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The Isomerisation of Unstable Organoelemental Radicals in Liquid-phase Reactions

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The studies carried out in recent years on the rearrangement of radicals involving the migration of Cl and Br atoms as well as the R_3Si, R_3Ge, RC = O, $RC\overset{O}{\underset{O}{<}}$, and RS groups in liquid-phase reactions are examined. Chemical and physicochemical data (obtained by EPR, stereochemical, tracer atom, etc. methods), supporting the idea of the intermediate formation of bridging radicals in 1,2- and 1,3-migrations of atoms and groups, are presented. The unusual rearrangements of aromatic perfluoro-radicals are discussed.
The bibliography includes 113 references.

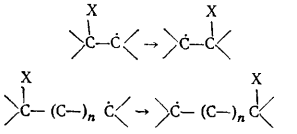
CONTENTS

I. Introduction 828
II. Rearrangements of radicals with migration of chlorine, bromine, and fluorine atoms 829
III. Rearrangements of radicals with migration of organoelemental groups 833

I. INTRODUCTION

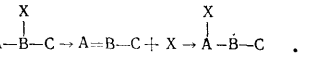
Studies on the rearrangements of organic radicals in the liquid phase constitute a rapidly developing field of modern radical chemistry[1-8]. The wide variety of the known types of rearrangements of radicals is due to the differences in the nature of the migrating groups, the variable nature of the atoms from which the migrating group is split off, the nature of the radical centre, and the length of the chain separating the radical centre from the migrating atom or group.

This review deals with true intramolecular rearrangements associated with the migration of atoms or groups via the mechanisms



It includes the rearrangements of radicals involving the migration of Cl, Br, and F atoms and of the R_3Si, R_3Ge, $RC\overset{O}{\underset{O}{<}}$, RCO, and RS groups; the literature on these rearrangements up to 1978 inclusive is considered. Despite all the differences between them, the above types of rearrangements have the following common features: the structure of the hydrocarbon skeleton of the radical remains unchanged in the rearrangement; heteroatoms (halogens) or groups incorporating heteroatoms (R_3Si, R_3Ge, RCO, RCOO, or RS) migrate; the migrating atoms or groups contain lone electron pairs, π-bonds, or unoccupied *d* orbitals.

All the known rearrangements of short-lived radicals can apparently be divided into two types: (1) rearrangements of radicals involving the migration of a hydrogen atom; (2) rearrangements involving the migration of atoms and groups containing lone electron pairs, π-bonds, and vacant *d* orbitals. These two types of rearrangements differ in their characteristics. For example, the 1,2-migration of hydrogen in radicals is virtually unknown; on the other hand, 1,2-migration and to a lesser extent 1,3-migration of atoms and groups are characteristic of all the rearrangements considered in the present review. An important problem for the understanding of 1,2-rearrangements involves criteria which make it possible to distinguish an intramolecular rearrangement from the formation of rearranged radicals via an elimination–addition mechanism, which can be formally represented schematically as follows:



In certain cases it is possible to distinguish these two types of reaction. The detection of the eliminated migrating group with the aid of a suitable trapping agent is sometimes used as proof that the reaction proceeds via an elimination–addition mechanism. It is noteworthy that this method does not provide an unambiguous answer, since the migrating group can be split off simultaneously with an intramolecular rearrangement.

The formation of intermediate three-membered bridged intermediate radicals or a bridged transition state is postulated for all the rearrangements involving 1,2-migration of atoms enumerated above. Indeed, it has been shown by EPR in instances where it was possible to obtain a resolved spectrum that the presence of chlorine and silyl, germyl, and certain other groups in the β-position with respect to the radical centre has a marked influence on the conformation of the radical. Thus a detailed study of the spectroscopic parameters of β-chloroalkyl radicals and their temperature variation showed[8] that in the most stable conformation of this radical the chlorine atom is located in the "eclipsed" position relative to the *p* orbital of the radical centre, which is favourable for the interaction between them.

The formation of bridged radicals can be to some extent detected by chemical methods. Thus anchimeric cooperation with the selective elimination of hydrogen from the β-position with respect to the atom or group which is capable of forming a bridged radical is observed in some reactions. A characteristic feature of the intermediate formation of a bridged radical is also the retention of optical activity in reactions involving a rearrangement of radicals.

Most of the known rearrangements of radicals have been investigated by methods of preparative organic chemistry. It can now be assumed that the information obtained by these methods about the radical-chain mechanisms of the rearrangements, the structures of the rearranged and non-rearranged radicals, and the intramolecular nature of the reaction has been confirmed in

many instances by various physicochemical methods (EPR, stereochemistry, tracer atoms, etc.).

II. REARRANGEMENTS OF RADICALS WITH MIGRATION OF CHLORINE, BROMINE, AND FLUORINE ATOMS

1. 1,2-Migration of Chlorine

Nesmeyanov et al.[9] first demonstrated reliably, in the case of the rearrangement of polychloroalkyl radicals I to radicals II with 1,2-migration of chlorine (1,2-Cl), the possibility of the liquid-phase isomerisation of unstable aliphatic radicals:

$$\underset{(I)}{XCCl_2\dot{C}YCH_2Z} \rightarrow \underset{(II)}{X\dot{C}ClCYClCH_2Z} \ ;$$

X=H, F, Cl, or CH_3; Y=H, Cl, Br, or CH_3; Z=Br, CCl_3, or SR.

The possibility of such a rearrangement in the above investigation has been questioned[10]. Radicals of type (I) have been generated by the addition of the radicals Ż to polychloropropenes $CH_2 = CYCCl_2X$. For the reaction of 3,3,3-trichloropropene with HBr initiated by benzoyl peroxide, the following scheme has been put forward:

$$HBr + C_6\dot{H}_5 \rightarrow C_6H_6 + \dot{B}r \ :$$
$$\dot{B}r + CH_2{=}CHCCl_3 \rightarrow BrCH_2\dot{C}HCCl_3 \ :$$

$$BrCH_2\dot{C}HCCl_3 \xrightarrow{\text{rearrangement}} BrCH_2CHCl\dot{C}Cl_2 \ :$$
$$BrCH_2CHCl\dot{C}Cl_2 + HBr \rightarrow BrCH_2CHClCCl_2H + \dot{B}r \text{ etc.} \qquad (1)$$

Data on this rearrangement (literature up to 1964) have already been surveyed[4] (see also Wilt[2] and Walling[5]). In recent years rearrangements of this type have been investigated vigorously, but comparatively few new examples have been described. In particular, a study has been made of the rearrangement of primary radicals (III) to radicals (IV):

$$\underset{(III)}{CCl_3\dot{C}H_2} \rightarrow \underset{IV}{\dot{C}Cl_2CH_2Cl} \ .$$

This rearrangement was investigated by methods of preparative chemistry[11], EPR,[12,13] and the spin trapping technique[14,15]. Other examples of rearrangements of this type have been found[16-18] in the decomposition of acetyl peroxide in polychloroethanes and polychloropropanes containing the CCl_3, $CHCl_2$, or CCl_2 groups; among other products, there are compounds whose formation is treated as a 1,2-Cl rearrangement via mechanisms analogous to mechanism (1).

The rearrangement of β-monochloroalkyl radicals with 1,2-migration of chlorine has been described in recent years for radicals obtained by the abstraction of hydrogen from $(CH_3)_3CCl$ by t-butoxy-radicals[19]:

$$(CH_3)_3CCl \xrightarrow{RO^{\cdot}} (CH_3)_2CCl\dot{C}H_2 \rightarrow (CH_3)_2\dot{C}CH_2Cl \xrightarrow{ROBr} (CH_3)_2CBrCH_2Cl \ .$$

Analogous rearrangements have been observed with the aid of EPR at low temperatures. The rearranged radicals have been identified by this method in reactions involving the abstraction of bromine from $(CH_3)_2CClCH_2Br$ and $CH_3CBrHC(CH_3)_2Cl$ by $(C_2H_5)_3Si$ radicals[12] and the abstraction of hydrogen from $(CH_3)_3CCl$.[12] The rearranged radicals, obtained by γ-irradiation from $(CD_3)_3CCl$, have been identified by EPR.[20]

The rearrangement of radicals with 1,2-migration of chlorine from C to Si in the gas phase[21] and from S to C in the liquid phase[22] has been described.

