODUCTION.

As a result of the investigation of the action of bases on cinnamic acid dibromide (αβ-dibromo-β-phenylpropionic acid) and its esters Sudborough and Thompson[1] were able to show that—

(*a*) Good yields of *a*-bromo- and *a*-bromoallocinnamic acids are obtained by the action of alcoholic potash on cinnamic acid dibromide or its esters.

(*b*) The relative amounts of the two acids change when the acid dibromide is replaced by one of its esters. With the acid dibromide the ratio of *a*-bromo-acid to *a*-bromoallo-acid is usually 1 : 7, but with the methyl ester the ratio is 1 : 0·7.

(*c*) The proportions in which the two products are formed are also affected, but to a less extent, by the nature of the alkali and of the solvent.
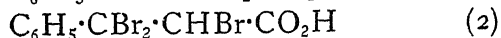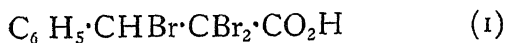
(*d*) When the acid dibromide is used there is a tendency for carbon dioxide to be eliminated and for ω-bromocinnamene, $C_6H_5 \cdot CH:CHBr$, to be formed unless low temperatures are employed. The bromocinnamene is not formed from either the two *a*-bromo acids and hence the elimination of carbon dioxide precedes or is concurrent with the elimination of hydrogen bromide.

(*e*) The formation of bromocinnamene is most marked when aqueous solutions of feeble alkalis are used, e.g. ammonia or sodium carbonate.
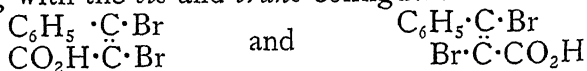
(*f*) With an alcoholic solution of dimethylaniline the chief acid product is cinnamic acid together with some bromocinnamene.

[1] *J. Chem. Soc.*, 1903, **83**, 666.

The object of our experiments has been to study the action of bases, under different conditions, on the compounds formed by the addition of bromine, to the a- and β-bromocinnamic acids and their esters,[1] viz. the $aa\beta$-tribromo-β-phenylpropionic acid (1) and its $a\beta\beta$-isomeride (2).

$$C_6H_5 \cdot CHBr \cdot CBr_2 \cdot CO_2H \qquad (1)$$
$$C_6H_5 \cdot CBr_2 \cdot CHBr \cdot CO_2H \qquad (2)$$

It is clear that, if the reaction proceeds normally and smoothly, the product would be an $a\beta$-dibromocinnamic acid, $C_6H_5 \cdot CBr : CBr.CO_2H$. Two stereoisomeric acids of this composition are actually known corresponding with the *cis* and *trans* configurations

$$\begin{array}{cc} C_6H_5 \cdot C \cdot Br & C_6H_5 \cdot C \cdot Br \\ CO_2H \cdot C \cdot Br & Br \cdot C \cdot CO_2H \end{array} \quad \text{and}$$

and our object has been to ascertain how far the relative proportions in which the two compounds are formed are affected by—

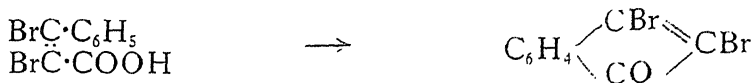(*a*) Replacing the $aa\beta$-acid by its isomeride.

(*b*) Substituting an ester for the free acid.

(*c*) Using different temperatures.

(*d*) Replacing a strong alkali by an organic base. We have also studied the action of water on the $aa\beta$-acid and have examined methods for separating the two dibromocinnamic acids.

The two stereoisomeric dibromocinnamic acids were first prepared by Roser and Haselhoff[2] by the addition of bromine to a chloroform solution of phenylpropiolic acid and were separated by crystallisation from a mixture of chloroform and light petroleum. The a-compound crystallises first in the form of well-defined colourless plates, melting at 139° and when treated with concentrated sulphuric acid does not lose water to form the cyclic compound, 2 : 3-dibromoindenone. From the mother liquor needles of the β-compound separate. This acid melts at 100° and yields dibromoindenone with sulphuric acid, whereas the isomeride only loses water when distilled under reduced pressure with phosphoric anhydride and then gives an 80 per cent. yield of the cyclic compound.[3]

According to Liebermann[4] the β-acid, which yields the 2 : 3-dibromoindenone with concentrated sulphuric acid possesses the *cis* structure.

$$\begin{array}{cc} BrC \cdot C_6H_5 \\ BrC \cdot COOH \end{array} \quad \longrightarrow \quad C_6H_4 \underset{CO}{\overset{CBr}{<}} \overset{}{>} CBr$$

[1] Sudborough and Williams, *This Journal*, 1922, **5**, 107. Lanser, *Ber.*, 1899, **32**, 2477.

[2] *Annalen*, **247**, 139.

[4] *Ibid.*, 1898, **31**, 2096.

II. DECOMPOSITION OF $aa\beta$-AND $a\beta\beta$-TRIBROMO-β-PHENYLPROPIONIC ACIDS WITH WATER.

Both acids are decomposed when boiled with water, the $aa\beta$-acid according to Kinnicutt and Palmer[1] yields 1 : 2-dibromocinnamene, a small amount of a-bromocinnamic acid melting at $132°$ and a little phenyldibromolactic acid melting at $184°$, but no yields are given.

We have carried out experiments by passing air, freed from carbon dioxide, through the boiling mixture of the acid and water placed in a reflux apparatus, drying the evolved gases with calcium chloride and absorbing the carbon dioxide in weighed caustic potash bulbs. The results of several experiments gave 92 per cent. of the theoretical yield of carbon dioxide assuming one molecule of the gas evolved from each molecule of the tribromo-acid originally present.

This proves that the main reaction follows the equation
$$C_6H_5 \cdot CHBr \cdot CBr_2 \cdot CO_2H \longrightarrow C_6H_5 \cdot CBr{:}CHBr + HBr + CO_2$$
and that the amounts of a-bromocinnamic acid and phenyldibromolactic acid must be small.

Michael[2] states that the $a\beta\beta$-tribromo-acid melting at $148°$ is completely decomposed into a neutral oil—presumably $a\beta$-dibromo-cinnamene, when brought into contact with warm water.

This reaction is interesting as an example of the effect of substituents in the molecule of an acid on the readiness with which carbon dioxide is evolved when the acid is warmed with water.

