## 578. *Reactions of Fluorocarbon Radicals. Part XVI.* Photolysis of Some Perhalogenoacetones.*

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The perhalogenoacetones $CF_2Cl \cdot CO \cdot CF_2Cl$, $CF_2Cl \cdot CO \cdot CFCl_2$, $CFCl_2 \cdot CO \cdot CFCl_2$, and $CCl_3 \cdot CO \cdot CCl_3$ have been photolysed alone and in the presence of halogen. The products, accounted for by free-radical mechanisms, suggest that acetones containing a predominance of fluorine are photolysed with carbon–carbon fission as the primary step, whereas those containing a predominance of chlorine are photolysed with carbon–chlorine fission.

THE photolysis of perhalogeno-ketones is of interest as a possible source of perhalogenoalkyl radicals. Thus, if photolysis of the ketones $CF_2Cl \cdot CO \cdot CF_2Cl$, $CF_2Cl \cdot CO \cdot CFCl_2$, $CFCl_2 \cdot CO \cdot CFCl_2$, and $CCl_3 \cdot CO \cdot CCl_3$ involves a free-radical mechanism, as established for acetone[1] and hexafluoroacetone,[2] the radicals $CF_2Cl \cdot$, $CFCl_2 \cdot$, and $CCl_3 \cdot$ would become available for further study, *e.g.*:

$$CF_2Cl \cdot CO \cdot CF_2Cl \xrightarrow{h\nu} CF_2Cl \cdot CO \cdot CF_2Cl^* \longrightarrow CF_2Cl \cdot + CF_2Cl \cdot CO \cdot \longrightarrow CF_2Cl \cdot + CO$$
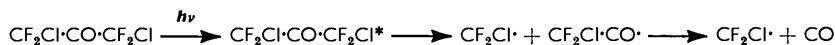
Perhalogenoacetones containing chlorine could, however, break down by an alternative primary process involving carbon–chlorine fission rather than carbon–carbon fission, *e.g.*:

$$CF_2Cl \cdot CO \cdot CF_2Cl \longrightarrow CF_2Cl \cdot CO \cdot CF_2 \cdot + Cl \cdot$$

since it is probable that the C–C and C–Cl bond-dissociation energies in such compounds are comparable. The photolysis would then take a different course from that found for hexafluoroacetone.

Photolysis of 1,3-dichlorotetrafluoroacetone in the vapour phase gives the compounds

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[1] Steacie, " Atomic and Free Radical Reactions," Reinhold, New York, 1954. Vol. I.
[2] Ayscough, Polanyi, and Steacie, *Canad. J. Chem.*, 1955, **33**, 743; Ayscough and Steacie, *Proc. Roy. Soc.*, 1956, *A*, **234**, 476.

$CF_2Cl \cdot CF_2Cl$ (71%), CF_2Cl_2 (18%), and $CF_2Cl \cdot CF_2 \cdot CF_2Cl$ (8%), and the following reaction scheme is suggested:

$$CF_2Cl \cdot CO \cdot CF_2Cl \xrightarrow{h\nu} CF_2Cl \cdot CO \cdot CF_2Cl^* \longrightarrow CF_2Cl \cdot CO \cdot + CF_2Cl \cdot$$

$$CF_2Cl \cdot CO \cdot \longrightarrow CF_2Cl \cdot + CO$$

$$CF_2Cl \cdot + CF_2Cl \cdot \longrightarrow CF_2Cl \cdot CF_2Cl$$

$$CF_2Cl \cdot + CF_2Cl \cdot CO \cdot CF_2Cl \longrightarrow CF_2Cl_2 + CF_2Cl \cdot CO \cdot CF_2 \cdot$$

$$CF_2Cl \cdot CO \cdot CF_2 \cdot + CF_2Cl \cdot \longrightarrow CF_2Cl \cdot CO \cdot CF_2 \cdot CF_2Cl$$

$$CF_2Cl \cdot CO \cdot CF_2 \cdot CF_2Cl \xrightarrow{h\nu} CF_2Cl \cdot + CF_2Cl \cdot CF_2 \cdot + CO$$

