177. *The Reactions of Metallic Salts of Acids with Halogens. Part II.* The Interaction of Silver Trifluoroacetate or Silver Perchlorate and Halogens in Various Solvents.*

By R. N. HASZELDINE AND A. G. SHARPE.

Silver trifluoroacetate and iodine in nitrobenzene yield a solution containing iodine trifluoroacetate, $CF_3\cdot CO_2I$, or a complex of probable composition $(CF_3\cdot CO_2)_2AgI$, the product depending on the molecular proportions of the reactants. Iodine trifluoroacetate (trifluoroacetyl hypoiodite) is a powerful iodinating agent by virtue of the " positive " iodine it contains, and iodinates aromatic compounds in the positions expected for attack by an electrophilic reagent. In nitrobenzene, which is only very slightly attacked, iodine trifluoroacetate undergoes thermal decomposition to yield trifluoroiodomethane and carbon dioxide as main products. Re-examination of the interaction of silver perchlorate and iodine in ether leads to the conclusion that there is no evidence for the existence of the chlorine tetroxide postulated by Gomberg (*J. Amer. Chem. Soc.*, 1923, **45**, 398) as a product of this reaction.

Bromine and silver trifluoroacetate form a powerful brominating mixture which at low temperatures reacts by a " positive " bromine mechanism. Uses of these new halogenating agents are indicated.

THE action of heat on a mixture of silver trifluoroacetate and excess of iodine is represented by the equation $CF_3\cdot CO_2Ag + I_2 = CF_3I + AgI + CO_2$ (Haszeldine, *Nature*, 1950, **166**, 192; *J.*, 1951, 584). Kleinberg (*Chem. Reviews*, 1947, **40**, 381; where full references are given) has classed reactions between silver salts of carboxylic acids and halogens in two groups: when one mol. of silver salt is treated with one or more mols. of halogen, a compound $R\cdot CO_2X$ is formed, and this undergoes thermal decomposition into RX and carbon dioxide; when, however, two mols. of silver salt are treated in an inert solvent with one mol. of iodine, a complex $(R\cdot CO_2)_2AgI$ is formed, and the action of heat then gives the ester $R\cdot CO_2R$, silver iodide, and carbon dioxide. The present paper gives an account of the interaction of halogens and silver trifluoroacetate in various solvents; and since silver trifluoroacetate, like silver perchlorate, is the salt of a very strong acid and is soluble in benzene and in ether, the bearing of our results on the disputed interpretation of the reaction between silver perchlorate and iodine in ether (Gomberg, *J. Amer. Chem. Soc.*, 1923, **45**, 398; Birckenbach and Goubeau, *Ber.*, 1932, **65**, 395; Gomberg and Gamrath, *Trans. Faraday Soc.*, 1934, **30**, 24; Goodeve, *ibid.*, p. 30; Sidgwick, " The Chemical Elements and their Compounds," Oxford Univ. Press, 1950; Kleinberg, " Unfamiliar Oxidation States and their Stabilization," Univ. Kansas Press, 1950) is considered. We conclude that, as was first suggested by Birckenbach and Goubeau, there is no evidence which requires Gomberg's supposition of the formation of chlorine tetroxide in this reaction.

The only inert solvent suitable for quantitative study of the interaction of iodine and silver trifluoroacetate is nitrobenzene. In this solvent, when iodine is shaken with excess of the silver salt, the colour of the iodine disappears, and one mol. of silver iodide is formed from every mol. of iodine. If potassium iodide solution is added, iodine equivalent in quantity to that taken as reactant is liberated, even if the mixture of reaction products is kept at room temperature for 24 hours before determination of the residual oxidising power. The first stage in the reaction is therefore $CF_3\cdot CO_2Ag + I_2 \longrightarrow CF_3\cdot CO\cdot OI + AgI$. It appears, however, that iodine trifluoroacetate (trifluoroacetyl hypoiodite) forms a complex with silver trifluoroacetate by a reaction analogous to those between iodine and silver salts of other carboxylic acids: $CF_3\cdot CO_2Ag + CF_3\cdot CO\cdot OI \longrightarrow (CF_3\cdot CO_2)_2AgI$. Hence, when iodine and silver trifluoroacetate are taken in exactly molar proportions in nitrobenzene, less than one mole of silver iodide is precipitated, and the iodine colour persists in the solution; iodine and iodine trifluoroacetate are therefore competing for the silver salt. If the iodine trifluoroacetate is removed, the equilibrium between iodine,

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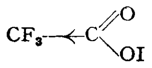
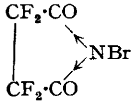
* Part I, *J.*, 1951, 584.

iodine trifluoroacetate, and the complex is disturbed, and precipitation of one mol. of silver iodide is quantitative; this may be effected by addition of phenol, which is very rapidly iodinated by iodine trifluoroacetate at room temperature. Uses of iodine and silver trifluoroacetate as an iodinating mixture in organic chemistry are described below; the high iodinating power makes it impossible to use benzene, ether, or chloroform as a volatile solvent suitable for the preparation and isolation of the iodine trifluoroacetate–silver trifluoroacetate complex (cf. Swarts, *Anal. Soc. Fis. Quim.*, 1929, **27**, 683). The use of trifluoroacetic acid as solvent is prevented by the insolubility of iodine in the acid. Iodine trifluoroacetate and the complex are stable in nitrobenzene for several hours at room temperature, but their isolation from solution cannot be effected: attempts to remove the solvent by distillation produce decomposition (see below).

