U.D.C. 541.151

Preparative Aspects of the Radiation Chemistry of Organic Compounds

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This review attempts to examine the preparative possibilities inherent in the use of ionising radiation, largely for the synthesis of organic compounds which are difficult to obtain or which are obtained for the first time.
The bibliography includes 86 references.

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I. INTRODUCTION

The first attempts to employ ionising radiation for the preparation of compounds more complicated than the initial components were made in the earliest days of radiation chemistry. The pioneer investigations of the radiation-induced synthesis of organic compounds were made in the 1950's. The wider availability and the improvement of the sources of ionising radiation led to a real possibility of a radiation-chemical synthesis of organic compounds not only on the laboratory scale but also on a preparative scale. However, preparative radiation-chemical synthesis is still not widely used. To some extent this is probably because organic chemists specialising in syntheses are still unaccustomed to regard this method as normal; on the other hand, the attention of chemists specialising in radiation chemistry is concentrated either on the study of the mechanism of radiation-chemical reactions or on devising large scale radiation-chemical technical processes.

Radiation-chemical syntheses are usually performed by irradiating liquid mixtures or solutions of organic compounds. The effects of ionising radiation are much more various and complex than those occurring in photochemical reactions†. Ionising radiation affects all the mixture components non-selectively, the radiation energy absorbed being distributed in proportion to the mole (more precisely electronic) fraction of each component. Frequently, particularly in those cases where aromatic compounds are present, effects occur which involve charge transfer from one component to another.

The general characteristic features of radiation-induced synthetic processes are as follows.

1. The feasibility of carrying out the process at temperatures as low as required; this makes it possible to increase the yield of the desired product by increasing the solubility of the gaseous components of reaction mixtures and to decrease the contribution of degradative and resinification processes by creating conditions suitable for the preparation of thermolabile compounds.

2. Absence from reaction mixtures of impurities due to added catalysts or initiators or their decomposition products.

3. Ease of inertialess regulation of the process and the possibility of altering very rapidly the dose rate or of stopping the process.

4. Lower fire risk and explosion risk, since the processes can be carried out under conditions far from the inflammation or detonation limits of the reaction mixtures.

Radiation-induced preparative synthesis has many specific advantages over photochemical synthesis: (1) the process can be carried out in highly coloured, opaque, turbid, or inhomogeneous systems; (2) the constancy of the radiation energy absorbed in the reaction space is ensured regardless of the formation on the vessel walls of a screening film or scale; (3) the harmful selective effect of light on reaction products having a high molar extinction coefficient in the spectral region close to the incident light is eliminated.

The radiation-chemical yields‡ of the products of the radiation-chemical synthesis may vary widely depending on the nature of the radiation-chemical process and its conditions. They are particularly high in the case of radiation-chemical initiation of chain reactions where the effect of radiation is virtually limited to the initiation stage, since for low absorbed doses the role of other radiation-chemical reactions is negligible [1,2].

When irradiating liquid-phase systems for preparative purposes, it is most convenient to employ cobalt-60

†The characteristics, phenomenology, and the theory of radiation-chemical processes have been described in a number of monographs [1-5].

‡The radiation-chemical yield is the absolute number of species (molecules, ions, free radicals, etc.) formed in the chemical system on absorption of 100 eV of the energy of ionising radiation. It is denoted by the symbol G. The radiation-chemical yield, sometimes called the energy yield, is an important quantitative characteristic of radiation-chemical reactions. The yield is calculated from the relation $G = 10^2 \Delta c/D$, where Δc is the absolute change in concentration, i.e. the absolute number of species referred to unit volume or unit mass, and D is the dose absorbed in electron-volts referred to the same unit volume or unit mass. An extensive compilation of G values has been made.

γ-radiation. A very important factor in such cases is the impossibility, in principle, of the generation of induced radioactivity in the object irradiated. The high penetrating power of the γ-radiation from the cobalt-60 isotope makes it possible to carry out synthetic reactions in both glass and metallic apparatus without a significant decrease of the dose rate in the object irradiated.

A number of isotopic devices of various designs have been constructed at scientific establishments and have been described in a monograph [7] and in technical papers [8-14]. MRKh-γ-100 apparatus, designed for radiation-chemical research, is manufactured on industrially [13].

In radiation-induced synthetic reactions with low radiation-chemical yields, it is desirable to employ electron accelerators. However, the relatively low penetrating power of accelerated electrons requires the use of fairly thin inlet windows or membranes in the irradiation vessels and virtually excludes the possibility of experiments at elevated pressures. Additional difficulties are associated with the intense heating of the irradiated system as a result of the absorption of a considerable amount of radiation energy and the complexity of thermostatic devices.

II. RADIATION-INDUCED SYNTHESIS OF HALOGENO-SUBSTITUTED HYDROCARBONS

The liquid-phase radiation-induced chlorination of 1,1,1,5-tetrachloropentane leads to the synthesis of highly chlorinated polychloropentanes [15-17]:

$$C_5H_8Cl_4 \rightarrow C_5H_7Cl_5 \rightarrow C_5H_6Cl_6 \rightarrow C_5H_5Cl_7 \rightarrow C_5H_4Cl_8 \rightarrow C_5H_3Cl_9 \rightarrow C_5H_2Cl_{10}.$$

The radiation-chemical yield of polychloropentanes diminishes with increasing extent of chlorination. Each succeeding chlorine atom is introduced into the polychloropentane molecule with greater difficulty than the previous one. The increase in the number of chlorine atoms diminishes the polarisability of the C–H bond, while the influence of the inductive effect increases, consequently the attack by chlorine on the C–H bond becomes the slowest stage. When the process was carried out under mild conditions at low temperatures (less than 120°C), a number of polychloropentanes were isolated from the reaction mixture and identified. Decachloropentane, the isomers of which probably have the structural formulae $CCl_3CHClCHClCCl_2CCl_3$ and $CCl_3CCl_2CH_2CCl_2CCl_3$, was synthesised for the first time. The isomer isolated is a white crystalline substance with a camphor smell [18].

The synthesis of tetrabromoxylene by radiation-induced bromination of xylene is also a multistage reaction with a parallel-consecutive mechanism [81].

In contrast to radiation-induced chlorination and bromination processes in which free chlorine or bromine participates, the radiation-induced fluorination is an indirect reaction. Studies on the radiolysis of fluorohydrocarbons showed that the radiolytic stability of the C–F bond is comparable to the radiolytic stability of bonds in hydrocarbons, but the radiation-chemical yields of the fluorohydrocarbon radiolysis products are somewhat lower than for hydrocarbons.

Fluorohydrocarbons have been used as fluorinating agents to form new fluorine–carbon bonds or to introduce fluorine-containing groups and also as components of mixtures subjected to ionising irradiation.

In sealed-tube experiments with γ-irradiation of benzene–carbon tetrafluoride mixtures, fluorobenzene and α-trifluorotoluene were synthesised in approximately equal amounts [19]:

$$C_6H_6 + CF_4 \rightarrow C_6H_5F + CHF_3,$$
$$C_6H_6 + CF_4 \rightarrow C_6H_5CF_3 + HF.$$

The radiation-chemical yield increases with the carbon tetrafluoride content in the mixture and is independent of temperature in the range investigated. The maximum value $G(C_6H_5CF_3) = 1.3$ was obtained in a mixture containing 37 wt.% CF_4. In CF_3Br–C_6H_6 mixtures $G(C_6H_5F)$ increases from about 0.22 to about 1.5 with increase of temperature from 27° to 250°C, while $G(C_6H_5CF_3)$ remains approximately 2.

