22. *A Study of the Action of Bromine on the Silver Salts of Organic Acids.*

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The action of bromine, dissolved in dry carbon tetrachloride, on the silver salts of five classes of organic acid has been investigated. (1) Monobasic aliphatic acids are decarboxylated with production of monobromides. This reaction gives a promising method of preparing *neo*pentyl halides, and is being further investigated. (2) Monobasic aromatic acids give less monobromide, and considerable quantities of the ester (formed by the loss of two atoms of silver and one molecule of carbon dioxide, from two molecules of the silver salt). (3) Monobasic aliphatic keto-acids, having the keto-group in or beyond the β-position, give about 50% of the monobromide, together with free parent acid and its bromination products. (4) Dibasic aliphatic acids give dibromides and/or lactones and bromo-acids, according to their structure. This reaction provides a method, better than any hitherto described, of obtaining alkylene dibromides where the bromine atoms are five or more carbon atoms apart. (5) Dibasic aromatic acids are sometimes unaffected by the reagent; others give some of the expected dibromide and larger quantities of the free parent acid.

For groups (1) and (2), and for some acids of group (4), the main reaction products from one or more members have been fully identified, either as known crystalline substances or, where they are oils, by conversion into known crystalline derivatives. The essentially similar analyses and properties of the products from other members of these groups point to the reactions being parallel. In group (3) and in the remaining acids of group (4) this procedure has been omitted owing to the unsatisfactory nature of the reaction. In group (5) little reaction occurred and crystalline products were recovered.

α-iso*Amyladipic* (*7-methyloctane*-1 : 4-*dicarboxylic*), m. p. 67—68°, and α-iso*amylglutaric* (6-*methylheptane*-1 : 3-*dicarboxylic*) *acid*, an oil, are described.

AN earlier paper (Oldham and Ubbelohde, *J.*, **1941**, 368) describes a new series of acyl derivatives of iodine prepared by the action of this halogen on the silver salts of aliphatic monobasic acids in the entire absence of water.

Although the action of bromine on the silver salts of the higher fatty acids has been studied by Mehta, Mehta, and Thosar (*J. Indian Chem. Soc.*, Indian Edn., **1940**, 137) and that on the half esters of many dibasic aliphatic acids by Hunsdiecker and Hunsdiecker (*Ber.*, **1942**, **75**, *B*, 291), very little has been published on the behaviour of the silver salts of aromatic or dibasic aliphatic acids. The work of the German authors on silver sebacate and adipate is in good agreement with the work described below. The behaviour of the following groups of compounds is now described: (1) monobasic aliphatic acids, (2) monobasic aromatic acids, (3) monobasic aliphatic monoketo-acids, (4) dibasic aliphatic acids, and (5) dibasic aromatic acids.

The advantages of the bromine reaction over the iodine reaction lie in the greater solubility of bromine, the greater speed of reaction, the production of fewer by-products, and the greater stability and lower boiling points of the bromo-compounds. The disadvantages are that with unsaturated acids it forms additive compounds, and with aliphatic keto-acids it has now been shown to form bromo-substituted derivatives with the consequent evolution of hydrogen bromide which, in turn, decomposes the silver salt to the original acid, causing a diminution of the yield. The choice of solvent for bromine is limited practically to carbon disulphide and carbon tetrachloride. In apparent disagreement with Hunsdiecker and Hunsdiecker (*loc. cit.*), bad yields were obtained in carbon disulphide, large quantities of the acid being recovered unchanged. Carbon tetrachloride was used throughout the present work, although the closeness of its boiling point to that of the lower alkyl bromides made the isolation of these products laborious.

It has already been shown (Oldham and Ubbelohde, *loc. cit.*) that the reaction of iodine with the silver salts of the monobasic aliphatic acids proceeds according to the equation

$$3R{\cdot}CO_2Ag + 2I_2 \longrightarrow (R{\cdot}CO_2)_3I + 3AgI \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

and that the unstable iodine acyls decompose rapidly in two ways simultaneously, the proportion of iodine present determining whether the ester, $R{\cdot}CO_2R$ (hereafter referred to as the Simonini ester), or the alkyl iodide, RI, predominate in the product:

$$(R{\cdot}CO_2)_3I \longrightarrow R{\cdot}CO_2R + RI + 2CO_2 \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$(R{\cdot}CO_2)_3I + I_2 \longrightarrow 3RI + 3CO_2 \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

It will be seen from equation (1) that three equivalents of iodine suffice to convert all the silver present into silver iodide; if an excess of iodine is present, further reaction occurs according to equation (3).

With bromine, on the other hand, it has now been shown that the reaction cannot be stopped at stage (1), no doubt because of the very great instability of the bromine acyls which, unlike the iodine acyls usually decompose rapidly at room temperature. For compounds of shorter chain length see Birkenbach, Goubeau, and Berninger (*Ber.*, 1932, **65**, 1339) and Bockemuller and Hoffman (*Annalen*, 1935, **519**, 165) who indicate that the decomposition is even more rapid. Special experiments were carried out with silver hexoate and sebacate from which, the proportion of bromine being less than two equivalents to one of silver salt, the formation of Simonini ester would be expected according to equation (4), which summarises the equivalents of equations (1) and (2) :

$$3R\cdot CO_2Ag + 2Br_2 \longrightarrow R\cdot CO_2R + RBr + 3AgBr + 2CO_2 \quad . \quad . \quad . \quad . \quad (4)$$

Contrary to expectation, the reaction actually took place according to equation (5), which summarises the equivalents of equations (1) and (3):

$$R\cdot CO_2Ag + Br_2 \longrightarrow RBr + AgBr + CO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

An equivalent amount of the silver salt was recovered unchanged. As both these salts gave similar results, only the experiments with silver hexoate are described.

In spite of the precautions taken to exclude water, some of the free parent acid, as distinct from unchanged silver salt, usually appears in the products. This can be accounted for by equation (6) :

$$6R\cdot CO_2Ag + 3H_2O + 3Br_2 \longrightarrow 6R\cdot CO_2H + 5AgBr + AgBrO_3 \quad . \quad . \quad . \quad (6)$$

When the reactions were carried out under conditions of less rigorous drying, as much as 50—60% of unchanged acid was found in the product; it can readily be seen that in small-scale experiments the air in the vessel will contain as much water as in a larger-scale experiment carried out in the same vessel, and that this water will have a relatively greater effect on the reaction.

In the detailed discussion which follows, the yields given represent the average from several experiments, the results of which, while in close agreement, were never identical. The figures are percentages of the calculated theoretical yield, any unchanged silver salt having been allowed for.

Group (1). *Monobasic Aliphatic Acids.*—With silver di*iso*amylacetate (2 : 8-dimethylnonane-5-carboxylate) and *cyclo*hexanecarboxylate the actual yield of bromide was low; this may have been due to its volatility, as in these cases it was actually isolated; with the hexoate and ββ-dimethylbutyrate however, the bromide was removed, along with the solvent, on drying *in vacuo* at 100°, its yield being calculated by difference.

