233. *Free Radicals and Radical Stability. Part XII. Fluorotriphenylmethyl and the Reactivity of Halogen Substituents in Free Radicals.*

By Sydney T. Bowden and Thomas F. Watkins.

A study has been made of the reactivity of fluorine in triphenylmethyl fluoride and fluorotriphenylmethyl for the purpose of comparing the aliphatic and aromatic C–F linkages and of ascertaining the influence of the free electron.

p-Fluorine increases the basicity of triphenylcarbinol and enhances the halochromism of the salts. It also raises the decomposition temperature of triphenylmethyl formate by about 30°. Measurements of the rate of decomposition of *p*-fluorotriphenylmethyl formate at 90° show that the reaction proceeds in normal manner to produce a good yield of the corresponding methane.

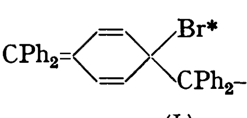
Fluorotriphenylmethyl has been isolated in the solid state. The reaction of the radical with oxygen has been examined, and the primary peroxide isolated. Tintometric measurements show that solutions of the radical change colour on standing in the dark. The amount of oxygen absorbed also decreases with the age of the radical system. This is shown to be due to isomerisation.

Agitation of the freshly prepared primary radical with molecular silver leads to the partial removal of fluorine and the formation of a secondary radical. This proves that the halogen atom in the aromatic C–F linkage of the free radical is more reactive than in the aliphatic C–F linkage of triphenylmethyl fluoride, whereas the opposite is true for the corresponding C–Br linkages. This behaviour is discussed from the standpoint of the quinonoid hypothesis, and an explanation based on the free-electron effect is proposed. Nuclear fluorine may also be replaced by sulphate on shaking nitrobenzene solutions of fluorotriphenylmethyl chloride with silver sulphate, and this is interpreted in terms of an ionic mechanism.

Rough estimates of the molecular weight of the radical system in benzene at the freezing point show that *p*-fluorine increases the unimolecular stability.

FREE radicals containing chlorine, bromine, or iodine in one or more of the phenyl groups of triphenylmethyl were obtained by Gomberg and his co-workers (*Ber.*, 1904, **37**, 1633; 1906, **39**, 3278; *J. Amer. Chem. Soc.*, 1923, **45**, 1765), but owing to their peculiar properties the radicals could not be isolated from solution nor could their molecular weights be determined by the customary indirect cryoscopic methods.

When a solution of *p*-bromotriphenylmethyl chloride is shaken with excess molecular silver, the metal effects rapid removal of all the chlorine and slow removal of part of the nuclear bromine. This reactivity of nuclear bromine is remarkable inasmuch as no bromine is removed from compounds of the type $C_6H_4Br{\cdot}CPh_2X$, where $X = H$, OH, or OCH_3. Still more remarkable, perhaps, is the fact that only one-half of the total amount of nuclear bromine is removed when $X = Cl$ or Br. To account for this behaviour Gomberg postulated the tautomerisation of the primary radical to a quinonoid form, which then combined with the benzenoid radical to produce a bimolecular compound (I) from which one only of the two bromine atoms is removed by metals. According to Gomberg, the bromine atom * simulates an aliphatically combined atom and must therefore differ in function from the "aromatic bromine." The latter atom resists attack by silver while the former is removed to produce a secondary radical. Although the secondary radical cannot be isolated, its presence is proved by the fact that it forms a characteristic peroxide. The theory finds further confirmation in the behaviour of *p*-bromodiphenyl-1-naphthylmethyl and diphenyl-4-bromo-1-naphthylmethyl chlorides which lose half the nuclear bromine, and in the behaviour of di-*p*-bromo- and tri-*p*-bromo-derivatives of triphenylmethyl which lose $\frac{3}{4}$ and $\frac{7}{8}$ of the bromine, respectively.



(I.)