$$CF_2Cl \cdot + CF_2Cl \cdot CF_2 \cdot \longrightarrow CF_2Cl \cdot CF_2 \cdot CF_2Cl$$
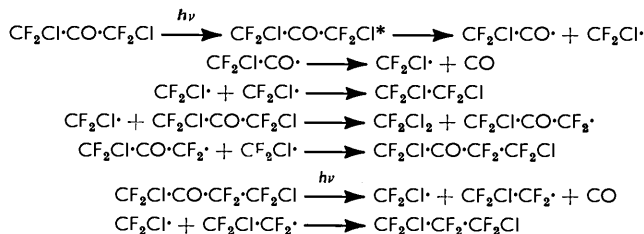
The main product then arises by photolysis involving initial carbon–carbon bond fission, as with acetone or hexafluoroacetone. Formation of dichlorodifluoromethane shows that some of the $CF_2Cl \cdot$ radicals attack 1,3-dichlorotetrafluoroacetone by abstraction of chlorine, leaving the $CF_2Cl \cdot CO \cdot CF_2 \cdot$ radical; this becomes the source of the 1,3-dichlorohexafluoro-propane, by combination of $CF_2Cl \cdot$ and $CF_2Cl \cdot CF_2 \cdot$ radicals. The concentration of $CF_2Cl \cdot$ radicals is relatively high, whereas that of $CF_2Cl \cdot CF_2 \cdot$ radicals at a given time is low, thus explaining why at most only very small amounts of 1,4-dichloro-octafluorobutane are produced by another radical combination:

$$2CF_2Cl \cdot CF_2 \cdot \longrightarrow (CF_2Cl \cdot CF_2)_2$$
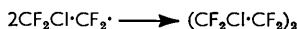
The formation of $CF_2Cl \cdot$ radicals was also shown by photolysis of the ketone in presence of chlorine, bromine, or iodine, which gave mainly dichlorodifluoromethane (96% yield), bromochlorodifluoromethane (93% yield), or chlorodifluoroiodomethane (57% yield), respectively:

$$CF_2Cl \cdot CO \cdot CF_2Cl \longrightarrow 2CF_2Cl \cdot \xrightarrow{X_2} 2CF_2ClX \quad (X = Cl, Br, \text{ or } I)$$
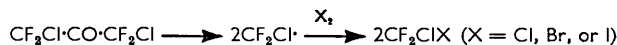
The reaction in presence of bromine also gave a low yield of chlorodifluoroacetyl bromide, providing evidence for the existence of the $CF_2Cl \cdot CO \cdot$ radical as an intermediate:

$$CF_2Cl \cdot CO \cdot CF_2Cl \longrightarrow CF_2Cl \cdot + CF_2Cl \cdot CO \cdot \xrightarrow{Br_2} CF_2Cl \cdot COBr$$
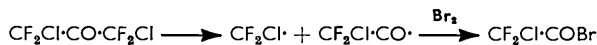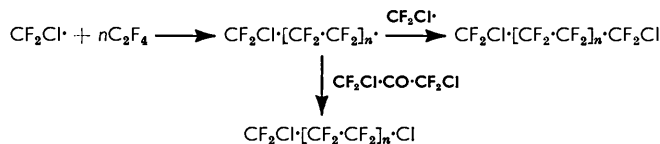
and indicating that the primary photolysis step involves liberation of one, rather than two, chlorodifluoromethyl radicals.

It is unlikely that initial photolysis of the added halogen X_2 facilitates reaction by a change in basic mechanism, *e.g.*, by initial abstraction:

$$X_2 \xrightarrow{h\nu} X \cdot \xrightarrow{CF_2Cl \cdot CO \cdot CF_2Cl} XCl + CF_2Cl \cdot CO \cdot CF_2 \cdot$$
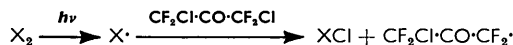
since when $X = Br$ or I products such as CF_2Br_2, CF_2I_2, $CF_2Cl \cdot CF_2Br$, or $CF_2Cl \cdot CF_2I$ would be expected from the further reactions of the $CF_2Cl \cdot CO \cdot CF_2 \cdot$ radical.

