

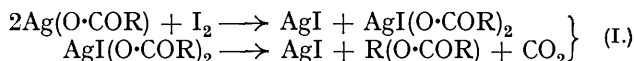
71. *Some Acyl Derivatives of Iodine.*

By J. W. H. OLDHAM and A. R. UBBELOHDE.

Iodine acyls are prepared by the action of iodine on silver salts, according to the reaction  $3R\cdot CO_2Ag + 2I_2 \longrightarrow 3AgI + I(O\cdot COR)_3$ . The production of solutions and of solid acyls is described. Important properties include a marked sensitiveness to moisture, and a ready decomposition on heating, possibly involving the liberation of free acyl radicals.

By boiling acyl derivatives with excess of iodine in non-reacting solvents, good yields of alkyl iodides are obtained. A convenient method of decarboxylation, based on this observation, is to heat the silver salt of the acid with excess of iodine under a dry solvent.

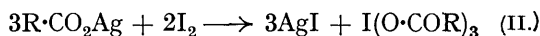
In connection with other investigations at the Davy Faraday Laboratory (Oldham and Ubbelohde, *Trans. Faraday Soc.*, 1939, **35**, 328; *Proc. Roy. Soc.*, 1940, **176**, A, 50) it has been necessary to review the application of standard organic reactions to the synthesis of long-chain aliphatic compounds (*idem*, J., 1938, 201; 1939, 201). The methods previously described have been extended by preparing rare long-chain alcohols with an odd number of carbon atoms from the more readily available fatty acids with an even number of carbon atoms (cf. Gascard, *Compt. rend.*, 1911, **153**, 1456). For this purpose, the method at first used was to warm the dry silver salt of the fatty acid with one equivalent of iodine, first at about 80°, with stirring, and then at about 120°. The reactions taking place have been stated to be (Simonini, *Monatsh.*, 1892, **13**, 320; 1893, **14**, 81) :



On account of side reactions, and of the fact that only half the acid is converted into the (esterified) alcohol, the method does not give very satisfactory yields; *e.g.*, from 206 g. of pure stearic acid there were obtained about 30 g. of recrystallised  $C_{17}H_{36}\cdot OH$ .

A preliminary account is now given of a new series of acyl derivatives of iodine. These can be used to give much more satisfactory yields of alkyl iodides from the corresponding fatty acids and thus provide a new method of decarboxylation, which may have considerable scope. In addition, the properties of the iodine acyls are of sufficient interest in connection with a number of other chemical problems to justify the rather incomplete description now attempted.

*Preparation of Solutions of Iodine Acyls.*—Provided suitable precautions be taken to exclude moisture, the preparation of solutions of iodine acyls is comparatively simple. The dry silver salt of the appropriate fatty acid is covered with a specially dried solvent, such as benzene, light petroleum ("AnalaR," free from unsaturated hydrocarbons), or carbon tetrachloride, and sufficient iodine added to convert all the silver salt into silver iodide. Tests showed that for the longer-chain fatty acids the amounts of iodine required are in accordance with the equation



For the shorter chains, other acyl derivatives appear to be formed in appreciable proportion.

The reactions are completed on gentle warming to about 40°, and the silver iodide is allowed to settle. It could be removed by filtration, but for many purposes the silver iodide does not interfere with subsequent reactions, and the rather tedious filtration is unnecessary.

*Isolation of Solid Iodine Acyls.*—Isolation of solid iodine acyls is somewhat more difficult than that of solid Grignard derivatives. The solutions, prepared as above and freed from silver salts by filtration, are cooled to about -20°, and the compound which separates is filtered off, care being taken to exclude moisture. Recrystallisation is usually necessary to remove impurities such as the free acid, and on some cases small quantities of other acyl derivatives are difficult to remove from the triacyl.

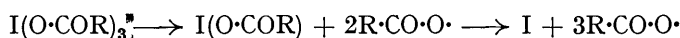
The solids resemble long-chain esters in appearance, but solutions of the triacyls have

a faint colour of vin rose even when freed as carefully as possible from the excess of iodine. After removal of all solvent by gentle warming in a vacuum, before exposure to the air, they have been kept for weeks in a desiccator, without undergoing serious decomposition. Dry acyls mixed with silver iodide can also be prepared as described below.