The study of the 1,2-Cl rearrangement on interaction of polyhalogenohydrocarbons with diazomethane has been developed to some extent[23]. The reactions of polyhalogeno-derivatives with diazomethane had been described earlier[24]:

$$CCl_4 + CH_2N_2 \xrightarrow{h\nu} (ClCH_2)_4C \ ;$$
$$XCCl_3 + CH_2N_2 \xrightarrow{h\nu} XCH_2C(CH_2Cl)_3 \ ;$$
X=H, Br, or CH_3CO_2 .

It has been suggested[24] that the reaction involves a series of consecutive stages in which methylene adds to the radical centre with subsequent 1,2-Cl migration. New examples of reactions of this type have been studied in recent years[23] and it has been shown that, depending on the reactant ratio and temperature, it is possible to isolate from the reaction mixture products obtained by the stabilisation of intermediate rearranged radicals formed by an exchange reaction with the initial polyhalogeno-derivative. For example, the reaction of diazomethane with $BrCCl_3$ led to the isolation of $BrCCl_2CH_2Cl$, $BrCCl.(CH_2Cl)_2$, $BrC(CH_2Cl)_3$, and $BrCH_2C(CH_2Cl)_3$. Analogous compounds were obtained in the reaction of diazomethane with $BrCCl_2CH_2Cl$, $BrCCl_2CH_3$, or $BrCCl_2H$.[23] A possible mechanism of this reaction has been discussed in detail in a review[2].

There are no data on the kinetics of the elementary stage of the 1,2-Cl rearrangement. The overall kinetics of reactions of this type, initiated by ultraviolet irradiation or benzoyl peroxide at 60°C, have been investigated in relation to the homolytic isomerisation of polyhalogenopropenes via the mechanism[25]

$$XCCl_2CBr{=}CH_2 \xrightarrow{h\nu} XCCl{=}CClCH_2Br \ (X{=}Cl, CH_3, \text{or } F) \ . \qquad (2)$$

It was established that the reaction is fastest in the case of 2-bromo-3,3,3-trichloropropene ($k = 2.2 \times 10^{-4}$ s^{-1}), which is followed by 2-bromo-3,3-dichlorobutene ($k = 1.5 \times 10^{-5}$ s^{-1}), the isomerisation of 2-bromo-3,3-dichloro-3-fluoropropene being slowest ($k = 5 \times 10^{-6}$ s^{-1}), It has been shown that the chain propagating species is the bromine atom. The quantum yield in the photochemical initiation of the isomerisation of 2-bromo-3,3,3-trichloropropene has been determined as 980 ± 30. The data obtained confirmed the mechanism of this rearrangement proposed by Nesmeyanov et al.[26] and made it possible to specify the chain initiation and termination stages. Presumably, the above series, in terms of decreasing rates of isomerisation of polyhalogenopropenes, corresponds to the series based on decreasing stabilities of the rearranged radicals:

$$Cl_2\dot{C}CBrClCH_2Br > CH_3\dot{C}ClCBrClCH_2Br > F\dot{C}ClCBrClCH_2Br \ .$$

It has been noted in the literature that most of the known rearrangements lead to the formation of more stable radicals from less stable ones. However, a number of instances are known in which the non-rearranged and rearranged radicals do not differ in stability; rearrangements have also been encountered in which more stable and relatively unreactive radicals rearranged to more reactive radicals with a lower stability. Certain examples of 1,2-Cl rearrangements of secondary chloroalkyl radicals to yield less stable primary radicals have been published[4]. However, comparatively few examples of such rearrangements are known and they give a low yield of the rearranged products. The calculation of the total electronic energies of two pairs of radicals is therefore of interest: $ClCH_2\dot{C}HCCl_3$ (V) and $ClCH_2CHCl\dot{C}Cl_2$ (VI); $ClCH_2\dot{C}ClCHCl_2$ (VII) and $ClCH_2CCl_2\dot{C}HCl$ (VIII). Radicals (VI) and (VIII) should be formed in the 1,2-Cl

rearrangement of radicals (V) and (VII) respectively. It had been shown earlier that radicals of type (V) do indeed rearrange to radicals (VI); under the same conditions, radical (VII) does not rearrange[4]. Calculation[27] showed that the relative stabilities of the radicals depend on their conformations and that, among the radicals enumerated above, radical (VI) is the most stable; the rearrangement of (V) to (VI) should be accompanied by an energy gain. The energies of radicals (VII) and (VIII) in the ground state differ little, but the rearrangement of radical (VII) to (VIII) nevertheless requires an expenditure of energy:

$$E\,(ClCH_2\dot{C}HCCl_3) - 0.85\ eV = E\,(ClCH_2CHCl\dot{C}Cl_2)\ ;$$
$$E\,(ClCH_2\dot{C}ClCHCl_2) + 0.06\ eV = E\,(ClCH_2CCl_2\dot{C}HCl)\ .$$

The absence of the rearrangement of radical (VII) to radical (VIII) with 1,2-migration of chlorine is thus apparently really associated with the unfavourable ratio of the stabilities of the above radicals, as had been suggested previously[4].

The rearrangement of radicals with 1,2-migration of chlorine has been observed also in the polymerisation of polyhalogenopropenes. It has been established[28,29] that the radical polymerisation of 3,3,3-trichloropropene and 3,3-dichloro-3-fluoropropene leads to polymers which contain mainly the rearranged $CH_2CClHCCl_2$ and $CH_2CH.ClCClF$ units respectively according to ^1H and ^{19}F NMR and ^{35}Cl NQR data.

Rearrangements with 1,5- and 1,6-migration of chlorine in chloroalkyl radicals proceed with difficulty if they are possible at all. Indirect data supporting the possibility of 1,5-Cl and 1,6-Cl rearrangements have been published[30-32].

The application of the EPR method and the spin trapping technique in the study of rearrangements with 1,2-migration of chlorine. Significant progress in identifying rearranged and non-rearranged radicals, formed in many reactions and in demonstrating the intramolecular nature of the rearrangements has been achieved in recent years with the aid of the EPR method, including the use of spin-trapping agents.

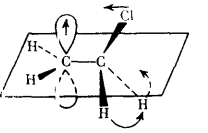
β-Chloroalkyl radicals. A number of workers have shown that the chlorine atom in the β-position with respect to the radical centre has a strong influence on the conformation of the radical[3,12,13,20,33,34], as had been observed earlier for certain other β-substituted alkyl radicals[35]. The EPR spectrum of the radicals obtained from t-butyl chloride under the influence of ^{60}Co γ-rays at 77 K exhibits a very large splitting between the components due to the hyperfine interaction (HFI) with the halogen atom[20].