Photolysis of 1,3-dichlorotetrafluoroacetone in presence of tetrafluoroethylene gave polytetrafluoroethylene and liquid polymers, probably telomers:

$$CF_2Cl \cdot + nC_2F_4 \longrightarrow CF_2Cl \cdot [CF_2 \cdot CF_2]_n \cdot \xrightarrow{CF_2Cl \cdot} CF_2Cl \cdot [CF_2 \cdot CF_2]_n \cdot CF_2Cl$$

$$\downarrow CF_2Cl \cdot CO \cdot CF_2Cl$$

$$CF_2Cl \cdot [CF_2 \cdot CF_2]_n \cdot Cl$$

Use of ethylene instead of tetrafluoroethylene similarly gave oils of b. p. 100—200°; infrared spectroscopy showed the presence of carbonyl groups, suggesting initiation or termination reactions involving $CF_2Cl \cdot CO \cdot$ and/or $CF_2Cl \cdot CO \cdot CF_2 \cdot$ radicals, *e.g.*:

$$CF_2Cl \cdot CO \cdot + CH_2 \colon CH_2 \longrightarrow CF_2Cl \cdot CO \cdot CH_2 \cdot CH_2 \cdot, \text{ etc.}$$

$$CF_2Cl \cdot [CH_2 \cdot CH_2]_n \cdot + CF_2Cl \cdot CO \cdot CF_2 \cdot \longrightarrow CF_2Cl \cdot [CH_2 \cdot CH_2]_n \cdot CF_2 \cdot CO \cdot CF_2Cl$$

Photochemical decomposition of 1,1,3-trichlorotrifluoroacetone gave 1,1,2-trichlorotri-fluoroethane (21%), 1,2-dichlorotetrafluoroethane (10%), 1,1,2,2-tetrachlorodifluoroethane (10%), and dichlorodifluoromethane (12%):

$$CF_2Cl \cdot CO \cdot CFCl_2 \xrightarrow{h\nu} CF_2Cl \cdot + CFCl_2 \cdot CO \cdot$$
$$CFCl_2 \cdot CO \cdot \longrightarrow CFCl_2 \cdot + CO$$
$$(or\ CF_2Cl \cdot CO \cdot CFCl_2 \xrightarrow{h\nu} CFCl_2 \cdot + CF_2Cl \cdot CO \cdot$$
$$CF_2Cl \cdot CO \cdot \longrightarrow CF_2Cl \cdot + CO)$$
$$2CF_2Cl \cdot \longrightarrow CF_2Cl \cdot CF_2Cl$$
$$2CFCl_2 \cdot \longrightarrow CFCl_2 \cdot CFCl_2$$
$$CF_2Cl \cdot + CFCl_2 \cdot \longrightarrow CF_2Cl \cdot CFCl_2$$

That the yield of 1,1,2-trichlorotrifluoroethane is twice that of the compounds $CF_2Cl \cdot CF_2Cl$ and $CFCl_2 \cdot CFCl_2$ indicates that decarbonylation of a perhalogenoacyl radical, *e.g.*, $CFCl_2 \cdot CO \cdot$, occurs soon after its formation, so that the $CFCl_2 \cdot$ radical so produced is in a favoured position for combination with the $CF_2Cl \cdot$ radical formed in the first step of the ketone photolysis:

$$CF_2Cl \cdot CO \cdot CFCl_2 \longrightarrow CF_2Cl \cdot + CFCl_2 \cdot CO \cdot \longrightarrow CFCl_2 \cdot + CO$$
$$CF_2Cl \cdot + CFCl_2 \cdot \longrightarrow CF_2Cl \cdot CFCl_2$$

Alternatively, the fact that the ratio of $CF_2Cl \cdot CF_2Cl : CF_2Cl \cdot CFCl_2 : CFCl_2 \cdot CFCl_2$ is 1 : 2 : 1 can be interpreted by assuming (*a*) formation of $CF_2Cl \cdot$ and $CFCl_2 \cdot$ radicals in equal numbers, without the formation of the $CFCl_2 \cdot CO \cdot$ radical as intermediate, and (*b*) equal rate constants for the three radical–radical combinations.