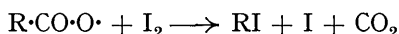
*Action of Heat on Solid Acyls.*—When solid acyls are warmed, melting is usually first observed. Marked evolution of gas then takes place suddenly round about 120°, and a complex mixture of products is formed, which includes the ester (*e.g.*, C<sub>17</sub>H<sub>35</sub>·O·CO·C<sub>17</sub>H<sub>35</sub> from iodine tristearate), carbon dioxide, iodine, some alkyl iodide, and possibly very small amounts of hydrocarbon. Noteworthy features of the thermal decomposition are the low temperature at which it occurs, and the fact that as the cl. in length of the acid is shortened, decomposition occurs with increasing violence. The significance of these features is discussed below.

*Action of Heat on Acyls in Solution: a New Method of Decarboxylation.*—When the iodine acyls are warmed in certain solvents, such as benzene or carbon tetrachloride, carbon dioxide is evolved. The products of thermal decomposition are qualitatively similar to those obtained from the dry solids. Other solvents such as toluene or xylene appear to react with the iodine acyls; in such cases the volume of free carbon dioxide from a given weight of acyl is much smaller and more complex products are formed.

A reaction of considerable value for a number of synthetic problems takes place when iodine acyls are warmed in non-reactive solvents in the presence of excess of iodine. This increases the evolution of carbon dioxide, and leads to the formation of comparatively high yields (up to 80% or more of the acid used) of alkyl iodides. On the basis of the hypothesis (see below) that the first action of heat on the iodine acyls is to liberate the free acyl radicals in solution,



the effect of excess of iodine appears to be to favour a reaction of the type



relative to a reaction leading to ester formation, such as



With a considerable excess of iodine and a low concentration of acyl in solution, the examples recorded below show that the formation of ester is repressed compared with the formation of alkyl iodide. The most suitable solvent appears to be benzene.

It is not necessary to filter off the silver iodide before using solutions of iodine acyls in this way. A simple method of decarboxylation is to heat the silver salt, under a solvent such as dry benzene or carbon tetrachloride, with excess of iodine till there is no further evolution of carbon dioxide (2—3 hours). In view of the difficulties frequently encountered in decarboxylation (*e.g.*, in sugar chemistry), extensions of this method promise to be of great interest. The salts of other metals are being compared with silver salts for this purpose, and the results will be recorded later.

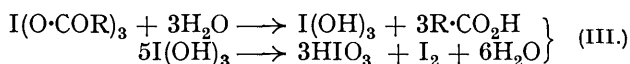
This method of decarboxylation has now been successfully applied to the production of the less common alkyl iodides, with an odd number of carbon atoms, from the commoner long-chain acids with an even number of carbon atoms. An amount of iodine approximately equal to that required by the reactions (II) and  $I(O\cdot COR)_3 + I_2 \longrightarrow 3CO_2 + 3RI$ , *i.e.*,  $R\cdot CO_2Ag + I_2 \longrightarrow AgI + CO_2 + RI$ , is added to the dry silver salt, which is then covered with the largest convenient volume of dry solvent, prepared as described below. The system is then boiled under reflux with exclusion of moisture for about 3 hours, and the alkyl iodide is isolated from the reaction mixture by the usual methods.

*Action of Water on the Iodine Acyls.*—The iodine acyls are remarkably sensitive to moisture, which probably explains why only one member of the series has been previously prepared, and that by quite different methods (Schutzenberger, *J. pr. Chem.*, 1861, **52**, 135; *Bull. Soc. chim.*, 1879, **31**, 104). When quite free from solvents, substances such as iodine tristearate can be transferred from one vessel to another without much decomposition, but if they are wetted even with supposedly hydrophobic organic solvents, they

rapidly become pink in the air, owing to the liberation of iodine. The water in benzene insufficiently dried over sodium can frequently be detected by adding it to a solution of an iodine acyl in really dry benzene (see below).

When solutions of iodine acyls in organic solvents are shaken with water, a golden colour appears momentarily in the aqueous layer, probably owing to the formation of a hydrated oxide of tervalent iodine (cf. Mellor, "A System of Inorganic Chemistry," Longmans, 1922, II, 285). Within a minute or two this colour disappears, and is replaced by that of free iodine, most of which migrates to the layer of organic solvent. When only small quantities of water are added, *e.g.*, as water dissolved in ether or benzene, crystals of iodic acid separate.