Group (1) *acids.*

Silver salt.	Loss of CO_2, %.	Unchanged acid, %.	Bromide, %.	Simonini ester, %.
Hexoate	91·4	5·5	92	2·4
ββ-Dimethylbutyrate	86·5	13·2	82·9	3·9
Di*iso*amylacetate	83·9	13·2	66·0	4·1
Stearate and palmitate *	93·6	5·5	89·4	0
*cyclo*Hexanecarboxylate	84·2	13·2	57·5	6·4

Equation (5) accounts for almost all the reaction of monobasic aliphatic acids (see table); when a ring is introduced, as in the *cyclo*hexanecarboxylate, more of the Simonini ester is formed, showing that reaction (4) is beginning to compete.

This reaction provides a convenient method of preparing the hitherto rather inaccessible halides of *neo*pentane, since ββ-dimethylbutyric acid is fairly easily prepared by the oxidation (best, by ozone) of di*iso*butene. In view of the importance of these compounds this is being further investigated.

Group (2). *Monobasic Aromatic Acids.*—Bromobenzene is volatile *in vacuo* at 100°, but it was isolated contaminated with less than 10% of carbon tetrachloride. The low yield of benzyl bromide may be due to its volatility *in vacuo* at 100°. The results show that here reaction (4) is competing strongly with reaction (5).

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* In cases marked thus, the principal products have been completely identified, being themselves crystallised or converted into crystalline derivatives. In other cases identity was partly inferred by analogy.

Silver salt.	Loss of CO_2, %.	Recovered acid, %.	Bromide, %.	Simonini ester, %.
Benzoate	66·1	10·6	45·8	43·9
Phenylacetate	74·5	14·0	53·7	21·0
o-Nitrobenzoate *	79·1	10·7	71·2	20·4

Group (3). *Monobasic Aliphatic Monoketo-acids.*—In this group, the reaction with bromine takes an unusual course, the greater part of the product consisting of the free parent acid, in spite of the fact that the conditions of rigorous drying were the same as in the other groups; in this reaction bromine substitution also occurs, leading to the formation of a bromo-acid. Similar results were obtained with 3-ketononane-1-carboxylic acid. With iodine on the other hand, the Simonini ester seemed to predominate in the product.

Silver salt.	Loss of CO_2, %.	Free parent acid, %.	Bromo-acid, %.	Bromide, %.	Simonini ester, %.
9-Ketodecane-1-carboxylate	42·0	50·7	4·8	39·8	Probably none

Group (4). *Dibasic Aliphatic Acids.*—If only one carboxyl group of dibasic acids is replaced by bromine, a bromo-acid results. With symmetrical acids, such as adipic, only one product, δ-bromovaleric acid can be formed; with asymmetrical acids on the other hand, such as α-methylglutaric acid, there are two possibilities: γ-bromovaleric and 4-bromobutane-2-carboxylic acid. The same considerations apply where one carboxyl group reacts with the halogen to give a lactone. Adipic acid could give only δ-valerolactone, while α-methylglutaric acid could give γ-valerolactone or α-methyl-γ-butyrolactone.

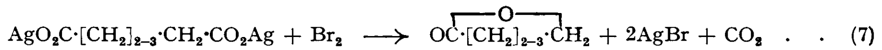
The salts in the annexed table are arranged in sub-divisions according to the distance between the carboxyl groups.

Group (4) *Acids.*

Silver salt, Sub-group A.	Loss of CO_2, %.	Dibromide, %.	Bromo-acid, %.	Lactone, %.	Free parent acid, %.
Sebacate *	94·5	81·3	7·3	0	0
Azelaäte	93·7	82·5	6·7	0	3·0
Pimelate	78·3	44·1	20·2	—	1·9
Sub-group B.					
α-*iso*Amyladipate	64·2	33·1	28·6	30·5	1·7
Adipate *	80·1	28·7	4·4	46·1	—
Sub-group C.					
α-*iso*Amylglutarate	58·7	15·8	18·6	60·5	2·8
ββ-Dimethylglutarate *	64·8	9·8	—	50·6	—
α-Methylglutarate	50·0	6·6	5·1	87·0	—
Glutarate	47·2	3·0	—	69·4	1·6
Sub-group D.					
*iso*Amylsuccinate	68·2	25·0	—	—	—
Methylsuccinate	77·0	12·6	—	—	—
Succinate	65·2	—	19·6	—	21·4
Sub-group E.					
Benzylmalonate	10—15	—	—	—	—

Sub-group A. Where the carboxyl groups are five or more carbon atoms apart the reaction is more like that of the aliphatic monobasic salts, the dibromide predominating in the product, some bromo-acid being also formed. In the case of pimelic acid some products of an ester-like type are produced which are still being investigated (see Experimental section).

Sub-group B. Here the yield of dibromide is diminished; the formation of a considerable quantity of lactone shows that, though both carboxyl groups apparently can react, the process tends to stop after one has reacted; this is even more marked in the next sub-group. In these cases, equation (4) becomes modified, and the lactone instead of the Simonini ester is formed.



$$AgO_2C\cdot[CH_2]_{2-3}\cdot CH_2\cdot CO_2Ag + Br_2 \longrightarrow \overbrace{OC\cdot[CH_2]_{2-3}\cdot CH_2}^{O} + 2AgBr + CO_2 \quad . \quad . \quad (7)$$

Silver adipate could not be dealt with by ordinary methods as, although the neutral fraction could be obtained by extracting the reaction product with aqueous sodium hydroxide, all attempts to recover the acid resulted in extremely bad yields. The alkaline

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* See footnote, p. 101.

extraction method was therefore only used to determine the amount of bromo-acid present. The procedure finally adopted consisted in heating the whole of the carbon tetrachloride extract with hydrogen bromide in a sealed tube at 100°, whereupon all the lactone present was converted into the bromo-acid. The mixture could then be separated into acid and neutral fractions with a total recovery of over 95%. Both fractions were converted in good yield into their crystalline phenoxy-derivatives.

Further, silver adipate seems particularly hard to dry. On a 10-g. scale, 20—35% of the amount of adipic acid theoretically present in the original silver adipate taken was recovered from an acetone extract of the silver residues; at the same time these residues showed no appreciable oxidising power, which would be expected from equation (6). For this reason, the amount of recovered adipic acid (calculated as silver salt) has been deducted from the original weight of silver adipate when assessing the figures quoted in the table.

Sub-group C. Here the lactone is the chief product, showing that reaction (7) predominates.

Sub-group D. Here no unimolecular lactone can be formed. There is however, some evidence for the formation of di- or poly-molecular compounds of the Simonini-ester type. More dibromide is formed than in the previous group. Nearly 50% of the product was a complex mixture of acids, the nature of which has not so far been elucidated.