The following HFI constants have been found for the EPR spectrum of $\dot{C}H_2CH_2Cl$: $a_\alpha(H) = 21.5$ G, $a_\beta(H) = 11.5$ G, and $a_\beta(Cl) = 17.4$ G at $-60°C$;[12] $a_\alpha(H) = 21.75$ G, $a_\beta(H) = 10.20$ G, $a_\beta(^{35}Cl) = 18.78$ G, and $a_\beta(^{37}Cl) = 15.65$ G at $-125°C$;[3] $g = 2.60199$. These data correspond to an asymmetric bridged structure (A) in which the chlorine atom eclipses the orbital of the odd electron, which requires a definite deviation from the regular tetrahedral geometry at the β-carbon atom[36]:



(A)

The EPR spectra have been investigated in greatest detail for a series of β-chloroalkyl radicals[3,13,33,37]. A detailed study of the spectral parameters—the g-factor, the hyperfine interaction constants for the β-protons and β-chlorine atoms, their temperature dependence, and the width of the lines in the spectrum—led to the conclusion[3] that the most stable conformation of the β-chloroethyl radical is of the type illustrated below†:



In this "eclipsed" conformation the chlorine atom is located at the optimum position for interaction with the radical centre. In conformity with Kochi's cautious formulation[3], the EPR data suggest that the structure of the β-chloroalkyl radicals can be regarded as the bridged type in a broad sense of the term. Radicals with chlorine in a more remote position relative to the radical centre cannot exist in the analogous conformation and do not isomerise with 1,3-, 1,4-, or 1,5-migration of chlorine. Bearing this fact in mind as well as the observed conformation of the β-chloroalkyl radicals, one can regard it as established that the 1,2-migration of chlorine in monochloroalkyl radicals has an intramolecular mechanism.

Table 1. EPR study of the rearrangement of radicals with 1,2-migration of chlorine.

Initial compound	Attacking radical	t, °C	Non-rearranged radicals (unidentified)	Rearranged radicals (identified)	Refs.
CH_3CCl_3	$CF_3O^\cdot$	−140	$\dot{C}H_2CCl_3$	$ClCH_2\dot{C}Cl_2$	13
$BrCH_2CCl_3$	$Et_3\dot{S}i$	−140	$\dot{C}H_2CCl_3$	$ClCH_2\dot{C}Cl_2$	13
ICH_2CCl_3	$n\text{-}Bu_3\dot{S}i$	−120	$\dot{C}H_2CCl_3$	$ClCH_2\dot{C}Cl_2$	12
$(CH_3)_2CClCH_2Br$	$Et_3\dot{S}i$	−110 −130	$(CH_3)_2CCl\dot{C}H_2$	$(CH_3)_2\dot{C}CH_2Cl$	12, 33
$(CH_3)_2CClCHBrCH_3$	$Et_3\dot{S}i$	−60	$(CH_3)_2CCl\dot{C}HCH_3$	$(CH_3)_2\dot{C}CHClCH_3$	12, 33
$(CH_3)_3CCl$	t-BuO·	−200	$(CH_3)_2CCl\dot{C}H_2$	$(CH_3)_2\dot{C}CH_2Cl$	12, 33
$(CD_3)_3CCl$	($\gamma^{60}Co$)	−196	$(CD_3)_2CCl\dot{C}D_2$	$(CD_3)_2\dot{C}CD_2Cl$	20

Rearranged radicals were identified by EPR in the liquid phase at low temperatures in the reactions presented in Table 1; non-rearranged radicals were not detected. Despite the incompleteness of the information obtained, these data are extremely important. They confirm the radical mechanism of the rearrangements, the high rate of 1,2-migration of chlorine in the radicals, and the greater stability of the rearranged radicals compared with the non-rearranged radicals.

gem-Polychloroalkyl radicals. For the purpose of the identification of both rearranged and non-rearranged radicals, the EPR method combined with the spin-trapping technique proved to be fruitful (Table 2).[34] The method has definite advantages for the solution of this problem. The spin-adducts (nitroxy-radicals) formed

† The arrows indicate the direction of the shifts of atoms in the transition state.

Table 2. EPR study of the rearrangements with 1,2-migration of chlorine using spin trapping agents.

No.	Initial compound	Attacking radical	t, °C	Non-rearranged radical (NR)	Trapping agent for NR	Rearranged radical (RR)	Trapping agent for RR	Refs.
1	$BrCH_2CCl_3$	$Et_3\dot{S}i$	−60	$\dot{C}H_2CCl_3$	MNP	$ClCH_2\dot{C}Cl_2$	Nitrosodurene	41
2	$ClCH_2CCl_3$	$P\dot{h}$	25	$Cl\dot{C}HCCl_3$	MNP	$Cl_2CH\dot{C}Cl_2$	MNP	14
3	$CH_2=CHCCl_3$	$(CH_3)_3C\dot{O}$	25	$(CH_3)_3COCH_2\dot{C}HCCl_3$	MNB	$(CH_3)_3COCH_2CHCl\dot{C}Cl_2$	MNP	43
4	$CH_2=CHCCl_3$	$\dot{C}Cl_3$	25	$CCl_3CH_2\dot{C}HCCl_3$	MNB	$CCl_3CH_2CHCl\dot{C}Cl_2$	MNP	43
5	$CH_2=CHCCl_2F$	$\dot{C}Cl_3$	55—60	$CCl_3CH_2\dot{C}HCCl_2F$	MNB	$CCl_3CH_2CHCl\dot{C}ClF$	MNP	42
6	$CH_2=CHCHCl_2$	$\dot{C}Cl_3$	55—60	Unidentified	MNP	$CCl_3CH_2CHCl\dot{C}HCl$	MNP	42
7	$ClCH_2CHClCCl_3$	$P\dot{h}$	25	$ClCH_2C\dot{C}lCCl_3$		$ClCH_2CCl_2\dot{C}Cl_2$		14

are sufficiently stable for their study by EPR in the liquid phase at the usual temperatures [38-40]. The large selection of spin-trapping agents available makes the method virtually universal for the detection of a wide variety of radicals. The method is experimentally simple. It has been shown [14,41,42] that various radicals formed in the reaction system can be identified by employing the selectivity of the spin-trapping agents [34,43]. Thus in a series of reactions (Table 2, Nos. 3–6) rearranged radicals of the type $R\dot{C}Cl_2$, $R\dot{C}ClF$, and $R\dot{C}HCl$ were identified in experiments carried out in the presence of methylnitrosopropane $(CH_3)_3CNO$(MNP) as the spin-trapping agent. Non-rearranged radicals of the type $R\dot{C}HR$ could be identified by carrying out the same reactions in the presence of another spin-trapping agent, namely 2-methyl-2-nitrosobutan-3-one $CH_3COC(CH_3)_2NO$ (MNB); Table 2 shows that other applications of the selectivity of spin-trapping agents have also been made.

Particularly important results have been obtained by employing the EPR method in the study of the detailed mechanism of the rearrangement of $XCCl_2\dot{C}H_2$ radicals with 1,2-migration of chlorine. Hoag and Heiba [44] suggested (without carrying out their own experiments on this subject) that the rearrangement proceeds via an elimination–addition mechanism. Significant evidence in support of an intramolecular mechanism of this rearrangement has been adduced in a number of papers and reviews [4,5,13]; it can now be assumed that this has been rigorously demonstrated by EPR. [14,41] It has been shown in a number of instances [14] that the EPR spectra of the spin adducts of the radicals $RCCl_2\dot{C}Cl^1Cl^2$ with $(CH_3)_3CNO$ and other trapping agents contain signals which show that the Cl^1 and Cl^2 atoms are equivalent in relation to the p_z orbital, when their environments in the nitroxy-radical are the same, but are non-equivalent when the environments are not the same. This observation has been used in the study of the rearrangements of radicals (IX) to (X) and of (XI) to (XII):

$$\underset{\text{(IX)}}{CCl_3\dot{C}HCl} \rightarrow \underset{\text{(X)}}{\dot{C}Cl_2CCl_2H} \quad \underset{\text{(XI)}}{CCl_3\dot{C}ClCH_2Cl} \rightarrow \underset{\text{(XII)}}{\dot{C}Cl_2CCl_2CH_2Cl} \ .$$

Radicals (IX) and (XI) were generated by the abstraction of hydrogen from CCl_3CH_2Cl or $CCl_3CHClCH_2Cl$ by phenyl radicals (Table 2, Nos. 2 and 7). The radicals C_6H_5 were obtained by the method of Razuaev et al. [45] The parameters of the EPR spectra of the spin-adducts of these radicals with MNP are presented in Table 3. In both cases the EPR spectra consist of a superposition of signals due to the spin-adducts of both non-rearranged and rearranged radicals with $(CH_3)_3CNO$. It was found that the β-chlorine atoms in the spin-adducts of the rearranged radicals are non-equivalent with respect to the $2p_z$ orbital of the nitrogen atom; this establishes unambiguously that the migrating chlorine atom in the radical is located in the plane of the $2p_z$ orbital of the carbon atoms to which the chlorine migrates and hence the intramolecular nature of the rearrangement is demonstrated [14,41].