In iodine trifluoroacetate or the iodine trifluoroacetate–silver trifluoroacetate complex, the powerful inductive effect of the trifluoromethyl group as in (I) will render the iodine more positive than in analogous derivatives of other carboxylic acids. The possession of halogenating powers by iodine or bromine and silver trifluoroacetate is in accord with

(I) 

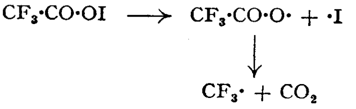
 (II)

recent work by Henne and Zimmer (*J. Amer. Chem. Soc.*, 1951, **73**, 1103) on positive bromine from perfluoro-*N*-bromosuccinimide (II), which is a more powerful and more specific brominating agent than *N*-bromosuccinimide itself, and is also in accord with the increased positive nature of iodine in trifluoroiodomethane (Banus, Emeléus, and Haszeldine, *J.*, 1951, 60).

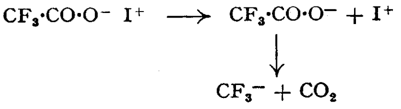
Iodine and silver trifluoroacetate as an iodinating mixture are similar to, but less powerful than, the iodine and silver perchlorate mixture described by Birckenbach and Goubeau (*loc. cit.*). Iodine perchlorate and benzene at room temperature react completely within a few minutes, but iodination with iodine and silver trifluoroacetate requires several hours. Iodine trifluoroacetate has, however, important advantages: trifluoroacetic acid, formed by the reaction $RH + CF_3{\cdot}CO{\cdot}OI \longrightarrow RI + CF_3{\cdot}CO_2H$, is volatile (b. p. 71·5°) and is therefore readily removed by distillation; the dangers and by-products attending the use of silver perchlorate (an exceedingly powerful oxidising agent) are avoided; and silver trifluoroacetate is more soluble in organic solvents than silver trichloroacetate, acetate, perchlorate, or sulphate (cf. Derbyshire and Waters, *J.*, 1950, 3694).

Iodination by iodine trifluoroacetate is rapid at higher temperatures, and the following substances have been iodinated (main products are shown in parentheses): benzene (iodobenzene), iodobenzene (*p*-di-iodobenzene), bromobenzene (*p*-bromoiodobenzene), chlorobenzene (*p*-chloroiodobenzene), toluene (*p*-iodotoluene), thiophen (2 : 5-di-iodothiophen), aniline (*p*-iodoaniline), and anisole (*p*-iodoanisole). It should be emphasised that the conditions described in the Experimental section are not necessarily the mildest which can be used; many of the iodinations described will take place more slowly at room or moderate temperatures, and such temperatures can be used if, in a particular instance, the iodinated product would be thermally unstable. For the preparation of simple aromatic iodo-compounds, most of which are thermally stable, the rapid iodination at higher temperatures is more convenient.

The iodination of benzene gave some *p*-di-iodobenzene in yields inversely proportional to the amount of benzene used as solvent. In the iodination of the substituted benzenes mentioned above it is noteworthy that the *p*-iodo-isomer predominates. Small amounts of the *o*-derivative were detected from chlorobenzene and toluene, but in no instance was the *m*-derivative found. The fission of the oxygen–iodine bond in iodine trifluoroacetate can clearly occur by two distinct mechanisms:

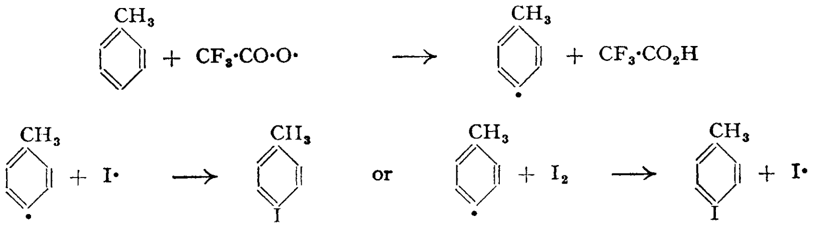
(*a*) 

$$CF_3{\cdot}CO{\cdot}OI \longrightarrow \underset{\displaystyle \downarrow \atop \displaystyle CF_3{\cdot} + CO_2}{CF_3{\cdot}CO{\cdot}O{\cdot}} + {\cdot}I$$

(*b*) 

$$CF_3{\cdot}CO{\cdot}O^-\ I^+ \longrightarrow \underset{\displaystyle \downarrow \atop \displaystyle CF_3^- + CO_2}{CF_3{\cdot}CO{\cdot}O^-} + I^+$$

If bond fission in iodine trifluoroacetate in solution were by a free-radical mechanism of type (*a*), nuclear iodination would be improbable, since iodine atoms are not known to attack aromatic nuclei; side-chain iodination might occur, but the products of such a reaction were not found in the examples considered. It is unlikely that nuclear iodination is effected by the abstraction of nuclear hydrogen by the $CF_3{\cdot}CO{\cdot}O{\cdot}$ or $CF_3{\cdot}$ radical followed by combination of the resulting radical with iodine, *e.g.*,



since, in general, free radicals will not abstract nuclear hydrogen from aromatic compounds but will react either by attack on side-chain hydrogen atoms or by substitution in the aromatic nucleus. For the attack of the $CF_3{\cdot}CO{\cdot}O{\cdot}$ radical on toluene, possible products would be :