Dichlorodifluoromethane (12%) and products of high b. p. (25%) are also produced by photolysis of 1,1,3-trichlorotrifluoroacetone. Trichlorofluoromethane is not a major photolysis product, and this implies (i) that the chlorine abstraction

$$CF_2Cl \cdot \xrightarrow{CF_2Cl \cdot CO \cdot CFCl_2} CF_2Cl_2$$

is distinctly faster than the reaction

$$CFCl_2 \cdot \xrightarrow{CF_2Cl \cdot CO \cdot CFCl_2} CFCl_3$$

and (ii) that abstraction of chlorine occurs preferentially from the $CFCl_2$ group of 1,1,3-tri-chlorotrifluoroacetone; this is as expected from the properties and reactions of other compounds containing these groups.

Some of the $CFCl_2$ groups must be involved in formation of the products of high b. p., either by initial carbon–chlorine fission, or by combination with $CF_2Cl \cdot CO \cdot CFCl \cdot$ radicals:

$$CF_2Cl \cdot CO \cdot CFCl_2 \longrightarrow \begin{cases} \xrightarrow{h\nu} CF_2Cl \cdot CO \cdot CFCl \cdot + Cl \cdot \\ \xrightarrow{CF_2Cl \cdot} CF_2Cl \cdot CO \cdot CFCl \cdot + CF_2Cl_2 \end{cases}$$
$$\downarrow$$
$$CF_2Cl \cdot CO \cdot + CFCl_2 \cdot$$
$$CF_2Cl \cdot CO \cdot CFCl \cdot + CFCl_2 \cdot \longrightarrow CF_2Cl \cdot CO \cdot CFCl \cdot CFCl_2 \xrightarrow{h\nu} \text{etc.}$$

Photolysis of 1,1,3,3-tetrachlorodifluoroacetone and of hexachloroacetone also suggests that as the percentage of chlorine in these perhalogenoacetones increases, the primary photolysis step changes from predominantly carbon–carbon to predominantly carbon–chlorine fission. Photolysis of 1,1,3,3-tetrachlorodifluoroacetone in presence of chlorine is very slow, and the rate of reaction is much the same as for photolysis in absence of chlorine.

5 G

Only trichlorofluoromethane is produced. Presence of chlorine would have facilitated photolysis by carbon–carbon fission, by trapping the radicals produced, *e.g.*:
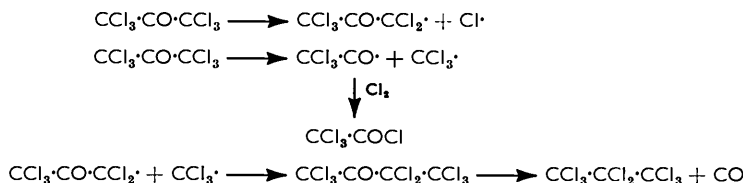
$$CFCl_2 \cdot CO \cdot CFCl_2 \longrightarrow CFCl_2 \cdot CO \cdot + CFCl_2 \cdot \xrightarrow{Cl_2} CFCl_3$$

$$\downarrow$$

$$CO + CFCl_2 \cdot \xrightarrow{Cl_2} CFCl_3$$

whereas it would inhibit photolysis by carbon–chlorine fission:

$$CFCl_2 \cdot CO \cdot CFCl_2 \rightleftharpoons CFCl_2 \cdot CO \cdot CFCl \cdot + Cl \cdot$$

The primary process in photolysis of monochloroacetone has recently been shown [3] to involve carbon–chlorine fission rather than the carbon–carbon fission expected by analogy with acetone, so even one chlorine has a marked influence in ketones that do not contain fluorine.