Table 3. Parameters of the EPR spectra [14] of the nitroxy-radicals $RN(\dot{O})C(CH_3)_3$.

Non-rearranged radical	a_N, G	a_{Cl}, G	Rearranged radical	a_N, G	a_{Cl}, G
$CCl_3\dot{C}HCl$	17.9	4.8	$\dot{C}Cl^1Cl^2CCl_2H$	12.7	Cl^1 4,5; Cl^2 1,0
$CCl_3\dot{C}ClCH_2Cl$	12.1	4.0	$\dot{C}Cl^1Cl^2CCl_2CH_2Cl$	12.2	Cl^1 4,0; Cl^2 1,0

2. The 1,2-Migration of Bromine

The rearrangement of radicals with 1,2-migration of bromine was described for the first time by Skell et al. [46] in 1961 in relation to the photochemical chlorination of t-butyl bromide and isopropyl bromide by t-butyl hypochlorite with formation of 1-bromo-2-chloro-methylpropane and 1-bromo-2-chloropropane respectively. Rearrangements of this type have been investigated vigorously in recent years in the photochemical halogenation of bromohydrocarbons [20,44,46-52]. The primary radical rearranges to a tertiary radical with a higher yield than in the rearrangement to a secondary radical, which is consistent with the general behaviour [4]. Thus the rearrangement in the photochemical chlorination of t-butyl bromide, resulting in 1-bromo-2-chloro-2-methylpropane, proceeds with a nearly quantitative yield [46], while the rearrangement of isopropyl bromide under the same conditions gives rise to 1-bromo-2-chloropropane with a yield which is only 15% of theoretical [46]. It is noteworthy that in the series of examples investigated a formally unusual rearrangement of more stable radicals to less stable radicals takes place, which undoubtedly reflects the characteristics of the mechanism of this rearrangement. For example, the photochemical bromination of labelled butyl bromide,

$$CH_3CH_2CH_2CH_2^{81}Br \xrightarrow{Br_2} CH_3CH_2CH^{81}BrCH_2Br \ ,$$

results in the conversion of a secondary radical into a primary radical [48].

There are no reliably established examples of rearrangements with migration of bromine to a more remote radical centre [53]. It has been suggested [31] that the

formation of $[(CH_3)_2CBrCH_2CBr_2]_2SO_2$ in the reaction of bis(tribromomethyl)sulphone with isobutene includes a stage where the radicals rearrange with 1,5-migration of bromine:

$$CBr_3SO_2CBr_2CH_2\dot{C}(CH_3)_2 \rightarrow \dot{C}Br_2SO_2CBr_2CH_2CBr(CH_3)_2 \quad .$$

The mechanism of the rearrangement of radicals with 1,2-migration of bromine. The problem of the mechanism of the rearrangement of radicals with 1,2-migration of bromine proved to be closely related to the problem of the anchimeric cooperation in the elimination of the β-carbon atom in bromoalkanes and the formation of a bromine bridge in the radical. In this case the rearrangement involves the mechanism

$$R_2CBr-CHR'_2 \xrightarrow[-HX]{+X^\cdot} R_2C(\overset{\cdot}{Br})-CR'_2 \xrightarrow{+X^\cdot} R_2CX-CR'_2Br \quad .$$
X = Cl, or Br

The anchimeric cooperation in the abstraction of a β-hydrogen atom and the formation of a bridged radical is also indicated by data published in a number of reports[46, 48,50,54,55].

The high selectivity of the radical hydrogenation of bromohydrocarbons with formation of vicinal dihalogeno-derivatives, noted by many workers[46-52], confirms the bridged structure of bromoalkyl radicals. However, in another series of studies data have been adduced in support of an elimination–addition mechanism for reactions of this kind[40,56,57]. It has also been stated[48] that there are no data whereby one could distinguish the situation where the intermediate bromoalkyl radicals are static symmetrical bridged structures from one where there is an equilibrium conversion of a pair of asymmetric intermediate bridged species ($\tau_{1/2} \simeq 10^{-11}$ s).

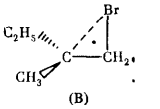
Data have also been presented in support of the intermediate formation of the classical radicals $\dot{C}-C-Br$ [44,52] (see also Cristol et al.[58]). It is noteworthy that none of the above series of studies can explain without contradictions all the observed facts in terms of a single reaction mechanism[47,58].

The attempts to obtain the EPR spectra of β-bromoalkyl radicals in the liquid phase were unsuccessful even at −120°C owing to the instability of these radicals[59]. The reaction of HBr with *cis*- and *trans*-but-2-ene as well as certain other unsaturated compounds has been investigated[60] by EPR at 70 K; the authors have attributed the observed spectra to the radical-adducts of bromine and but-2-ene. These spectra are compatible with the idea that bridged radicals of the type

$$CH_3CH(\overset{\cdot}{Br})-CHCH_3$$

are formed. However, the possibility of another assignment of the spectral signals and of a different interpretation of the results of Abel and Peitte[60] has been pointed out[61].

Chemical data, in particular the results of the study of the stereochemistry of the photochemical halogenation of bromoalkanes, support the bridged structure of the β-bromoalkyl radicals. Thus the liquid-phase photobromination of the optically active 1-bromo-2-methylbutane with bromine[62] yielded 1,2-dibromo-2-methylbutane with a high optical purity. The rearrangement in the photochlorination of (+)(2*S*)-bromobutane by t-butyl hypochlorite leads to the formation of optically active 1-bromo-2-chlorobutane[48]. Analogous results were obtained in a study[63] where the authors were able to trap an asymmetric intermediate radical (B) in the form of a product $C_2H_5CD.(CH_3)CH_2Br$ of the addition of deuterium (from DBr) to the bridged radical with retention of the initial configuration to an extent greater than 96%:[63]


(B)

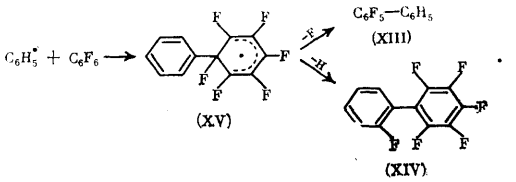
These facts cannot be accounted for either by an elimination-addition mechanism or by the hypothesis of the classical structure of β-bromoalkyl radicals, since in these cases racemic compounds should have been obtained[48,64,65]. From a study of the tritium isotope effect in the reaction

$$R\dot{C}HCH_2Br + TBr \rightarrow RCHTCH_2Br + \dot{B}r \quad , \qquad (3)$$

it was concluded[66] that the presence of Br in the β-position relative to the radical centre lowers the energy of the bromoalkyl radical, possibly by the formation of a radical analogue of the cyclic bromonium ion.