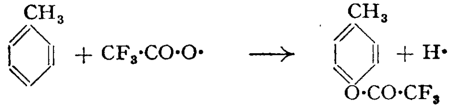
(1) $$Ph{\cdot}CH_3 + CF_3{\cdot}CO{\cdot}O{\cdot} \longrightarrow Ph{\cdot}CH_2{\cdot} + CF_3{\cdot}CO_2H$$

$$2Ph{\cdot}CH_2{\cdot} \longrightarrow Ph{\cdot}CH_2{\cdot}CH_2Ph$$

or

$$Ph{\cdot}CH_2{\cdot} + I{\cdot} \longrightarrow Ph{\cdot}CH_2I$$

(2)



cf.

$$C_6H_6 + C_6H_5{\cdot} \longrightarrow C_6H_5{\cdot}C_6H_5 + H{\cdot}$$

The resonance-stabilised benzyl radical when prepared by other routes is known to react mainly by dimerisation : neither dibenzyl nor benzyl iodide was a product of reaction. Fluorine-containing benzene derivatives were not isolated, and, after allowance for handling losses, most of the silver trifluoroacetate was recovered as trifluoroacetic acid.

The *op*-iodination of the compounds studied is in complete accord with iodination by an entity which carries a positive charge, *i.e.*, with ionisation of the type (*b*) above; the compounds concerned contain groups known to activate the aromatic nucleus to electrophilic attack.

Both nitrobenzene and benzoic acid resist attack by electrophilic reagents, and if substitution is to occur at all it will be at the *m*-positions. Nitrobenzene is not affected by iodine trifluoroacetate, and the main products obtained on heating are trifluorciodomethane and carbon dioxide arising by thermal decomposition, $CF_3{\cdot}CO{\cdot}OI \longrightarrow CF_3I + CO_2$, of the type observed in the absence of a solvent. Benzoic acid in nitrobenzene solution is attacked by iodine trifluoroacetate to yield *m*-iodobenzoic acid [cf. iodine and silver benzoate at 150° which yield *m*-iodobenzoic acid (Birnbaum and Reinherz, *Ber.*, 1882, **15**, 456), presumably *via* $C_6H_5{\cdot}CO{\cdot}OI$ as iodinating agent]. Even if the trifluoroacetoxy-radical were capable of substituting into benzoic acid, then the *p*- and not the *m*-trifluoroacetoxybenzoic acid would be expected, since the *p*-position is favoured for free-radical attack on substituted benzenes. Trifluoroacetoxybenzoic acid and *p*-iodobenzoic acid were not isolated.

The above evidence indicates strongly that iodine trifluoroacetate iodinates in solution by a positive iodine mechanism.

The decarboxylation with simultaneous iodination which occurs when iodine trifluoroacetate is heated in nitrobenzene solution could occur by a free-radical mechanism or, since nitrobenzene is an ionising solvent, by an ionic mechanism : $CF_3{\cdot}CO{\cdot}O^- \; I^+ \longrightarrow$

$CF_3^- + I^+ + CO_2 \longrightarrow CF_3I + CO_2$. This decomposition would be opposed by the stability of the $CF_3{\cdot}CO{\cdot}O^-$ ion; studies on sodium trifluoroacetate by Auerbach, Verhoek, and Henne (*J. Amer. Chem. Soc.*, 1950, **72**, 299) have shown that the activation energy for the decarboxylation of $CF_3{\cdot}CO{\cdot}O^-$ is 42 kcal. mole^{-1} as compared with 31·6 kcal. mole^{-1} for $CCl_3{\cdot}CO{\cdot}O^-$. This would mean that if iodine trifluoroacetate decomposed by this mechanism, it could be used as an iodinating agent at a higher temperature than iodine trichloroacetate or iodine acetate, as well as being a more powerful agent than either of these. The radical decomposition of iodine trifluoroacetate will clearly be favoured by higher temperatures.

Simonini's reaction (*Monatsh.*, 1892, **13**, 320) by which the ester of the acid under investigation is prepared, *e.g.*,

$$CH_3{\cdot}[CH_2]_n{\cdot}CO_2Ag \xrightarrow{I_2} CH_3{\cdot}[CH_2]_n{\cdot}CO{\cdot}O{\cdot}[CH_2]_n{\cdot}CH_3$$

presumably occurs by an ionic mechanism

$$CH_3{\cdot}[CH_2]_n{\cdot}CO_2Ag + I_2 \longrightarrow CH_3{\cdot}[CH_2]_n{\cdot}CO{\cdot}OI + AgI$$

$$CH_3{\cdot}[CH_2]_n{\cdot}CO{\cdot}O{\cdot}I \longrightarrow CH_3{\cdot}[CH_2]_n{\cdot}I + CO_2$$

$$CH_3{\cdot}[CH_2]_n{\cdot}CO_2Ag + CH_3{\cdot}[CH_2]_n{\cdot}I \longrightarrow CH_3{\cdot}[CH_2]_n{\cdot}CO{\cdot}O{\cdot}[CH_2]_n{\cdot}CH_3 + AgI$$

The predominance of the formation of trifluoroiodomethane (as distinct from the ester, trifluoromethyl trifluoroacetate, by the reaction $CF_3{\cdot}CO_2Ag + CF_3I \longrightarrow CF_3{\cdot}CO{\cdot}O{\cdot}CF_3 + AgI$) when iodine and silver trifluoroacetate are heated alone or in nitrobenzene solution is in accord with the absence of reactions of trifluoroiodomethane which would involve heterolytic fission of the carbon–iodine bond to give CF_3^+ and I^- (Banus, Emeléus, and Haszeldine, *loc. cit.*).