It has been suggested that the radiolytic reactions of fluorohydrocarbons take place both by an ionic and a radical mechanism. The ionic intermediate, for example CF_3^+, acts upon the C–F bond; radical processes take place simultaneously.

In the radiolysis of two-component mixtures of CF_4, SiF_4, BF_3, and C_2F_6 with benzene, nitrobenzene, or toluene, fluorine-containing compounds were synthesised [20]. In the CF_4–$C_6H_5NO_2$ mixture the yield of *m*-fluoronitrobenzene increases linearly with the electronic fraction of CF_4 and is independent of irradiation temperature. In the radiolysis of toluene-containing mixtures, trifluoromethyl derivatives are mainly formed.

The radiation-induced synthesis of ethyl bromide from gaseous ethylene and hydrogen bromide is the first industrial radiation-chemical synthetic process [21]. The reaction is carried out in ethyl bromide solution, the composition being chosen so that ethylene and hydrogen bromide are largely consumed during passage through the irradiation zone. The reaction is carried out at −2°C and a dose rate of about 40 rad s^{-1}. The chain reaction is initiated by bromine atoms produced by the radiation. The radiation-chemical yield reaches 3.9×10^4.

The competitiveness of the radiation-induced process depends to a considerable degree on the relative costs of anhydrous hydrogen bromide used in the radiation-chemical synthesis and of 48% hydrobromic acid employed in the "usual" chemical reaction with ethyl alcohol:

$$C_2H_5OH + HBr \rightarrow C_2H_5Br + H_2O.$$

The water formed carries away an appreciable amount of the hydrogen bromide dissolved in it.

The radiation method, which permits the synthesis of ethyl bromide from simple starting materials, virtually without side products, has advantages over other synthetic methods such as initiation with peroxides or reaction with aluminium bromide.

The addition of HBr to various α-olefins ranging from propene to octene has been investigated at temperatures between −79° and 25°C. The addition takes place predominantly contrary to the Markovnikov rule and leads to the formation of primary bromoalkanes (up to 90% of products). The radiation-chemical yield is about 10^3 in the gas phase and about 10^5 in the liquid phase [22].

The preparative synthesis of 1-bromo-2-chloro-1,1,2-trifluoroethane, used as an inhalation anaesthetic, is also an example of radiation-induced hydrobromination of halogeno-substituted ethylene:

$$F_2C{=}CFCl + HBr \rightarrow BrF_2C{-}CHFCl.$$

The reaction is performed at temperatures between −70° and +20°C over a wide range of dose rates, from 0.5 rad h^{-1} to 15 Mrad h^{-1}, and pressures up to 20 atm. The yield of the desired product reaches 89% of theoretical [23].

III. RADIATION-INDUCED SYNTHESIS OF ORGANIC SULPHIDES AND DISULPHIDES

The addition of butanethiol to pent-1-ene resulted in the synthesis of the corresponding dialkyl sulphide [24]:

$$RSH + CH_2{=}CHR' \rightarrow RSCH_2CH_2R'.$$

The reaction was carried out in cyclohexane solution under the action of X-rays; n-butyl pentyl sulphide was formed in 75–95% yield, G reaching 8×10^4.

Disulphides may be obtained from substituted mercaptans. The introduction of an OH group into the mercaptan molecule reduces significantly its radiation stability and gives rise to the possibility of the preparative synthesis of substituted disulphides. While in the γ-irradiation of ethanethiol the yield of decomposition products does not exceed 5, on irradiation (at a dose rate of 0.8×10^{15} eV $ml^{-1}\ s^{-1}$) of β-hydroxyethanethiol, G reaches 400. Crystals of the disulphide [25] $HOCH_2CH_2SSCH_2CH_2OH$ are isolated from the reaction mixture in yields up to 70%.

IV. RADIATION-INDUCED SYNTHESIS OF NITROGEN-CONTAINING ORGANIC COMPOUNDS

Among the radiation-induced syntheses of nitrogen-containing compounds, it is necessary to consider primarily the processes which result in the formation of compounds with C–N bonds.

1. Syntheses Based on Nitrogen Oxides

The reactions with nitrogen oxides have been little investigated to date. The trapping of unstable products by nitrous oxide, widely used in radiation-chemical experiments, has not found preparative application.

Among reactions with nitric oxide, the radiation-chemical synthesis of nitroso-derivatives of halogeno-substituted methane and ethane is of preparative interest. They are obtained by irradiating carbon tetrachloride (or chloroform, bromoform, trichloronitromethane, trichloroethane) with a stream of electrons (dose 10^8 rad) at room temperature in the presence of a stream of NO (15 litre h^{-1}). [26,27] The CCl_3 or CH_3CCl_2 radicals formed by radiolysis react with NO:

$$\dot{C}Cl_3 + NO \rightarrow CCl_3NO$$

or

$$CH_3\dot{C}Cl_2 + NO \rightarrow CH_3CCl_2NO.$$

$G(CCl_3NO)$ is in the range between 4.4 and 6.0; the chemical yield is 50% at 10% conversion: $G(CH_3CCl_2NO) = 0.5$. In the reaction with chloroform, dichloronitrosomethane was synthesised together with dichloroformaldoxime:

$$CHCl_3 \rightarrow \dot{C}HCl_2 + \dot{C}l$$
$$\dot{C}HCl_2 + NO \rightarrow CCl_2{=}NOH \rightarrow HCCl_2NO$$

This new compound, stable only at low temperatures, is obtained with $G = 0.5$ and a chemical yield of 20%.

The synthesis of dimeric nitrosobenzeneiron tricarbonyl, obtained by γ-irradiation of a benzene solution of nitrobenzene and iron pentacarbonyl, has been described [28]:

$$C_6H_5NO_2 + Fe(CO)_5 \rightarrow C_6H_5NO_2Fe(CO)_4 + CO,$$
$$2C_6H_5NO_2Fe(CO)_4 \rightarrow [C_6H_5NOFe(CO)_2]_2 + 2CO_2.$$

2. The Addition of Acetonitrile to Unsaturated Compounds

The addition of acetonitrile to olefins under the action of ionising radiation takes place fairly successfully [29], in contrast to photochemical addition sensitised by acetone or benzophenone. Sealed-tube experiments with a considerable excess of acetonitrile in an argon atmosphere lead to the formation of addition products (Table 1).

Table 1. Radiation-chemical yields of products of addition of acetonitrile to unsaturated compounds under the action of cobalt-60 γ-radiation, (dose rate 3.84×10^5 rad h^{-1}).

Olefin	Product	Yield, %	G
Hex-1-ene	heptyl cyanide	35	1.2
Hept-1-ene	octyl cyanide	36	1.2
Oct-1-ene	nonyl cyanide	45	1.2
Dec-1-ene	undecyl cyanide	40	1.2
Dodec-1-ene	tridecyl cyanide	42	1.2
Cyclopentene	cyclopentylacetonitrile	38	1.2
Cyclohexene	cyclohexylacetonitrile	45	1.2
Cyclo-octene	cyclo-octylacetonitrile	47	1.2
Cyclodecene	cyclodecylacetonitrile	43	1.2
Cyclododecene	cyclododecylacetonitrile	35	1.1
Norbornene	norbornylacetonitrile	65	1.7
Norbornadiene	nortricyclylacetonitrile	60	1.6
Benzene	benzyl cyanide	10–15	0.2

Table 2. Radiation-induced synthesis of diamines [31,32] by γ-irradiation in the absence of air (dose $\simeq 10^{21}$ eV ml^{-1}).