3. The Migration of Fluorine

Very little is known about the possibility of the rearrangement of radicals with migration of fluorine. It has been shown[67,68] that the interaction of phenyl radicals, generated by the decomposition of nitrobenzene, with perfluorobenzene in the gas phase at 600°C leads to a mixture of products, the principal of which are pentafluorobiphenyl(XIII) and hexafluorobiphenyl (XIV):

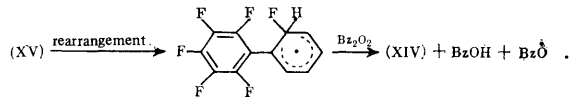


Compound (XIII) is formed via the usual aromatic substitution mechanism involving the addition of a phenyl radical to perfluorobenzene with formation of the radical-adduct (XV) containing the cyclohexadienyl group, this being followed by the elimination of fluorine. The formation of compound (XIV) has been explained[67,68] by the intramolecular substitution of hydrogen in the benzene ring by fluorine. Thus in this instance an unusual rearrangement of radical (XV) takes place with migration of fluorine to the neighbouring aromatic ring and not to the radical centre. The homolytic abstraction of fluorine from radical (XV) in this process is unusual. In the liquid phase hexafluorobiphenyl is not formed in the reaction of perfluorobenzene with benzoyl peroxide.

The reaction of hexafluorobenzene with phenyl radicals generated from other sources (phenylazotriphenylmethane[69], benzoyl peroxide[69,70]) has been investigated[69,70] at much lower temperatures. A detailed study has been made of the decomposition of benzoyl peroxide in hexafluorobenzene at 78.2°C [the kinetics of the decomposition process, the influence of the addition of benzoic or *p*-fluorobenzoic acid and the ratio of the yields of (XIII) and (XIV)]. This study established that the elimination of

fluorine from the σ-complex (XV) takes place in the reaction with an arenecarboxylic acid with formation of compound (XIII), HF, and ArCOO. This reaction of carboxylic acids is of independent interest.

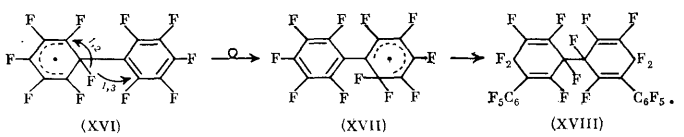
A study[70] of the kinetics of the decomposition of Bz_2O_2 in hexafluorobenzene showed that, together with the dissociation of the O–O bond (a first-order reaction), sensitised decomposition of the peroxide takes place (a reaction order of 1.5). The formation of the rearranged product (XIV) and benzoic acid is coupled with the last reaction:



It has been stated[70] that the high-boiling fraction apparently contains isomeric dodecafluorotetrahydroquaterphenyls. Thus a deeper understanding of the individual stages of this interesting process has been achieved. The mechanism of the stage involving a rearrangement with migration of fluorine to the neighbouring ring is at present least clear.

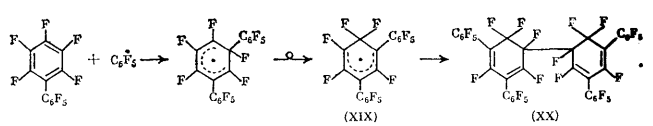
The interaction of hexafluorobenzene with nitromethane at 550°C gives a low yield of hexafluorotoluene $C_6F_5CH_2F$; this process also involves a rearrangement stage[71]. It is of interest to note that at 150°C hexafluorobenzene interacts with acetyl peroxide without a rearrangement; the main reaction products are 4,4′-dimethylperfluoro-1,1′,4,4′-tetrahydrobiphenyl and its isomers[72].

Interesting results were obtained in a study of the reaction of perfluorobenzene with perfluorobenzoyl peroxide[73] (in sealed tubes at 200°C). The pure substance (XVIII) was isolated from the mixture of products on repeated recrystallisation; according to ^1H and ^{19}F NMR, the substance is 3,3′-bis(pentafluorophenyl)perfluoro-1,1′,4,4′-tetrahydro-1,1′-biphenyl. The authors suggest that the radical-adduct (XVI), formed as a result of the addition of the pentafluorophenyl radical to perfluorobenzene, rearranges to the perfluorophenylcyclohexadienyl radical (XVII), whose dimerisation leads to compound (XVIII):



The authors[73] state that this example does not permit a choice between 1,2- and 1,3-migration of fluorine in the radical-adduct (XVI), since the rearranged radical-adduct (XVII) is formed in both cases.

The study of the reaction of pentafluorobenzoyl peroxide with decafluorobiphenyl[74] and with octafluorotoluene[75] suggested the migration of fluorine to a neighbouring carbon atom. For decafluorobiphenyl, the reaction involves the mechanism[74]



Perfluoro-3,3′,5,5′-tetraphenyl-1,1′,2,2′-tetrahydro-1,1′-biphenyl (XX), which is formed by the recombination of radicals (XIX), was isolated from the mixture of isomers.

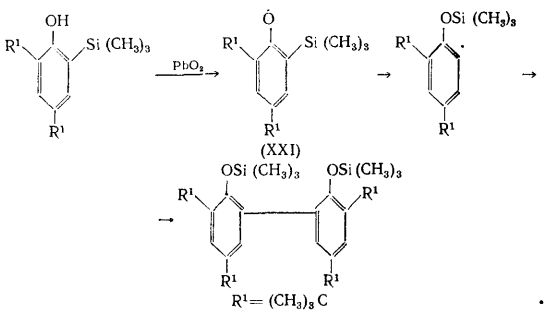
III. REARRANGEMENTS OF RADICALS WITH MIGRATION OF ORGANOELEMENTAL GROUPS

One of the new fields of study involving the rearrangement of radicals comprises the detection and investigation of rearrangements where the migrating group incorporates a heteroatom, which participates in the formation of a transition state via free *d* orbitals or π-bonds. Instances of the migration of the R_3Si, R_3Ge, RC(O)O, RCO, and RS groups are examined below.

1. The Migration of Silicon-, Germanium-, and Tin-Containing Groups

An interesting series of studies have been devoted to the investigation of the radical 1,3-migration of the R_3Si group from carbon to oxygen. This rearrangement was apparently first discovered in the thermolysis of 2,4,6-bis(trimethylsilyl)phenol,[76,77] but a detailed and systematic investigation of this type of migration of the trialkylsilyl group was undertaken by Razuvaev and coworkers[78–83], who demonstrated, in particular, the radical mechanism of this process.

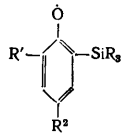
The oxidation of 4,6-di-(t-butyl)-2-trimethylsilylphenol by PbO_2 or $K_3Fe(CN)_6$ in a neutral solvent in the absence of oxygen leads to the formation of the relatively stable phenoxy-radical (XXI), whose rearrangement and subsequent recombination give a quantitative yield of the corresponding dimers[78,79]:



The formation of the phenoxy-radical was observed by EPR (1 : 2 : 1 triplet spectrum due to splitting by the *meta*-protons of the aromatic ring). It was shown that the R_3Si group migrates exclusively from the *ortho*-position[80] regardless of the number and positions of other such groups in the ring.

There is no rearrangement (1,5-, from C to O) in 2,6-di-t-butyl-4-trimethylsilylphenol. On the other hand, the degree of rearrangement involving the migration of the R_3Si group from the *ortho*-position depends significantly on the nature of the substituents in the *para*-position[81]. The yields of the rearranged dimers of 2,6-bis(trimethylsilyl)-4-R-phenols are presented in Table 4. The absence of a rearrangement for R = CH_3 (Table 4) is attributed to the lower stability of the corresponding rearranged phenoxy-radical[81]. When the capacities of the $(C_6H_5)_3Si$ and $(CH_3)_3Si$ groups for migration were compared, an unusual dependence of the rate on the nature of the substituent R′ in the phenoxy-radical (XXII) was

noted[82].