If the ionic mechanism for the Simonini reaction is valid, the last step, $R{\cdot}CO_2Ag + RX \longrightarrow R{\cdot}CO_2R + AgX$, should be facilitated if R is electron-releasing, *e.g.*, if R is an unfluorinated alkyl radical. When R is aromatic, ester formation from RX is much more difficult, and RX and nuclear-halogenated by-products are formed from $R{\cdot}CO_2X$ in proportions depending on the nature of substituents in the nucleus. Silver *m*-methoxybenzoate and bromine in carbon tetrachloride, for example, yield 2-bromo-3-methoxybenzoic acid as the main product (Dauben and Tilles, *J. Amer. Chem. Soc.*, 1950, **72**, 3185). Nuclear bromination by $CH_3{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}OBr$ is apparently the main reaction, and the failure of bromine and silver perchlorate to react with *m*-methoxybenzoic acid under the same conditions (—20°) is probably due to the insolubility of silver perchlorate in carbon tetrachloride, and not to a difference in brominating power between acyl hypobromite and bromine perchlorate.

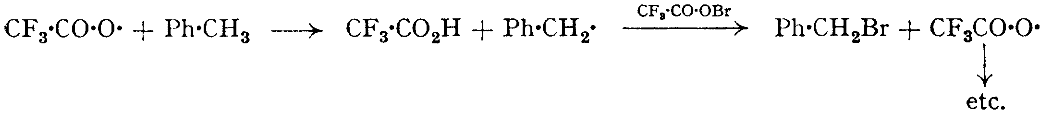
When R contains an electronegative group such as NO_2, the positive nature of X in $R{\cdot}CO_2X$ and RX will be increased, with further reduction in the amount of ester formed; in addition, the aromatic ring in R will be less susceptible to attack by X^+, and decarboxylation of $R{\cdot}CO_2X$ should become the main reaction. Thus silver *m*-nitrobenzoate and bromine in carbon tetrachloride yield *m*-bromonitrobenzene (68%) as the main product (Dauben and Tilles, *loc. cit.*).

The stoicheiometry of the reaction between bromine and silver trifluoroacetate has not been investigated. These substances when heated together in the absence of a solvent yield bromotrifluoromethane, silver bromide, and carbon dioxide (Haszeldine, *loc. cit.*); in solution, however, they constitute a powerful and useful brominating mixture (cf. Henne and Zimmer, *J. Amer. Chem. Soc.*, 1951, **73**, 1362). Bromination of the following compounds has been effected by a procedure similar to that used with iodine trifluoroacetate: benzene (to bromobenzene), bromobenzene (*p*-dibromobenzene), chlorobenzene (*p*-bromochlorobenzene), toluene (*p*-bromotoluene), anisole (*p*-bromoanisole), aniline (*p*-bromoaniline), and benzoic acid (*m*-bromobenzoic acid). These results are in accord with attack by a positive brominating entity, probably Br^+ from bromine trifluoroacetate. The reactions are similar to those between bromine, silver perchlorate, and organic compounds investigated by Birckenbach and Goubeau (*loc. cit.*), and although bromine perchlorate is the more powerful brominating agent, bromine trifluoroacetate has marked advantages similar to those indicated above for iodine trifluoroacetate. Bromine and silver trifluoroacetate react at once in trifluoroacetic acid, and the use of this acid as an inert solvent is being explored.

The conditions recorded in the Experimental section are probably more vigorous than actually required. The bromination of anisole, for example, proceeds steadily at 0°, although the reaction can be hastened by slowly raising the temperature from 20° to 120°. With toluene, product and yield were the same when the reaction was carried out by raising the temperature to reflux as when the reactants were kept at room temperature. The reaction, which clearly occurs rapidly at room temperature, and yields exclusively the *p*-bromo-isomer, undoubtedly involves an ionic mechanism. A radical decomposition of $CF_3{\cdot}CO{\cdot}OBr$ to yield bromine atoms ($CF_3{\cdot}CO{\cdot}OBr \longrightarrow CF_3{\cdot}CO{\cdot}O{\cdot} + Br{\cdot}$) would result in bromination in the side chain (as in bromination by bromine in the presence of heat, peroxides, or light) and not in the nucleus.

When the bromine was added to silver trifluoroacetate in toluene at 110° in the absence of light, nuclear bromination was still the main reaction but some benzyl bromide and small amounts of dibenzyl were formed. These could arise either by the free-radical decomposition of bromine trifluoroacetate to give bromine atoms as above, or by the reaction of bromine with the methyl group of toluene rather than with silver trifluoroacetate.

At higher temperatures, or with compounds which resist ionic halogenation, it may be possible to use bromine trifluoroacetate as a brominating agent analogous to *N*-bromosuccinimide. A chain reaction analogous to that postulated for bromination by the latter reagent can be visualised :



$$CF_3{\cdot}CO{\cdot}O{\cdot} + Ph{\cdot}CH_3 \longrightarrow CF_3{\cdot}CO_2H + Ph{\cdot}CH_2{\cdot} \xrightarrow{CF_3{\cdot}CO{\cdot}OBr} Ph{\cdot}CH_2Br + \underset{\text{etc.}}{\underset{\downarrow}{CF_3CO{\cdot}O{\cdot}}}$$

The competing reaction involving the thermal decomposition of bromine trifluoroacetate to bromotrifluoromethane and carbon dioxide may predominate, however, with compounds less susceptible to radical attack. Reactions with unsaturated compounds such as *cyclo*hexene will be described in a later communication.

The bromination of benzoic acid in nitrobenzene yielded the *m*-derivative; the isolation of *m*-bromonitrobenzene and the evolution of some carbon dioxide without simultaneous formation of bromotrifluoromethane indicated that slight attack on the solvent also took place. Nitrobenzene itself gave a low yield of *m*-bromonitrobenzene; bromotrifluoromethane and unidentified products were also formed.