Initial amine	Diamine synthesised	Radion-chemical yield, G
Diethylamine	*meso*-* and racemic* *NN*-diethylbutane-2,3-diamine	0.77
Triethylamine	*meso*-* and DL-2,3-di(diethylamino)-butane	2.9
Trimethylamine	*NNN'N'*-tetramethylethylenediamine	2.5
N-Methyldiethylamine	*meso*-*NN*-diethyl-*N'N'*-dimethylbutane-2,3-diamine*	0.5
	NNN'N'-tetraethylethylenediamine	
	1-diethylamino-2-ethylmethylamino-propane*	
1-Methylpiperidine	1,2-dipiperidinoethane	0.37
	meso-1,1'-dimethyl-2,2'-dipiperidyl*	0.75
	1-methyl-2-(piperidinomethyl)piperidine*	0.39
Benzylamine	*meso*-stilbenediamine	2.76
	N-Benzylidenebenzylamine	0.11
t-Butylamine	*NN'*-di-t-butylformamidine*	0.026
	2-amino-1-t-butylamino-2-methylpropane*	0.025
	2,5-dimethylhexane-2,5-diamine	0.008

*Synthesised for the first time.

The addition takes place exclusively contrary to the Markovnikov rule:

$$RCH{=}CH_2 + CH_2CN \rightarrow RCH_2CH_2CH_2CN.$$

Nitriles, products of the addition of the CN radical to olefins, are also formed in low yields (2–3%).

3. Synthesis of Amines and Radiation-induced Amidation

Under the action of γ-radiation, aliphatic and aromatic amines enter into reactions not involving C–N bonds. As a result of the removal of a hydrogen atom from the α-position, radicals are formed which dimerise to form diamines [30–33].

The following reactions take place with mono-, di-, and trialkylamines in which all the alkyl groups attached to the same nitrogen atom are identical:

$$(C_2H_5)_2NCH_2CH_3 \rightarrow (C_2H_5)_2N\dot{C}HCH_3 + H,$$

$$2\,(C_2H_5)_2N\dot{C}HCH_3 \rightarrow CH_3CH(N(C_2H_5)_2)CH(N(C_2H_5)_2)CH_3.$$

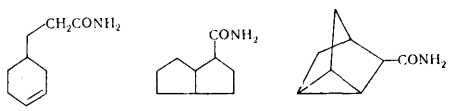
If the irradiation of amines results in the formation of radicals of various compositions and structures, then the set of diamines (dimerisation products) becomes more complex (Table 2). The low G in the case of t-butylamine is due to the absence of a hydrogen atom in the α-position relative to the nitrogen atom. The radiolysis gives rise to the radicals $CH_2C(CH_3)_2NH_2$ and $(CH_3)_3CNH$.

Table 3. Yields and radiation-chemical yields of diene amidation products[37].

Initial diene	Addition product	Yield, %	G
4-Vinylcyclohexene	I	35	3
1,5-cyclo-octadiene	II	50	3.5
Norbornadiene	III	75	5

Attempts at radiation-induced synthesis of quaternary ammonium salts containing a phenyl group from aryl halides were unsuccessful[34]. Trialkylamines react with aryl halides to form trialkyl- or dialkyl-ammonium salts ($G < 7$), but this reaction is of no preparative interest.

The amidation of olefins by formamide under the action of γ-radiation or as a result of a photochemical reaction initiated by acetone leads to the synthesis of 1 : 1 addition products. The high chemical yield makes both methods suitable for synthetic purposes[35]. In contrast to the addition to olefins, photochemical addition of formamide to dienes with formation of 1 : 1 products takes place with a low yield[36]. Under the action of γ-radiation, the addition to dienes occurs with an appreciable yield (Table 3) and may be used for synthetic purposes.



(I) (II) (III)

Carbamoyl radicals $CONH_2$ are formed as a result of the direct action of radiation on formamide, while the diene, the concentration of which in the reaction mixture is low, is little affected by the radiolytic processes.

V. RADIATION-INDUCED SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS

Several trends have now been established in the field of radiation-induced synthesis of compounds with C–P bonds. The radiation-chemical reactions of aliphatic or cyclic hydrocarbons with phosphorus trichloride or its alkyl-(cycloalkyl)-substituted derivatives, leading to the synthesis of compounds of the type $RPCl_2$ and $RR'PCl$, constitute a large group of processes. Reactions involving addition of PCl_3 to unsaturated compounds constitute another group. The use of γ-irradiation has led to interesting preparative possibilities based on the introduction of aryl groups R into quaternary phosphonium salts $[RP(R')_3]Hal$ and phosphonic acid esters $RP(O)(OR')_2$.

1. Synthesis of Alkyl(cycloalkyl)-substituted Phosphorus Trichloride Derivatives

The reactions of phosphorus trichloride with a number of aliphatic and cyclic hydrocarbons have been investigated[38,39]. The main products of the synthesis are alkyl- or cycloalkyl-phosphorus dichloride—the products of the substitution of a chlorine atom by a hydrocarbon group. When the alkyl(cycloalkyl)-substituted derivatives are used as the initial phosphorus compounds, disubstituted derivatives[38] and various compounds with a more complex structure are formed (Table 4). The synthesis is carried out in simple glass apparatus in an inert gas at atmospheric pressure and room temperature, the hydrogen chloride evolved being passed through an absorber. A finely dispersed orange deposit, the amount of which is proportional to the dose absorbed, is formed as a side product. This deposit is the product of the decomposition of tetrachlorodiphosphine P_2Cl_4 and is a polymeric substance of variable composition: $R(H_2)ClP_n$, where n = 20–30.

A reaction mechanism involving the participation of free radicals and excited molecules of the initial components has been proposed:

$$RH \rightarrow R^{\cdot} + H^{\cdot},$$
$$PCl_3 \rightarrow {}^{\cdot}PCl_2 + Cl^{\cdot},$$
$$H^{\cdot} + PCl_3 \rightarrow HCl + {}^{\cdot}PCl_2,$$
$$Cl^{\cdot} + RH \rightarrow HCl + R^{\cdot},$$
$$R^{\cdot} + {}^{\cdot}PCl_2 \rightarrow RPCl_2,$$
$$R^{\cdot} + R^{\cdot} \rightarrow R_2,$$
$$R^{\cdot} + Cl^{\cdot} \rightarrow RCl,$$
$${}^{\cdot}PCl_2 + {}^{\cdot}PCl_2 \rightarrow P_2Cl_4$$

and also

$$RH^{*} + PCl_3 \rightarrow HCl + RPCl_2,$$
$$PCl_3^{*} + RH \rightarrow HCl + RPCl_2.$$

Table 4. Yields of organophosphorus compounds synthesised under the action of γ-radiation[39].