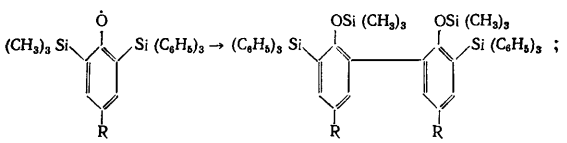
(XXII)
$R^2 = (CH_3)_3C$

Thus, when $R' = CH_3$, the trimethylsilyl group (where $R = CH_3$) migrates to the oxygen atom and the triphenylsilyl group ($R = C_6H_5$) does not migrate; for $R' = Br$, the opposite behaviour is observed.

Table 4. The 1,3-migration of the $(CH_3)_3Si$ group in 4-R-2,6-$[(CH_3)_3Si]_2C_6H_2\dot{O}$.

R	CH_3	$CH(CH_3)_2$	$C(CH_3)_3$	$Si(CH_3)_3$
Yield of rearranged dimer, %	0	77	95	81

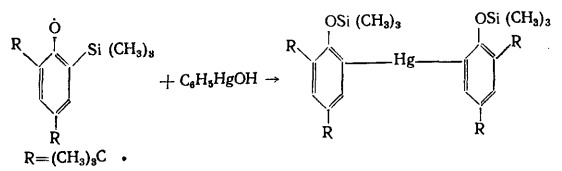
A phenoxy-radical in which there is a possibility of a competitive migration of these groups has also been investigated:



(XXIII)
$R = (CH_3)_3C$.

The dimer (XXIII) is the only reaction product, i.e. under these conditions only the $(CH_3)_3Si$ group migrates.

Only silylphenoxy-radicals capable of rearrangement yield mercurated derivatives on interaction with C_6H_5HgOH:[83]



$R = (CH_3)_3C$.

Less sterically hindered phenols react without rearrangement.

The radical mechanism of the migration of organosilicon radicals and the significant role of bulky *ortho*-substituents, ensuring the stability of the phenoxy-radical, was undoubtedly demonstrated in this series of studies; an intramolecular process mechanism appears to be extremely probable. On the other hand, the nature of the transition state and the special role of the silicon atom are still obscure, in view of the fact that the carbon analogues of silicon-containing phenoxy-radicals do not rearrange under these conditions with migration of $C(CH_3)_3$ groups[81].

The study of the decomposition of silicon-containing peracid esters made it possible to observe, together with other processes, the 1,4-migration of the trimethylsilyl group from carbon to oxygen[84]:

$$(CH_3)_3SiCH_2CH(CH_3)C(O)OOC(CH_3)_3 \xrightarrow[CCl_4]{120-130^\circ} \rightarrow (CH_3)_3SiCH_2CH(CH_3)COO\cdot \xrightarrow{\text{rearrangement}} \dot{C}H_2CH(CH_3)COOSi(CH_3)_3 \rightarrow \rightarrow CH_2{=}C(CH_3)COOSi(CH_3)_3 .$$

An analogous rearrangement was noted also for organogermanium compounds[85]:

$$(C_2H_5)_3GeCH_2CH_2C(O)OOC(CH_3)_3 \xrightarrow[CCl_4]{100-105^\circ} \rightarrow (C_2H_5)_3GeCH_2CH_2COO\cdot \xrightarrow{\text{rearrangement}} \dot{C}H_2CH_2COOGe(C_2H_5)_3 \rightarrow \rightarrow CH_2{=}CHCOOGe(C_2H_5)_3 .$$

The acrylate formed as a result of the rearrangement has been obtained in a yield of ~10%.

Such parallelism in the ability of organosilicon and organogermanium radicals to migrate has been discovered also in the rearrangement of *N,O*-bisorganosilyl(germyl)-hydroxylamines with 1,2-migration from oxygen to nitrogen[86]. When $RSi(CH_3)_2NHOSi(CH_3)_2R$ [$R = CH_3$, C_2H_5, $C(CH_3)_3$, or C_6H_5] was irradiated in the presence of t-butyl peroxide, only the signal due to the nitroxy-radical (XXV) (triplet with $a_N = 6.5$ G) was observed:

$$\underset{\text{(XXIV)}}{RSi(CH_3)_2\dot{N}OSi(CH_3)_2R} \rightarrow \underset{\text{(XXV)}}{[RSi(CH_3)_2]_2N\dot{O}} . \qquad (4)$$

The signal of the non-rearranged radical (XXIV) could not be detected even at −80°C. For the analogous germyl radical $[RGe(CH_3)_2]_2N\dot{O}$, the EPR signal consisted of a triplet with $a_N = 8.8$ G.

The migration of the $(CH_3)_3Si$ and $(CH_3)_3SiSi(CH_3)_2$ groups from silicon to the sulphur atom in the thiyl radicals (XXVI) and (XXVII) proceeds under mild conditions in the presence of radical initiators[87]:

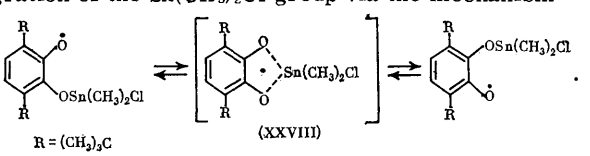
$$[(CH_3)_3Si]_2Si(CH_3)SH \xrightarrow{Bz_2O_2} \underset{\text{(XXVI)}}{[(CH_3)_3Si]_2Si(CH_3)\dot{S}} \rightarrow$$

$$\rightarrow (CH_3)_3Si\dot{S}i(CH_3)SSi(CH_3)_3 \rightarrow (CH_3)_3SiSiH(CH_3)SSi(CH_3)_3 . \qquad (5)$$

$$\underset{\text{(XXVII)}}{(CH_3)_3SiSi(CH_3)_2Si(CH_3)_2\dot{S}} \rightarrow \dot{S}i(CH_3)_2SSi(CH_3)_2Si(CH_3)_3 . \qquad (6)$$

Both reactions are inhibited by hydroquinone. It has been suggested that the transfer of the radicals $(CH_3)_3Si\dot{S}i(CH_3)_2$ proceeds via a three-membered transition state.

In stable phenoxy-radicals there is reversible 1,4-migration of the $Sn(CH_3)_2Cl$ group via the mechanism[88]



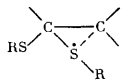
$R = (CH_3)_3C$ (XXVIII)

The rearrangement was inferred from the EPR spectra.

2. The Migration of Oxygen- and Sulphur-Containing Groups

When the behaviour of O- and S-containing radicals is compared in rearrangements, one often has to emphasise differences rather than similarities in the capacity of O- and S-containing groups for migration in the radical. The

differences are apparently due to the ability of the sulphur atom to interact with the neighbouring carbon atom carrying the unpaired electron (possibly with participation of the *d* orbitals of sulphur). Hence arose the hypothesis of the three-membered transition state (XXIX) in the 1,2-migration of the RS group:



(XXIX)

1,2-Migration is in fact characteristic of radicals containing two geminal alkylthio- or arylthio-groups in the β-positions relative to the radical centre.

On the other hand, a rearrangement of radicals with migration of alkoxy- or aryloxy-groups has not been described. The 1,2-migration of the acyloxy-group has been most thoroughly investigated for oxygen-containing radicals; it is suggested that the rearrangement proceeds via a five-membered transition state with unpairing of the electrons in the π-bond of the C=O group.

On the other hand, the preferential migration to the vicinal carbon atom is a common characteristic of these rearrangements.

(a) Migration of Oxygen-Containing Groups

Migration of the acyloxy-group. The Unusual behaviour of the acyloxy-group in the radical rearrangement consists in the fact that the oxygen atom of the carbonyl group can participate in the formation of an intermediate transition state.