The analytical tests described below show that for the longer chains the main sequence of reactions can be represented by the equations



There is some evidence for the formation of uni- and quinque-valent acyl derivatives of iodine, but further investigation is required to prove their presence. With water, these could give rise to iodic acid and free iodine by disproportionation, just as in the case of triacyls, but the ratio of free iodine to iodic acid would be different.

Other properties of solutions of iodine acyls are the rapid interaction with metallic mercury at room temperature, and also with unsaturated hydrocarbons, with diethyl sulphide, and with *m*- and *p*-xylene. The course of these reactions can be followed from the visible changes in the system, and by analysis of the solutions at intervals, but a more detailed description must be deferred.

#### DISCUSSION.

The main facts which emerge from the experimental work can be summarised as follows :

(1) In the acyl iodides, as in the Simonini compounds containing silver, the linkage between iodine and the acyl groups is hydrolysed with remarkable ease by traces of water. It has not yet been possible to compare the effect of other hydroxylic compounds, so as to determine whether the mechanism of hydrolysis involves the attack of hydroxyl ions, or an interaction with hydroxyl groups bound by covalent links to other atoms.

(2) The linkage between iodine and the acyl groups breaks down with ease at comparatively low temperatures. In the absence of solvents, the decomposition appears to be autocatalytic, and is probably preceded by an induction period whose duration increases at lower temperatures. Further work is required before these physicochemical characteristics of the reaction can be regarded as finally proved. As the chain length of the acyl group is shortened, the thermal decomposition proceeds with increasing violence.

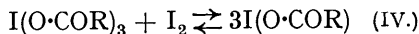
(3) When iodine acyls are warmed with solvents, the thermal decomposition can be followed from the evolution of carbon dioxide or from analysis of samples of the solution. Solvents such as carbon tetrachloride appear to act as inert diluents in the thermal decomposition, whereas toluene, xylene, and unsaturated hydrocarbons change the course of reaction, and give rise to much smaller quantities of carbon dioxide in the thermal decomposition.

(4) When the acyl iodides are boiled in dilute solution in inert solvents with excess of iodine, the preponderating reaction involves formation of alkyl iodides and free carbon dioxide. This reaction promises to be of use in synthetic organic chemistry.

(5) Analysis of the solids isolated as described below, and of solutions, shows that the main product when sufficient iodine acts on the silver salt of an organic acid is the tervalent iodine acyl, formed according to the equation (II) (p. 368). The formation of other acyls at the same time is not excluded.

These facts may be reviewed in conjunction with the known chemistry of multivalent iodine. Amongst the inorganic compounds, the additional valency links formed in passing from uni- to ter-valent iodine are known to be comparatively labile; a well-established

example is the thermal dissociation of iodine trichloride:  $\text{ICl}_3 \rightleftharpoons \text{ICl} + \text{Cl}_2$ . With the iodine acyls, some of the observations suggest an equilibrium of the type



but there is as yet no suggestion of a reversible dissociation according to the scheme  $\text{I(O}\cdot\text{COR)}_3 \rightleftharpoons \text{I(O}\cdot\text{COR)} + (\text{R}\cdot\text{CO}\cdot\text{O})_2$ .

As a working hypothesis, the thermal decomposition of iodine acyls is most simply regarded as primarily giving free acyl radicals, the iodine reverting to the univalent state, e.g.,  $\text{I(O}\cdot\text{COR)}_3 \longrightarrow \text{I(O}\cdot\text{COR)} + 2\text{R}\cdot\text{CO}\cdot\text{O}\cdot$ . As in the Kolbe reaction, these acyl radicals can split off carbon dioxide without much change of energy, but unlike the radicals in the Kolbe reaction, they are liberated in the melt or solid, instead of at a metal electrode.

When any molecule has just liberated a pair of radicals, they must necessarily be in close juxtaposition. The known instability of the peroxide link  $-\text{O}-\text{O}-$  (cf. Ubbelohde, *Proc. Roy. Soc.*, 1935, **152**, A, 371) makes a pairing of the radicals to form acyl peroxides unlikely, since there would not be much diminution in free energy. If one of the radicals loses carbon dioxide before pairing, the much more stable ester will be formed:  $\text{R} + \text{R}\cdot\text{CO}\cdot\text{O}\cdot \longrightarrow \text{R}\cdot\text{O}\cdot\text{COR}$ . Finally, if other reaction partners are available, a wide range of chemical possibilities might be realised. The present paper gives details only of the reaction with iodine.