Thus : Nitroacetic acid yields nitromethane [3]
  Trichloroacetic acid yields chloroform [4]
  Tribromoacetic acid yields bromoform [5]
  Triiodoacetic acid yields iodoform [6]
  s-Trinitrobenzoic acid yields s-trinitrobenzene [7]
  s-Trihydroxybenzoic acid yields phloroglucinol [8]

According to Raikow and Tischkow [9] certain substituents such as OH, NO_2, NH_2 in the ortho- and sometimes in the para-position facilitate the removal of carbon dioxide from an aromatic acid when

[1] *Amer. Chem. J.*, 1883, 5, 384. This acid is termed by them β-phenyltribromo-propionic acid but melts at $151°$ and is identical with the acid described in this Journal, 1922, 5, 113.

[2] *Ber.*, 1886, 19, 1380. [6] Angeli, *Ber.*, 1893, 26, 596.

[3] Steinkopf, *Ber.*, 1909, 42, 2030, 3927. [7] *Int. Cong. Applied Chem.* 1909, IV-A.1, p. 94.

[4] Lossen, *Annalen*, 1905, 342, 122. [8] V. Hemmelmayr, *Monatsh.*, 1913, 34, 365.

[5] *Ibid.*, 123.

[9] *Int. Cong. Applied Chem.*, 1909 Section IV-A.1, p. 94.

the acid is gradually heated with phosphoric acid to 200°. The influence of Cl, Br and I is far less marked, the relative values being 1·3, 2·5 and 39·9 as compared with 90 to 100 for the substituents previously named.

V. Hemmelmayr[1] has shown that hydroxyl groups in the meta-positions have a stabilising effect, and Fry[2] has attempted to show that many of these phenomena are explicable on the electronic structure of the benzene molecule.

The elimination of carbon dioxide from cinnamic acid dibromide and the dibromides of the a- and β-bromocinnamic acids may be due to a different cause. The elimination of carbon dioxide in these cases is accompanied by the elimination of hydrogen bromide and it is possible that during the elimination of hydrogen bromide the stability of the molecule is affected and the elimination of carbon dioxide facilitated.

III. EXPERIMENTS ON ESTIMATING CIS-AND TRANS-DIBROMOCINNAMIC ACIDS IN MIXTURES.

A. In the earlier experiments the mixtures of the two acids were separated by crystallisation from a mixture of chloroform and light petroleum.

A preliminary experiment to test the accuracy of this method of separation gave the following results :—

0·437 gram of each acid were mixed and crystallised from a mixture of 3 cc. of chloroform and 6 cc. of light petroleum (boiling at 80°). Three fractions were collected but each consisted of a mixture of colourless flat prisms and sulphur yellow prisms. These were separated by hand and 0·384 gram of *trans* acid and 0·356 gram of *cis* acid were obtained and 0·036 gram of mixture which could not be separated.

The method is obviously not a very convenient or reliable one for quantitative separations.

B. Liebermann's method[3] of treating the mixture of the two acids with concentrated sulphuric acid, converting the *cis* acid into dibromoindenone and isolating and weighing the *trans* acid can also be used. It has the drawback that one of the acids is destroyed, but is useful in estimating small amounts of *cis* acid mixed with *trans* acid.[4]

[1] V. Hemmelmayr, *Monatsh.*, 1913, 34, 365.
[2] Electronic conception of valency and the constitution of benzene, 1921, p. 63.
[3] *Ber.*, 1898, 31, 2096.   [4] *Ibid.*, 1913, 46, 1264.

Two experiments gave the following results :—

(1) 0·881 gram of *cis* acid and 1·033 of *trans* acid were mixed with 20 cc. of concentrated sulphuric acid at 0° and left over night ; the temperature rose to 25°. The mass was poured into water, extracted three times with ether, the ethereal solution shaken three times with 2 N. sodium carbonate solution, the alkaline solution acidified and extracted three times with ether. After drying the ethereal solution with anhydrous sodium sulphate and removal of the ether 1·043 grams of impure *trans* acid melting at 105-123° were obtained.

(2) 0·542 gram of *cis* and 1·177 grams of *trans* acid were treated in exactly the same manner. 1·060 grams of acid were isolated corresponding with 90 per cent. of the original *trans* acid. The melting point was 115-132°.

C. A method devised by Stoermer and Heymann consists in converting the acids into their sodium salts and separating these by means of the difference in solubility of the two salts in 10 per cent. sodium chloride solution at the ordinary temperature.

We have adopted this method of separation in all the later experiments, but as our separations were carried out at a temperature of 25° as compared with Stoermer's temperature of 15° and as also we worked with mixtures containing very different proportions of the two acids we have carried out a series of experiments in order to ascertain the best concentrations of sodium chloride to use at 25° and also to see if the same concentration is advisable for all proportions of *cis* and *trans* mixtures.

The simple method of estimating the percentages of the two components by comparing the solidifying point with those of a solidifying point curve is not available in this case as slight decomposition occurs during melting, and the solidifying point varies according to the length of time of heating.

Table I however gives the rough melting points of different mixtures of the two acids.

Table II gives the results of experiments of separating the two acids at 25° with different concentrations of sodium chloride when the relative proportions of the two acids are *cis : trans* = 1 : 3, and Table III when the proportions are 1·67 : 1.

TABLE I

Melting points of mixtures of cis-*and* trans-*dibromocinnamic acids*

Per cent. *cis* acid	M.P	Per cent. *cis* acid	M.P.
100	98-99°	40	81-113°
90	82-95	30	85-119
80	79-92	20	108-126
70	79-82	10	122-131
60	79-80	0	135-136
50	80-81		

TABLE II

Separation of a mixture of 1·0 gram cis-*acid and 3·0 grams* trans-*acid by difference in solubility of sodium salts in common salt solution*

Experiment No.	Percentage concentration of common salt	Grams of *cis* acid recovered	M.P.	Weight of *trans* acid recovered	M.P.	Weights of *cis* and *trans* acids corrected from melting points		Percentage loss
						cis	*trans*	
R1	10	1·50	82-86°	2·40	133°	1·05	2·85	2·5
R2	11	1·47	83-86	2·43	133-134	1·03	2·87	3·0
R3	12	1·40	82-87	2·47	135-136	1·05	2·82	2·5
R4	15	1·18	84-90	2·72	132-134	0·94	2·96	3·0
R5	20	0·89	87-93	2·99	128-132	0·95	2·93	3·0
R6	20	0·91	85-93	2·97	127-132	0·97	2·91	2·0

TABLE III

Separation of a mixture of 2·5 grams of cis-acid and 1·5 grams of trans-acid by difference in solubility of sodium salts in common salt solution

No. of Experiment	Percentage concentration of common salt	Grams of *cis* acid recovered	M.P.	Grams of *trans* acid recovered	M.P.	Weights corrected by M.P's		Percentage loss
						cis	*trans*	
R7	11	3·17	80-90°	0·74	133-134°	2·54	1·37	2·0
R8	15	2·66	80-90	1·17	129	2·25	1·58	4·0
R9	16	2·54	83-89	1·37	115-125	2·31	1·60	2·0
R10	17	2·20	78-86	1·70	95-115	2·27	1·63	3·0
R11	18	1·69	86-93	2·08	100-110	2·35	1·42	6·0
R12	20	1·50	85-92	2·37	100-110	2·33	1·54	3·0
R13	16	1·91	80-86	1·79	110-125	1·89	1·81	2·5
R14	16	1·98	80-86	1·73	110-125	1·93	1·78	2·5

In all the experiments the concentration of the sodium salts of the dibromo-acids was approximately 10 per cent. and solid sodium chloride was added to give the required concentration of common salt.