Sub-group E. Here the reaction appears to follow an entirely different course. Although only 10—15% of the carbon dioxide is lost, extensive bromine substitution occurs, the products being dark glasses or stiff syrups. This seems to indicate polymerisation, which most probably involves free radicals. These products darken greatly when boiled with alkali, and no definite compounds have been isolated from them.

There is little evidence in group (4) that bromine reacts with one carboxyl group in preference to the other. Because of the absence of crystalline compounds in the reaction products from the unsymmetrically substituted acids, some of the lactone from the silver α-*iso*amylglutarate reaction was converted into the amide which, if pure, would be expected to crystallise readily. The fact that the product could not be induced to crystallise seems to indicate the presence of a mixture of amides, resulting from a mixture of lactones formed by the indiscriminate reaction of both carboxyl groups as follows (R = *iso*amyl) :

$$\mathrm{R{\cdot}\overbrace{CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO}^{O}} \longleftarrow \mathrm{HO_2C{\cdot}CHR{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H} \longrightarrow \mathrm{\overbrace{OC{\cdot}CHR{\cdot}CH_2{\cdot}CH_2}^{O}}$$

Group (5). *Dibasic Aromatic Acids.*—Results are recorded in the table. In the case of *iso*phthalate the figures for the loss of carbon dioxide and for dibromide refer to the small amount of product and take no account of the fact that the great bulk of the silver salt is unchanged.

Group (5). *Dibasic Aromatic Acids.*

Silver salt.	Loss of CO_2, %.	Recovered acid, %.	Dibromide, %.	Unchanged silver salt, %.
Terephthalate	—	—	—	98·0
*iso*Phthalate	25·8	—	4·0 ?	78·4
Phthalate	38·4	29·0	10·1	0

With the phthalate, silver bromide is produced quantitatively, but the dark products of the reaction consist largely of unchanged acid; there is also evidence that some bromine substitution has occurred.

EXPERIMENTAL.

General.

(Yields are expressed as weights-%, unless otherwise stated, and were determined to the nearest mg.)

Preparation of Silver Salts.—The silver salts were prepared as described previously (Oldham and Ubbelohde, *loc. cit.*), except that AnalaR sodium carbonate was used instead of ammonia solution. Analyses were within about 1% of the calculated values.

Reaction with Bromine.—Reaction was carried out in a current of rigorously dried air, previously passed through concentrated sulphuric acid, phosphoric oxide, and again concentrated sulphuric acid. A concentrated sulphuric acid trap was placed at the exit. If these precautions are not taken, 50% or more of unchanged acid is recovered.

The apparatus consists of an U-tube, one limb of which is connected directly to the air supply, the other by means of a three-way adapter to a reflux condenser which in turn is connected to the terminal sulphuric acid trap. The second limb of the adapter carries a dropping funnel, while the third is used for the air stream, which can be passed either through the U-tube or directly into the adapter, by means of a T-piece provided with taps.

The silver salt is placed in the U-tube, through which air is passed for 1½ hours, maintained at 100° in a water-bath. (Precautions must be taken against the condensation of water round the joints at the top of the U-tube.) The water-bath is then removed, and the air is caused to pass directly into the adapter by use of the appropriate taps on the T-piece. An excess over the calculated amount of a 15—18% solution of bromine in carbon tetrachloride (made up in bulk, and stored over phosphoric oxide) is added as quickly as possible through the dropping funnel, due regard being paid to the, sometimes vigorous, evolution of carbon dioxide. When the colour no longer fades, the red solution is warmed for a few minutes to ensure that the reaction is complete. Much longer boiling is sometimes necessary. The mixture is then filtered and the silver residues well washed with hot carbon tetrachloride.

Examination of the Silver Residue.—In quantitative work it is necessary to determine the amount of unchanged silver salt by extracting the silver residues with aqueous ammonia as already described (Oldham and Ubbelohde, *loc. cit.*). In the details given below the weight of silver salt recovered in this way has been allowed for.

Examination of the Product.—The filtered solution was evaporated on a water-bath and the residue usually dried *in vacuo* at 100°. In the case of the lower monobasic acids the carbon tetrachloride distillate contains the bulk of the bromo-compounds and these must be separated by distillation through a column. The procedure thereafter varied: various methods of separation were employed in each case, those recorded in the individual experiments being the most suitable. Sometimes the product was distilled; generally the neutral and the acid fraction of the product were separated by extraction three times from ether with aqueous sodium hydroxide. In the case of the higher fatty acids, alcohol must be added to this system which otherwise forms stable emulsions.

Any acids present are recovered by acidifying the alkaline extract with sulphuric acid, followed by extraction with ether; in the case of the dibasic acids it is advisable to determine any bromine in this water, since some bromo-acids produced during the reaction are decomposed by cold aqueous sodium hydroxide.

The neutral ethereal solution contains the bromides, any ester of the Simonini type, and, in the case of the dibasic acids, lactones. The product, after removal of the ether, was dried *in vacuo* at 100° and usually fractionally distilled. For the removal of lactones it was sometimes necessary to boil it with N/10-aqueous alcoholic sodium hydroxide.

Analyses.—The bromine content of the product was determined by the Stepanow method, except in the cases of the bromo-acids, for which titration with boiling N/10-alkali was usually sufficient. The carboxyl group was determined by titration with an excess of boiling N/10-alkali, followed by back-titration with N/10-nitric acid, and calculated as carbon dioxide.

Yields.—Yields quoted below for the crude products of the reaction are expressed as percentages of the weight of silver salt employed. Subsequent yields are calculated as percentages of the weight of crude product. The percentages of the theoretical yields have been given above in the tables and will not be repeated.

Details.

Group (1). *Aliphatic Monobasic Acids.*—*Special experiments with silver hexoate.* The two following experiments were designed to ascertain in what proportions bromine reacts with this salt. The quantities are expressed in g.-equivs. The calculation was complicated by the persistence of a trace of water, which gave rise to reaction (6) in which one equivalent of free parent acid is produced by one equivalent of bromine. The amount of acid present, determined by titration, must therefore be deducted from the original amount both of silver salt and of bromine. Any remaining bromine (determined by titration) or silver salt (determined as described above) must also be deducted from the original amounts. The amounts that remain then indicate the proportions in which the silver salt and the bromine have actually reacted. The determination of excess of bromine calls for no comment, but in determining the acid the carbon tetrachloride solution should be well shaken with excess of N/10-aqueous alkali, the carbon tetrachloride removed, and the excess of alkali back-titrated with acid.

(i) *Use of an excess of bromine.* $0{\cdot}485 \times 10^{-3}$ g.-equivs. of silver hexoate and 10^{-3} g.-equiv. of bromine gave $0{\cdot}076 \times 10^{-3}$ g.-equiv. of acid, $0{\cdot}105 \times 10^{-3}$ g.-equiv. remaining unchanged. Therefore the amount of silver salt used in the reaction was $0{\cdot}485 - 0{\cdot}076 = 0{\cdot}409 \times 10^{-3}$ g.-equiv. and that of bromine $1{\cdot}000 - 0{\cdot}076 - 0{\cdot}105 = 0{\cdot}819 \times 10^{-3}$ g.-equiv. These figures are in the proportion of 2 : 1 and indicate that reaction (5) has indeed taken place.