In making a comparison with the Kolbe reaction, it seems noteworthy that not more than minute traces of the hydrocarbon  $\text{R}_2$  appear to be formed in the thermal decomposition of iodine acyls. Experiments are being made to test whether this can be correlated with the action of metal surfaces in the Kolbe reaction, or whether it means that the working hypothesis about the formation of acyl radicals will have to be modified.

The action of water on iodine triacyls leads to the transitory appearance of an orange compound, which then disproportionates to iodic acid and free iodine. The greater stability of higher oxides is probably to be ascribed to the increased possibilities of resonance when several oxygen atoms are linked to iodine (cf. the oxides of chlorine; Goodeve and Marsh, *J.*, 1939, 1332). Information on the relative stability of iodine acyls of different valencies is as yet incomplete, but promises to throw light on the higher valencies of iodine. Reference may also be made to recent work (Masson *et al.*, *J.*, 1938, 1699, 1702, 1708) on other derivatives of trivalent iodine, whose properties throw light on the behaviour of the iodine acyls.

#### EXPERIMENTAL.

*Preparation of Dry Silver Salts.*—Dry silver salts of the fatty acids are conveniently prepared by adding a very slight excess of ammonia to the acid, warming to dissolve it in a convenient volume of water or aqueous alcohol, and stirring in a slight excess of concentrated silver nitrate solution. The precipitate is stirred, set aside for some minutes, and then filtered off and washed, first with water and then repeatedly with acetone; the final product is dried at about  $100^\circ$ . Although these repeated washings were necessary to remove the water tenaciously held in the silver salt, yet the dry salts did not appear to absorb water from the atmosphere. Dry salts are essential for success in the subsequent operation; on account of the high molecular weight of some of the silver salts, a small percentage of water by weight can lead to a serious loss of iodine derivatives.

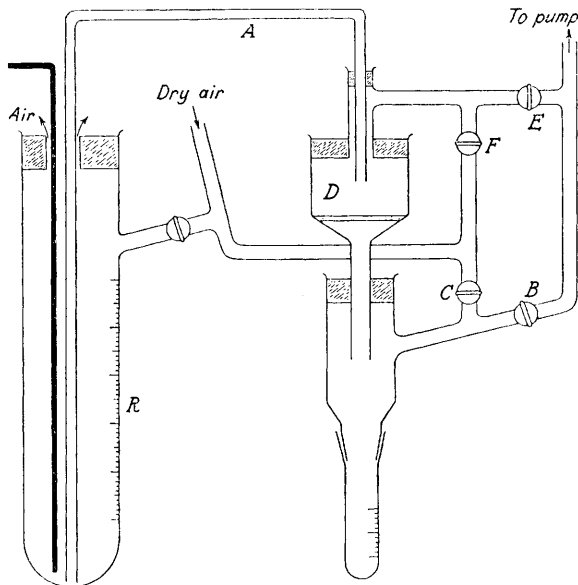
*Preparation of Dry Acyl Derivatives, mixed with Silver Iodide.*—This mixture suffices for many purposes. The Simonini compound is said to be obtained when the appropriate amount of iodine is mixed with the silver salt of a fatty acid at the bottom of a long test-tube. The mixture is maintained at about  $80^\circ$  and is stirred with a stainless steel rod for a few minutes, during which the colour of iodine gradually disappears. A counter-current of dry air at the top of the tube (see below) may be necessary with some silver salts, but has not been found to be important with salts of the fatty acids. The nominal equation for reaction is given in (I) (p. 368), but some iodine acyls must inevitably be formed under the conditions described. A simple test of further reaction with iodine is obtained by heating the reaction mixture to about  $120^\circ$ , so as to drive off carbon dioxide. The volume of carbon dioxide obtained from a given weight of silver salt is increased by about 50% when sufficient additional iodine is used to correspond with the equation



Owing to the imperfect mixing of two solids, it seems likely that the Simonini compound will react with further iodine in regions of the mix where the concentration of iodine is high, even if on the average the proportions of iodine and silver salt are maintained at 1 : 1. In practice, the preparation of acyl derivatives was usually carried out in the presence of solvents, to obtain more uniform mixing.