Liquid hexachloroacetone is photolysed only extremely slowly, to give hexachloroethane, octachloropropane, and trichloroacetyl chloride:

$$CCl_3 \cdot CO \cdot CCl_3 \longrightarrow CCl_3 \cdot CO \cdot CCl_2 \cdot + Cl \cdot$$

$$CCl_3 \cdot CO \cdot CCl_3 \longrightarrow CCl_3 \cdot CO \cdot + CCl_3 \cdot$$

$$\downarrow Cl_2$$

$$CCl_3 \cdot COCl$$

$$CCl_3 \cdot CO \cdot CCl_2 \cdot + CCl_3 \cdot \longrightarrow CCl_3 \cdot CO \cdot CCl_2 \cdot CCl_3 \longrightarrow CCl_3 \cdot CCl_2 \cdot CCl_3 + CO$$

whereas photolysis in presence of chlorine, also extremely slow, yields only carbon tetrachloride:

$$CCl_3 \cdot CO \cdot CCl_2 \cdot \longrightarrow CCl_3 \cdot + CCl_2 \colon C \colon O$$

$$\downarrow Cl_2 \qquad \downarrow Cl_2$$

$$CCl_4 \qquad CCl_3 \cdot COCl \longrightarrow CCl_4 + CO$$

$$CCl_3 \cdot CO \cdot CCl_3 \longrightarrow CCl_3 \cdot CO \cdot + CCl_3 \cdot$$

$$\downarrow Cl_2 \qquad \downarrow Cl_2$$

$$CCl_4 + CO \quad CCl_4$$
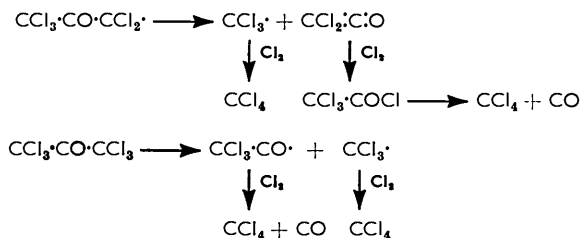
Photolysis of these highly chlorinated acetones is primarily a liquid-phase process (*e.g.*, $CCl_3 \cdot CO \cdot CCl_3$, b. p. 202°), and a combination of " cage-effect " and relatively high stability of radicals such as $CCl_3 \cdot CO \cdot CCl_2 \cdot$ leading to recombination of the radicals produced in the primary step, may well be responsible for the very slow rates of photolysis, rather than a very difficult primary step. That radical recombination plays a major rôle is suggested by the observation that photolysis of hexachloroacetone in presence of oxygen is considerably faster. Oxygen is known [4] to be a particularly efficient scavenger for perhalogenoalkyl radicals, and to lead to the formation of carbonyl halides; hexachloroacetone similarly yields only carbon dioxide and carbonyl chloride:

$$CCl_3 \cdot CO \cdot CCl_3 \longrightarrow CCl_3 CO \cdot CCl_2 \cdot + Cl \cdot$$

$$CCl_3 \cdot CO \cdot CCl_2 \cdot \xrightarrow[\text{several steps}]{O_2} CCl_3 \cdot CO \cdot CCl_2 \cdot O \cdot \longrightarrow CCl_3 \cdot CO \cdot + COCl_2$$

$$CCl_3 \cdot CO \cdot \longrightarrow CCl_3 \cdot \xrightarrow{O_2} CCl_3 \cdot O \cdot \longrightarrow COCl_2 + Cl \cdot$$
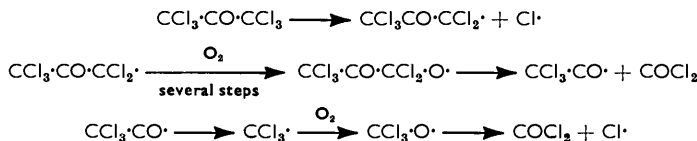
[3] Strachan and Blacet, *J. Amer. Chem. Soc.*, 1955, **77**, 5254.
[4] Haszeldine and Nyman, *J.*, 1959, 387, 420, 1084.

The available evidence is thus consistent with a primary step for a highly chlorinated acetone $CXCl_2 \cdot CO \cdot CXCl_2$ (X = F or Cl) involving quite rapid carbon–chlorine fission, but with the equilibrium

$$CXCl_2 \cdot CO \cdot CXCl_2 \rightleftharpoons CXCl_2 \cdot CO \cdot CXCl \cdot + Cl \cdot$$

lying to the left, whereas the more highly fluorinated acetones, like the corresponding ketones containing only hydrogen, are photolysed by carbon–carbon fission.