(ii) *Use of an excess of silver salt.* Silver hexoate (0·612) and bromine (1·00) produced acid (0·062) (all 10^{-3} g.-equiv.), $0{\cdot}081 \times 10^{-3}$ g.-equiv. of silver salt being recovered. Therefore the amount of silver salt used is $0{\cdot}612 - 0{\cdot}081 - 0{\cdot}062 = 0{\cdot}469$ and that of bromine used is $1{\cdot}000 - 0{\cdot}062 = 0{\cdot}938 \times 10^{-3}$ g.-equiv. These figures also are in the proportion of 2 : 1, showing that again reaction (5) has taken place.

Silver hexoate. The low yield (3·9%) shows that the bulk of the product has been removed with the carbon tetrachloride and must therefore be the bromide. Found: CO_2, 27·9% by cold titration, 31·2% by hot titration; Br, 5·8%. The cold titration corresponds to the presence of 73·6% of the free parent acid (Calc. for $C_6H_{12}O_2$: CO_2, 37·9%) and the difference between the two titrations probably indicates the presence of 13·9% of the Simonini ester (Calc. for $C_{11}H_{22}O_2$: CO_2, 23·6%). The bromine content corresponds to the presence of 10·9% of amyl bromide.

The carbon tetrachloride distillate was redistilled through a column till the temperature of the vapour reached 82°. The bromine content of the residual mixture of amyl bromide and carbon tetrachloride was 21·5%, corresponding to a 40·6% yield of amyl bromide, based on the original weight of silver salt. By calculation, a 60% yield would be expected, so presumably 33% of the product remained in the carbon tetrachloride.

Silver ββ-dimethylbutyrate. The bulk of the product (12·2% yield) consists of the bromide (Found: CO_2, 18·3% by cold titration, 21·5% by hot titration). The cold titration corresponds to the presence of 48·5% of free parent acid (Calc. for $C_6H_{12}O_2$: CO_2, 37·9%), while the difference between the two titrations probably represents 13·5% of Simonini ester (Calc. for $C_{11}H_{22}O_2$: CO_2 23·6%). The remaining 38% of the product is undoubtedly the bromo-compound, but the bromine of *neo*pentyl derivatives cannot be determined by ordinary methods. For this reason the carbon tetrachloride distillate was not further examined.

*Silver di*iso*amylacetate.* The yield of product was 74·6% (Found : CO_2, 3·1%), of which 11·6% was a solid acid (Found : CO_2, 22·1. Calc. for $C_{12}H_{24}O_2$: CO_2, 22·0%). The neutral fraction (81·2%) gave a distillate, b. p. 85—87°/2 mm. (yield 83·4%) (Found : CO_2, 0 ; Br, 35·2. Calc. for $C_{11}H_{23}Br$: Br, 34·0%). The yield of residue was 12·5% (Found : CO_2, 2·2 ; Br, 44·0. The CO_2 content may represent 17·7% of Simonini ester. Calc. for $C_{23}H_{46}O_2$: CO_2, 12·4%).

Silver stearate. The product (78·5%) (Found : CO_2, 0·9%) gave a solid acid fraction (5·5%) (Found : CO_2, 15·4%. Calc. for $C_{18}H_{36}O_2$: CO_2, 15·4%) and a neutral fraction (93·0%), m. p. 29—30° (Found : Br, 25·7. Calc. for $C_{17}H_{35}Br$: Br, 25·0%), the residue from the evaporation of the mother-liquors having m. p. 27·8—28·2° (Found : CO_2, 0 ; Br, 25·1%). The m. p. of 1-bromoheptadecane is 32°.

Silver cyclo*hexanecarboxylate.* The product (65·9%, dried *in vacuo* at 60°) (Found : CO_2, 4·5%) gave a solid acid fraction (10·9%) (Found : CO_2, 34·0. Calc. for $C_7H_{12}O_2$: CO_2, 34·3%) and a neutral fraction (88·0%), which gave fractions, (i) b. p. 75—77°/2 mm. (57·3%) (Found : CO_2, 0 ; Br, 51·6. Calc. for $C_6H_{11}Br$: Br, 49·0%), and (ii) b. p. 70—90° (15·8%) (Found : CO_2, 6·7 ; Br, 31·8%. This corresponds to a mixture of 64·2% of *cyclo*hexyl bromide, calc. on the bromine, and 32·0% of the Simonini ester, calculated on the carbon dioxide values. Calc. for $C_{13}H_{22}O_2$: CO_2, 20·9%). The residue (4·4%) was a black tar. The loss in weight in this distillation is probably due to the volatility of *cyclo*hexyl bromide.

Group (2). *Aromatic Monobasic Acids.—Silver benzoate.* The yield of product (Found : CO_2, 20·1%) was 32·0%. As phenyl benzoate is very unstable to alkalis the ethereal solution of the product was extracted with aqueous potassium hydrogen carbonate and gave a crystalline acid fraction (27·2%) (Found : CO_2, 30·9. Calc. for $C_7H_6O_2$: CO_2, 36·0%). The low value for CO_2 indicates the presence of 14·2% of non-acidic material, probably phenol, which in turn would represent 30·1% of phenyl benzoate which has been hydrolysed even under these mild conditions. The neutral fraction (66·9%) was partly solid (Found : CO_2, 17·0%. This indicates the presence of 76·5% of phenyl benzoate. Calc. for $C_{13}H_{10}O_2$: CO_2, 22·2%), the rest being probably bromobenzene. The carbon tetrachloride distillate was distilled through a column till the temperature of the vapour reached 81°. The amount of carbon tetrachloride remaining in the residue was 8·3% (Found : Br, 46·7%) making the yield of bromobenzene 26·1% of the original silver benzoate.

Silver phenylacetate. The product (57·9%) (Found : CO_2, 7·9 ; Br, 30·5%) gave a solid acid fraction (14·4%) (Found : CO_2, 30·6. Calc. for $C_8H_8O_2$: CO_2, 32·3%) and a neutral fraction (81·0%), yielding fractions, (i) b. p. 73—80°/2 mm. (60·0%) (Found : CO_2, 0·8 ; Br, 44·9%. The CO_2 content indicates the presence of 4·1% of the Simonini ester. Calc. for $C_{15}H_{14}O_2$: CO_2, 19·4%. Calculation on the bromine content gives 96·1% of benzyl bromide. Calc. for C_7H_7Br : Br, 46·7%), and (ii) b. p. 80—130°/2 mm. (31·9%) (Found : CO_2, 9·6 ; Br, 23·2%. This corresponds to a mixture of 49·4% of the Simonini ester, calculated on the CO_2, and 49·9% of benzyl bromide, calculated on the bromine content). The loss in weight may be due to the volatility of benzyl bromide.