*Preparation of Dry Solvents for Reactions in Solutions.*—Owing to the remarkable sensitiveness of iodine acyls to water, special care is necessary to obtain sufficiently dry solvents. These are first dried as completely as possible by standard methods, sodium wire being used for "AnalaR" light petroleum (b. p. 60–80°, free from unsaturated hydrocarbons), benzene, and xylene, and calcium chloride for carbon tetrachloride.

A sufficient bulk of the last solvent is then warmed to about 10° below its b. p., and a fine stream of rigorously dried air is passed through it for about 90 minutes, a sintered-glass bubbler being used. For drying, the air stream is washed with 30% potassium hydroxide, concentrated sulphuric acid, 20% oleum, another tower of concentrated acid to absorb any sulphur trioxide, and two towers of phosphoric oxide, and is filtered from dust. Furthermore, the top of the tube containing the solvent to be dried is protected from entry of atmospheric moisture. A side



limb is fitted to the opening, and a stream of dry air is by-passed through it, to hinder diffusion inwards (see the reaction vessel on the left of the figure). For the other solvents, the same method could be used, or alternatively, fresh sodium wire could be added daily for a number of days.

After the heated solvent has been dried, it is allowed to cool with the air stream running, and can then be transferred with ordinary caution from one vessel to another, by syphoning and protecting any openings to the air with counter-currents of dry air. Larger bulks of carbon tetrachloride dried in this manner were occasionally used over a period of 2 or 3 days, but in most cases reaction between iodine and the silver salt was carried out in a vessel containing the solvent dried *in situ*.

This simple and economical method of obtaining really dry solvents is based on infra-red absorption measurements by

Fox and Martin (*Proc. Roy. Soc.*, 1940, **174**, *A*, 273), and was adopted after the presence of water in ordinary solvents had been detected from its reaction with iodine tristearate.

*Preparation of Solutions of Iodine Acyls.*—These preparations are carried out in a vessel of the type indicated on the left of the figure. For convenience in subsequent manipulation, this vessel may be graduated by volume. 10–15 C.c. of solvent per g. of iodine can be used, and the requisite amounts of silver salt and iodine are dropped in, according to equation (II) (p. 368). The reaction system is warmed at about 45° till the colour of free iodine disappears. Some reappearance of a reddish tint was noticed, particularly with palmitates and stearates, on cooling the reaction mixture. Provisional evidence has been obtained suggesting that this is due to some reversible equilibrium, such as (IV).

If the counter-current of dry air at the top of the tube is inadequate, in preparing solutions of iodine acyls, the entry of atmospheric moisture is at once evident from the appearance of a flush of free iodine where the moisture meets the dry reaction mixture. This flush is quite distinct from the reddish tint described in the preceding paragraph, as the tint is observed throughout the body of the solution, and not at an interface.

Solutions of iodine acyls so prepared contain suspended silver iodide. This can be allowed to settle, and for many purposes it does not interfere with subsequent applications of the acyls.

*Removal of Suspended Silver Iodide from Solutions.*—Whenever possible, reactions with solutions of iodine acyls are carried out *in situ*, the original reaction vessel being modified as required to suit subsequent operations. Removal of the silver iodide is complicated by its

fine state of division, and by the necessity to exclude atmospheric moisture at every stage of the filtration; it can be effected in the apparatus shown in the figure. After all the iodine has reacted with the silver salt in the vessel *R*, the solution is allowed to settle for 5—10 mins.; the supernatant liquid is then sucked over into the filter chamber *D* by manipulating the taps *F* and *E* which connect respectively to dry air and to vacuum. Before this transfer, the whole of the apparatus is washed several times with dry air, the tube *A* being closed at the reaction vessel end. Towards the end of the filtration, the silver iodide in *R* is sucked over, and is washed with fresh portions of dry solvent on the filter septum (porosity 3). The vacuum used for filtration is controlled by the tap *B*, which has a second tap immediately in sequence with it, not shown in the diagram, to facilitate control of the pressure.