The evidence presented above shows that in solution the halogen trifluoroacetates (trifluoroacetyl hypohalites) can act as sources of positive halogens, thereby providing powerful and specific halogenating agents.

It was reported by Gomberg (*loc. cit.*) that in ether (though not in other solvents) prolonged interaction of iodine and silver perchlorate proceeds according to the equation $2AgClO_4 + I_2 \longrightarrow 2AgI + 2ClO_4$, yielding a solution of chlorine tetroxide, which is distinguished from perchloric acid by its liberation of iodine from hydrogen iodide. The stoicheiometry, however, and in particular the retention of oxidising power after 2·00 mols. of silver iodide had been precipitated at the end of a slow reaction, were not rigidly established. Birckenbach and Goubeau (*loc. cit.*) suggested the intermediate formation of iodine perchlorate, $AgClO_4 + I_2 \longrightarrow AgI + IClO_4$, followed by iodination of the ether to give an unstable iodo-ether which slowly reacted with the second mol. of silver perchlorate, forming another mol. of silver iodide, $AgClO_4 + RI \longrightarrow AgI + RClO_4$. They found that at the end of the reaction the characteristic oxidising properties claimed for the oxide ClO_4 had vanished, and attributed this to complete consumption of the iodine perchlorate in iodinating the solvent. Later authors have disagreed on the interpretation of the facts without presenting further experimental material : Gomberg and Gamrath (*loc. cit.*) have affirmed their faith in the existence of the tetroxide, and their conclusions have been very recently accepted by Kleinberg (*loc. cit.*); Goodeve (*loc. cit.*) and Sidgwick (*loc. cit.*) regard its existence as unproven.

Birckenbach and Goubeau showed conclusively that when iodine and silver perchlorate react with an aromatic compound the overall reaction is $C_6H_5X + I_2 + AgClO_4 \longrightarrow C_6H_4XI + AgI + HClO_4$, nuclear iodo-compounds not being affected by the presence of excess of silver perchlorate in ether. Their postulated ready reaction between the iodinated ether and the silver salt could not, however, be verified, owing to the instability of the iodinated ether. Later work by Meyer and Spormann (*Z. anorg. Chem.*, 1936, **228**, 341), however, strongly supports the postulate: alkyl iodides in general react with silver perchlorate in ether at ordinary temperatures, *e.g.*, $C_2H_5I + AgClO_4 \longrightarrow C_2H_5ClO_4 + AgI$. We find that the stoicheiometry of the iodine–silver trifluoroacetate reaction in ether is similar to that for the iodine–silver perchlorate reaction; the first precipitation of silver iodide is followed by a slow secondary precipitation, and much more than one mol. of silver iodide per mol. of iodine is obtained, while the oxidising power of the solution decreases. Reinvestigation of the reaction between iodine and silver perchlorate showed that within thirty minutes of mixing ethereal solutions of iodine and silver salt the weight of silver iodide formed corresponded to 1·4 mols. per mol. of iodine, and part of the oxidising power remained; when, after a few hours, the yield of silver iodide approached 2·0 mols. per mol. of iodine, all of the oxidising power had vanished. Gomberg's assumption that ether is an inert solvent in the reaction is therefore incorrect; and with the demonstration that, for the formation of more than one mol. of silver iodide per mol. of iodine, reaction with the solvent is an essential step, all need for supposing the formation of chlorine tetroxide in the reaction between iodine and silver perchlorate disappears.

EXPERIMENTAL

Materials.—Silver trifluoroacetate, prepared as described earlier (Haszeldine, *loc. cit.*), was purified by ether extraction, and dried *in vacuo* before use. Organic reactants and solvents were carefully purified and dried by standard techniques, and moisture was excluded from all reactions. Silver perchlorate, prepared by Hill's method (*J. Amer. Chem. Soc.*, 1921, **43**, 254), iodine, and bromine were dried over phosphoric anhydride before use.

Interaction of Iodine and Silver Trifluoroacetate in Nitrobenzene.—In nitrobenzene, 0·523 g. (2·07 m.-moles) of iodine yielded with excess of silver trifluoroacetate 0·506 g. (2·14 m.-moles) of silver iodide (filtered on a Gooch crucible, washed with nitrobenzene and acetone, and dried at 120°). In another experiment, a solution of iodine in nitrobenzene completely retained its oxidising power towards potassium iodide 24 hours after addition of the silver trifluoroacetate. Interaction of 0·686 g. (2·70 m.-moles) of iodine and 0·596 g. (2·70 m.-moles) of silver trifluoroacetate yielded 0·470 g. (2·00 m.-moles) of silver iodide, the colour of the iodine persisting in the solution; 0·908 g. (4·10 m.-moles) of silver trifluoroacetate and a five-fold excess of iodine similarly gave 0·735 g. (3·15 m.-moles) of silver iodide. The iodine trifluoroacetate–silver trifluoroacetate complex is therefore not decomposed by iodine to any considerable extent.

When 0·806 g. (3·64 m.-moles) of silver trifluoroacetate and 0·930 g. (3·65 m.-moles) of iodine were allowed to react, the iodine colour again remained in the solution; on addition of 2 g. of phenol it immediately disappeared; the yield of silver iodide was then 0·845 g. (3·60 m.-moles). The titre of a solution of iodine in nitrobenzene was not affected by addition of phenol.