In Experiments R13 and R14 2·1 grams of *cis* and 1·7 grams of *trans* acid were used.

The results show that for a mixture of *cis* and *trans* acids in the proportions 1 : 3 the best results are obtained with a 15-20 per cent. sodium chloride solution at 25°. With lower concentrations much of the *trans* salt is found in the filtrate and with higher concentrations much of the *cis* salt is found in the precipitate. The loss of acids during the operation is usually about 3 per cent. If the weights of *cis* and *trans* acids are corrected by means of the melting points given in Table I then the calculated weights agree quite well with the weights taken.

Even with a mixture of 2·5 grams of *cis* and 1·5 gram of *trans* acid the best results are obtained with a 16-17 per cent. solution of sodium chloride.

2

IV. ACTION OF POTASSIUM HYDROXIDE ON ααβ-TRIBROMO-β-PHENYL-PROPIONIC ACID.

A. *Aqueous potassium hydroxide.*

Experiment J12.—Five grams of the acid and 30·4 cc. of aqueous potassium hydroxide solution (two equivalents) were shaken for 66 hours at 15°, but the solution was still distinctly alkaline. The solid was removed and when acidified gave 1·73 grams of the original acid, the aqueous solution was precipitated with barium chloride and from the insoluble barium salt a further 0·79 gram of unaltered acid was recovered. A certain amount of neutral oil was formed and only 0·13 gram of acid was isolated from the soluble barium salts and the melting point was 110-120°.

Experiment B35.—9·7 grams of acid and two equivalents of aqueous potassium hydroxide heated on boiling water bath for five hours gave 3·3 grams of neutral oil containing 56·9 per cent. of bromine and 1·56 equivalents of hydrogen bromide were liberated, practically no organic acid was precipitated on acidifying but 2·52 grams were isolated on extracting with ether. These acids were oily and had a neutralisation equivalent 264, i.e. intermediate between mono- and dibromocinnamic acids.

B. *Alcoholic potassium hydroxide.*

Experiment R5.—From 1·2 grams of the acid shaken for forty hours at 25° with two equivalents of alkali dissolved in 50 per cent. alcohol only oil was isolated.

Experiment J1.—When 10 grams of the acid in 90 per cent. alcohol was mixed with an alcoholic solution containing two equivalents of potassium hydroxide an immediate white precipitate was obtained. When this was removed, washed and acidified, 10 grams of acid were recovered, but the melting point was low, 112 to 140° and only a trace of bromide was found in the aqueous solution.

Experiment J8.—When a similar mixture was shaken for 6·5 hours, the solution was still alkaline and on evaporation on the water bath gave 4·6 grams of neutral oil and only 0·46 gram of acid melting at 110-115°.

Experiment J9.—From 10 grams of acid dissolved in absolute alcohol and two equivalents of potassium hydroxide also dissolved

in absolute alcohol, after shaking for twenty-four hours at 15° and evaporating off alcohol at ordinary temperature, the following results were obtained.

(*a*) 0·25 equivalents of HBr eliminated.

(*b*) 0·08 gram of neutral oil.

(*c*) 3·59 gram of sodium salt insoluble in water.

(*d*) 4·93 gram of sodium salt soluble in water.

The acid liberated from (*c*) was pure $\alpha\alpha\beta$-acid and the acid liberated from (*d*) was mainly $\alpha\alpha\beta$-acid.

Experiment R1.—9·68 grams of acid were shaken with 125 cc. of 0·1 N. alcoholic potassium hydroxide (two equivalents) for ninety-three hours at 25°, and portions of the solution titrated against standard acid at given intervals. Initially 16·6 cc. of acid were required and after ninety-three hours 4·8 cc. indicating the decomposition of about 70 per cent. of the $\alpha\alpha\beta$-acid. After ninety-three hours the insoluble potassium salt was removed and acidified and gave $\alpha\alpha\beta$-acid equal to 30 per cent. of amount taken and from the soluble potassium salts a mixture of acids melting at 100-127° was obtained and if this contained nothing but *cis* and *trans* dibromo-acids would have the composition *cis* : *trans* = 1 : 4. The amount of neutral oil was small.

Experiment R3.—5·12 grams of the tribromo-acid were shaken at 25° for seventy-five hours with 2·5 equivalents of potassium hydroxide in the form of normal solution in 90 per cent. alcohol. After removal of alcohol and isolation of free acids from the potassium salts 2·45 grams or a 61 per cent. yield of mixed acids was obtained melting at 116-128°, together with 0·2 gram of neutral oil. After separation by means of salt solution 0·22 gram of *cis* and 1·82 grams of *trans* acid were isolated. The ratio *cis* to *trans* is 1 : 8·5.

Experiment J2.—Five grams of tribromo-acid were dissolved in alcohol warmed to 75° and a warm solution of alcoholic potash run in. Rapid reaction occurred accompanied by brisk effervescence and odour of brominated cinnamene. The precipitate formed weighed 2·7 grams and consisted of a mixture of potassium carbonate and potassium bromide. From the alcoholic liquor an acid was obtained which melted at 136° after crystallisation from chloroform. It was pure *trans* dibromo-acid but the weight was only one gram. Much neutral oil was formed.

Experiment R4.—0·4 gram of tribromo-acid was shaken for 0·5 hour at 50-55° with two equivalents of potassium hydroxide in the form of 0·1 N solution in alcohol showed 37 per cent. decomposition and after 2·5 hours the product was neutral but when worked up gave as the chief product dibromocinnamene.

Experiment R6.—6·57 grams of tribromo-acid were shaken for three hours at 50° with 2·01 equivalents of potassium hydroxide in the form of 0·8 N. alcoholic solution and when worked up gave one gram of unaltered *ααβ*-acid and 4·6 grams of mixed dibromo-acids melting at 102-120° and corresponding with a mixture of *cis* and *trans* acids in the proportion 1 : 3.