The filtrate so obtained is practically free from suspended silver iodide. By measuring its volume, and titrating a small part for total oxidising power (see below), it is possible to determine what fraction of the iodine originally used has passed into the filtrate as a soluble iodine derivative. This titration is a useful check on the precautions against moisture. By using Pyrex apparatus, filled with dry air before use, and by applying counter-currents of dry air at every stage during which the solution might come into contact with atmospheric moisture, an average yield of 95% of soluble iodine derivative can be obtained. Any entry of moisture leads to the precipitation of iodic acid—oxidising power is retained in the residue instead of passing into the filtrate.

Solutions prepared and filtered in this way included acyls of the acids  $C_nH_{2n+1}\cdot CO_2H$  with  $n = 2, 3, 5, 7, 11, 15$ , and 17. With silver acetate the results were unsatisfactory.

The rate of spontaneous decomposition of the filtered solutions at room temperature may be illustrated for some experiments with iodine trilaurate.  $4.04 \times 10^{-2}$  Equiv. of iodine was treated with  $2.95 \times 10^{-2}$  equiv. of silver laurate at 40°, 136 c.c. of benzene, including the washings, being used. The solution was protected from atmospheric moisture as described, and 5 c.c. of the filtrate were analysed at intervals, to test how much oxidising power remained in solution, and also how much organic acid was formed on adding water. Unchanged iodine trilaurate would give an oxidising power equivalent to the iodine used, and would liberate organic acid equivalent to the silver laurate used. The rate of decay can be followed from the data below.

*Decomposition of a solution of iodine trilaurate at room temperature.*

Time of analysis.	Oxidising power, equivs. $\times 100$ .	Organic acid, equivs. $\times 100$ .
Used in preparation .....	4.04	2.95
After filtering AgI .....	3.59	2.78
"  "  after 24 hours ...	3.51	2.75
"  "  "  48  "  ...	3.10	2.53
"  "  "  96  "  ...	2.80	2.26
"  "  "  11 days .....	1.22	1.44
"  "  "  11  "  .....	0.47	1.11

The decomposition products appeared to be similar to those obtained on boiling (see below).

*Preparation of Solid Iodine Acyls.*—The isolation of solid acyls was attempted in a number of cases, in order to characterise more closely this new series of iodine derivatives. For this purpose we used a filtration apparatus similar to that shown in the figure, except that the sintered filter *D* was replaced by a longer, narrower model of porosity 2. A temperature jacket round this filter could be filled with alcohol, stirred by a stream of air. The acyl solution itself was freed as far as possible from silver iodide, and after transference to the sintered filter it was stirred by dry air bubbling up through the sintered glass septum. By adding fragments of solid carbon dioxide to the alcohol bath, this could be cooled so as to freeze out the acyl compound. A temperature of about  $-20^\circ$  was used for compounds having the longer chains. When sufficient solid had separated, suction was applied to the septum, and the mother-liquor was removed as completely as possible.

The solid acyl which remained was usually recrystallised by syphoning a fresh quantity of dry solvent into the filter at room temperature, so as to dissolve it. The resulting solution was again cooled to about  $-20^\circ$ , to separate the acyl a second time. This procedure was apt to clog the filter, in spite of the air bubbling up through the septum during the cooling. After cooling, the mother-liquor was again sucked off; analysis of the two mother-liquors showed that recrystallisation tended to leave behind a solid with a ratio of iodine to acyl more nearly 1 : 3 than in the crude product.

Finally, a stream of dry air was again passed up through the septum; the top of the filter

was partly exhausted, and the temperature of the outer jacket was gradually raised to about 45°, so as to remove any traces of solvent from the solid acyl, before exposing it to the atmosphere.

*Analytical Tests on the Reaction between Iodine and Silver Salts.*—The main analytical tests may be illustrated by specimen investigations. *Iodine propionate.*  $6.41 \times 10^{-2}$  Equiv. of iodine was treated with  $4.81 \times 10^{-2}$  equiv. of silver propionate in 117 c.c. of dry benzene. The mixture was stirred with a stainless steel rod, and was warmed at 40° till all the solid iodine had disappeared. After the silver iodide had settled, titration of 5 c.c. of the supernatant benzene solution showed that on the average the benzene contained  $6.40 \times 10^{-2}$  equiv. of oxidising power in all, thus verifying that all the oxidising power remained in solution.