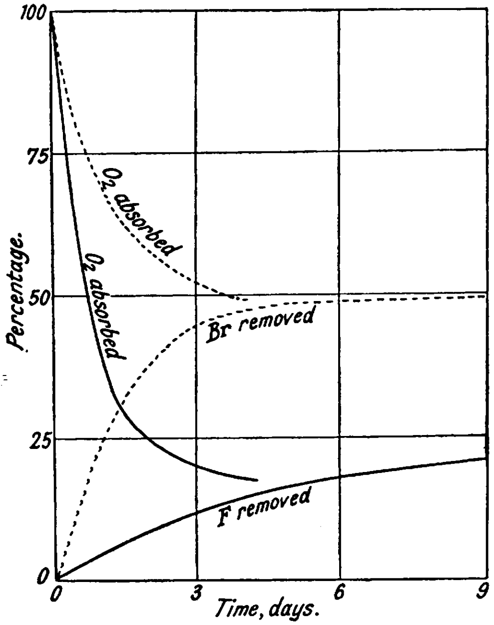
The reactivity of the fluorine atom in triarylmethane derivatives was first examined by Blicke (*J. Amer. Chem. Soc.*, 1924, **36**, 1515), who found that triphenylmethyl fluoride, unlike the corresponding chloride and bromide, is a remarkably stable compound from which not a trace of fluorine is removed even on prolonged boiling of the benzene solution with molecular silver. Since, moreover, the fluoride shows little tendency to hydrolyse, it is evident that the simple aliphatic C–F linkage is extremely strong in these derivatives. The fact that the fluorine atom is not removed by silver makes it reasonable to suppose that it would be still less subject to attack when present as a nuclear substituent. In other words, *p*-fluorotriphenylmethyl should be stable towards silver and no secondary radical would be produced. If such is actually the case, it should be possible to determine the molecular weight of the system and thus ascertain the influence of the halogen on the unimolecular stability of the radical.

The basicity of *p-fluorotriphenylcarbinol*, as measured by Baeyer's method, is nearly twice that of triphenylcarbinol. The presence of halogen substituents also enhances the halochromic properties, and the salts derived from the fluoro-derivative are reddish-yellow, whereas those corresponding to the bromo-substituted carbinol are yellowish-red. The behaviour of heated solutions of *p*-fluorotriphenylmethyl formate indicates that the fluorine atom increases the thermal stability of the salt. Whereas triphenylmethyl formate evolves 46% of the theoretical amount of carbon dioxide in 30 mins. at 77°, not a trace of the gas is evolved from the fluoro-derivative under these conditions. At 100°, however, the decomposition of the latter takes place rapidly, and a high yield of fluorotriphenylmethane may be isolated when the solution is nearly decolorised.

Certain substituents promote internal instability of radical systems and increase the tendency to isomerisation or disproportionation with the formation of colourless saturated derivatives. Owing to these phenomena and the destruction of the free radical during the concentration of the solution, it is generally impossible to isolate the corresponding hexaarylethane in the solid state. In the case of the halogenotriphenylmethyls hitherto examined, there is the further complication arising from the reactivity of the nuclear substituent towards silver and the formation of a secondary radical with a unimolecular stability entirely different from that of the original free radical. *A priori* considerations would suggest that these complications would be much less evident in the fluoro-substituted radical owing to the lower polarisability of the fluorine atom and its low reactivity in triphenylmethyl fluoride.

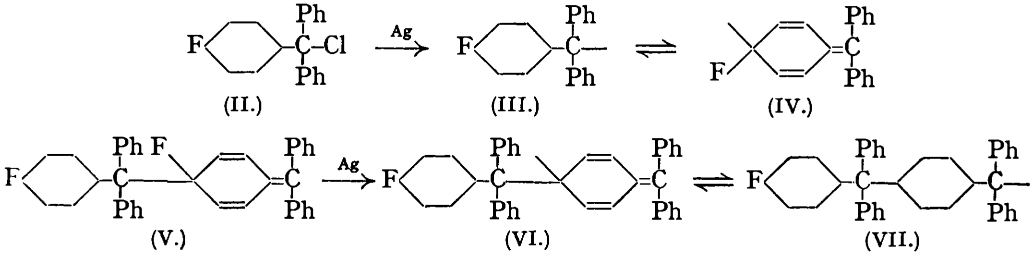
p-Fluorotriphenylmethyl may be prepared by the reduction of the corresponding chloride by means of silver or mercury, and the solutions are bright yellow. The influence of substituents on the colour of the free radical in 2% benzene solution is shown in the following table. In the halogenotriphenylmethyls, it is evident that the colour is displaced towards the red with increasing polarisability of the substituent. Actually, the colour differences are more pronounced in more concentrated solutions.