As these preliminary experiments showed that the reaction is too slow at 25° and too vigorous at 75°, but at 50-55° proceeds smoothly when the alcoholic potash is not too dilute, a series of experiments was carried out at 50-60° and the results obtained are recorded in Table IV.

V. ACTION OF POTASSIUM HYDROXIDE ON *αββ*-TRIBROMO- PHENYLPROPIONIC ACID.

Experiment J14.—Ten grams of the tribromo-acid dissolved in a little absolute alcohol were mixed with a solution of two equivalents of potassium hydroxide also dissolved in absolute alcohol, the temperature rose from 15-35°, a white precipitate was formed immediately and after a short time the solution was practically neutral, 1 cc. of the alcoholic potash was then added and the mixture shaken for two minutes and remained alkaline. After removal of the alcohol on the water bath the residue weighed 11·85 grams. This was dissolved in water and the neutral oil extracted with ether. The following values were obtained :—

Weight of neutral oil = 0·42 gram.

Hydrogen bromide eliminated = 1·0 equivalent.

Total acids = 6·07 grams as compared with a theoretical value of 7·9 grams.

The acids crystallised from a mixture of chloroform and light petroleum gave 1·97 grams of flat colourless plates melting at 135-136° and 3·51 grams of yellow needles melting at 90-94°. This gives a ratio of *cis* : *trans* = 1 : 0·56.

TABLE IV

Decomposition of aaβ-tribromo-β-phenylpropionic acid with normal alcoholic potassium hydroxide and sodium hydroxide

No. of Experiment	Grams of aaβ acid	Equivalents of potassium hydroxide	Temperature	Time in hours	Grams of mixed acids obtained	Percentage yield	Grams of oil	Concentration of common salt used for separation	Grams of cis acid	Grams of trans acid	Ratio cis : trans	Remarks
R7	5·0	2·5	50-55°	7	2·62	66	...	10	0·19	1·79	1 : 9	R7 to R31 with potassium hydroxide Occasional shaking by hand.
R8	10·0	2·5	50-55	7	4·77	60	...	10	1·40	3·22	1 : 2·3	do. do.
R9	10·0	2·5	53	10	2·85	36	1·3	20	0·19	2·61	1 : 13·5	oily acid not taken into account.
R10	10·0	2·5	53	10	2·61	33	1·0	20	0·02	2·34	1 : 120	
R11	10·0	2·5	56	6	4·68	59	0·82	20	0·70	3·76	1 : 5·4	R11 to R18 continuous stirring
R12	10·0	2·5	56	6	4·19	53	0·77	20	1·06	2·98	1 : 3	by means of air current saturated
R13	10·0	2·5	56	6	6·63	84	0·17	20	1·59	4·74	1 : 3	with alcohol.
R14	10·0	2·0	60	4	3·34	42	2·12	20	0·65	2·48	1 : 4	
R15	10·0	2·5	58	4	5·20	66	0·44	20	1·19	3·61	1 : 3	
R16	10·0	2·5	60	4	5·42	69	0·86	20	1·33	3·87	1 : 3	
R17	15·6	3·0	56	6	6·41	52	...	20	0·74	5·12	1 : 7	
R18	10·0	2·0	60	5·5	4·10	52	...	20	1·02	2·73	1 : 2·8	
R26	7·83	2·5	25	65	4·20	68	...	20	1·06	2·90	1 : 2·8	R26 to R31. Continuous mechanical stirring. Apparatus provided with mercury trap.
R27	8·13	2·3	25	65	3·91	61	...	20	1·17	2·39	1 : 2·5	
R28	5·95	2·5	25	48	3·24	70	...	20	0·65	2·42	1 : 3·7	
R30	3·89	2·5	25	92	2·55	83	...	20	0·67	1·72	1 : 2·6	In dark.
R31	4·18	2·5	25	48	2·69	82	...	20	0·72	1·83	1 : 2·5	do.
R32	7·37	2·0	50	24	4·53	80	...	10	0·77	2·95	1 : 4	R32 to R37 with sodium hydroxide. Stirred by air.
R33	7·48	2·0	50	18	4·50	80	...	16	0·92	3·10	1 : 3·5	do. do.
R35	7·40	2·0	55	21	4·30	75	...	16	0·92	3·17	1 : 3·5	do. do.
R37	5·36	2·0	75	6	1·58	40	...	16	0·14	1·23	1 : 9	Not stirred.

Experiment J15.—In this experiment the alcoholic solution of the tribromo-acid was cooled to $-5°$ and two equivalents of potassium hydroxide dissolved in alcohol run in. The temperature rose to 18° and then fell to 3°. One equivalent of hydrogen bromide was eliminated and 7·4 grams of mixed acids corresponding with a 94 per cent. yield were obtained and on crystallising from chloroform and light petroleum 2·59 grams of colourless plates melting at 135–136° and 4·32 of yellow needles corresponding with a ratio *cis* : *trans* of 1 : 1·7.

Further experiments are given in Table V.

VI. DECOMPOSITION OF METHYL $aa\beta$-TRIBROMO-β-PHENYLPROPIONATE WITH ALCOHOLIC POTASH.

Experiment J4.—When a solution of five grams of the ester in alcohol was mixed with a slight excess of alcoholic potash (two equivalents) the temperature rose from 15 to 28° and a fine precipitate gradually separated. The mixture was allowed to stand, then heated to 50° and again allowed to stand. The precipitate weighed 2·64 grams and when acidified gave 1·2 grams of acid ($aa\beta$-acid) and the alcoholic liquid evaporated gave 3·30 grams of residue from which 1·3 grams of acid melting at 118° were obtained on acidifying.

Experiment J11.—Ten grams of the acid dissolved in absolute alcohol was shaken with two equivalents of alcoholic potash at room temperature during twenty-four hours. At the end the solution was neutral, so 1 cc. of alcoholic potash was added and the shaking continued for four hours, then another 1 cc. added and the shaking continued for six hours, when the liquid was still alkaline. After removal of the alcohol at the ordinary temperature 12·9 grams of residue were obtained. This was completely soluble in water and the solution acidified gave 5·95 grams of mixed acids melting at 103-115°. On crystallising this mixture from chloroform and light petroleum 3·75 grams of *trans* acid were isolated melting at 133-134° but very little pure *cis* acid could be isolated. The ratio *cis* to *trans* is 1 : 1·8.

Experiment J13.—This was similar to J11, but the alcohol was removed on the water bath. 0·94 equivalents of hydrogen bromide were eliminated, only a very little neutral oil was formed and 5·73 grams of mixed acids were isolated corresponding with a 75 per cent. decomposition. On cystallising, 2·91 grams of colourless *trans* acid were isolated, but pure *cis* acid could not be isolated from the mother liquor. Assuming the pasty residue was *cis* acid the proportion is *cis* : *trans* = 1 : 1·2.