Initial hydrocarbon	Initial phosphorus compound	Molar ratio	Dose absorbed, eV, ml^{-1}	Compound synthesised	B.p. (p, mmHg)	d_4^{20}	n_D^{20}	Yield, mole $litre^{-1}$
Cyclopentane	PCl_3	1.0:1.2	3.4×10^{20}	cyclopentyldichlorophosphine*				0.5
Cyclohexane	PCl_3	1.0:1.2	5.0×10^{20}	cyclohexyldichlorophosphine				0.5
Cyclohexane	cyclo-$C_6H_{11}PCl_2$	1.3:1.0	5.0×10^{20}	dicyclohexyldichlorophosphine*	T. m.p.23°	—	—	0.05
–	PCl_3 and cyclo-$C_6H_{11}PCl_2$	1.0:1.3	5.0×10^{20}	dicyclohexylchlorophosphine cyclohexenyltetrachlorodiphosphine*	130—135 (0.5)	1.4582	1.5865	0.2 0.2
n-Hexane	PCl_3	1.0:1.2	4.0×10^{20}	isohexyldichlorophosphine				0.5
			5.6×10^{21}	hexenyltetrachlorodiphosphine*	111—120 (0.5)	1.3205	1.5402	0.2
n-Hexane	$C_6H_{13}PCl_2$	1.0:1.0	5.0×10^{21}	dihexylchlorophosphine*	105—113 (0.2)	0.959	1.4862	0.2
n-Heptane	PCl_3	1.0:1.2	4.0×10^{20}	isoheptyldichlorophosphines				0.6
n-Octane	PCl_3	1.0:1.2	4.0×10^{20}	iso-octyldichlorophosphines*				0.6

*Compound synthesised for the first time.

The reaction mixtures consist mainly of $RPCl_2$, R_2PCl, and $R'(PCl_2)_2$, the proportions of which depend on the dose absorbed. The fraction of R_2PCl and $R'(PCl_2)_2$ in the reaction mixture increases with the dose. This suggests that these compounds are formed largely from alkyldichlorophosphines

$$RPCl_2 \rightarrow R'PCl_2 + H^{\cdot} \text{ or } \rightarrow R\dot{P}Cl + Cl^{\cdot},$$
$$R'PCl_2 + {}^{\cdot}PCl_2 \rightarrow Cl_2PR'PCl_2,$$
$$R\dot{P}Cl + RH \rightarrow R_2PCl + H^{\cdot},$$
$$R\dot{P}Cl + R^{\cdot} \rightarrow R_2PCl.$$

The radiation-induced synthesis of higher dichlorophosphines, various dialkylchlorophosphines, and other compounds based on them is of considerable preparative interest, since chemical methods for their preparation via organomercury, organocadmium, and organomagnesium compounds or by oxidative chlorophosphonation using a fast stream of oxygen are relatively complex and the yield is low.

In the radiation-induced synthetic reactions described above phosphorus trichloride is the main phosphorus-containing starting material. Another possible version of the synthetic reaction is based on the use of free (elemental) white phosphorus and alkyl chlorides as reactants. When solutions of white phosphorus in carbon tetrachloride are γ-irradiated, a number of products are formed[40], the yields of which depend significantly on temperature (Table 5).

Table 5.

Temp., °C	Radiation-chemical yield, G						
	Red P	PCl_3	CCl_3PCl_2	C_2Cl_6	Polymer $(CCl_2)_n$	consumption	
						CCl_4	P
25	22	1.4	4.5	3.1	1	10	28
130	<0.5	9.5	41	3.1	12	100	51

From the point of view of the preparation of compounds with a C–P bond, the synthesis of trichloromethylphosphorus dichloride is of greatest preparative interest. There are competitive reactions involving the formation of red phosphorus and low-molecular-weight products, which show different temperature dependences. While at room temperature red phosphorus is formed preferentially, at temperatures above 100°C the products are almost exclusively PCl_3 and CCl_3PCl_2. The mechanism of the reactions involves the addition of free radicals R, formed by the radiolysis of CCl_4, to dissolved P_4 phosphorus species:

$$R^{\cdot} + P_4 \rightarrow RP_4 \quad (R = CCl_3 \text{ or } Cl).$$

Further reactions of this adduct lead either to the formation of a red phosphorus polymer[41] or to the synthesis of low-molecular-weight products:

$$RP_4 + CCl_4 \rightarrow RP_4Cl + {}^{\cdot}CCl_3.$$

The activation energy for this chain propagation reaction is 8.2 kcal mole^{-1}.

Interesting preparative possibilities arise when red phosphorus activated by radiation and containing terminal CCl_3 groups is treated with chlorine, bromine, or other reagents which rupture P–P bonds[40]. When such activated phosphorus was dissolved in bromine, the previously unknown trichloromethylphosphorus dibromide CCl_3PBr_2 was synthesised.

2. Synthesis of Products of Addition of Phosphorus Trichloride to Unsaturated Hydrocarbons

Whe mixtures of liquid olefins with phosphorus trichloride are irradiated, radical-chain addition takes place:

$$RCH{=}HCR' + PCl_3 \rightarrow \underset{\displaystyle PCl_2}{\overset{\displaystyle |}{RCH}}{-}\underset{\displaystyle Cl}{\overset{\displaystyle |}{CHR'}}.$$

Olefins which do not show a tendency towards polymerisation by a free-radical mechanism (cyclo-olefins, n-olefins) give rise mainly to 1 : 1 addition products (Table 6)—α-chloroalkylphosphorus dichlorides; telomerisation products are formed with other types of olefin[42,43].

Table 6. Yields and radiation-chemical yields of products of addition of phosphorus trichloride to unsaturated hydrocarbons (irradiation with cobalt-60 γ-rays at room temperature).

Initial hydrocarbon	Hydrocarbon : PCl_3 (vol.%)	Dose absorbed, eV, ml^{-1}	Substance synthesised	Yield, mole litre^{-1}	G*, mol./100 eV	Refs.
Cyclopentene	1:2**	$7 \cdot 10^{18}$	(cyclo-$C_5H_8Cl)PCl_2$	0.6		44
	1:1				173	43
Cyclohexene	1:2**	$8.2 \cdot 10^{18}$	(cyclo-$C_6H_{10}Cl)PCl_2$	0.6		44
	1:1				240	43
	1:2**	$1.2 \cdot 10^{22}$	cyclo-$C_6H_9PCl_2$	0.8		44
		$1.0 \cdot 10^{22}$	(cyclo-$C_6H_8ClPCl_2$)	0.07		44
			PCl(cyclo-C_6H_9)			
Cycloheptene	1:1		(cyclo-$C_7H_{12}Cl)PCl_2$		103	43
Hept-1-ene			$CH_3(CH_2)_4CHClCH_2PCl_2$			45
Hept-2-ene			$CH_3(CH_2)_3CHClCHPCl_2CH_3$			45
Hept-3-ene			$CH_3(CH_2)_3CHClCHPCl_2CH_2CH_3$			45
Pent-1-ene	1:1		$CH_3(CH_2)_2CHClCH_2PCl_2$		278	43
Hex-1-ene	1:1		$CH_3(CH_2)_3CHClCH_2PCl_2$		192	43
Dec-1-ene	1:1		$CH_3(CH_2)_7CHClCH_2PCl_2$		89	43
Oct-2-ene	1:1		$CH_3(CH_2)_4CHClCHPCl_2CH_3$		252	43
Isobutene	1:1		$CH_3(CH_2)CClCH_2PCl_2$		430	43
			$(CH_3)_2CPCl_2CH_2Cl$		270	43
2-Ethylbutene	1:1		$(C_2H_5)_2CClCH_2PCl_2$		195	43
2-Methylbut-1-ene	1:1		$C_2H_5(CH_3)CClCH_2PCl_2$		245	43
2-Methylbut-2-ene	1:1		$(CH_3)_2CClCH(CH_3)PCl_2$		350	43

*Dose rate 7×10^{-3} r h^{-1}.
**Molar ratio.