Radical.	Colour.	Radical.	Colour.
Triphenylmethyl	Yellow	*p*-Iodotriphenylmethyl	Orange
p-Fluorotriphenylmethyl	Bright yellow	*p*-Methyltriphenylmethyl	Yellow
p-Chlorotriphenylmethyl	Bright yellow	*p*-Methoxytriphenylmethyl	Orange-yellow
p-Bromotriphenylmethyl	Orange		



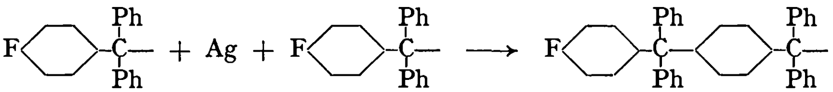
Freshly prepared solutions of *p*-fluorotriphenylmethyl in organic solvents react rapidly with oxygen, and the colour is largely but not completely discharged during the process. Nearly 1 mol. of oxygen is absorbed in a few minutes, and the normal *peroxide* $CPh_2(C_6H_4F)\cdot O\cdot O\cdot CPh_2(C_6H_4F)$ can be isolated as a white crystalline solid. In the presence of silver, however, the reddish-yellow solution of fluorotriphenylmethyl becomes pale yellow after standing for several days in the dark. The colour change, which can be followed by tintometric observations, is due to an inherent isomerisation process or to the formation of a secondary radical through the removal of fluorine by the metal.

The effect of shaking solutions of the radical with excess molecular silver was examined by measuring the amount of oxygen absorbed by the systems and by estimating the amount of silver fluoride produced. As shown by the dotted curves in the diagram, Gomberg and Blicke (*J. Amer. Chem. Soc.*, 1923, **45**, 1768) found that approximately 50% of the nuclear bromine is removed from *p*-bromotriphenylmethyl when it is shaken with silver for several days, and that the amount of oxygen absorbed falls to correspond finally with that required for the oxidation of the secondary radical. Fluorine is also removed by similar treatment of *p*-fluorotriphenylmethyl, and if we adopt the quinonoid hypothesis, the reactions may be represented by the scheme:



The reduction of the chloride (II) yields the benzenoid form of the primary radical (III) and the corresponding quinonoid modification (IV). The two forms of the radical unite to produce the bimolecular derivative (V), from which the fluorine atom attached to the quinonoid ring is removed by the action of silver. This leads to the formation of the secondary radical (VI) and the corresponding benzenoid modification (VII). The explanation of the behaviour of *p*-bromotriphenylmethyl is based on the assumption that the bromine atom in the bimolecular compound analogous to (V) should function as though it were linked to " an aliphatic rather than an aromatic carbon atom and should therefore be removable by silver." This is in harmony with the fact that the reactivity of the halogen in triphenylmethyl bromide is greater than in bromotriphenylmethyl. However, for compounds containing fluorine, this interpretation is untenable, since the reactivity of fluorine is greater in fluorotriphenylmethyl than in triphenylmethyl fluoride.

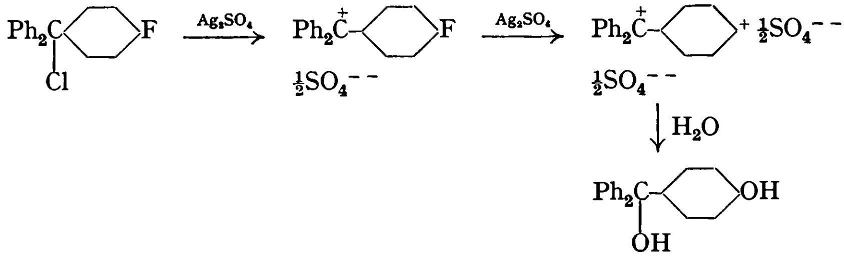
The reactivity of free radicals, as exemplified in dimerisation, oxidation, and other addition processes, is generally referred to the tendency of the tervalent carbon atom to complete its octet by direct sharing with external atoms. The behaviour of the halogenotriphenylmethyls, however, raises the question of the reactivity of the other atoms of the complex which are functioning with their normal valency. In view of the fact that the halogen atom X in the free radical $-CPh_2{\cdot}C_6H_4X$ is removed by silver while the saturated compounds $CHPh_2{\cdot}C_6H_4X$, $CPh_2(OH){\cdot}C_6H_4X$, and $CPh_2F{\cdot}C_6H_4X$ are unattacked, it is clear that the presence of the free electron on the methyl carbon atom leads to (*a*) a redistribution of the electron density, so that certain other atoms of the radical exhibit enhanced reactivity, or (*b*) the formation of some kind of bimolecular compound in which the reactivity of certain atoms is greater than normal owing to some other cause. Since the bimolecular compound must perforce be a saturated compound, and since the explanations hitherto proposed cannot be applied to derivatives containing fluorine, we favour the hypothesis based on the free-electron effect and the enhancement of reactivity through the redistribution of electron density. The reaction may proceed through unimolecular quinonoid forms but may for simplicity be represented:



This interpretation covers equally well the behaviour of all bromo-substituted triarylmethyls and accounts for the maximum percentage of halogen actually removed by silver. Incidentally, the free-electron effect is doubtless responsible for the intramolecular changes (isomerisation, disproportionation, and photodecomposition) which are characteristic of many triarylmethyl systems. Several of the reactions involved in the pyrolysis of aliphatic derivatives likewise indicate that this effect is operative in short-lived radicals. The effect is therefore a general one in all neutral polyatomic systems containing an unpaired electron, and its significance is further apparent from the wave-mechanical standpoint.

As shown in the diagram, less than 20% of the halogen is removed from *p*-fluorotriphenylmethyl by silver in 10 days. Since the completion of the present work, Bacon and Gardner (*J. Org. Chem.*, 1938, **3**, 281) have reported similar results, and so it might be concluded that the reactivity of halogen is lower in *p*-fluorotriphenylmethyl than in *p*-bromotriphenylmethyl. Actually, however, the present experiments do not allow of a comparison of the reactivities. This is clear from the fact that the absorption of oxygen does not correspond to the amount of fluorine removed and is much lower than would be shown by a mixture of the primary and secondary radicals alone. It follows therefore that the system also contains isomerisation or disproportionation products which do not react with oxygen. Experiments with solutions of *p*-fluorotriphenylmethyl in the absence of silver showed that the amount of oxygen absorbed decreases with the age of the system. Since disproportionation would not be expected to occur at room temperature, it may be concluded that the primary radical forms an isomerisation product which is not attacked by silver.

The polarisability of the halogens increases rapidly in the sequence F<Cl<Br<I, and this is also the general order of reactivity as exemplified by the thermal and photochemical dissociation of the hydrogen halides. In connexion with the general polar effects of halogens, the behaviour of *p*-fluorotriphenylmethyl chloride towards silver sulphate is of interest, since the bromine in *p*-bromotriphenylmethyl chloride is wholly replaced by SO_4 in suitable solvent media (Gomberg, *Ber.*, 1907, **40**, 1852). We find that fluorine is also replaced in the same way on shaking a nitrobenzene solution of *p*-fluorotriphenylmethyl chloride with silver sulphate, and that hydrolysis of the reaction mixture yields *p*-hydroxytriphenylcarbinol:



The reactions may proceed through quinonoid phases, but the ionic mechanism is doubtless operative since the triarylmethyl sulphates, unlike the corresponding chlorides, are typical halochromic salts. The reactivity of nuclear fluorine in this case is due to the fact that it forms part of the triarylmethyl cation. On hydrolysis of the sulphate the colour is destroyed with formation of the homopolar carbinol. It is noteworthy that Bacon and Gardner (*loc. cit.*) found that *p*-fluorotriphenylmethyl chloride undergoes partial rearrangement in liquid sulphur dioxide, and that prolonged shaking with silver chloride is without appreciable effect.

With regard to the influence of fluorine on the unimolecular stability of the neutral radical, it is not easy to predict on wave-mechanical grounds whether *p*-fluorotriphenylmethyl should have a higher or lower stability than triphenylmethyl itself. Apart from the number of factors involved, it is not possible to foretell whether the anomalous behaviour of fluorine in saturated derivatives would likewise be observable in the free radical. On the experimental side, accurate measurement of the radical stability is not possible owing to secondary reactions, but these may be largely avoided by carrying out the cryoscopic determinations as rapidly as possible. Rough estimates made in this way show that the unimolecular stability is about 20% in 2% benzene solution at the freezing point. The causes relating to the stabilising influences of *p*-fluorine and *o*-methyl (Part X; this vol., p. 883) must of course be different and the agreement in the observed values of the stability is fortuitous.

The radical may be obtained in the solid state by using rapid methods of isolation.

EXPERIMENTAL.

Halogenotriphenylcarbinols.