Silver o-*nitrobenzoate.* The product (70·4%) gave a solid acid fraction (9·3%) (Found : CO_2, 25·0. Calc. for $C_7H_5O_4N$: CO_2, 26·3%) and a crystalline neutral fraction (89·4%) (Found : CO_2, 2·6 ; Br, 32·9%). These figures correspond to a mixture of 83·0% of *o*-bromonitrobenzene (m. p. 41·5°) (Calc. for $C_6H_4O_2NBr$: Br, 39·6%) and 17·0% of the Simonini ester (Calc. for $C_{13}H_8O_6N_2$: CO_2, 15·2%). The substance softened at 32° and melted at 37—40°.

Group (3). *Aliphatic Monobasic Monoketo-acids.—Silver* 9-*ketodecane*-1-*carboxylate.* The product (72·1%) (Found : CO_2, 11·5 ; Br, 19·5%) was extracted from ether with sodium carbonate solution to give a largely solid acid fraction (47·3%) (Found : CO_2, 21·0 ; Br, 3·7%). This corresponds to a mixture of 87·1% of the free parent acid (Calc. for $C_{11}H_{20}O_3$: CO_2, 22·0%) with 12·9% of its mono-bromo-derivative (Calc. for $C_{11}H_{19}O_3Br$: CO_2, 15·7 ; Br, 28·6%), calculated from the bromine content ; or 84·2 and 15·8% respectively calculated from the CO_2 content. For the neutral fraction (46·9%) (Found : CO_2, 2·5 ; Br, 30·7%) the bromine content corresponds to the presence of 90·3% of the bromo-compound (Calc. for $C_{10}H_{17}OBr$: Br, 34·0%).

Group (4). *Silver Salts of the Aliphatic Dibasic Acids.*—In this group, the acid fraction is usually a mixture of the free parent acid and bromo-acid. The composition of the mixture was calculated from the CO_2 content, and also from the bromine content. In all cases these agreed within 3%, and the average value is given below.

Sub-group A. (i) *Silver sebacate.* The yield of product was 61·3%. A further 0·9% was obtained by extracting the silver residues with acetone, and this material, crystallised from acetone, had m. p. 108—118° (Found : CO_2, 27·7 ; Br, 2·3%) ; the nature of this substance, more of which was obtained from the main fraction, remains obscure. The acid fraction (8·6%) (Found : CO_2, 16·2 ; Br, 31·7%), on treatment with light petroleum, gave 7·9% of a white crystalline substance, m. p. 118—120° (Found : CO_2, 33·7 ; Br, 0%). This was doubtless the same as the product from the acetone extract described above. An oil (91·7%) obtained on removal of the light petroleum was dissolved in ether and again extracted with aqueous sodium hydroxide ; 8·7% was obtained from the ether and was added to the main neutral fraction ; 86·1% of an acid product was isolated which crystallised (m. p. 31—33°) and was so soluble in all solvents that recrystallisation was unsatisfactory [Found : CO_2, 17·2 ; Br, 31·8%. Calc. for 9-bromopelargonic acid (m. p. 36—36·5°), $C_9H_{17}O_2Br$: CO_2, 18·5 ; Br, 33·7%]. The neutral fraction (90·2%) gave a distillate (94·8%), b. p. 140°/5 mm. (Found : CO_2, 0 ; Br, 59·3. Calc. for $C_8H_{16}Br_2$: Br, 58·8%). The dark residue (4·7%) (Found : CO_2, 5·7 ; Br, 44·5%) was not further examined. The products of the reaction contained 85·4% of the dibromide, 6·7% of the bromo-acid, 2·1% of an unknown crystalline acid, and 4·2% of a dark residue.

The distillate was treated with sodium phenoxide as described by Ssolonina (*Zentr.*, 1899, I, 26), giving a 99% yield of the diphenoxy-derivative, m. p. (after recrystallisation from absolute alcohol) 84—86° (lit., 83—84°), while 8·1% of impure crystals, m. p. 44—51°. were obtained from the mother-liquors.

(ii) *Silver azelaäte.* The product (64·2%) gave an acid fraction (8·0%) (Found : CO_2, 26·7 ; Br, 25·6%). This corresponds to a mixture of 72·8% of the bromo-acid (Calc. for $C_8H_{15}O_2Br$: CO_2, 19·7 ; Br, 35·8%) and 27·2% of azelaic acid (Calc. for $C_9H_{16}O_4$: CO_2, 46·8%) and a neutral fraction (91·7%) which gave a distillate (89·9%), b. p. 125°/2 mm. (Found : CO_2, 0 ; Br, 61·0. Calc. for $C_7H_{14}Br_2$:

Br, 62·0%). The residue (7·3%) was not further investigated. The products contained 82·4% of the dibromide, 5·8% of the bromo-acid, and 2·2% of azelaic acid.

(iii) *Silver pimelate.* The product (59·3%) (Found: CO_2, 8·6%) give an acid fraction (19·2%) [Found: CO_2, 24·3; Br, 37·7. This corresponds to a mixture of 92·9% of the bromo-acid (Calc. for $C_6H_{11}O_2Br$: CO_2, 22·5 Br, 41·0%) and 7·1% of pimelic acid (Calc. for $C_7H_{12}O_4$: CO_2, 55·0%)]. The neutral fraction (72·2%) gave a distillate, b. p. 120°/2 mm. (63·4%) (Found: CO_2, 0; Br, 71·5. Mainly $C_5H_{10}Br_2$: Calc., Br, 69·9%). The residue (35·5%) was boiled with aqueous alcoholic sodium hydroxide but no very clear-cut results were obtained; the isolation of 8·5% of a neutral substance would seem to indicate the presence of a compound of the type of a Simonini ester, formed by the unsymmetrical loss of two molecules of CO_2 between two molecules of pimelic acid, such as  $\mathrm{O}{<}\begin{matrix}\mathrm{CO}\cdot[\mathrm{CH_2}]_5\cdot\mathrm{CO}\\ {[\mathrm{CH_2}]_5}\end{matrix}{>}\mathrm{O}$. The product of the reaction contained 45·8% of the dibromide, 17·8% of the dibromo-acid, 1·4% of free parent acid, and 25·6% of an unknown substance which is being further investigated.