Since this work was completed a report has appeared [5] of related studies in substantial agreement with some of the results reported above, but with minor differences in interpretation.

EXPERIMENTAL

The chlorofluoro-ketones, a gift from the Allied Chemical and Dye Corporation, General Chemical Division, U.S.A., were purified by distillation. Gas–liquid chromatography and infrared spectroscopy showed that other chlorofluoro-ketones were absent. Hexachloroacetone was a commercial sample, similarly purified.

General Technique.—Photolyses were carried out in sealed silica tubes. Reactants were either condensed into the evacuated tube, by standard vacuum techniques, or were put into the tube in a fragile glass ampoule which was broken after the reaction tube had been evacuated and sealed. A Hanovia S-250 ultraviolet lamp was used, without the Wood's filter, at 5—15 cm. from the reaction tube. In experiments where the compound to be photolysed was partly in the liquid phase, the reaction vessel was shaken vigorously in a horizontal position so that both liquid and vapour were irradiated simultaneously. Purely thermal reactions during long periods of photolysis were negligible.

The volatile products were transferred to a vacuum-system for distillation and identification. Products (*e.g.*, carbon monoxide) not condensed *in vacuo* by liquid nitrogen were discarded without further examination or were manipulated by use of a Töpler pump. Products with a b. p. too high for convenient manipulation in a vacuum-system were distilled through a vacuum-jacketed semimicro-column. Products were identified by b. p., molecular-weight determination (Regnault's method), analysis, etc., and their identity was confirmed by infrared spectroscopy (Perkin–Elmer model 21 spectrophotometer with sodium chloride optics). Mixtures of products which could not be separated by distillation on the scale employed were analysed by infrared spectroscopy, often combined with molecular-weight determination and, where appropriate, by removal of components of the mixture by chemical reactions, *e.g.*, treatment with mercury to remove free halogen, treatment with aqueous sodium hydroxide to remove compounds such as $COCl_2$, CO_2, COF_2, SiF_4, $CF_2Cl \cdot COBr$, $CCl_3 \cdot COCl$.

Analytically and spectroscopically pure samples of the following compounds were available from other work for reference spectra, etc.: CF_2Cl_2, $CF_2Cl \cdot CF_2Cl$, $CF_2Cl \cdot CF_2 \cdot CF_2Cl$, $CF_2 : CF_2$, COF_2, $COCl_2$, CO_2, $CF_2Cl \cdot COBr$, $CCl_3 \cdot COCl$, CF_2ClBr, CF_2ClI, SiF_4, $CFCl_2 \cdot CFCl_2$, $CF_2Cl \cdot CFCl_2$, CF_3Cl, C_2Cl_6, CCl_4, C_3Cl_8.

Photolysis of 1,3-Dichlorotetrafluoroacetone.—(i) *Alone.* 1,3-Dichlorotetrafluoroacetone (3·384 g., 17·0 mmole) was sealed in a 360 ml. silica tube (ketone entirely in the vapour phase) and exposed to ultraviolet light for 45 hr. The carbon monoxide produced was pumped off, and the volatile products were distilled to give (*a*) an unidentified residue, b.p. >80° (0·053 g.) (Found: C, 16·3%), (*b*) 1,3-dichlorohexafluoropropane (0·308 g., 1·39 mmole, 8%), (*c*) 1,2-dichlorotetrafluoroethane (2·065 g., 12·1 mmole, 71%), and (*d*) dichlorodifluoromethane (0·369 g., 3·0 mmole, 18%).

Irradiation of *liquid* 1,3-dichlorotetrafluoroacetone gave a similar distribution of products ($CF_2Cl \cdot CF_2 \cdot CF_2Cl$ 2%; $CF_2Cl \cdot CF_2Cl$ 78%; CF_2Cl_2 3%).