Alkyl p-*Fluorobenzoates.*—*p*-Fluorobenzoic acid was prepared in good yield by the method of Schiemann and Winkelmüller (*Organic Syntheses*, 1933, **13**, 52) and was converted into the methyl ester by means of methyl alcohol and hydrogen chloride (Meyer, *Monatsh.*, 1910, **31**, 935). The ester, which is readily volatile with the alcohol, was obtained pure by repeated fractionation; b. p. 195—197°. The ethyl ester, similarly prepared, was obtained as an oil solidifying at 26°. It was finally purified by steam distillation, followed by fractionation under reduced pressure. The pure material had b. p. 140°/12 mm. (Schmidt and Gehren, *J. pr. Chem.*, 1870, **1**, 400).

p-*Fluorotriphenylcarbinol.*—A filtered solution of phenylmagnesium bromide [from bromobenzene (95 g.) and excess magnesium] was treated with a solution of ethyl *p*-fluorobenzoate (38 g.) in ether (100 c.c.) and then heated on the steam-bath for 5 hours. The mixture was decomposed with ice and sulphuric acid, and the ethereal solution washed and dried. After removal of the ether, steam was passed through the residual oil until it solidified on cooling. After three recrystallisations from ligroin, the *carbinol* was obtained in perfectly white crystals (51 g.), m. p. 121—122° (Found: C, 82·5; H, 5·2. $C_{19}H_{15}OF$ requires C, 82·2; H, 5·3%). The carbinol was also prepared similarly from methyl fluorobenzoate, but the yield was appreciably lower. The above method is superior to that described by Bacon and Gardner (*loc. cit.*), who used *p*-fluorobenzophenone and phenylmagnesium bromide and obtained a low yield of impure carbinol for which no m. p. or analysis is given. The basicity of the carbinol as estimated by Baeyer's method (see J., 1939, 36) is 1·9 (triphenylcarbinol = 1). In so far as the *p*-position is concerned, the influence of substituents on the basicity is in the order $CH_3O > F > CH_3$.

p-Bromotriphenylcarbinol was prepared from ethyl *p*-bromobenzoate (Cone and Long, *J. Amer. Chem. Soc.*, 1906, **28**, 519) and purified by conversion into bromotriphenylmethyl chloride followed by hydrolysis, as recommended by Gomberg and Blicke (*ibid.*, 1923, **45**, 1770); m. p. 102°.

For the purpose of comparing the halochromic properties, solutions of the carbinols in pure concentrated sulphuric acid were examined tintometrically in a Lovibond cell (1 × 1 cm.) provided with a lightly greased cover-slip to exclude atmospheric moisture. The results for two dilutions are given below:

Colour values of triarylmethyl salts.

	10^{-5} Millimols. per c.c.	10^{-3} Millimols. per c.c.
Triphenylmethyl	2·2 yellow	29 yellow; 0·1 red
p-Fluorotriphenylmethyl	1·6 yellow	27·2 yellow; 1·7 red; 3·0 neutral
p-Bromotriphenylmethyl	1·7 yellow	29·9 yellow; 4·1 red; 3·1 neutral

These results reveal that in very dilute solution the halochromism is diminished in the substituted derivatives. In the more concentrated solutions, however, the halochromism is markedly increased by the halogen substituents and in the order of their polarisability.

p-*Fluorotriphenylmethyl Chloride.*—The dry, finely powdered carbinol (5 g.) was suspended in ether, and the mixture saturated with hydrogen chloride. The carbinol dissolved to form a yellow solution, and *p*-fluorotriphenylmethyl chloride was deposited as yellowish-brown crystals. The filtrate was kept over a few lumps of anhydrous calcium chloride, and the solution was then concentrated to obtain a further quantity of the fluoro-derivative. The compound was obtained pure by recrystallisation from light petroleum; the colourless crystals melted at 91—92°. Bacon and Gardner (*loc. cit.*) record m. p. 90—91° for material prepared in benzene solution (Found: Cl, 11·8. Calc. for $C_{19}H_{14}FCl$: Cl, 11·8%).

The substance exhibits the normal halochromic properties of triarylmethyl chlorides, and on treatment with ethereal solutions of zinc chloride and ferric chloride forms yellowish-red addition compounds, which are obtained as oils at ordinary temperature and are readily hydrolysed with regeneration of the carbinol.

Thermal Stability of p-*Fluorotriphenylmethyl Formate.*—The addition of the carbinol to anhydrous formic acid leads to formation of a yellow solution of *p*-fluorotriphenylmethyl formate. The thermal stability of the salt was examined by observing the temperature at which carbon dioxide was evolved from the system in the apparatus previously described (Part VIII, this vol., p. 878). The decomposition temperature was found to be 79°, compared with 49° for triphenylmethyl formate. The reducibilities of these derivatives were compared by measuring the rate of evolution of carbon dioxide at 90°. In the following table the volumes refer to *N.T.P.*

Triphenylmethyl Formate.