This benzene solution was filtered as described, and 5 c.c. at a time were removed, shaken with water, and analysed. To determine the oxidising power, freshly standardised sodium hydrogen sulphite solutions were used. It was found that the aqueous layer contained  $0.16 \times 10^{-2}$  equiv. and the benzene layer  $0.02 \times 10^{-2}$  equiv. of oxidising power. After allowance for the samples removed from the original reaction system for analysis, and the total volume of filtrate being known, these tests showed that the filtrate contained 97% of the original iodine, in the form of a practically colourless derivative soluble in benzene.

The residue on the sintered filter (10.944 g.) was washed with hot aqueous ammonia and dried. The remaining weight of silver iodide (10.878 g.) was 96% of the theoretical for the reaction (II) (p. 368).

The ammoniacal washings were acidified, and found to contain 0.04 g. of silver iodate and 0.026 g. of silver propionate. The remaining 3.4% of silver salt unaccounted for in the residue may in part be due to experimental error, but some of it may have passed into the benzene filtrate as a silver derivative of an iodine acyl (*e.g.*, the Simonini compound) or as colloidal silver iodide.

The benzene filtrate containing the soluble iodine derivative was repeatedly shaken with water to decompose it, and the aqueous extracts were shaken with more benzene to remove free iodine. Titration of the aqueous layer showed that its total content of oxidising power (due to iodic acid) was  $4.47 \times 10^{-2}$  equiv., and that its total acidity corresponded with  $4.25 \times 10^{-2}$  equiv. of acid. By distilling off the propionic acid in a vacuum at 100°, it was shown that of this acidity  $3.5 \times 10^{-2}$  equiv. corresponded with propionic acid. The experimentally found ratios, *i.e.*, propionic acid : iodic acid (acidity) : iodic acid (oxidising power) = 1 : 0.21 : 1.28, may be compared with the theoretical ratios 1 : 0.20 : 1.20 which would be given by the equations (III) (p. 370). The iodic acid in the aqueous layer was further identified by evaporating some of the solution in a water-pump vacuum at 100°. Slightly red crystals were obtained; 1 g. of these gave 3.66, 0.57, and 0.61 centi-equivs. of oxidising power, acidity, and iodine (estimated as silver iodide), respectively (Calc. for  $\text{HIO}_3$  : 3.4, 0.57, and 0.57 centi-equivs., respectively). The rather high oxidising power may be due to the presence of some higher oxide of iodine, though the addition of aqueous potassium iodide and bicarbonate did not lead to the liberation of free iodine, so that little if any periodic acid can have been present.

The red crystals of crude iodic acid were dissolved in ammonia, leaving 0.5% of a red residue, too small in amount to permit further investigation. From the ammoniacal solution precipitates of silver iodate gave 99% of the oxidising power and 99.8% of the silver iodide required by theory for silver iodate.

In attempts to isolate the solid propionyl derivative, it was necessary to use light petroleum as solvent. With this solvent, as much as 10% of the silver passed into the filtrate. On cooling, the solid acyl derivative separated, but analysis showed that it contained appreciable amounts of silver derivatives. The compound melted and then decomposed with marked violence on warming.

With silver butyrate and iodine, crystals of an acyl derivative separated from light petroleum at  $-20^\circ$ , but as these melted below  $0^\circ$  they were not further isolated, owing to the difficulties of purification. An acyl derivative of lauric acid was readily isolated from light petroleum (*b. p.* 60–80°). On warming, it melted between 50° and 60°, and evolved carbon dioxide with violence at about 120°. It was completely soluble in cold benzene, giving a clear solution with a colour of vin rose. Analysis showed that, although its composition was not far from that for iodine trilaurate, it still contained appreciable amounts of a silver derivative.

*Iodine tristearate.* With this substance, purification was more successful. In a specimen preparation,  $4.15 \times 10^{-2}$  equiv. of iodine was warmed with  $3.02 \times 10^{-2}$  equiv. of silver stearate, about 100 c.c. of dry carbon tetrachloride being used as solvent. The solution could only be filtered with difficulty, and about 10% of the possible silver iodide passed into the first filtrate. The bulk of this was, however, removed by a second filtration. On cooling, the acyl derivative

separated from the solution. This was recrystallised once *in situ*, and gave a solid with a little free iodine. The free iodine was estimated by making up a dilute solution of the solid in benzene, and comparing the iodine colour with standard solutions of iodine in benzene. (In dilute solution the amount of free iodine estimated colorimetrically was independent of the dilution, but in concentrated solution the presence of the acyl derivative interfered with the estimation.)