To elucidate the optimum conditions for the radiation-chemical synthesis of the 1 : 1 addition product, the accumulation of chlorocyclohexyldichlorophosphine (CCHDCP) was investigated as a function of three principal parameters: temperature in the range 33–140°C, dose rate in the range between 1.5 and 55 rad s^{-1}, and the proportions of the initial components in the reaction mixture[44].

The linear variation of the yield of CCHDCP with the dose absorbed is observed only at low conversions. When the dose absorbed and hence the conversion is high, the reaction product (CCHDCP) accumulates and the proportions of the components begin to differ appreciably from the optimum values. The effective activation energy was determined from the temperature variation of the radiation-chemical yield as 5.9 kcal mole^{-1}. The rate of accumulation of CCHDCP is proportional to the square root of the dose rate and the order of the reaction with respect to each component is unity.

The radical-chain addition of PCl_3 to cyclohexene is described by the following mechanism:

$$PCl_3 \rightarrow {}^{\cdot}PCl_2 + Cl^{\cdot},$$
$$C_6H_{10} \rightarrow {}^{\cdot}C_6H_9 + H^{\cdot},$$
$$C_6H_{10} + {}^{\cdot}PCl_2 \rightarrow {}^{\cdot}C_6H_{10}PCl_2,$$
$$C_6H_{10}PCl_2 + PCl_3 \rightarrow ClC_6H_{10}PCl_2 + {}^{\cdot}PCl_2.$$

Chain termination takes place by the reactions:

$$\cdot PCl_2 + \cdot PCl_2 \rightarrow P_2Cl_4,$$
$$\cdot C_6H_{10}PCl_2 + \cdot PCl_2 \rightarrow PCl_2C_6H_{10}PCl_2,$$
$$\cdot C_6H_{10}PCl_2 + \cdot C_6H_{10}PCl_2 \rightarrow (C_6H_{10}PCl_2)_2.$$

When the dose rate is high, alkenyldichlorophosphine and alkyldichlorophosphine are formed, probably due to disproportionation and dehydrochlorination reactions.

Very similar kinetics were observed in the study of the radiation-chemical addition of phosphorus trichloride to linear mono-olefins, in liquid and gaseous phases[45]. The formation of two isomers of the main product and the increased reactivity of the olefins on displacement of the double bond from a terminal carbon atom to an inner carbon atom has been explained by postulating the formation in the initiation stage of a bridge-type dichlorophosphinealkyl radical.

The radiation-chemical yields of chloroalkyldichlorophosphines, reaching 10^4 mol./100 eV, suggest that γ-initiated reactions of phosphorus trichloride with unsaturated compounds could be successfully carried out on a larger scale[46,47].

3. Synthesis of Phosphonium Salts from Aryl Halides

While the synthesis of phosphonium and other quaternary 'onium salts from alkyl halides takes place readily on heating, the synthesis of 'onium salts from aryl halides is fairly complicated. γ-Irradiation of mixtures containing halogeno-substituted aromatic hydrocarbons has proved a very effective method for the synthesis of a number of quaternary phosphonium salts (Table 7). The radiation-chemical yields of arsonium salts are much lower and stibonium salts are formed with a negligible G.

The radiation-chemical synthesis has the following characteristic features: (1) a pronounced dependence of G of the 'onium salt on the mole fraction of the aryl halide in the mixture; the maximum is displaced towards higher contents of the aryl halide; (2) a significant increase in the percentage incorporation of triphenylphosphine on addition to the reaction mixture of various types of solvent; the curves relating the percentage incorporation to the amount of added solvent show a tendency towards saturation.

A mechanism with participation of positive ions and electrons derived from the solvent (S) has been proposed for dilute solutions:

$$S \rightarrow S^+ + e^-,$$
$$S^+ + (C_6H_5)_3P \rightarrow S + (C_6H_5)_3P^+,$$
$$e^- + C_6H_5Br \rightarrow C_6H_5 + Br^-,$$
$$(C_6H_5)_3P^+ + C_6H_5 \rightarrow (C_6H_5)_4P^+.$$

4. Synthesis of Phenylphosphonates

Trialkyl phosphites react with alkylhalides to form dialkyl esters of alkylphosphonic acid (Arbuzov rearrangement):

$$P(OR')_3 + RHal \rightarrow RP(O)(OR')_2 + R'Hal.$$

A similar thermal reaction cannot be achieved with aryl halides, but the use of γ-radiation allows the preparative synthesis of a number of phenyl phosphonates (Table 8).

The data presented in Table 8 show that the radiation-chemical yields of phenyl phosphonates are a maximum when iodobenzene is used as one of the reactants. In this case other characteristics of the reaction are a decrease of G proportional to the square root of the dose rate and a negative temperature coefficient of the reaction rate.

Table 7. Properties and yields of quaternary 'onium' salts synthesised under the action of cobalt-60 γ-radiation (dose rate $6 \times 10^3 - 8 \times 10^5$ r h^{-1}).[48,49]

Starting materials	Mole %	Phosphonium salt	G	Rel. incorp. of phosphine(arsine) %	Rel. incorp. of phosphine(arsine) Dose × 10^{-7}, r	M.p., °C properties of substance
Chlorobenzene	76	$[P(C_6H_5)_4]Cl$	1.4	15	25	274 - 278
Triphenylphosphine	24					white crystals
Bromobenzene	73.5	$[P(C_6H_5)_4]Br$	3.4	43	25	286 - 294
Triphenylphosphine	26.5					white crystals
Iodobenzene	91.7	$[P(C_6H_5)_4]I$	6.5	78	5.6	335 - 343
Triphenylphosphine	8.3					transparent needles
Fluorobenzene	90	$[(C_6H_5)_4P]F$	0.2	2.1	5.6	277 - 282
Triphenylphosphine	10					white needles
1,3-Dichlorobenzene	90	$[(C_6H_5)_3PC_6H_4Cl]Cl$	2.0	80	10	207 - 208
Triphenylphosphine	10					white crystals
1,4-Dichlorobenzene	71.5	$[(C_6H_5)_3PC_6H_4Cl]Cl$	3.9	90	20	157 - 158
Triphenylphosphine	28.5					white crystals
1,4-Dibromobenzene	79.7	$[(C_6H_5)_3PC_6H_4Br]B$	5.1	25	2	134 - 150
Triphenylphosphine	20.3					white crystals
1-Chloro-4-iodobenzene	74.8	$[(C_6H_5)_3PC_6H_4Cl]I$	4.4	55	3.5	219 - 222
Triphenylphosphine	25.2					yellow crystals
p-Chlorotoluene	92	$[(C_6H_5)_3PC_7H_7]Cl$	2.0	21	6	215 - 223
Triphenylphosphine	8					white crystals
o-Chlorotoluene	85	$[(C_6H_5)_3PC_7H_7]Cl$	1.4	3	1.6	260 - 262
Triphenylphosphine	15					white crystals
o-Bromotoluene	85	$[(C_6H_5)_3PC_7H_7]Br$	2.4	7	1.6	228 - 237
Triphenylphosphine	15					white crystals
p-Bromotoluene	64	$[(C_6H_5)_3PC_7H_7]Br$	2.1	41	4	228 - 237
Triphenylphosphine	36					white crystals
1-Chloronaphthalene	82	$[(C_6H_5)_3PC_{10}H_7]Cl$	0.3	4	14	288 - 291
Triphenylphosphine	18					white crystals
1-Bromonaphthalene	82	$[(C_6H_5)_3PC_{10}H_7]Br$	1.0	23	14	243 - 248
Triphenylphosphine	18					white crystals
2-Bromothiophen	80	$[(C_6H_5)_3PC_4H_3S]Br$	6.2	13	1.2	250 - 253
Triphenylphosphine	20					yellow crystals
Bromobenzene	78	$[(C_6H_5)P(C_4H_9)_3]Br$	5.8	13	2.3	162 - 164
Tributylphosphine	22					white crystals
Iodobenzene	78	$[(C_6H_5)P(C_4H_9)_3]I$	2.1	13	4	151 - 152
Tributylphosphine	22					white lustrous crystals
Chlorobenzene	92	$[(C_6H_5)_4As]Cl$	0.06	2.5	19	256 - 260
Triphenylarsine	8					white crystals
Bromobenzene	92	$[(C_6H_5)_4As]Br$	0.25	5.5	7.5	272 - 281
Triphenylarsine	8					elongated colourless needles
Iodobenzene	88	$[(C_6H_5)_4As]I$	0.08			228 - 230
Triphenylarsine	12					dark-red crystals
Bromobenzene	90	$[(C_6H_5)_4Sb]Br$	~0.005	—	25	212 - 218
Triphenylstibine	10					