The rearrangement of radicals with 1,2-transfer of the AcO group was first demonstrated in 1967 for the addition of radical species to α,α-dimethylallyl acetate[89,90]:

$$(CH_3)_2C(OAc)CH{=}CH_2 + \dot{R} \rightarrow \underset{(XXX)}{} \rightarrow (CH_3)_2C(OAc)\dot{C}HCH_2R \begin{cases} \longrightarrow (CH_3)_2C(OAc)CH_2CH_2R \\ \longrightarrow (CH_3)_2\dot{C}CH(OAc)CH_2R \xrightarrow{RH} \underset{(XXXI)}{(CH_3)_2CHCH(OAc)CH_2R} \end{cases} \quad (7)$$

The degree of rearrangement then depends significantly on the nature of the addend RH and the structure of the non-rearranged radical. A rearrangement involving migration to a more remote radical centre does not occur, nor does it take place when one of the methyl groups has been replaced by hydrogen. If a malonate ester [R = $CH(CO_2.C_2H_5)_2$] is used as an addend, then the yield of the rearranged acetate (XXXI) is 95%, while with R = $CH(CN).CO_2C_2H_5$ it is only 25–30%, which the authors attribute to the different efficiencies of these compounds as hydrogen donors. For the relatively ineffective cyclohexane (R = C_6H_{11}), it was possible to detect the acetate (XXXI) (yield 4%) even when one of the CH_3 groups in the initial acetate (XXX) has been replaced by hydrogen[90].

It is of interest to note that the analogous reaction with the thioloacetate $(CH_3)_2C(SAc)CH = CH_2$ takes place without a rearrangement even for cyclohexane[90].

The migration of the acetoxy-group was observed by studying the radical decarbonylation of 3-acetoxy-3-methylbutanal in the presence of benzoyl peroxide[91]:

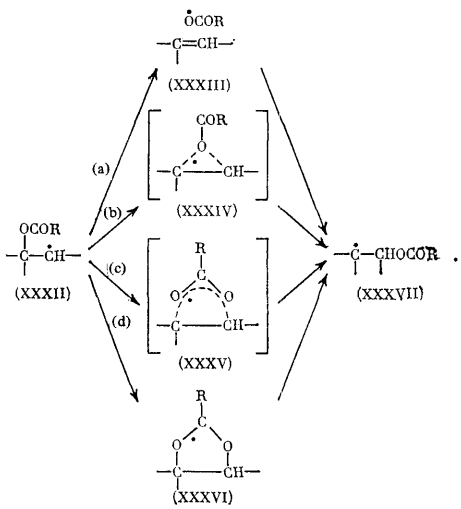
$$(CH_3)_2C(OAc)\dot{C}H_2 \rightarrow (CH_3)_2\dot{C}CH_2OAc \quad .$$

Further studies of rearrangements of this type were devoted mainly to the investigation of the mechanism of the migration of the AcO group[92,93]. In principle, several mechanisms can be put forward for the 1,2-transfer of the acyloxy-group[92].

One of these (*a*) involves elimination-addition and two others (*b* and *c*), involve the transfer of the AcO group via a three-membered (XXXIV) or five-membered (XXXV) unstable transition state; the last mechanism (*d*) involves 1,2-transfer with formation of the 1,3-dioxolanyl radical (XXXVI) as an intermediate.

The elimination–addition mechanism has been rejected[94] because it had been established previously[95] that the free acetoxy-radical ȮC(O)R rapidly decomposes to CO_2 and $\dot{C}H_3$ even in the presence of effective radical trapping agents. In addition it has been shown[91] that a decrease of the concentration of the initial aldehyde (in the decarbonylation reaction) promotes a relative increase in the yield of the rearranged product, which is also inconsistent with an elimination–addition mechanism.

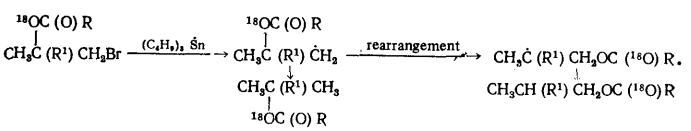
The spectrum of the dioxolanyl radical (XXXVI), known to have been obtained (Scheme 8) was detected by EPR;[92] it did not contain signals which could be attributed to the rearranged radical (XXXVII).



(8)

On the other hand, by studying the abstraction of hydrogen by OH radicals from $(CH_3)_3COAc$, Beckwith and Tivdal[96] obtained a set of signals characterising the radicals $\dot{C}H_2C(CH_3)_2OAc$ and $(CH_3)_2\dot{C}CH_2OAc$, but did not observe any signs of the formation of the cyclic radical (XXXVI).

The choice between pathways *b* and *c* was made in favour of *c* in the study of radicals labelled with ^{18}O. It was shown[92] that the rearrangement involves the inversion of the label in the molecule of the labelled specimen:



An analogous result was obtained with a specimen labelled at the oxygen atom of the carbonyl group. Naturally, in the three-membered transition state (XXXIV) (Scheme 8) there should be no inversion.

The only example of the 1,3-migration of the acetoxy-group has been found[97] in the oxidation of γ-acetoxy-carboxylic acid (XXXVII):

$$\begin{array}{l} \mathrm{AcOCRR^1CH_2CHR^2COOH} \xrightarrow[60^\circ]{S_2O_8^{2-}} \\ \quad (\mathrm{XXXVIII}) \\ \rightarrow \mathrm{AcOCRR^1CH_2\dot{C}HR^2} \left\{ \begin{array}{l} \longrightarrow \mathrm{AcOCRR^1CH_2CH_2R^2} \\ \longrightarrow \mathrm{\dot{C}RR^1CH_2CHR^2OAc} \rightarrow \mathrm{CHRR^1CH_2CHR^2OAc} \end{array} \right. \\ \quad (\mathrm{XL}) \qquad\qquad\qquad\qquad (\mathrm{XLI}) \qquad\quad (\mathrm{XXXIX}) \end{array} \quad (9)$$

The yield of the isomerised ester (XXXIX) ranges from 3 to 10%, depending on the nature of the substituent: 3% for $R = R^1 = H$, $R^2 = CH_3$; 6% for $R = R^2 = H$, $R^1 = CH_3$; 10% for $R = R^1 = CH_3$, $R^2 = H$; i.e. the greater the difference between the stabilities of the initial radical (XL) and the rearranged radical (XLI), the greater the degree of rearrangement.

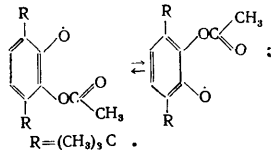
The migration of the acyl group. In the decomposition of the peracid ester (XLII) [Scheme (10)] both the non-rearranged ketone (XLIII) and the ketone (XLIV), corresponding to the radical (XLV) formed as a result of the 1,2-migration of the acyl group[98] in the radical (XLVI), were identified among the reaction products:

$$\begin{array}{l} \mathrm{CH_3C(O)CR^1R^2CH_2C(O)OOC(CH_3)_3} \xrightarrow{130^\circ} \\ \quad (\mathrm{XLII}) \\ \rightarrow \mathrm{CH_3C(O)CR^1R^2\dot{C}H_2} \left\{ \begin{array}{l} \longrightarrow \mathrm{CH_3C(O)CR^1R^2CH_3} \\ \qquad (\mathrm{XLIII}) \\ \longrightarrow \mathrm{\dot{C}R^1R^2CH_2C(O)CH_3} \xrightarrow{\mathrm{DH}} \mathrm{CHR^1R^2CH_2C(O)CH_3} \end{array} \right. \\ \quad (\mathrm{XLVI}) \qquad\qquad\qquad (\mathrm{XLV}) \qquad\qquad (\mathrm{XLIV}) \end{array} \quad (10)$$

For $R^1 = R^2 = H$, there is no rearrangement; for $R^1 = R^2 = CH_3$, the ratio of the yields (XLIV)/(XLIII) is approximately unity; for $R^1 = CH_3$ and $R^2 = C_6H_5$, the ratio (XLIV)/(XLIII) $\simeq$ 1.3. In the generation of the radicals (XLVI) in the $CH_3C(O)C(CH_3)_2CH_2X + R_3SnH + R^1\dot{O}$ system this ratio is 0.4 for X = Br and $R = C_6H_5$, 0.15 for X = Cl and $R = C_6H_5$, and 0.18 for X = Cl and $R = C_4H_9$ respectively.