(ii) *In the presence of tetrafluoroethylene.* 1,3-Dichlorotetrafluoroacetone (2·710 g., 13·6 mmole) and tetrafluoroethylene (1·980 g., 19·8 mmole), irradiated in a 320 ml. silica tube for 42 hr., rapidly deposited polytetrafluoroethylene (1·5 g.), and an involatile liquid polymer (0·8 g.). Distillation of the volatile products gave (*a*) 1,3-dichlorohexafluoropropane (0·146 g., 0·66 mmole, 5%), (*b*) 1,2-dichlorotetrafluoroethane (1·150 g., 6·82 mmole, 50%), and (*c*) dichlorodifluoromethane (0·224 g., 2·71 mmole, 20%).

[5] Bowles, Majer, and Robb, *Nature*, 1960, **187**, 314; Bowles, Derbyshire, Majer, and Patrick, *Nature*, 1960, **185**, 683.

(iii) *In the presence of ethylene.* 1,3-Dichlorotetrafluoroacetone, (2·926 g., 14·7 mmole) and ethylene (0·390 g., 13·9 mmole) were sealed in a 150 ml. silica tube and exposed to ultraviolet light for 40 hr. The volatile products were fractionally distilled *in vacuo*, to give (*a*) 1,3-dichloro-hexafluoropropane (0·095 g., 0·43 mmole, 3%), (*b*) 1,2-dichlorotetrafluoroethane (0·420 g., 2·46 mmole, 18%), and (*c*) dichlorodifluoromethane (0·026 g., 0·21 mmole, 2%). The liquid products (2·30 g.) were distilled to give a series of fractions boiling between 54°/23 mm. and 120°/23 mm. Infrared spectroscopy showed that each fraction contained one or more carbonyl groups, but together with analytical data indicated that they were complex mixtures. Further resolution was not achieved on the scale employed.

(iv) *In the presence of chlorine.* 1,3-Dichlorotetrafluoroacetone (1·088 g., 5·46 mmole) and chlorine (0·591 g., 8·32 mmole) in a 150 ml. silica tube were irradiated for 80 hr. The volatile products were shaken with mercury to remove chlorine, transferred to the vacuum-system, then distilled to give unchanged 1,3-dichlorotetrafluoroacetone (0·421 g., 2·12 mmole, 39% recovery), and a mixture shown to consist of dichlorodifluoromethane (0·678 g., 6·43 mmole, 96%) and carbonyl fluoride (0·016 g., 0·25 mmole).

(v) *In the presence of bromine.* 1,3-Dichlorotetrafluoroacetone (0·894 g., 4·50 mmole) and bromine (0·944 g., 5·90 mmole) in a 150 ml. silica tube were exposed to ultraviolet light for 72 hr. The volatile products were shaken with mercury to remove bromine, and distilled *in vacuo* to give unchanged 1,3-dichlorotetrafluoroacetone (0·617 g., 3·10 mmole, 69% recovery), bromochlorodifluoromethane (0·429 g., 2·59 mmole, 93%), and chlorodifluoroacetyl bromide (0·016 g., 0·06 mmole, 4%).

(vi) *In the presence of iodine.* 1,3-Dichlorotetrafluoroacetone (0·755 g., 3·79 mmole) and iodine (1·20 g., 4·70 mmole) were sealed in a 150 ml. silica tube and irradiated for 88 hr. The volatile products, treated with mercury to remove iodine, were chlorodifluoroiodomethane (1·01 g., 4·29 mmole, 57%), dichlorodifluoromethane (0·060 g., 0·50 mmole), and a mixture (0·135 g., 2·5 mmole) of carbon dioxide, carbonyl fluoride and a trace of silicon tetrafluoride.

(vii) *In presence of oxygen.* The ketone (0·410 g., 2·06 mmole) and oxygen (0·513 g., 16·0 mmole), irradiated for 7·5 hr. in a 260 ml. tube (initial pressure *ca.* 2 atm.), gave unchanged ketone (0·100 g., 0·502 mmole, 24%), chlorine (removed by reaction with mercury), and a mixture (0·183 g., 3·09 mmole) of the compounds CO_2, SiF_4, COF_2, and COFCl (trace).