Interaction of Iodine and Silver Trifluoroacetate in Benzene.—A slow attack on benzene at 20° by iodine trifluoroacetate was demonstrated by determining the oxidising activity of a solution containing 0·413 g. (1·62 m.-moles) of iodine and excess of silver trifluoroacetate after 18 hours; this was only equivalent to 1·49 m.-moles of iodine. Evaporation *in vacuo* over silica gel of the filtrate from 0·244 g. (0·96 m.-mole) of iodine and 0·425 g. (1·92 m.-moles) of silver trifluoroacetate yielded a pale yellow residue which had a faint odour of trifluoroacetic acid and liberated iodine from potassium iodide only in the presence of acid (iodine liberated, 0·67 m.-mole). In concentrated solution, therefore, decomposition of the complex or marked attack on the solvent had taken place.

Phenol reacts much faster than benzene with iodine trifluoroacetate, and it was shown that very nearly one mol. of iodine is converted into the reactive iodinating entity by one mol. of silver salt. Solutions of 0·711 g. (3·22 m.-moles) of silver trifluoroacetate and 1·212 g. (4·78 m.-moles) of iodine were mixed, and 5 g. of phenol were added. Determination of the residual iodine (by thiosulphate titrate) after 5 minutes showed 0·430 g. (1·68 m.-moles) to be present; 3·10 m.-moles had therefore yielded 3·10 m.-moles of CF_3·CO·OI on treatment with 3·22 m.-moles of silver salt.

Interaction of Iodine and Silver Trifluoroacetate in Ether.—When solutions of iodine and silver trifluoroacetate were mixed, an immediate precipitate formed; if this was filtered off and the filtrate set aside, a further precipitate slowly developed. When 0·554 g. (2·18 m.-moles) of iodine and excess of silver salt were left in contact with ether during 6 hours, 0·682 g. (2·90 m.-moles) of silver iodide was precipitated; the filtrate still had oxidising powers equivalent to 0·83 m.-mole of iodine. This formation of much more than one mol. of silver iodide per mol. of iodine taken contrasts sharply with results in nitrobenzene.

Interaction of Iodine and Silver Perchlorate in Ether.—This is a more powerful iodinating mixture than silver trifluoroacetate and iodine: when 0·262 g. (1·03 m.-moles) of iodine was treated in 25 ml. of pure ether with an excess of silver perchlorate, the oxidising power was reduced to 0·057 m.-mole within 30 minutes. From 0·371 g. (1·46 m.-moles) of iodine and excess of the silver salt, no oxidising power remained after 6 hours, 0·658 g. (2·80 m.-moles) of silver iodide then having been precipitated. Addition of potassium iodide 5 minutes after that of silver perchlorate to a solution of 0·286 g. (1·13 m.-moles) of iodine resulted in the liberation of 1·12 m.-moles of iodine; slow attack on the ether therefore takes place under the conditions reported by Gomberg for the preparation of chlorine tetroxide.

Iodination and Bromination Experiments.—The experiments described below were carried out in a 250- or 500-ml. flask fitted with water condenser and rubber tubing connection to liquid-air traps.

Iodination experiments. (i) Benzene. AnalaR Benzene (10 ml.) and silver trifluoroacetate (4·40 g., 0·02 mole) were placed in the flask, heated to boiling, and cooled to room temperature; iodine (5·10 g., 0·02 mole) and AnalaR benzene (10 ml.) were then added. A precipitate of silver iodide appeared immediately. After 1 hour the clear red solution obtained by filtration was heated to 50° during 30 minutes, whereupon a further quantity of silver iodide was precipitated. The benzene solution, which had a strong odour of trifluoroacetic acid, was filtered, shaken with dilute sodium hydroxide solution to remove acid and the slight excess of iodine, washed with water, dried (Na_2SO_4), and distilled to give unchanged benzene, iodobenzene (3·5 g., 85%) (Found: C, 35·5; H, 2·6. Calc. for C_6H_5I: C, 35·3; H, 2·4%), b. p. 85°/15 mm., 190°/763 mm., n_D^{20} 1·620, and *p*-di-iodobenzene (0·1 g., 6%), m. p. 128—129°.

(ii) Iodobenzene. Iodobenzene (12 ml.) and silver trifluoroacetate (4·40 g.) were heated to 100° and cooled to room temperature. Powdered iodine (5·10 g.) was then added, causing an immediate precipitation of silver iodide. The solution was heated rapidly to 160°, cooled to room temperature, and filtered. The liquid-air traps contained only a small amount of trifluoroacetic acid and no trifluoroiodomethane. Distillation of the solution gave: trifluoroacetic acid (1·85 g., 80%), b. p. 71—72°; iodobenzene, b. p. 80°/12 mm., and *p*-di-iodobenzene (5·1 g., 77%), which recrystallised from ethanol as plates, m. p. 128°.

(iii) Bromobenzene. The above experiment was repeated but with bromobenzene and heating to 130°. No trifluoroiodomethane was detected, and trifluoroacetic acid (*ca.* 70% of theory), unchanged bromobenzene, and *p*-bromoiodobenzene (4·0 g., 71%), b. p. *ca.* 250°, m. p. 90—91° (from ethanol), were detected in the products.

(iv) Chlorobenzene. Chlorobenzene, silver trifluoroacetate, and iodine similarly yielded trifluoroacetic acid, unchanged chlorobenzene, and *p*-chloroiodobenzene (2·96 g., 62%) (Found: C, 29·7; H, 1·9. Calc. for C_6H_4ClI: C, 30·2; H, 1·7%), b. p. 224—228°, m. p. 55—56·5° (from ethanol). The crude chloroiodobenzene fraction was semi-solid and consisted mainly of the *p*-derivative. Infra-red spectroscopic examination of the liquid portion revealed the presence of some *o*-derivative.