Sub-group B. (i) *Silver* α-*isoamyladipate.* The product (54·2%) (Found: CO_2, 13·5%) gave a distillate, b. p. 115—130°/2 mm. (44·1%). The CO_2 content (2·0%) corresponds to the presence of 7·4% of the lactone (Calc. for $C_{10}H_{18}O_2$: CO_2, 25·8%); allowing for this, the bromine content (53·9%) is revalued at 58·3%, showing that the substance is mostly the dibromide (Calc. for $C_9H_{18}Br_2$: Br, 55·8%). The residue (53·0%) (Found: CO_2, 21·7 Br, 17·6%) corresponds to a mixture of 55·3% of the bromo-acid) (Calc. for $C_{10}H_{19}O_2Br$: CO_2, 17·5; Br, 31·8%), 41·7% of the lactone, and 3% of *iso*amyladipic acid (Calc. for $C_{11}H_{20}O_4$: CO_2, 40·7%). In this case also the residue was boiled with excess of alkali, giving results similar to those described for pimelic acid; the isolation of 13·2% of a neutral substance indicates the presence of a compound of the Simonini ester type. The reaction products contained 40·7% of the dibromide, 29·3% of the bromo-acid, 1·6% of *iso*amyladipic acid, and 22·1% of lactone + Simonini-like compound. This is being further investigated

(ii) *Silver adipate.* (*a*) The yield obtained in carbon tetrachloride was 29·5% (Found: CO_2, 16·4%). The silver residues were extracted with hot acetone, giving a further 11·9% of crystalline product (cf. p. 103) (Found: CO_2, 55·3%), softening at 136°, m. p. 141—146°, unchanged on admixture with adipic acid. As it remained impure after recrystallisation from glacial acetic acid, it was converted into the ethyl ester and distilled (88·5% yield) (Found: CO_2, 43·6. Calc. for $C_{10}H_{18}O_4$: CO_2, 43·5%). The residue was a dark gum. The ester was hydrolysed to adipic acid (99·5%) (Found: CO_2, 59·2. Calc. for $C_6H_{10}O_4$: CO_2, 60·2%), m. p. 151—153°, unchanged on mixing with adipic acid. Allowance being made for this amount of adipic acid, the yield of other products in the carbon tetrachloride extract is 40·1%.

Although the neutral portion of the usual alkaline extraction could be isolated without difficulty, it proved impossible to isolate the acid portion in good yield. The amount of bromo-acid present was determined by boiling the strongly alkaline extract for ½ hour and determining the bromine content. This was equivalent to the presence of 5·7% of the bromo-acid in the original carbon tetrachloride extract.

(*b*) The crude product from the carbon tetrachloride was heated in a sealed tube for 2 hours at 100° with four times the theoretical amount of hydrogen bromide in glacial acetic acid and an excess of acetic anhydride to destroy any water present; the product was evaporated to dryness *in vacuo* at 100°. As the dibromide is considerably volatile under these conditions, the total distillate was flooded with water, neutralised with sodium carbonate, and extracted with ether, comparatively large quantities of the dibromide being recovered. The total yield of product was 130·4%. The alkaline extract thereof (all solutions were kept ice-cold) was immediately run into ice-cold acid. The acid fraction (52·1%) (Found: CO_2, 25·8; Br, 44·3. Calc. for $C_5H_9O_2Br$: CO_2, 24·3; Br, 44·2%) failed to crystallise, and its subsequent identification is described below. The neutral fraction (45·2%) gave a distillate (71·8%), b. p. 80—90°/5 mm. Analysis (CO_2, 13·3; Br, 5·4%) of the residue (24·2%) might indicate presence of 4-bromobutyl δ-bromovalerate (Calc. for $C_9H_{16}O_2Br_2$: CO_2, 13·6; Br, 50·0%); this substance would easily have distilled under the conditions employed. As this material represented only 12—15% of the reaction product, it was not further investigated. The bulked distillates from several experiments were redistilled (yield 93·7%), b. p. 75—85°/5 mm. (Found: CO_2, 0; Br, 71·3. Calc. for $C_4H_8Br_2$: Br, 74·0%), a residue (3·3%) (Found: Br, 31·0%) not being further investigated.

The products of the reaction contained 31·1% of the dibromide, 28·7% of adipic acid, 22·8% of the lactone, 4·0% of the bromo-acid, and 10·1% of unidentified material. If the carbon tetrachloride extract only is considered, these figures become 42·3, 32·0, 5·7, and 14·2%, respectively.

The distillate was converted into 1 : 4-diphenoxybutane as described above (yield 92·0% of theory). Recrystallisation from absolute alcohol yielded crystals, m. p. 99—100° (lit., 99°). The mother-liquors yielded 15·0% of material, m. p. 30—40°.

The bromo-acid was heated with twice its volume of thionyl chloride on a water-bath, and then treated cautiously with a small quantity of alcohol, evaporated to dryness *in vacuo* at 100° (yield 99·3%) (Found: CO_2, 22·9; Br, 33·7. Calc. for $C_7H_{13}O_2Br$: CO_2, 22·1; Br, 38·2%), and distilled (distillate: 71·7%; b. p. 100—105°/5 mm.; residue: 7·6% of a black tar). As treatment of the ester with sodium phenoxide in alcohol gave a very poor yield of the acid (presumably owing to the formation of δ-valerolactone), it was boiled in acetone with the acetone compound of sodium phenoxide (Segaller, *J.*, 1914, **105**, 112). Two treatments with this reagent removed the bromine completely. In this case hydrolysis also occurred, the acid, and no δ-valerolactone being formed. Ethyl δ-phenoxyvalerate (59·9% of theory) (Found: CO_2, 18·9; Br, 0. Calc. for $C_{13}H_{18}O_3$: CO_2, 19·8%) was isolated by removing the acetone on a water-bath, shaking the residue with water–ether, and washing the ethereal layer with sodium hydroxide solution. This was hydrolysed with aqueous-alcoholic sodium hydroxide and, as the solution became cloudy on removal of the alcohol, it was extracted with ether, from which 5·2% of a neutral crystalline compound was obtained in insufficient quantity for further work. The solution was then acidified and extracted with ether, yielding 96·1% of the calculated amount of δ-phenoxyvaleric acid (after allowance for the neutral substance mentioned above), m. p. 62—63°.

The substance was too soluble in all solvents to be satisfactorily recrystallised, but on being pressed between filter paper had m. p. 63—65° (lit., 66°) (Found : CO_2, 21·9. Calc. for $C_{11}H_{14}O_3$: CO_2, 22·6%). More acid (impure) was recovered from the alkaline washings from the ester ; these were bulked, acidified, neutralised with potassium hydrogen carbonate solution, extracted 3 times with ether to remove phenol, again acidified, and extracted with ether. The yield of impure dark acid was 32·4%, making the total yield 93·3% of theory (Found : CO_2, 20·8%).

The bromo-ester was treated with excess of ethyl sodiomalonate, hydrolysed by alkali, decarboxylated at 180—200°, and dried *in vacuo* at 100°. This gave 81·0% of pimelic acid, m. p. 101—104° (after recrystallisation from benzene) (Found : CO_2, 53·4. Calc. for $C_7H_{12}O_4$: CO_2, 55·0%), unchanged on mixing with an authentic specimen. The mother-liquors yielded 36·0% of impure product. The somewhat unsatisfactory yield of pimelic acid is a feature common to many decarboxylations of malonic derivatives.