Photolysis of 1,1,3-*Trichlorotrifluoroacetone.*—1,1,3-Trichlorotrifluoroacetone (3·946 g., 18·2 mmole), irradiated in a 360 ml. tube for 47 hr., gave carbon monoxide and (*a*) a fraction containing 1,1,3-trichlorotrifluoroacetone (0·200 g., 0·93 mmole, 5% recovery) and 1,1,2,2-tetra-chlorodifluoroethane (0·335 g., 1·64 mmole, 10%), (*b*) 1,1,2-trichlorotrifluoroethane (0·694 g., 3·70 mmole, 21%), and (*c*) a mixture of 1,2-dichlorotetrafluoroethane (0·300 g., 1·75 mmole, 10%) and dichlorodifluoromethane (0·260 g., 2·15 mmole, 12%). The liquid (*ca.* 1·0 g.) boiling in the range 100—200°, which remained in the reaction tube, was not characterised further; spectroscopic examination revealed the presence of keto-groups of the $>$CF·CO·CF$<$ type.

Photolysis of 1,1,3,3-Tetrachlorodifluoroacetone in Presence of Chlorine.—When 1,1,3,3-tetra-chlorodifluoroacetone (1·215 g., 5·24 mmole) and chlorine (0·659 g., 9·27 mmole) were irradiated in a 150 ml. silica tube for 19 days, only chlorine (removed by treatment with mercury), tri-chlorofluoromethane (0·070 g., 0·67 mmole, 67%) and unchanged tetrachlorodifluoroacetone (1·10 g., 4·74 mmole, 91% recovery) were obtained.

Photolysis of Hexachloroacetone.—(i) *Alone.* Hexachloroacetone (2·00 g., 7·85 mmole) in a 150 ml. silica tube was irradiated for 4 months. Carbon monoxide was the only gaseous product. The oily liquid remaining in the tube consisted of unchanged hexachloroacetone (50%), hexa-chloroethane (30%), octachloropropane (10%), and trichloroacetyl chloride (10%). The more difficult analysis of these products means that the precise yields are open to greater error (±5%) than in the photolysis of the other ketones.

(ii) *In the presence of chlorine.* Hexachloroacetone (3·40 g., 13·3 mmole) and chlorine (1·007 g., 14·2 mmole), irradiated in a 150 ml. silica tube for 9 days, gave chlorine (removed by treat-ment with mercury), carbon tetrachloride (0·025 g., 0·16 mmole, 12%), and unchanged hexa-chloroacetone (3·20 g., 12·0 mmole, 90% recovery).

(iii) *In the presence of oxygen.* Hexachloroacetone (0·810 g., 3·17 mmole) and oxygen (0·551 g., 17·2 mmole) in a 320 ml. silica tube were irradiated for 24 hr. The volatile products were shaken with mercury to remove chlorine and distilled to give carbonyl chloride (0·010 g., 0·10 mmole) and carbon dioxide (0·195 g., 4·44 mmole). The less volatile product consisted only of unchanged hexachloroacetone (0·20 g., 0·78 mmole, 25% recovery).

Infrared Spectra.—These were determined on a Perkin–Elmer 21 instrument with sodium chloride optics. Bands (cm.$^{-1}$) observed were:

$CF_2Cl \cdot CO \cdot CF_2Cl$ (vapour): 2·79w, 5·53s, 7·92s, 8·37vs, 8·67s, 9·36vs, 10·13s, 11·40vs, 11·57s, 12·33s, 13·53m, 14·45m.

$CF_2Cl \cdot CO \cdot CFCl_2$ (vapour): 2·80w, 5·55s, 8·07s, 8·47vs, 8·90s, 9·24s, 10·43s, 11·67s, 12·27m, 12·74s, 14·05s, 14·60s.

$CFCl_2 \cdot CO \cdot CFCl_2$ (liquid film): 5·60s, 8·38m, 8·54w, 8·97s, 9·19s, 9·35s, 10·55, 10·65m (doublet), 11·20vs, 13·0s, 14·32s, 14·95, 15·00s (doublet).

$CCl_3 \cdot CO \cdot CCl_3$ (liquid film): 5·61s, 5·74m, 8·98m, 11·15s, 11·75, 11·90vs (doublet), 15·13s.