Wt. of carbinol = 0·8125 g. Theoretical evolution of CO_2 = 70 c.c.

Time (mins.)	1	2	3	4	5	6	7	8	10	15	20	30
CO_2 evolved (c.c.)	7·8	16·7	23·7	29·3	33·4	35·3	37·4	38·6	40·3	43·5	45·0	45·0

p-*Fluorotriphenylmethyl Formate.*

Wt. of carbinol = 0·8662 g. Theoretical evolution of CO_2 = 70 c.c.

Time (mins.)	1	2	3	4	5	6	7	8	10	15	20	30
CO_2 evolved (c.c.) ...	1·7	12·9	22·9	31·0	36·4	39·7	43·4	44·7	47·2	50·7	52·3	53·6

Although the temperature of incipient decomposition of fluorotriphenylmethyl formate is higher than that of the unsubstituted derivative, it is evident that apart from the early stages the speed of reduction at 90° is greater for the fluoro-derivative. The figures, however, actually indicate the thermal behaviour of formates in the presence of the water produced initially through salt-formation and accordingly reflect the effects arising from the different hydrolysability of the two formates. These, however, are the conditions which obtain in the preparation of triarylmethanes, and it is evident that the method is a suitable one for the reduction of fluorotriphenylcarbinol.

The Halogenotriphenylmethyl Radicals.

Reaction of Primary Radicals with Oxygen.—The absorption of oxygen by the nascent radical and by the radical which had stood for various periods was measured in the apparatus previously described (Part X). The experiments were carried out at 17·5°, and the system was adequately protected from light to avoid photodecomposition. The results of typical experiments are recorded below.

Experiment 1. Reducing metal: mercury, 10 g. Wt. of *p*-fluorotriphenylmethyl chloride, 0·3008 g. Materials agitated for 6 hours in sealed tube and allowed to stand for 12 hours.

Time, mins.	3	5	25	85	120
O_2 absorbed, c.c.	4·9	5·3	5·8	6·1	6·2
Absorption, %	41·0	46·8	50·8	53·5	54·8

Similar experiments with triphenylmethyl chloride showed that there is a very rapid absorption amounting to 97·4% of the theoretical value corresponding to the formation of the simple peroxide. The low value for the fluoro-derivative may be due to the formation of a secondary radical in the presence of mercury, or to isomerisation. These alternatives were examined by estimating the amount of metal fluoride, as described later.

Experiment 2. Reducing metal: molecular silver, 3 g. Wt. of *p*-fluorotriphenylmethyl chloride, 0·7665 g. The reduction was carried out *in situ* in the absorption apparatus, so that the primary radical was oxidised as it was produced in the system.

Time, mins.	2	4	6	12	20	30
O_2 absorbed, c.c.	14·1	24·1	26·3	27·5	27·9	28·0
Absorption, %	48·6	83·1	90·4	95·6	95·9	96·4

The reduction of fluorotriphenylmethyl chloride is rapid, but the speed is naturally dependent on the state of division of the silver and the degree of agitation. The oxygen absorbed corresponds fairly closely to the theoretical value when the radical is oxidised as soon as it is formed in solution. It follows, therefore, that the rate of oxidation is much higher than the rate of formation of the secondary radical or the rate of isomerisation.

Experiment 3. Reducing metal: molecular silver, 3 g. Wt. of *p*-fluorotriphenylmethyl chloride, 0·7545 g. The radical solution was allowed to stand for 30 mins. before the oxygen absorption was measured.

Time, mins.	1	2	3	4	5	10	20	30
O_2 absorbed, c.c.	14·9	24·6	25·3	25·7	25·8	26·2	26·9	27·4
Absorption, %	52·3	86·4	88·8	90·2	90·5	91·9	94·4	96·2

Similar experiments with *p*-bromotriphenylmethyl showed that 94·2% of the amount of oxygen corresponding to normal peroxide formation is absorbed in 10 mins. The volume of oxygen absorbed by freshly prepared halogenotriphenylmethyls is slightly lower than that found in the case of triphenylmethyl and the methoxytriphenylmethyls (J., 1939, 36). It is clear, however, that reactions involving isomerisation or the removal of nuclear halogen do not proceed to any great extent during the periods under consideration.