TABLE V

Decomposition of aββ-tribromo-β-phenylpropionic acid with alcoholic potash (0·5 N.)

No. of Experiment	Grams of acid taken	Equivalents of alkali	Temperature	Time in hours	Grams of mixed acids	Percentage yield	Gram of oil	Concentration of sodium chloride	Grams of *cis* acid	Grams of *trans* acid	Ratio *cis* : *trans*	REMARKS
R4	5·81	2·0	−10 to +15°	1·0	3·4	74	0·42	11	1·61	1·59	1 : 1	Occasional shaking by hand.
R5	5·81	2·2	−10 to +15°	1·0	4·9	91	0·06	11	2·30	1·77	1 : 0·8	do.
R6	5·81	2·2	−10 to +15°	1·0	3·83	83	...	16	1·60	1·73	1 : 1·7	do.
R7	5·81	2·2	−10 to +15°	1·0	4·1	89	...	16	1·49	2·15	1 : 1·5	do.
R8	5·81	2·2	−10 to +15°	1·5	3·22	70	...	16	1·30	1·68	1 : 1·3	do.
R9	5·81	2·5	− 5 to − 3	1·0	4·03	88	...	16	1·90	1·91	1 : 1	do.
R10	5·81	2·3	− 3 to 0	1·0	3·66	80	...	16	1·41	1·79	1 : 1·3	do.
R11	5·81	2·2	− 3 to 0	1·0	3·93	86	...	16	1·58	2·16	1 : 1·4	do.

Experiment J16.—Twenty grams of ester were used and the mixture was shaken for 18·5 hours, after which the solution was only faintly alkaline. 0·95 equivalents of HBr were eliminated, and 12·73 grams of mixed acids, including 1·17 grams obtained by extraction with ether, were isolated corresponding with an 83 per cent. decomposition. From the mixture 6·96 grams of pure *trans* acid were obtained by crystallisation, giving a ratio of *cis* : *trans* = 1 : 1·2.

Further experiments with alcoholic potash and one with alcoholic soda are given in Table VI.

VII. DECOMPOSITION OF METHYL $\alpha\beta\beta$-TRIBROMO-β-PHENYLPROPIONATE WITH ALCOHOLIC POTASH.

Experiment J17.—A solution of 14·1 grams of the tribromo-ester in absolute alcohol was mixed with an alcoholic solution of two equivalents of potassium hydroxide at 15°. The temperature rose to 21° and a white precipitate at once made its appearance. After shaking for ten minutes the solution was neutral and the alcohol was then removed on the water bath. 0·99 equivalents of hydrogen bromide were eliminated, some neutral oil was formed and 7·4 grams of mixed acids, corresponding with a 74 per cent. decomposition were isolated. On crystallising, 2·95 grams of colourless *trans* acid were isolated giving a ratio of *cis* : *trans* = 1 : 0·7.

Experiment J18.—Similar to J17. 3·89 grams of neutral oil were obtained and 6·65 grams of mixed acids melting at 75-91° and from this mixture only 1·52 grams of pure *trans* acid was obtained on crystallisation giving a ratio *cis* : *trans* = 1 : 0·4.

The results of other experiments are given in Table VII.

VIII. ACTION OF DIMETHYLANILINE ON THE TRIBROMO-ACIDS AND THEIR METHYL ESTERS, AND ALSO ON CINNAMIC ACID DIBROMIDE AND ITS METHYL ESTER.

A. *Cinnamic acid dibromide.*—Attention has already[1] been drawn to the fact that when cinnamic acid dibromide, $\alpha\beta$-dibromo-β-phenyl-propionic acid is heated with an alcoholic solution of dimethylaniline, bromine and not hydrogen bromide appears to be eliminated as the acid product formed is cinnamic acid itself.

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[1] Sudborough and Thompson, *J. Chem. Soc.*, 1903, 83, 681.

TABLE VI

Decomposition of Methyl αaβ-tribromo-β-phenylpropionate with alcoholic potash

Weight of ester = 10·4 grams and normality of potash = 1

No. of Experiment	Equivalents of potassium hydroxide	Temper- ature	Time in hours	Grams of mixed acids	Percentage decompo- sition	Grams of neutral oil	Concen- tration of Sodium Chloride	Grams of *cis* acid	Grams of *trans* acid	Ratio *cis* : *trans*
R I	2·5	58°	5	6·27	79	0·08	20	1·30	4·61	1 : 3·5
R II	2·0	58	5	5·30	67	0·62	20	0·97	3·76	1 : 4·0
R III	2·03	55	3·5	4·29	54	2·52	20	0·77	3·00	1 : 4·0
R IV	2·03	55	3·5	5·89	73	0·52	20	1·20	4·03	1 : 3·3
R V	2·03	60	3·5	4·90	62	0·36	20	0·88	3·70	1 : 4·2
R VI	2·03	60	3·5	5·86	73	0·06	20	1·31	4·35	1 : 3·3
Alcoholic Sodium hydroxide										
R 39 *	2·5	75	4	2·34	80	...	16	0·58	1·76	1 : 3

* 3·74 grams.

83

TABLE VII

Decomposition of Methyl αββ-tribromo-β-phenylpropionate with alcoholic potash

4·01 gram of ester used and normality of the alcoholic potash = 0·5.

No. of Experiment	Equivalents of potassium hydroxide	Temperature	Time in hours	Gram of mixed acids	Percentage decomposition	Concentration of sodium chloride	Grams of *cis* acid	Grams of *trans* acid	Ratio *cis* : *trans*	Remarks
R1	2·2	− 15 to + 6 and 25°	3	2·92	95	16	1·09	1·70	1 : 1·6	Stirred by means of air saturated with alcohol.
R2	2·2	25-37	12	2·90	95	16	1·14	1·62	1 : 1·4	
R3	2·2	25-37	12	1·98	65	16	0·53	1·32	1 : 2·5	
R4	2·2	25-37	12	2·73	90	16	1·09	1·54	1 : 1·4	
R5	2·4	25-37	12	2·60	85	16	1·05	1·41	1 : 1·4	
R6	2·4	25-37	12	2·87	93	16	1·07	1·61	1 : 1·5	
R7	2·4	25-37	12	2·73	90	16	0·92	1·68	1 : 1·8	

Experiment R23.—A mixture of 1·28 grams of cinnamic acid dibromide, 1·33 grams of dimethylaniline (two equivalents) and 10 cc. of benzene were heated for seven hours in a reflux apparatus on a boiling water bath. It was found that 1·16 equivalents of hydrogen bromide had been eliminated, 0·092 grams of a neutral oil formed and 0·29 grams of acid were isolated. The melting point 132° and the neutralisation equivalent proved this acid to be cinnamic acid and confirmation was obtained in the fact that when mixed with cinnamic acid its melting point was unaffected.