(v) Thiophen. Benzene (20 ml.; not AnalaR) was heated under reflux for 5 minutes with silver trifluoroacetate (4·40 g.) and cooled to room temperature. Iodine (5·10 g.) was then added, and the mixture kept at room temperature for 1 hour. The silver iodide was removed by filtration, and distillation gave trifluoroacetic acid, benzene, and 2 : 5-di-iodothiophen (Found: C, 14·4; H, 0·9. Calc. for $C_4H_2I_2S$: C, 14·3; H, 0·6%), b. p. 128°/8 mm., white plates, m. p. 41° (from ethanol).

(vi) Toluene. The experiment with AnalaR benzene was repeated but with toluene and 10 minutes' heating under reflux. After filtration, distillation gave *p*-iodotoluene (3·85 g., 88%) (Found: C, 38·7; H, 3·5. Calc. for C_7H_7I: C, 38·5; H, 3·2%), b. p. 210°, m. p. 35°. The infra-red spectrum of the iodotoluene material showed that no *meta*- and only traces of *ortho*-derivative were present. A portion of the product, distilled *in vacuo* (to avoid decomposition of any benzyl iodide), gave no reaction with alcoholic silver nitrate or aqueous sodium hydroxide, thereby proving that iodination was exclusively nuclear. The trifluoroacetic acid recovered was 70% of the theoretical amount.

(vii) Anisole. Anisole (20 ml.) was heated to 100° with silver trifluoroacetate (4·40 g.), cooled to room temperature and powdered iodine (5·10 g.) added; silver iodide was immediately deposited. The mixture was heated to 100° for 15 minutes, cooled, filtered, and distilled. Trifluoroacetic acid (65%), unchanged anisole, and *p*-iodoanisole (3·5 g., 75%), b. p. 235—237°, needles, m. p. 50—51° (from aqueous methanol), were isolated.

(viii) Aniline. The last experiment was repeated, but with aniline. After cooling to room temperature the reaction mixture was filtered, washed with aqueous sodium hydroxide, dried, and distilled to yield *p*-iodoaniline (2·25 g., 51%) as a still residue; recrystallised from ethanol, it had m. p. 66—67°. The *N*-acetyl derivative had m. p. 184° (lit., 184°). The acetyl derivative of *o*-iodoaniline (m. p. 60—61°) is reported to have m. p. 109—110°.

(ix) *NN*-Dimethylaniline. This gave a 41% yield of *p*-iodo-*NN*-dimethylaniline, m. p. 80° (from ethanol) (lit., 82°).

(x) Nitrobenzene. Nitrobenzene (25 ml.) was mixed with silver trifluoroacetate (4·40 g.) and iodine (5·10 g.) and heated under reflux. Silver iodide was deposited at room temperature, and at *ca.* 120° a gas was evolved and collected in the liquid-air traps. Examination of the nitrobenzene solution failed to indicate the presence of *m*-iodonitrobenzene, and only a small amount of trifluoroacetic acid was detected. The volatile material consisted mainly of carbon dioxide and trifluoroiodomethane (75% yield) (*M*, 193. Calc. for CF_3I: *M*, 196), but in addition a volatile product still under investigation was isolated.

(xi) Benzoic acid. Benzoic acid (6·0 g.), silver trifluoroacetate (11·2 g.), and iodine (13 g.) were added to nitrobenzene (100 ml.) and the mixture was heated to 150° for 20 minutes. Carbon dioxide and trifluoroacetic acid were observed in the liquid-air trap and were completely absorbed by aqueous alkali. No trifluoroiodomethane was observed. The nitrobenzene solution was heated for recovery of trifluoroacetic acid (3·2 g.) and was then extracted by 5% sodium hydroxide solution. The alkaline solution was filtered from silver iodide and extracted by ether to remove traces of nitrobenzene. Acidification of the alkaline solution with dilute nitric acid caused precipitation of a solid which was taken up in ether. The aqueous solution was extracted by ether. The ether was removed from the combined, dried, ethereal extracts and the residual solid (10·2 g., 84%) was recrystallised from aqueous ethanol, giving *m*-iodobenzoic acid, m. p. 184—185° (Found: C, 33·8; H, 2·1. Calc. for $C_7H_5O_2I$: C, 33·9; H, 2·0%). Infra-red spectroscopic examination of the crude solid product failed to reveal the presence of *o*- or *p*-iodobenzoic acid.

Bromination experiments. (i) Benzene. AnalaR Benzene (10 ml.) and silver trifluoroacetate (4·40 g., 0·02 mole) were heated to reflux and cooled to room temperature. Addition of bromine (3·3 g., 0·02 mole) and AnalaR benzene (10 ml.) caused an immediate precipitation of silver bromide, which, after 1 hour, was removed by filtration. The brown solution, which had a strong odour of trifluoroacetic acid, was then slowly heated (30 minutes) to 50°, cooled, and shaken with dilute sodium hydroxide solution. After being washed with water, the dried benzene solution was distilled to yield benzene, and bromobenzene (2·80 g., 89%), b. p. 51°/23 mm., 154—155°/765 mm., n_D^{20} 1·561. A small amount of higher-boiling material, m. p. 83—85°, was probably crude *p*-dibromobenzene (m. p. 87°), but was not definitely identified as such.