Sub-group C. (i) *Silver γ-*iso*amylglutarate.* The product (45·9%) (Found : CO_2, 19·0 ; Br, 24·6%) gave a distillate, b. p. 110—120°/2 mm. (67·9%) (Found : CO_2, 2·3% by cold titration, 17·6% by hot titration ; titratable Br, 4·2% ; total Br, 25·1%). The bromine content by titration agrees with the CO_2 content by cold titration to indicate the presence of 12·4% of the bromo-acid (Calc. for $C_9H_{17}O_2Br$: CO_2, 18·5 ; Br, 33·7%). The remaining 15·3% of CO_2 corresponds to 54·2% of the lactone (Calc. for $C_9H_{16}O_2$: CO_2, 28·2%). With allowance for these factors the bromine content of the remainder is revalued at 62·7% (Calc. for $C_8H_{16}Br_2$: Br, 58·8%). Analysis (CO_2, 26·6 ; Br, 16·8%) of the residue (29·1%) corresponds to a mixture of 49·9% of the bromo-acid, 26·6% of the lactone, and 23·6% of α-*iso*amylglutaric acid (Calc. for $C_{10}H_{18}O_4$: CO_2, 43·5%). To confirm this the residue was boiled with excess of alkali, whereupon it gave 11·8% of a neutral substance, which was not further examined, 16·8% of bromine, and 69·4% of an acid (Found : CO_2, 32·6%), corresponding to a mixture of 71·3% of the lactone and 28·7% of *iso*amylglutaric acid. The expected amount of α-*iso*amylglutaric acid was only 11·8%, but the neutral material could correspond to a further 15·9% of this acid. The reaction products consisted of 22·6% of the dibromide, 22·9% of the bromo-acid, 49·5% of the lactone, and 2·8% of *iso*amylglutaric acid.

(ii) *Silver ββ-dimethylglutarate.* The product (29·2%) (Found : CO_2, 28·4 ; Br, 15·1%) was boiled with a slight excess of N/10-aqueous-alcoholic sodium hydroxide, giving a neutral fraction (21·6%) (Found : CO_2, 1·4 ; Br, 65·7%), the CO_2 content of which corresponds to the presence of 3·6% of the lactone (Calc. for $C_6H_{10}O_2$: CO_2, 38·5%). With allowance for this, the bromine content of the remainder becomes 68·2% (Calc. for $C_5H_{10}Br_2$: Br, 69·9%). The acid fraction (61·5%) [Found : CO_2, 39·4%. The aqueous portion contained 11·4% of bromine which corresponds to 27·8% of the bromo-acid (Calc. for $C_6H_{11}O_2Br$: CO_2, 22·5 ; Br, 41·0%)] gave a distillate, b. p. 80°/2 mm. (84·5%) (Found : CO_2, 38·4%). In spite of its good analysis the distillate crystallised badly, and a cold titration showed CO_2, 1·3%. The *residue* was 11·2% (Found : CO_2, 52·5. Calc. for ββ-dimethylglutaric acid, $C_7H_{12}O_4$: CO_2, 55·0%). The reaction products consisted of 20·8% of the dibromide, 27·8% of the bromo-acid, 36·5% of the lactone, and 6·8% of ββ-dimethylglutaric acid.

(iii) *Silver α-methylglutarate.* The product (31·7%) (Found : CO_2, 38·5%) gave a distillate, b. p. 65—80°/2 mm. (76·3%) [Found : CO_2, 36·7 ; Br, 12·0%. This corresponds to a mixture of 83·6% of the lactone (Calc. for $C_5H_8O_2$: CO_2, 44·0%) and 16·4% of the bromo-compound (Calc. for $C_4H_8Br_2$: Br, 74·0%). The bromine content (17·7%) of the residue (21·7%) (Found : CO_2, 34·6%) indicates the presence of 40% of the bromo-acid (Calc. for $C_5H_9O_2Br$: CO_2, 24·3 ; Br, 44·2%) with 60% of the lactone, but such a mixture would require CO_2, 36·1%. The reaction products consisted of 12·5% of the dibromide, 8·2% of the bromo-acid, and 76·1% of the lactone.

(iv) *Silver glutarate.* There was no evidence of the presence of trimethylene bromide. The product (24·4%) gave a distillate, b. p. 70—80°/2 mm. (54·0%) (Found: CO_2, 44·4 ; Br, 10·9%). These values indicate a mixture of 83·6% of the lactone (Calc. for $C_4H_6O_2$: CO_2, 51·1%) and 16·4% of the dibromide (Calc. for $C_3H_6Br_2$: Br, 79·2%). They do not agree so well with any mixture containing the bromo-acid. The residue (36·4%) (Found : CO_2, 52·2 ; Br, 0%) is a mixture of the lactone and 7·0% of glutaric acid (Calc. for $C_5H_8O_4$: CO_2, 66·6%). The reaction product consisted of 7·2% of the dibromide, 70·6% of the lactone, and 2·6% of glutaric acid. The deficiency shown by these figures is possibly due to the loss of the volatile dibromide.

Sub group D. (i) *Silver* iso*amylsuccinate.* The product (50·7%) (Found : CO_2, 13·7 ; Br, 35·0%) gave a neutral fraction (71·0%) (Found : CO_2, 7·1 ; Br, 44·6%), b. p. 85—95°/2 mm. (63·7%) (Found : CO_2, 4·3 ; Br, 55·4%), and a residue (35·0%) (Found: CO_2, 11·0 ; Br, 26·6%), presumably consisting of products of the Simonini-ester type. The CO_2 content of the distillate indicated the presence of an ester, a lactone being impossible. The distillate was therefore boiled with aqueous-alcoholic N/10-sodium hydroxide, to give 70·2% of a neutral material [Found : CO_2, 0·8 ; Br, 61·0. Mostly dibromide (Calc. for $C_7H_{16}Br_2$: Br, 62·0%)] and 12·1% of an acid (Found : CO_2, 24·5%). The residual aqueous solution contained 6·5% of bromine. The CO_2 content of the acid could correspond to that required by a dihydroxy-acid (Calc. for $C_8H_{16}O_4$: CO_2, 25·0%). To confirm this it was treated with silver oxide and ethyl iodide, but it gained only 11·2% in weight. The CO_2 content however proved to be 17·3% which is close to that required by the ethyl ester of a diethoxy-acid (Calc. for $C_{14}H_{28}O_4$: CO_2, 16·9%). The acid fraction (26·9%) (Found : CO_2, 24·1 ; Br, 17·7%) was a complex mixture from which no definite product could be isolated. The products of the reaction contained 31·7% of the dibromo-compound.