Experiment R34.—16·46 grams of the acid, 13 grams of dimethylaniline (2 mols.) and 20 cc. of benzene were heated in a reflux apparatus for nine hours on a boiling water bath. The mixture was diluted with ether and shaken with sodium carbonate, the alkaline extract was acidified with nitric acid and 6·2 grams of acids melting at 127-129° were obtained. The (after recrystallisation) neutralisation equivalent 154, and mixed melting point proved the acid to be cinnamic acid. The filtrate from the acids contained 1·07 equivalents of soluble bromide.

The ethereal solution was washed with dilute hydrochloric acid, then with water, dried and the ether removed. 2·37 grams of neutral oil with a bromine content of 26·1 per cent. were obtained. This oil is evidently a mixture of cinnamene and α-bromocinnamene (Br = 43·1). When distilled the oil gave two fractions one boiling up to 110° and the other at 206°, under a pressure of 683 mm. The hydrochloric acid solution when made alkaline and extracted with ether gave 14·9 grams of base, which was distilled and gave 7·9 grams of dimethylaniline (190°) and 6 grams of solid base melting at 52-54° [1].

B. *Methyl αβ-dibromo-β-phenylpropionate.*

Experiment 24.—2·26 grams of ester, 1·57 grams of base (two equivalents) and 10 cc. of benzene were heated for seven hours on the boiling water bath. 1·02 equivalents of hydrogen bromide were liberated and 0·86 gram of bromine-free ester were liberated, corresponding with an 80 per cent. yield of methyl cinnamate. The recovered base was found to contain bromine and weighed 1·38 grams.

Experiment 41.—7·74 grams of ester, 3·93 grams of base (1·2 equivalents) and 20 cc. of benzene were boiled in a reflux apparatus during twenty-four hours. The products isolated were—(a) 4·00 grams of neutral ester containing 0·6 per cent. of bromine. On standing the ester gave 3·6 of crystals melting 35-36° the melting point of

[1] The melting point of pure *p*-bromodimethylaniline is 55°.

methyl cinnamate. (*b*) 5·6 grams of base melting at 50-53° after distillation (b.p. 252-253° /683 mm.). (*c*) 0·96 equivalent of hydrogen bromide was eliminated.

C. *aaβ-tribromo-β-phenylpropionic acid.*

Experiment 1.—3·88 grams of the tribromo-acid, 4·5 grams of base (four equivalents) and 10 cc. of alcohol were heated for five hours in a reflux apparatus on a boiling water bath. Only 0·4 gram of an acid could be isolated. The chief product was 2·1 grams of neutral oil.

Experiment 19.—10 grams of the acid, 7 grams of base (2·3 equivalents) and 25 cc. of benzene were heated for 5 hours on the boiling water bath. It was found that 0·98 equivalent of hydrogen bromide had been eliminated and 6·7 grams of neutral oil were isolated. The boiling point (250° under pressure of 683 mm.) and bromine content, 60·9 compared with the theoretical value 61·1 proved this to be dibromocinnamene. The recovered base weighed 6·8 grams and on distillation gave 5·6 grams boiling at 186-196° (dimethylaniline).

Experiment 15.—A mixture of acid (1·86 grams), base (1·16 grams) and benzene 5 cc. were shaken at 23-25° during ninety-one hours. 1·04 equivalents of hydrogen bromide were eliminated, a trace of an acid melting at 128-129° presumably *a*-bromocinnamic acid, and 1·14 grams of neutral oil were isolated. This oil was dibromocinnamene as it contained 60·3 per cent. of bromine as compared with the theoretical value 61·1 per cent.

D. *Methyl aaβ-tribromo-β-phenylpropionate.*

Experiment 3.—4·68 grams of ester, 5·5 grams of base (four equivalents) and 15 cc. of alcohol were heated for four hours on the boiling water bath. 1·08 equivalents of hydrogen bromide were eliminated and 2·68 grams of an ester boiling at 153-155° under a pressure of 5·5 mm. and containing 37·2 per cent. of bromine. The theoretical yield of product for methyl *a*-bromocinnamate is 2·81, its boiling point is 155-157° under 7 mm. pressure and its bromine content is 33·2 per cent. It is thus clear that the main product is an ester of a monobromo- and not a dibromocinnamic acid. From the bromine content the composition of the product would be 75 per cent. methyl *a*-bromocinnamate and 25 per cent. methyl dibromocinnamates. This indicates that the organic base has removed Br_2 rather than HBr from the original tribromo-ester.

Experiment 4.—This was similar to No. 3 but larger amounts of materials were used, viz. 17·0 grams of the tribromo-ester, 20 grams of base and 50 cc. of alcohol.

0·96 equivalents of hydrogen bromide were found in the liquid and 10·04 grams of ester were isolated corresponding with a theoretical value of 10·2 grams if the product is methyl *α*-bromocinnamate. The percentage of bromine in the ester was again 37·2 (theory 33·2) and when hydrolysed with dilute alkali an acid melting at 128° was obtained.

When the base was isolated and distilled it gave first unaltered dimethylaniline boiling at 80° under a pressure of 6 mm. and finally a solid brominated product melting at 52° and corresponding with *p*-bromodimethylaniline which melts at 55°.

Experiment 11.—10·3 grams of ester, 3·1 grams of base (one equivalent) and 40 cc. of benzene were heated for four hours on a boiling water bath. The yield of ester from the product was 7·1 grams whereas the theoretical yield for methyl *α*-bromocinnamate is 6·2. The bromine content of the ester was 39·6 as compared with the theoretical value 33·2. The base when isolated solidified and proved to be *p*-bromo-dimethylaniline as it melted at 52 to 55°.

E. *αββ-tribromo-β-phenylpropionic acid.*

Experiment 40.—8·65 grams of acid, 6·34 grams of dimethylaniline (2 mols.) and 7 cc. of benzene were heated on the boiling water bath for seven hours ; at the beginning copious effervescence occurred. 5·76 grams of neutral oil were obtained boiling at 251-254° and corresponding with *αβ*-dibromocinnamene. 0·63 gram of oily acids with an equivalent of 264 was also isolated.

F. *Methyl αββ-tribromo-β-phenylpropionate.*

Experiment 16.—6·68 grams of ester, 5·79 grams of base (2·9 equivalents) and 30 cc. of benzene were shaken for 336 hours at 20-25°. Only 0·33 equivalents of hydrogen bromide were eliminated and 5·57 grams of ester were isolated as compared with the theoretical value of 4·01 grams for methyl *β*-bromocinnamate. When distilled the product evolved bromine indicating the presence of unaltered tribromo-ester.