Table 8. Yields of phenyl phosphonates synthesised under the action of cobalt-60 γ-radiation (dose rate 2.6×10^5 r h^{-1}).[50]

Starting materials	Mole %	Phosphonate synthesised	G	Dose × 10^{-7}, r	B.p., °C
$(CH_3O)_3P + C_6H_5F$	50:50	$C_6H_5P(O)(OCH_3)_2$	0.25	9.5	247
$(CH_3O)_3P + C_6H_5Cl$	50:50		2.6	5.8	
$(CH_3O)_3P + C_6H_5Br$	50:50		4.9	5.4	
$(CH_3O)_3P - C_6H_5I$	50:50		250	0.1	
$(C_2H_5O)_3P + C_6H_5Br$	50:50	$C_6H_5P(O)(OC_2H_5)_2$	4.0	8.0	267
$(C_2H_5O)_3P + C_6H_5I$	50:50		28	0.6	
$(iso\text{-}C_3H_7O)_3P + C_6H_5I$	50:50	$C_6H_5P(O)(O\text{-}iso\text{-}C_3H_7)_2$	11	0.7	—
$(CH_3O)_3P + p\text{-}ClC_6H_4I$	70:30	$(CH_3O)_2P(O)C_6H_4Cl$	68	0.6	264—268
$(CH_3O)_3P + p\text{-}BrC_6H_4CH_3$	70:30	$(CH_3O)_2P(O)C_7H_7$	2.5	1	262—265
$(CH_3O)_3P + m\text{-}C_6H_4Cl_2$	70:30	$(CH_3O)_2P(O)C_6H_4Cl$	1.9	1.5	265—268
$(CH_3O)_3P + 2\text{-bromothiophen}$	50:50	$(CH_3O)_2P(O)C_4H_3S$	9.7	1	248—255

It has been suggested that the process has a chain mechanism:

$$\cdot C_6H_5 + P(OR)_3 \rightarrow C_6H_5P(OR)_3,$$
$$C_6H_5P(OR)_3 + C_6H_5I \rightarrow [C_6H_5P(OR)_3]^+I^- + \cdot C_6H_5.$$

The quasi-phosphonium salt formed as a result of the addition of an iodine atom to a phosphorus(IV) free radical breaks down with formation of the desired product:

$$[C_6H_5P(OR)_3]^+I^- \rightarrow C_6H_5P(O)(OR)_2 + RI.$$

Quadratic chain termination can occur via reactions of the phenyl radicals with one another or with intermediate phosphorus-containing radicals. The rate of the processes is probably determined by the formation of the quasi-phosphonium salt, which depends on the strength of the C–H bond in the aryl halide, the electron affinity of the halogen, and the solvation of the ions produced.

VI. RADIATION-INDUCED SYNTHESIS OF ORGANOTIN COMPOUNDS

The radiation-chemical synthesis of organotin compounds of the type R_2SnBr_2 and R_3SnBr is based on the reaction of an alkyl bromide RBr with metallic tin under the action of γ-radiation. The synthesis of dibutyltin dibromide (DBTDB) have been most thoroughly investigated [51–56]. The compound was synthesised in a bench-type apparatus and described by Miretskii et al. [56] n-Butyl bromide with a purity of 99% and tin powder containing not less than 99.5% of tin were employed. The experiments were performed mainly at 85–90°C and atmospheric pressure with vigorous stirring. The average absorbed dose rate was about 100 rad s^{-1}.

The interaction of n-butyl bromide with tin in the presence of γ-radiation is fairly selective, the main product being DBTDB and a certain amount of tributyltin bromide and stannous bromide.

One of the characteristics of the radiation-chemical synthesis of DBTDB is the induction period. Application of various techniques led to the discovery of the optimum conditions for the reaction under which there is virtually no induction period. The introduction into the reaction mixture of various compounds activating the reaction, for example n-butyl alcohol or water, proved to be highly effective [57].

The study of the parameters of the reaction occurring virtually without an induction period led to the discovery of its principal macrokinetic features [58]. A very important factor in the radiation-chemical process proved to be temperature. The effective activation energy determined from the kinetic curves for the accumulation of DBTDB in the range 20–95°C proved to be 12 kcal $mole^{-1}$. The rate of formation of DBTDB is proportional to the square root of the dose rate in the range 175–2.5 rad s^{-1}.

The formation of DBTDB probably involves a chain mechanism. This is suggested by the following findings: (1) the radical-chemical yield reaches 10^3–10^4 mol./100 eV at a high conversion; (2) the reaction system shows characteristic behaviour on introduction of activating species; (3) the rate of reaction depends on the square root of the dose rate. When irradiation is stopped, the reaction ceases immediately, but recommences at the previous rate after the source of radiation is reintroduced. An additional piece of evidence in favour of a chain mechanism is provided by observations of the effect of inhibiting additives on the rate of formation of DBTDB. Special experiments showed that oxygen in the reaction system or the introduction of electron-accepting additives such as benzoquinone, hydroquinone, or *m*-dinitrobenzene cause appreciable inhibition of the reaction. The author of the review suggested the following probable mechanism for the chain process, the principal feature of which is that all the chain-propagation stages take place on the surface of tin.

Initiation:

$$RBr \rightarrow R^{\cdot} + Br^{\cdot},$$

and (or)

$$RBr + e \rightarrow R^{\cdot} + Br^{-}.$$

Chain propagation:

$$R^{\cdot} + Sn \rightarrow RSn,$$
$$RSn + RBr \rightarrow R_2SnBr,$$
$$R_2SnBr + RBr \rightarrow R_2SnBr_2 + R^{\cdot}.$$

Chain termination:

$$R^{\cdot} + Br^{\cdot} \rightarrow RBr,$$
$$R^{\cdot} + R^{\cdot} \rightarrow R_2,$$
$$R_2SnBr + Br^{\cdot} \rightarrow R_2SnBr_2,$$
$$Br^{\cdot} + Br^{\cdot} \rightarrow Br_2.$$

The formation of tributyltin monobromide and $SnBr_2$ may involve the reactions

$$R_2SnBr + R^{\cdot} \rightarrow R_3SnBr,$$
$$Br^{\cdot} + Sn \rightarrow SnBr,$$
$$SnBr + RBr \rightarrow SnBr_2 + R^{\cdot}.$$

The study of the radiation-induced synthesis of DBTDB homologues (from C_3 to C_9) showed that the macrokinetic features of all the reactions are very similar, dialkyltin dibromides being formed with fairly high radiation-chemical (500–1000 mol./100 eV) and chemical (80–85%) yields [59]. The synthesis of a number of dialkyltin dibromides in appreciable amounts permitted the determination for the first time of their physical constants (Table 9).