p-*Fluorotriphenylmethyl Peroxide.*—*p*-Fluorotriphenylmethyl chloride (2 g.) in dry ether (10 c.c.) was shaken with molecular silver (3 g.) in a stoppered tube for 30 minutes. The reddish-yellow solution of the free radical was filtered from silver chloride and unchanged metal, and was oxidised by a stream of air. In contrast to the behaviour of triphenylmethyl systems, the solution was not completely decolorised during the process, and the peroxide was deposited as a pale yellow microcrystalline solid on concentration to half-bulk. The *peroxide* was obtained free from colour by rapid recrystallisation from carbon disulphide, and melted at 169° (Found : C, 82·5; H, 5·1. $C_{38}H_{28}O_2F_2$ requires C, 82·3; H, 5·1%). The yield was 65%, and the compound is unusual in that it becomes slightly yellow on standing in a desiccator for some days. The freshly prepared peroxide gives a reddish-yellow solution with concentrated sulphuric acid, but there appears to be no action with anhydrous formic acid.

Colour Changes in the Free-radical Solution.—In order to obtain more precise information as to the colour changes in the primary radical–silver system, the solution was examined at intervals by means of a tintometer. The following results refer to a 2% benzene solution of *p*-fluorotriphenylmethyl in the presence of a five-fold excess of molecular silver. The system was kept in the dark, and the colour values determined in Lovibond units : 20 mins., 20·1 yellow, 2·2 red, 0·3 blue; 18 hrs., 20·0 yellow, 1·2 red; 2 days, 20·0 yellow, 0·9 red; 4 days, 20·0 yellow; 12 days, 18·0 yellow. The change of colour is comparatively slight, and so it may be concluded that the process of isomerisation involving the formation of colourless compounds is a slow reaction at room temperature. Since, moreover, other experiments reveal the formation of the secondary radical under these conditions, it is evident that the colour of this radical does not differ greatly from that of the primary radical. The change of colour appears to be more pronounced in other systems, and Gomberg and Blicke (*loc. cit.*) report that in the reduction of *p*-bromodiphenyl-α-naphthylmethyl chloride, the solution of the secondary radical is of indigo colour in contrast to the violet solution of the primary radical.

Removal of Fluorine by Silver.—The action of molecular silver on the primary radical was investigated in two series of experiments involving the measurement of oxygen absorption and the determination of the amount of silver fluoride formed. In the first series of experiments a number of sealed tubes containing a known amount of *p*-fluorotriphenylmethyl in benzene solution and excess molecular silver were agitated in the dark on a rotary shaking machine for predetermined periods, and the oxygen absorption then determined for each system. The times recorded below are the periods for which the systems were shaken, and the percentage absorption refers to the final maximum value of the oxygen absorbed. The fall in the percentage absorption is more rapid and proceeds further than in the corresponding reaction between *p*-bromotriphenylmethyl and silver.

Time, hrs.	0·33	1	4	12	24	48	72
O_2 absorbed, %	98·5	91·1	68·6	61·0	35·8	22·0	20·6

In a second series of experiments, the presence of silver fluoride was proved by heating the mixture with 300 c.c. of water, filtering it from silver chloride and excess silver, and removing bromobenzene by steam-distillation. The clear solution thus obtained immediately decolorised the zirconium lake of purpurin. The fluoride was estimated by treating the solution with a large excess of a saturated solution of lead chloride, allowing the mixture to stand for 12 hours, and then filtering off the lead chlorofluoride. The precipitate was washed successively with lead chloride solution and water before it was dried at 120° (Starck, *Z. anorg. Chem.*, 1911, **70**, 173). The results are summarised below.

Time, hrs.	4	24	48	72	240
F removed, %	2·74	5·69	7·91	9·07	19·67

It is clear that the fluorine atom is removed from the solution more slowly than the bromine atom from *p*-bromotriphenylmethyl, which suffers a 50% loss of halogen in 7 days. Since, however, the decrease in the amount of oxygen absorbed by the *p*-fluorotriphenylmethyl–silver systems does not correspond to the amount of fluorine removed, it follows that the primary or secondary radical is unstable and undergoes isomerisation or disproportionation to yield substances which do not absorb oxygen.

As a further confirmation, experiments were made with freshly prepared radical solutions which had been filtered through a fine sintered-glass filter in a stream of oxygen-free nitrogen. These solutions were hermetically sealed and kept in the dark for various periods before the oxygen absorption was measured. It was thus found that the total amount of oxygen absorbed was lower the longer the solution had been allowed to stand. This shows that it is the primary radical which undergoes isomerisation or disproportionation. Since the occurrence of disproportionation is unlikely at these low temperatures, we may conclude that *p*-fluorotriphenylmethyl undergoes an independent isomerisation process.