Experiment 22.—3·14 grams of ester, 2·68 grams of base (three equivalents) and 20 cc. of benzene were heated for eight hours on a

boiling water bath. 0·96 equivalents of hydrogen bromide were eliminated and 1·86 grams of an ester were isolated corresponding with 1·89 grams for methyl β-bromocinnamate. The ester boiled at 135-140° under a pressure of 4·4 mm. and contained 35·9 per cent. of bromine as compared with the theoretical value 33·2.

Experiment 30.—14·5 grams of ester, 4·44 grams of base (one equivalent) and 10 cc. of benzene were heated for seven hours on the boiling water bath. 0·95 equivalents of hydrogen bromide were eliminated and 8·86 grams of ester were isolated (theoretical value 8·70). The boiling point of the ester was 140-142° under a pressure of 3 mm. corresponding with methyl β-bromocinnamate. The recovered base was solid (m. p. 52-55°) and weighed 6·5 grams whereas if the bromination had been complete the theoretical value should be 7·4 grams.

IX. DECOMPOSITION OF METHYL αaβ-TRIBROMO-β-PHENYLPROPIONATE BY OTHER BASES.

Experiment 6.—3·15 grams of ester, 4 grams of quinoline (four equivalents) and 10 cc. of 90 per cent. alcohol were heated for four hours on a boiling water bath. 1·46 equivalents of hydrogen bromide were eliminated and 1·64 grams of ester containing 36·8 per cent. of bromine were obtained. On hydrolysis the ester gave an acid with a neutralisation equivalent of 236 and a melting point 130°. The ester isolated was, therefore, mainly methyl α-bromocinnamate. The high hydrogen bromide value is probably due to the decomposition of the brominated quinoline.

Experiment 9.—7·81 grams of ester, 8 grams of aniline (four equivalents) and 30 cc. of 98 per cent. alcohol were heated for 3·5 hours. 0·99 equivalents of hydrogen bromide were eliminated and 4·71 grams of ester boiling at 155-156° under 6 mm. isolated. The percentage of bromine in the ester was 38·6 as compared with the theoretical value 33·2 for methyl α-bromocinnamate.

X. DISCUSSION OF RESULTS.

1. The elimination of carbon dioxide from the αaβ-acid by boiling with water proceeds almost quantitatively according to the equation :—

$$C_6H_5 \cdot CHBr \cdot CBr_2 \cdot CO_2H = C_6H_5 \cdot CBr : CBr + HBr + CO_2 \text{—(1)}$$

as 92 per cent. of the theoretical amount of carbon dioxide can be absorbed by potassium hydroxide.

2. Of the three methods available for estimating the amounts of *cis*- and *trans*-dibromocinnamic acid in mixtures, viz.

(*a*) Separating by fractional crystallisation from a mixture of chloroform and light petroleum (b.p. 80-100°).

(*b*) Conversion of the *cis* acid into the neutral dibromoindenone by treatment with cold concentrated sulphuric acid.

(*c*) Separation of the sodium salts by means of common salt solutions in which the salt of the *cis* acid is readily soluble and that of the *trans* acid very sparingly soluble. The last is the most convenient for most purposes. Both acids can be recovered and the separation is fairly clean when the concentration of the common salt is 16 to 20 per cent., that of the sodium salts of the organic acids 10 per cent. and the temperature 25°.

3. Strong alkalis such as sodium or potassium hydroxide in alcoholic solution eliminate hydrogen bromide from either the $\alpha\alpha\beta$-tribromo-β-phenylpropionic acid or the $\alpha\beta\beta$-isomeride and produce mixtures of the two stereoisomeric dibromocinnamic acids

$$C_6H_5 \cdot CHBr \cdot CBr_2 \cdot CO_2H \longrightarrow HBr + C_6H_5 \cdot CBr : CBr \cdot CO_2H$$

$$C_6H_5 \cdot CBr_2 \cdot CHBr \cdot CO_2H \longrightarrow HBr + C_6H_5 \cdot CBr : CBr \cdot CO_2H.$$

4. The reaction is complicated by the readiness with which carbon dioxide is also eliminated and dibromocinnamene formed as represented in equation 1 above.

Conditions which facilitate the elimination of carbon dioxide are—

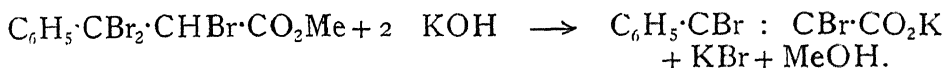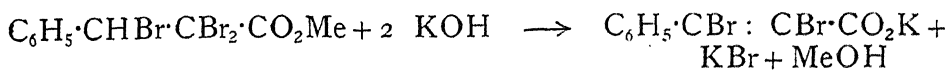(*a*) replacement of alcohol by water.

(*b*) using a dilute, e.g. 0·1 N. solution of the alkali.

(*c*) comparatively high temperatures.

By stirring during 18 to 24 hours at 50° or shaking ninety-two hours at 25° it is possible in the case of the $\alpha\alpha\beta$-acid to obtain an 80 per cent. yield of the mixed dibromo-acids, and from the isomeric $\alpha\beta\beta$-acid 90 per cent. yields of mixed dibromo-acids can be obtained by working at −5 to +15°.

5. Similar reactions take place when the esters are shaken with an alcoholic solution of 2·0 to 2·5 equivalents of alkali. The product

in both cases consists of a mixture of the two stereoisomeric $\alpha\beta$-dibromocinnamic acids.

$$C_6H_5 \cdot CHBr \cdot CBr_2 \cdot CO_2Me + 2\ KOH \longrightarrow C_6H_5 \cdot CBr : CBr \cdot CO_2K + KBr + MeOH$$

$$C_6H_5 \cdot CBr_2 \cdot CHBr \cdot CO_2Me + 2\ KOH \longrightarrow C_6H_5 \cdot CBr : CBr \cdot CO_2K + KBr + MeOH.$$

In the case of the $\alpha\alpha\beta$-ester 75-80 per cent. yields of mixed dibromo-acids can be obtained by warming the mixture for 4 to 5 hours at 55 to 60° and with the $\alpha\beta\beta$-ester 95 per cent. yields can be obtained by keeping the mixture at —15 to + 6° for three hours and then at ordinary room temperature for twelve hours.