Table 9. Properties of dialkyltin dihalides synthesised by the radiation-chemical method [59].

Dialkyltin dibromide	n_D^{20}	d^{20}	M.p., °C
$(C_3H_7)_2SnBr_2$	1.5480	1.87	43
$(C_6H_{13})_2SnBr_2$	1.5270	1.537	8.3
$(C_7H_{15})_2SnBr_2$	1.5230	1.4720	20.5
$(C_8H_{17})_2SnBr_2$	1.5180	1.4157	20.2
$(C_9H_{19})_2SnBr_2$	1.5147	1.383	20.1

The radiation-chemical synthesis of dialkyltin dibromides has a number of useful characteristics: it is a single-stage selective process, the desired product is formed in high yield, there is no fire or detonation risk, and the process is readily controlled.

VII. RADIATION-INDUCED SYNTHESIS OF OXYGEN-CONTAINING COMPOUNDS

The radiation-induced oxidation of hydrocarbons at moderate temperatures is of no interest from the standpoint of the selective synthesis of oxidation products because of the lack of selectivity and low radiation-chemical yield of the products.

The oxidation of halogeno-olefins, in particular chloroethylenes, is of definite importance for the synthesis of valuable organic substances used as intermediates for various syntheses. Laboratory studies established that liquid tetrachloroethylene is oxidised by gaseous oxygen to tetrachloroepoxyethane and trichloroacetyl chloride on

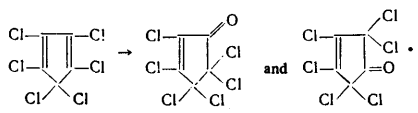
γ-irradiation at temperatures in the range 20–120°C.[60] The oxidation was carried out in a bench-type radiation-chemical apparatus[61] with a linear radiation source located coaxially in the reaction space, the average dose rate in the apparatus being about 100 rad s^{-1}. The flow rate of gaseous oxygen at atmospheric pressure was 1–2 litre min^{-1} per litre of the tetrachloroethylene taken for oxidation (with vigorous stirring of the reactants). The process was carried out in batches at 120°C and above, the duration of a single operation being 5–10 h. Trichloroacetic acid obtained by the radiation-chemical method is 4–5 times cheaper than the acid usually obtained by the oxidation of chloral with a mixture of nitric and sulphuric acids[62].

Liquid trichloroethylene is oxidised by gaseous oxygen to dichloroepoxyethane and dichloroacetyl chloride on γ-irradiation. Trichloroepoxyethane was obtained for the first time; 146 g of trichloroethylene treated with a stream of oxygen for 150 min at a flow rate of 0.3 litre min^{-1}, heated to 72°C, and exposed to γ-radiation (dose rate 0.4 rad s^{-1}) gave a mixture containing 60% of trichloroepoxyethane[63]. The optimum parameters for the synthesis of the acid chloride using the bench-type apparatus mentioned above at an average dose rate of about 25 rad s^{-1} are as follows: oxidation at 50–60°C at atmospheric pressure of oxygen flowing at a rate of 1–2 litre min^{-1} per litre of trichloroethylene. The process is carried out in batches and the duration of the oxidation is about 10 h.

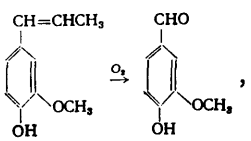
The radiation-chemical synthesis of trichloroethylene oxidation products has considerable advantages. Firstly, the cost of methyl dichloroacetate obtained from the acid chloride is approximately three times smaller than that of the product obtained by the usual chemical synthesis via chloral[64].

The radiation-induced oxidation of chloroethylenes and tetrafluoroethylene[65], leading to the synthesis of carbonyl fluoride COF_2, epoxytetrafluoroethane $(CF_2)_2O$, and a liquid polyperoxide $(-CF_2-CF_2-O-O-)_n$ is a typical chain process with an appreciable radiation-chemical yield.

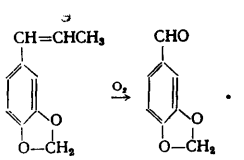
The radiation-chemical oxidation of hexachlorocyclopentadiene leads to the synthesis of hexachlorocyclopentenone[66]:



The radiation-chemical oxidation involving a double bond in the α-position relative to an aromatic ring is highly selective[67–70]. Thus vanillin was synthesised by the radiation-chemical oxidation of isoeugenol:



and heliotropin was obtained from isosafrole:



The addition of aldehydes to acetylenedicarboxylate esters has not been described previously[71]. On γ-irradiation in evacuated tubes (dose rate 4×10^5–4.5×10^5 rep h^{-1}) at 22°C, butyraldehyde, isobutyraldehyde, and acetaldehyde add to dimethyl- or diethyl-acetylenedicarboxylates with formation of diacylsuccinates (Table 10).

Table 10.

Starting materials	Dose absorbed, 10^6 rep	Addition product	Yield, %	G, mol./100 eV
Butyraldehyde (0.264 M)	10.4	dimethyl 2,3-dibutyryl-succinate	23	54
Dimethyl acetylene-dicarboxylate (0.06 M)				
Acetaldehyde (0.30 M)	18.8	dimethyl 2,3-diacetyl-succinate	31	54
Dimethyl acetylene-dicarboxylate (0.072 M)				
Acetaldehyde (0.304 M)	18.8	diethyl 2,3-diacetyl-succinate	2	46
Diethyl acetylene-dicarboxylate (0.072 M)				
Isobutyraldehyde (0.225 M)	17.4	diethyl 2,3-di-isobutyryl-succinate		
Diethyl acetylene-dicarboxylate (0.051 M)				

The addition takes place by a free radical mechanism:

$$RCHO \rightarrow RC\dot{O} + H,$$

$$RC\dot{O} + R'O_2CC \equiv CCO_2R' \rightarrow R'O_2C-\underset{\displaystyle COR}{C}=\dot{C}-CO_2R',$$

$$R'O_2C-\underset{\displaystyle COR}{C}=\dot{C}CO_2R' + RCHO \rightarrow R'O_2C-\underset{\displaystyle COR}{C}=CHCO_2R' + RC\dot{O},$$

$$R'O_2CC=\underset{\displaystyle COR}{CHCO_2R'} + RC\dot{O} \rightarrow R'O_2C-\underset{\displaystyle COR}{\dot{C}}-\underset{\displaystyle COR}{CHCO_2R'},$$

$$R'O_2C-\underset{\displaystyle COR}{\dot{C}}-\underset{\displaystyle COR}{CHCO_2R'} + RCHO \rightarrow RC\dot{O} + R'O_2C-\underset{\displaystyle COR}{CH}-\underset{\displaystyle COR}{CH}-CO_2R'.$$

VIII. RADIATION-INDUCED SYNTHESIS OF ORGANOSILICON COMPOUNDS

The addition of silanes to ethylene under the action of radiation leads to the formation of telomerisation products[72]. In the gas phase methylsilane and dimethylsilane form 1 : 1 and 1 : 2 telomers. For a silane : ethylene ratio of 3 : 1 at 50°C the radiation-chemical yields are $G(CH_3CH_2CH_2SiH_3) = 38$ and $G(CH_3CH_2CH_2SiH_2CH_3) = 15$. At temperatures close to 250°C $G(CH_3CH_2CH_2SiH_3)$ reaches several hundreds. The mechanism of the telomerisation chain reaction is evidently ionic.