Replacement of Fluorine by Sulphate.—The effect of shaking solutions of *p*-fluorotriphenylmethyl chloride with silver sulphate was investigated according to Gomberg and Blicke's procedure (*loc. cit.*) for the bromo-derivative. Sealed tubes containing nitrobenzene solutions of the halide and powdered silver sulphate were shaken for different periods in a thermostat at

50°. After the specified period of shaking, each tube was opened, and the dark nitrobenzene solution filtered. The solid material was treated with water to dissolve the silver fluoride, and the latter was estimated as lead chlorofluoride. The results for four experiments were as follows:

Period of agitation, hrs.	24	48	72	80
F removed, %	28·02	52·71	64·71	70·30

The behaviour is thus similar to that of *p*-bromotriphenylmethyl chloride which loses 74% of the nuclear bromine under these conditions.

The nitrobenzene solutions were extracted with 3% sodium hydroxide, and the extract neutralised with dilute acetic acid. The yellow solid which separated was identified as impure *p*-hydroxytriphenylcarbinol.

Degree of Dissociation of Difluorohexaphenylethane.—The indirect method of molecular-weight determination (J., 1939, 37) cannot be applied in the ordinary manner owing to the occurrence of isomerisation and the formation of a secondary radical. However, a rough estimate of the dissociation was obtained by carrying out the reduction and the cryoscopic measurements as rapidly as possible. For this purpose sodium-dried benzene, pure *p*-fluorotriphenylmethyl chloride, and excess molecular silver were shaken under nitrogen in the cryoscopic vessel for 15 minutes at room temperature and for the period necessary to cool the solution to the freezing point. The stirring was continued after each determination until two or three fairly concordant values for the depression were obtained. The results of a typical experiment are recorded below.

Dissociation of Difluorohexaphenylethane.

Wt. of *p*-fluorotriphenylmethyl chloride, 0·5196 g.; wt. of benzene, 18·1 g.; *K* for benzene, 52·5°.

Molecular weight of difluorohexaphenylethane, 522.

,, ,, ,, fluorotriphenylmethyl, 261.

Depression	0·319°	0·328°	0·326°	0·323°
Apparent molecular weight	437·9	425·9	428·5	432·5
Dissociation, %	19·2	22·5	21·8	20·7

Inasmuch as the determinations were completed within 2 hours, the amount of secondary radical produced in the solution was very small. Moreover, the occurrence of isomerisation (which would lead to a decrease in the measured dissociation) and of disproportionation (which would lead to a higher value for the observed dissociation) was slight, since these processes take place slowly under the present experimental conditions. The colour of the final solution was yellowish-red.

Isolation of the Radical.—The general method of isolating radicals in the solid state (Part II, *loc. cit.*, p. 33) was adopted, but in view of the changes suffered by the radical, special precautions were taken in order to carry out the various operations as rapidly as possible.

The deep yellowish-red solution of the radical (prepared from a benzene solution of the chloride in 15 mins.) was filtered, and the solvent removed at 45° under reduced pressure in a stream of carbon dioxide. The residual dark red oil was dissolved in the minimum amount of acetone and kept at −16° for 30 mins. Since the solution did not crystallise, the acetone was removed at 35°, and the oil taken up in light petroleum. On cooling to −16°, the associated radical separated as a pale yellow crystalline mass. The mother-liquor was decanted, and the solid carefully washed with small amounts of cold light petroleum. It was dried at 35° and then at 50° under reduced pressure in a slow stream of carbon dioxide. During these operations, the solid became yellowish-brown, and more rigorous drying processes could not be applied. The m. p. of the substance in an evacuated capillary tube was not sharp; it liquefied, but not completely, in the range 115—124°. It is evident therefore that the radical isolated in these experiments was contaminated with other products. That the radical was actually present, however, was proved by its conversion into the peroxide.

Gomberg and Blicke (*loc. cit.*) made several attempts to isolate *p*-bromotriphenylmethyl and *p*-bromodiphenyl-α-naphthylmethyl, but obtained oils which failed to crystallise. The isolation of *p*-fluorotriphenylmethyl as described above leads us to believe that the *m*-fluoro-derivative, being less prone to isomerise, may be prepared in the pure state by this method.

We wish to record our great indebtedness to Professor W. J. Jones, through whose good offices the work reported in this series (Parts I—XII) has been made possible.

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