(ii) Iodobenzene. Silver trifluoroacetate (4·40 g.) and iodobenzene (14 ml.) were heated to 100°, and cooled to room temperature. Addition of bromine (3·3 g.) caused immediate precipitation of silver bromide. The solution was heated rapidly to 150°, cooled, and filtered. No bromotrifluoromethane was isolated from the cooled traps. Distillation gave trifluoroacetic acid (1·5 g., 66%), b. p. 70—72°, and unchanged iodobenzene, b. p. 90°/20 mm., and left a residue of *p*-bromoiodobenzene (4·81 g., 85%), m. p. 91—92° after two recrystallisations from ethanol. The *ortho*-derivative was not isolated.

(iii) Bromobenzene. The use of bromobenzene instead of iodobenzene, with conditions as in the previous experiment, yielded *p*-dibromobenzene (3·05 g., 65%) (Found: C, 30·3; H, 2·3. Calc. for $C_6H_4Br_2$: C, 30·3; H, 1·7%), b. p. *ca.* 220°/760 mm.; recrystallised twice from ethanol, it had m. p. 86—87°. Infra-red spectroscopic examination of the liquid obtained by filtration of the dibromobenzene fraction indicated the presence of *o*-dibromobenzene, but a quantitative separation was not attempted.

(iv) Chlorobenzene. This compound similarly yielded *p*-bromochlorobenzene (2·21 g., 58%) (Found: C, 37·2; H, 2·6. Calc. for C_6H_4ClBr: C, 37·6; H, 2·1%), b. p. 194—197°,

m. p. 67° (from ethanol), trifluoroacetic acid (*ca.* 55%), and a small amount of *o*-bromochlorobenzene detected by infra-red spectroscopic examination.

(v) Toluene. Silver trifluoroacetate (4·40 g.) and toluene (10 ml.) after being heated and cooled were treated with bromine (3·3 g.), and the temperature was then raised to cause refluxing for 10 minutes. Filtration and distillation gave trifluoroacetic acid, toluene, and *p*-bromotoluene (3·09 g., 90%) (Found: C, 49·5; H, 4·5; Br, 45·9. Calc. for C_7H_7Br: C, 49·1; H, 4·1; Br, 46·8%), b. p. 183—186°, identical with a genuine specimen on infra-red spectroscopic examination. No side-chain bromination had occurred since there was no reaction of a portion of the crude material distilled *in vacuo* with alcoholic silver nitrate or sodium hydroxide solution. Furthermore, the infra-red spectrum failed to reveal the presence of *o*- or *m*-bromotoluene or of benzyl bromide.

The experiment was repeated with the temperature kept below 20° during and after the addition of bromine. After 1 hour at this temperature, the silver bromide was removed; the solution was then washed with sodium hydroxide solution and water (to remove trifluoroacetic acid), dried, and distilled, to give essentially the same product (91% yield of *p*-bromotoluene).

When the mixture of toluene (10 ml.) and silver trifluoroacetate (4·40 g.) was heated under reflux and shielded from light whilst bromine (3·3 g.) was slowly added by an inlet-tube dipping under the surface of the liquid, unchanged toluene, *p*-bromotoluene (68%), and side-chain brominated compounds were isolated. The yield of these compounds, estimated by their reaction with sodium hydroxide and silver nitrate solutions, was 14%. The *o*- and *m*-bromotoluenes were not formed. Dibenzyl, m. p. 51—52°, identified spectroscopically, was isolated from the reaction mixtures from two such experiments in 3% yield.

(vi) Anisole. Anisole when heated to 120° with silver trifluoroacetate and bromine gave *p*-bromoanisole (2·86 g., 76%) (Found: C, 44·9; H, 4·2. Calc. for C_7H_7OBr: C, 44·9; H, 3·7%), b. p. 110—115°/23 mm., shown to be identical with a known specimen by comparison of infra-red spectra. The yield of *p*-bromoanisole when the reaction was carried out at 0° for 12 hours was 58%.

(vii) Aniline. In a similar experiment the yield of *p*-bromoaniline (Found: C, 41·7; H, 3·6. Calc. for C_6H_6NBr: C, 41·9; H, 3·5%), m. p. 65—66° (*N*-acetyl derivative, m. p. 167°), was 2·12 g. (62%).

(viii) Nitrobenzene. Nitrobenzene, heated with silver trifluoroacetate and bromine as above, yielded *m*-bromonitrobenzene (19%), bromotrifluoromethane (21%), carbon dioxide (41%), and unidentified volatile and high-boiling products.

(ix) Benzoic acid. This compound (6·0 g.), silver trifluoroacetate (11·2 g.), and bromine (9·0 g.) were added to nitrobenzene (100 ml.), and the mixture was heated to 150° for 20 minutes. Carbon dioxide was evolved but no bromotrifluoromethane was observed. After cooling and removal of the trifluoroacetic acid (*ca.* 60%) by distillation, the solution was filtered and extracted by 5% sodium hydroxide solution. The alkaline extracts were combined with the alkaline extracts of the silver bromide and treated with ether to remove traces of nitrobenzene. Acidification and ether-extraction gave, on removal of the dried ether, a crude solid which, after recrystallisation from aqueous ethanol, yielded *m*-bromobenzoic acid (6·12 g., 61% calc. on silver trifluoroacetate) (Found: C, 42·3; H, 2·7. Calc. for $C_7H_5O_2Br$: C, 41·8; H, 2·5%), m. p. 155°, shown to be identical with a known specimen by infra-red spectroscopic examination. There was no indication of *o*- or *p*-bromobenzoic acid, although a small amount (5%) of *m*-bromonitrobenzene was isolated from the nitrobenzene solution.

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