After allowance for the free iodine, analysis of the solid gave  $n = 2.95$  in the formula  $I(O\cdot CO\cdot C_{17}H_{35})_n$ , based on its oxidising power and yield of fatty acid on hydrolysis, and  $n = 3.09$ , based on the content of iodine and yield of fatty acid. Other samples in independent preparations gave values of  $n$  with extreme limits of about 2.7 and 3.1. The solid was stored in a desiccator containing phosphoric oxide, together with a dish of silver stearate and some solid sodium hydroxide, to absorb any iodine vapour evolved. Over one month the loss of oxidising power did not exceed 3%. When the solid was warmed to about 140°, carbon dioxide was evolved corresponding roughly with one-third of the acyl groups present.

*Action of Heat on Iodine Acyls.*—When solid acyls are warmed, the action of heat leads to the formation of carbon dioxide, the ester  $R\cdot CO_2R$ , some alkyl iodide, and some of the original acid or anhydride. The thermal decomposition presents points of physicochemical interest, owing to the possible liberation of free acyl radicals, but detailed comment is reserved.

In the presence of solvents, the thermal decomposition of the acyls was studied by boiling silver salts of organic acids with iodine under a reflux condenser, various dry solvents being used. A slow stream of dried air was passed through the solution, to carry forward any carbon dioxide liberated through weighed bubblers containing concentrated potassium hydroxide solution. Numerous experiments were also carried out on solutions of iodine acyls obtained after filtering off the silver iodide, but no significant difference could be detected as a result of filtration.

Specimen results obtained under various conditions are given in the table for silver laurate and silver stearate with iodine. Similar results were obtained with the other acyls. The main point to note in these results is the high yield of alkyl iodide obtained on boiling with excess of iodine in fairly dilute solution. In many cases this method of obtaining alkyl iodides may be the most direct and convenient available.

Analysis of the decomposition products may be summarised for  $I(O\cdot CO\cdot C_{11}H_{23})_3$ . The solution was first shaken with aqueous sodium hydrogen sulphite, to remove free iodine, and then with standard baryta, to estimate the free acid or anhydride. The solvent was next distilled, and the residue separated by fractional distillation in a vacuum. Analyses by Stepanov's method of the alkyl iodide fraction ( $C_{11}H_{23}I$ , b. p. 125—130°/5 mm.) gave results about 3% low in iodine, and on conversion of the iodide into the ester, by heating with silver laurate, small quantities of an unsaturated compound were left unconverted. This substance was completely soluble in concentrated sulphuric acid, but the amounts were too small for identification.

*Reaction products obtained on boiling solutions of iodine acyls.*

Ag : I.	Solvent.	Wt. % of iodine acyl.	CO <sub>2</sub> liberated, % (3 mols. = 100%).	Alkyl iodide, %.	Acid recovered, %.
<i>Silver laurate.</i>					
1 : 2	Benzene	5.1	95.6	87.7	12.2
1 : 2	"	8.8	77.5	73.7	12.4
1 : 1.37	"	7.1	72.5	72.5	11.5
1 : 2	Light petroleum	5.3	63.8	65.7	11.8
1 : 2	" "	9.5	73.7	55.5	18.4
1 : 1.37	" "	7.2	70.2	51.7	16.9
1 : 2	CCl <sub>4</sub>	4.9	90.9	78.0	11.4
1 : 2	"	9.3	83.3	70.2	10.8
1 : 1.36	"	9.5	67.2	(48.0)	10.4
<i>Silver stearate.</i>					
1 : 1.33	Benzene	6.3	65.3	—	7.0
1 : 1.33	"	7.4	71.9	64.4	26.1

After separation of the alkyl iodide by distillation, the high-boiling residue was shown by m. p. and mixed m. p. to be mainly the ester  $C_{11}H_{23}\cdot O\cdot CO\cdot C_{11}H_{23}$ . Hydrolysis with alcoholic sodium hydroxide, followed by extraction with benzene, gave mainly the alcohol  $C_{11}H_{23}\cdot OH$ , identified similarly.

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