(ii) *Silver methylsuccinate.* No dibromide could be found in the carbon tetrachloride distillate. The product (28·5%) (Found : CO_2, 20·5%) gave a neutral fraction (60·0%) (Found : CO_2, 14·5 ; Br, 57·3%), b. p. 110—115°/2 mm. (58·3%) (Found : CO_2, 7·9 ; Br, 58·8%), probably mostly the dibromide (Calc. for $C_3H_6Br_2$: Br, 79·2%) mixed with an acidic substance of similar nature to that obtained from silver *iso*amylsuccinate. The residue (40·0%) (Found : CO_2, 17·7 ; Br, 50·1%) was not further investigated. The acid fraction (36·5%) was a complex mixture from which no definite product could be isolated. The reaction products contained a maximum of 26·0% of the dibromo-compound, which would be lowered if the ester in the neutral fraction itself contained bromine. The rest of the product was indefinite.

(iii) *Silver succinate.* The reaction mixture required 1½ hours' boiling. Fractionation of the carbon tetrachloride disclosed no ethylene dibromide. Dissolution of the product (20·2% yield) (Found: CO_2, 45·9%) in ether gave 37·7% of succinic acid (Found: CO_2, 74·6. Calc. for $C_4H_6O_4$: CO_2, 74·5%). The material (61·0%) (Found: CO_2, 32·8; Br, 39·1%) from the ethereal solution was again dissolved in ether, the solution was washed 3 times with water, and the washings were extracted with ether. Titration of the water showed CO_2, 40·3. 89% of material (Found: CO_2, 30·9; Br, 43·1%) was recovered from the ether. The bromine content corresponds to the presence of 82·5% of the bromo-acid (Calc. for $C_3H_5O_2Br$: CO_2, 28·7; Br, 52·2%), and 17·5% of a substance containing CO_2, 41·1%. The nature of the latter, as of the substance in the water, remains obscure. The reaction product contains 44·8% of bromo-acid, and 37·7% of succinic acid.

Sub-group E. (i) *Silver benzylmalonate.* The reaction mixture was boiled for ½ hour, and the silver residue well washed with hot carbon tetrachloride and then hot acetone. The carbon tetrachloride solution yielded 14·9% of a stiff syrup (Found: CO_2, 21·1; titratable Br, 31·6%). The yield of product from the acetone was 64·2% (Found: CO_2, 24·6°; titratable Br, 27·4; total Br, 38·1%); it was a glass, insoluble in ether. The analysis shows that only 12·0% of "CO_2" content had been lost, and that extensive bromination had occurred, some of the bromine having apparently even entered the ring. Treatment with alkali caused great darkening, even in the cold, and nothing but dark syrups or glasses could be isolated.

Group (5). *Aromatic Dibasic Acids.—Silver terephthalate.* The reaction mixture was boiled for 3 hours with occasional addition of more bromine. Examination of the silver residues by standard methods showed the presence of only 2·0% of silver bromide, 98·0% of the silver salt being recovered unchanged. Analysis of the product (5·8%) showed CO_2, 19·2%. Bromobenzoic acid $C_7H_5O_2Br$ requires CO_2, 21·8%, but as the product did not crystallise there can have been none of this acid present. There was too little product for further investigation.

Silver iso*phthalate.* The mixture was boiled for 3 hours. The silver residues were extracted with hot acetone in addition to carbon tetrachloride. The yield from both extracts was 13·6% (Found: CO_2, 26·8%). The neutral fraction (18·3%) was not further examined, but was probably the dibromide. The acid fraction (80·3%) (Found: CO_2, 36·0%), m. p. >300°, was boiled with benzene, in which *iso*phthalic acid is insoluble, and filtered. The crystalline residue (Found: CO_2, 52·0. Calc. for $C_8H_6O_4$: CO_2, 55·0%), was not further examined. Analysis of the silver residues indicated the presence of 21·6% of silver bromide, showing that 78·4% of the salt was unchanged. The reaction products appeared to consist of 37·7% of *iso*phthalic acid and 15·7% of a neutral substance, probably the dibromide, the rest of the product being unidentified.

Silver phthalate. The mixture was boiled for ½ hour. The carbon tetrachloride gave 34·7% of material (Found: CO_2, 25·7%). A further 12·6% were obtained by extracting the silver residues with hot acetone (Found: CO_2, 44·9%), this being dark and having m. p. 190—200°, unchanged by admixture with phthalic acid (Calc. for $C_8H_6O_4$: CO_2, 53·0%). The main product was extracted from ether with aqueous sodium hydroxide, leaving a neutral fraction (18·2%) (Found: CO_2, 0; Br, 62·6. Calc. for $C_6H_4Br_2$: Br, 68·3%). The dark acid fraction (80·9%) (Found: CO_2, 30·9%) was purified by treatment with silver oxide and ethyl iodide, to give an ester, b. p. 155—170°/2 mm. (88·7%) (Found: CO_2, 20·3; Br, 12·9%). The residual black tar was not further examined. The distillate was hydrolysed and the acidified solution (*A*) extracted with chloroform, in which phthalic acid is insoluble; the yield of partly crystalline product was 27·7% (Found: CO_2, 15·7%). Dibromobenzoic acid (Calc. for $C_8H_3O_2Br_2$: CO_2, 15·1%) is a strongly crystalline substance. Further extraction of (*A*) with ether yielded an oil (49·1%) (Found: CO_2, 39·9%), which when rubbed with chloroform afforded phthalic acid (m. p. and mixed m. p.); 62·4% of the ether-extracted material was recovered from the chloroform mother-liquors (Found: CO_2, 27·3%). This reaction gave 13·3% of the dibromide, 26·8% of phthalic acid, and a number of unidentified acidic products.

Note on the Purity of the Acids used.—Azelaic acid was made from Kahlbaum's monomethyl azelaäte; stearic and palmitic acids were Kahlbaum's and Schuchardt's respectively. The following were pure commercial products: hexoic, benzoic, nitrobenzoic, phenylacetic, phthalic, *iso*phthalic, terephthalic, adipic, and succinic acid. The sebacic acid, being coloured, was recrystallised once from glacial acetic acid. The keto-acids were made by Ruzicka and Stoll's method (*Helv. Chim. Acta*, 1927, **10**, 691). The other acids were made from ethyl malonate.

γ-iso*Amyladipic acid.* Ethyl sodiomalonate was treated successively with ethyl γ-bromobutyrate (from ethyl sodiomalonate and 2-phenoxyethyl bromide) and *iso*amyl bromide, and the product then hydrolysed, decarboxylated, and purified by re-esterification and distillation (Found: CO_2, 40·8. Calc. for $C_{11}H_{20}O_4$: CO_2, 40·7%); it had m. p. 66—68° and gave a silver salt (Found: Ag, 50·1. Calc. for $C_{11}H_{18}O_4Ag_2$: Ag, 50·2%).

α-iso*Amylglutaric acid.* Ethyl sodiomalonate was treated successively with ethyl β-bromopropionate and *iso*amyl bromide; the product, isolated as above, failed to crystallise, even on long storage (Found: CO_2, 43·4. Calc. for $C_{10}H_{18}O_4$: CO_2, 43·5%). The silver salt was also analysed (Found: Ag, 51·0. Calc. for $C_{10}H_{16}O_4Ag_2$: Ag, 51·9%).

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