Under the action of γ-radiation, triphenylsilane adds to the double bond of oct-1-ene and cyclohexene[73]. Irradiation for 63 h of a mixture of 0.15 M triphenylsilane and 0.05 M octene in a sealed tube in an atmosphere of nitrogen at 65°C at a dose rate of 810 000 rep h^{-1} leads to the synthesis of 1-octyltriphenylsilane (700 mg) and hexaphenyldisiloxane (210 mg). A mixture of triphenylsilane and cyclohexene gives triphenylcyclohexylsilane and hexaphenyldisiloxane.

The addition of chlorosilane olefins takes place readily under the action of ultraviolet light[74]. When mixtures

of various ethylene derivatives with trichlorosilane, dichlorosilane, methyldichlorosilane, or ethyldichlorosilane were exposed to ionising radiation, a large number of compounds were synthesised, some for the first time [75,76]. The telomerisation reaction takes place at a temperature not exceeding 120°C.

The preparative possibilities of the method, which permits the synthesis of the compounds $R'SiCl_2$ and $R'R'SiCl_3$ from fluoro-olefins $C_nH_{2n-m}F_m$ are illustrated in Table 11, where certain compounds synthesised for the first time are listed.

Table 11. Fluorine-containing chlorosilanes obtained by radiation-induced synthesis [75].

Starting materials	Product of synthesis	d^{25}	n_D^{20}	B.p., °C/mmHg	Percentage utilisation of starting materials	$\frac{G,\ \text{mol.}}{100\ \text{eV}}$
$C_3F_6 + HSiCl_3$	$(C_3HF_6)SiCl_3$	1.6170	1.3610	84/756.5	95	190
$C_3F_6 + H_2SiCl_2$	$(C_3HF_6)_2SiCl_2$	1.7202	1.3413	160	80	100
$C_3F_6 + CH_3HSiCl_2$	$(C_3HF_6)CH_3SiCl_2$	1.4610	1.3338	94/749	85	225
$C_3F_6 + C_6H_5HSiCl_2$	$(C_3HF_6)C_6H_5SiCl_2$	1.4342	1.3710	110—112/752	95	180
$C_2F_4 + HSiCl_3$	$(C_2HF_4)ClSiCl_2$	1.5138	1.3645	--	11	1.6

The chain reaction is initiated by $SiCl_3$ radicals formed from trichlorosilane under the action of radiation:

$$HSiCl_3 \rightarrow H^{\cdot} + {}^{\cdot}SiCl_3\ ,$$

$$RCH{=}CH_2 + {}^{\cdot}SiCl_3 \rightarrow R\dot{C}HCH_2SiCl_3,$$

$$R\dot{C}HCH_2SiCl_3 + HSiCl_3 \rightarrow RCH_2CH_2SiCl_3 + {}^{\cdot}SiCl_3.$$

The reactions with other substituted chlorosilanes takes place similarly.

The CH_3 and C_6H_5 groups in methylphenyldichlorosilane and dimethylchlorosilane can be chlorinated by the radiation method [77].

Another method for synthesising a number of organosilanes involves the condensation of unsubstituted and alkyl(aryl)-substituted chlorosilanes $(R'R'')_nSiHCl_{3-n}$, the molecule of which must contain a mobile hydrogen atom, with alkyl and aryl halides [79-82]:

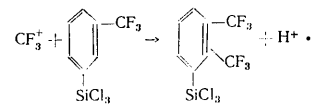
$$(R'R'')_nSiHCl_{3-n} + RCl \rightarrow (R'R'')_nSiRCl_{3-n} + HCl.$$

The reaction results in the introduction of a new group R into the chlorosilane molecule. A large series of chlorosilanes containing a wide variety of substituents was synthesised in this way with appreciable radiation-chemical yields (Table 12). The condensation reaction takes place at a temperature not exceeding 360°C. It has been established that the radiation-chemical synthesis of chloroperfluoroalkyl(aryl)-silanes takes place at lower temperatures than the synthesis of non-fluorinated alkyl-(aryl) chlorosilanes [82].

An interesting example of the radiation-induced synthesis of fluoroaryl-substituted chlorosilanes is provided by the preparation of trichloro-2,3-di(trifluoromethyl)phenylsilane, which has not been described previously [83]. Irradiation of evacuated sealed tubes with a mixture of equal volumes of $\alpha\alpha\alpha$-trifluorotoluene and tetrachlorosilane at an average dose rate of 87 rad s^{-1} resulted in the synthesis of the desired product with $G \simeq 3$. The set of processes leading to the synthesis may include the following radical and ionic reactions:

$$SiCl_4 \rightarrow {}^{\cdot}SiCl_3 + {}^{\cdot}Cl\ ,$$

$$R_FH \rightarrow \begin{cases} {}^{\cdot}R_F + H^{\cdot} \\ Ph^{\cdot} + {}^{\cdot}CF_3 \\ {}^{\cdot}CF_3^+ + {}^{\cdot}C_6H_5 + e^- \end{cases},$$



Although the data presented in the review are unquestionably fragmentary, there is hardly any doubt that preparative radiation-induced synthesis of many organic compounds is the simplest and the most rational procedure.

Table 12. Radiation-chemical synthesis of substituted chlorosilanes [81].

Chlorosilane	Aryl halide	Component ratio	Temp., °C	Product of synthesis	G
$HSiCl_3$	C_6H_5Cl	1:1	175	$C_6H_5SiCl_3$	300
$HSiCl_3$	p-$C_6H_4Cl_2$	1:3	170	p-$C_6H_4(SiCl_3)Cl$	100
$HSiCl_3$	p-$C_6H_4Cl_2$	2:1	300	p-$C_6H_4(SiCl_3)_2$	100
$HSiCl_3$	o-$C_6F_4Cl_2$	4:1	250	o-$C_6F_4(SiCl_3)_2$	60
$HSiCl_3$	1,2,4-$C_6H_3Cl_3$	1.2:1	175	$C_6H_3Cl_3(SiCl_3)$	70
CH_3SiHCl_2	C_6H_5Cl	1:2	300	$CH_3(C_6H_5)SiCl_2$	300
$C_6H_5SiHCl_2$	C_6H_5Cl	1:1	300	$(C_6H_5)_2SiCl_2$	150
$(CH_3)_2SiHCl$	p-$C_6H_4Cl_2$	4:1	300	p-$C_6H_4[Si(CH_3)_2Cl]Cl$	80
				p-$C_6H_4[Si(CH_3)_2Cl]_2$	87
$(CH_3)_2SiHCl$	m-$C_6H_4Cl_2$	4:1	300	m-$C_6H_4[Si(CH_3)_2Cl]Cl$	80
$CH_3(C_6H_5)SiHCl$	p-$C_6H_4Cl_2$	2:1	300	p-$C_6H_4[SiCH_3(C_6H_5)Cl]_2$	20
$(C_6H_5)_2SiHCl$	p-$C_6H_4Cl_2$	2:1	300	p-$C_6H_4[(C_6H_5)_2SiCl]_2$	15

Together with the preparative radiation-induced synthesis described above, carbonylation, carboxylation, hydroxylation, nitration, and nitrosation reactions, synthesis of glycols, reactions involving the addition to olefins of telogens such as, for example, alcohols, aldehydes, mercaptans, etc. (see the relevant reviews [84-86]), occurring under the action of radiation, are also known. One cannot exclude the possibility that in certain cases some of the reactions enumerated may find preparative applications.

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