6.   It is clear that hydrogen bromide is eliminated more readily from the $\alpha\beta\beta$-acid and its ester than from the isomeric $\alpha\alpha\beta$-acid and its ester under the influence of alcoholic potash. This is in agreement with the well-known fact that an $\alpha\beta$-dibromo-substituted acid by loss of hydrogen bromide gives the α-substituted olefinic acid and not the β-isomeride.

The tribromo-acid which loses its hydrogen bromide the more readily is also the acid from which the neutral dibromocinnamene is the more readily obtained by the action of water.

7.   The relative proportions of *cis*- and *trans*-dibromo-acids is not appreciably affected by—

(*a*) replacement of alcoholic potash by alcoholic soda;

(*b*) substituting an ester for the free tribromo-acid.

This latter point is of interest as when cinnamic acid dibromide is used the relative proportions of the two stereoisomeric *a*-bromo-cinnamic acids is considerably affected when the ester is used in place of the acid.
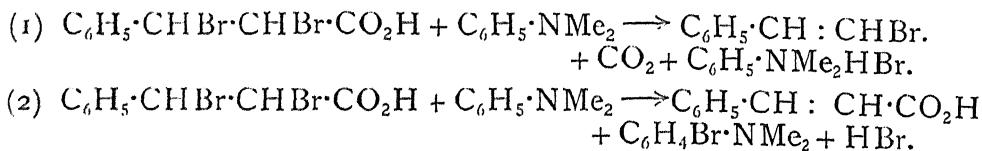
8.   By the action of alcoholic potash on the two isomeric $\alpha\alpha\beta$- and $\alpha\beta\beta$-acids the relative proportions of *cis*- and *trans*-dibromocinna-mic acids are quite different.

With the $\alpha\alpha\beta$-acid or its ester the ratio of *cis*- to *trans*-acid is 1 : 3·0, whereas with the $\alpha\beta\beta$-acid or its ester the proportion is 1 : 1·4.

When much neutral oil—dibromocinnamene—is formed the ratio can fall to 1 : 9 or even 1 : 12.

9. The reaction with an organic base such as dimethylaniline appears to be different from that of a strong alkali like alcoholic potash.
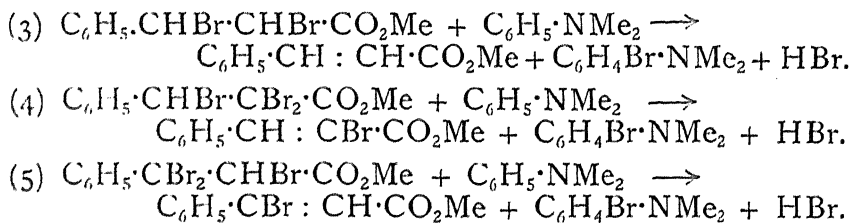
With cinnamic acid dibromide and dimethylaniline two reactions occur as represented by the two equations :—

(1) $C_6H_5 \cdot CHBr \cdot CHBr \cdot CO_2H + C_6H_5 \cdot NMe_2 \longrightarrow C_6H_5 \cdot CH : CHBr.$
$+ CO_2 + C_6H_5 \cdot NMe_2HBr.$

(2) $C_6H_5 \cdot CHBr \cdot CHBr \cdot CO_2H + C_6H_5 \cdot NMe_2 \longrightarrow C_6H_5 \cdot CH : CH \cdot CO_2H$
$+ C_6H_4Br \cdot NMe_2 + HBr.$

The first reaction is similar to that with potassium hydroxide the products formed being monobromocinnamene, carbon dioxide and hydrogen bromide. About 20 per cent. of the dibromide appears to react in this manner.

The second reaction is quite different. Bromine is eliminated from the dibromide and reacts with the base forming *p*-bromodimethylaniline and hydrogen bromide. About 60 per cent. of the dibromide appears to react in this manner. At the same time carbon dioxide is eliminated and some cinnamene is formed. With the $\alpha\alpha\beta$-and $\alpha\beta\beta$-tribromo-acids the reaction is mainly of the type represented by equation (1). The products are chiefly neutral oil, dibromocinnamene, carbon dioxide and hydrogen bromide. Small amounts of acids are also formed, but the mixture is oily and appears to be a mixture of mono-and dibromocinnamic acids.

With the esters on the other hand the main reaction consists in the elimination of bromine from the ester and the production of *p*-bromodimethylaniline as represented in equations (3) to (5.)

(3) $C_6H_5 \cdot CHBr \cdot CHBr \cdot CO_2Me + C_6H_5 \cdot NMe_2 \longrightarrow$
$C_6H_5 \cdot CH : CH \cdot CO_2Me + C_6H_4Br \cdot NMe_2 + HBr.$

(4) $C_6H_5 \cdot CHBr \cdot CBr_2 \cdot CO_2Me + C_6H_5 \cdot NMe_2 \longrightarrow$
$C_6H_5 \cdot CH : CBr \cdot CO_2Me + C_6H_4Br \cdot NMe_2 + HBr.$

(5) $C_6H_5 \cdot CBr_2 \cdot CHBr \cdot CO_2Me + C_6H_5 \cdot NMe_2 \longrightarrow$
$C_6H_5 \cdot CBr : CH \cdot CO_2Me + C_6H_4Br \cdot NMe_2 + HBr.$

At the same time, however, a reaction analogous to that with alcoholic potash also occurs, but only to a small extent, so that the ester formed is a mixture, in the first case of methyl cinnamate with a little methyl monobromocinnamate and in the second and third cases of monobromocinnamate with a little dibromocinnamates. The formation of such mixtures is shown by the bromine contents and boiling points of the products.

10.   Other organic bases such as aniline and quinoline appear to behave in a manner exactly similar to dimethylaniline.

11.   The reaction between dimethylaniline and the esters is of interest as the elimination of bromine from $\alpha\beta$-dibromo-compounds under the influence of bases is not a common phenomenon.   An example of such elimination has recently been noticed by Chandrasena and Ingold [1] who obtained glutaconic acid by the action of sodium hydroxide on glutaconic acid dibromide and muconic acid by the action of methyl alcoholic potassium hydroxide on methyl muconate dibromide.

Gupta and Thorpe [2] have also shown that certain dibromo-derivatives such as ethyl dibromomalonate, $CBr_2(CO_2Et)_2$, and dibromo-cyanoacetamide, $CN \cdot CBr_2 \cdot CO \cdot NH_2$, act as brominating agents towards dimethylaniline losing one atom of bromine and yielding p-bromo-dimethylaniline but no hydrogen bromide.

Note.—The preliminary experiments were made by Mr. W. Jones during the session 1907-08 in the Edward Davies Chemical Laboratories, Aberystwyth, and the experiments made by him are characterised in this paper by the letter J.

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