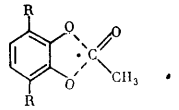
The most probable mechanism of the rearrangement involves the formation of the unstable cyclopropoxy-radical in the transition state. However, it has been suggested[99] that the isomerisation can proceed, at least partially, via an elimination–addition mechanism. In the case of the radical $CH_3C(O)CH_2\dot{C}H_2$ the authors were able to detect the formation of $CH_3\dot{C}O$ and ethylene. The radical $CH_3\dot{C}O$ reacted with cyanopyridine to give a substitution product. The radicals (XLVI, $R^1 = H$, $R^2 = CH_3$) and (XLV, $R^1 = H$, $R^2 = CH_3$) were also detected as substitution products. Thus the occurrence of the reaction via two mechanisms simultaneously can be postulated.

For stable radicals, the reversible 1,4-migration of the acetyl group was observed by EPR:[100]



$R = (CH_3)_3C$.

It was suggested[100] that the migration proceeds via the cyclic transition state



(b) Migration of Sulphur-Containing Groups

The rearrangement of radicals with 1,2-migration of the thiyl group was discovered for the first time in 1963 in relation to the isomerisation of acetone diphenyl mercaptole under the influence of t-butyl peroxide[101]:

$$\begin{array}{l} \mathrm{CH_3C(SC_6H_5)_2CH_3} \xrightarrow[140^\circ]{(\mathrm{CH_3})_3\mathrm{C\dot{O}}} \mathrm{CH_3C(SC_6H_5)_2\dot{C}H_2} \longrightarrow \left[\begin{array}{c} \mathrm{CH_3C(SC_6H_5)CH_2} \\ \mathrm{SC_6H_5} \end{array} \right] \longrightarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (\mathrm{ILVII}) \\ \longrightarrow \mathrm{CH_3\dot{C}(SC_6H_5)CH_2SC_6H_5} \xrightarrow{\mathrm{H^\bullet}} \mathrm{CH_3CH(SC_6H_5)CH_2SC_6H_5} \end{array} , \quad (11)$$

A radical chain mechanism of the process was demonstrated and evidence was adduced in support of an intramolecular mechanism of the transfer of the RS radical[101]. On heating in the absence of an initiator, acetone mercaptoles do not isomerise. It has been suggested[4] that the migration of the RS group proceeds via a cyclic three-membered transition state (XLVII) as a result of the ability of sulphur to delocalise the unpaired electron at the neighbouring carbon atom.

Soon examples of the thermal isomerisation of mercaptoles in the absence of radical initiators were described[102,103]. Thus, on heating without the peroxide, acetophenone diphenyl mercaptole gives rise to 1,2-diphenylthioethylbenzene (~10%), but the main products are α-phenylthiostyrene and diphenyl disulphide:

$$\mathrm{C_6H_5C(SC_6H_5)_2CH_3} \xrightarrow{135^\circ} \mathrm{C_6H_5C(SC_6H_5)=CH_2} + \mathrm{C_6H_5CH(SC_6H_5)CH_2SC_6H_5} + (\mathrm{C_6H_5S})_2 .$$

A similar behaviour was observed also for pinacolone diphenyl mercaptole; the formation of appreciable amounts of an unsaturated compound, diphenyl disulphide, and traces of thiophenol justified the hypothesis[103] that thermal rearrangements proceed via an elimination–addition mechanism. Depending on the reaction conditions and the structure of the initial mercaptoles, both mechanisms can apparently operate. The pathway leading to the initiation of thermal rearrangement and the problem of the possible chain transfer by the extremely stable benzyl radicals $C_6H_5\dot{C}(SC_6H_5)CH_2SC_6H_5$, formed as a result of the rearrangement, remains obscure.

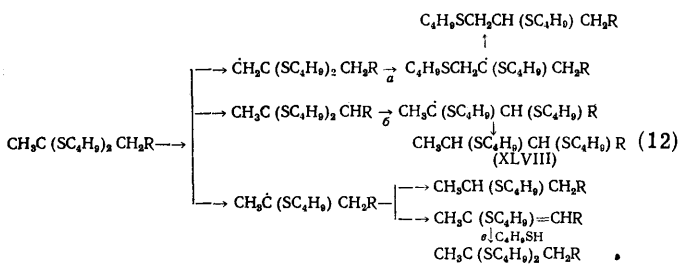
The use of the EPR method with spin trapping agents in the study of the rearrangement of mercaptoles capable of thermal isomerisation (in the absence of an initiator) confirmed the radical nature of the process and led to the determination of the nature of the initiating radicals[104]. Together with signals due to the known radicals, the spectrum obtained on irradiation of acetophenone diphenyl mercaptole in the presence of 2-methyl-2-nitrosopropane (as the spin trapping agent), showed the presence of a triplet (a = 25.7 G), which was assigned to the spin-adduct of the oxy-radical $C_6H_5C(\dot{O})(SC_6H_5)CH_3$, formed as a result of the oxidation of the $C_6H_5\dot{C}(SC_6H_5)CH_3$ radicals formed initially in the thermolysis. The oxy-radicals abstract hydrogen from the methyl group of the mercaptole regenerating the initial radical $C_6H_5C(SC_6H_5)_2\dot{C}H_2$. It has been shown[102] that acetophenone diphenyl mercaptole is capable

of initiating the rearrangement of acetone diphenyl mercaptole in the absence of a peroxide. Presumably the rearrangement is in this case initiated by the oxy-radicals formed in the thermolysis of the acetophenone mercaptole.

The mechanism of the 1,2-migration of thiyl radicals as well as the influence of various factors on the course of the rearrangement of mercaptoles became the subject of further discussion and investigations carried out in recent years in relation to the mercaptoles of higher symmetrical and asymmetric ketones [105,106], cyclic ketones [107], and ketones containing functional groups [108]. In a few studies it has been suggested [94,109] that the radical migration of the RS groups takes place in all cases via an elimination–addition mechanism. The authors based their conclusion on the absence of a rearrangement, which they demonstrated in the reaction of α,α-dimethylallyl phenyl sulphide with free radicals, where the intermediate radical fragments with elimination of the RS group:

$$(CH_3)_2C(SC_6H_5)-CH=CH_2 + R^{\cdot} \rightarrow (CH_3)_2\dot{C}(SC_6H_5)CHCH_2R \rightarrow (CH_3)_2C=CHCH_2R$$

However, subsequent studies showed that such analogy between monosulphides and *gem*-bis-sulphides is insufficiently well-founded. The intramolecular mechanism of the 1,2-migration of the thiyl group was clearly demonstrated in a study of the isomerisation of the dibutyl mercaptole of acetoacetic ester (R = $CO_2C_2H_5$) in the presence of t-butyl peroxide [Scheme (12)], where the authors obtained for the first time a complete material balance and were able to trace the fate of all the radicals formed [108]:



(12)

Here there is a possibility of two competitive pathways involving the migration of RS groups (*a* and *b*); it was shown that the migration proceeds preferentially to the carbon of the methyl group (*a*). Presumably this pathway in the transition of the RS group is related to the more favourable conditions for the formation of a transition state of type (XLVII) with participation of the terminal CH_2 group. Special experiments have shown that the addition of butanethiol to ethyl 3-butylthiocrotonate [Scheme (12), pathway *c*] results in a low yield of only the initial ketone mercaptal and not the rearranged product (XLVIII). Thus, by virtue of the mode of addition, the elimination–addition mechanism cannot account for the formation of the products of the rearrangement in this instance.

Acetone mercaptoles isomerise also on irradiation with ultraviolet light [110]. When the reaction was carried out at different temperatures (70° and 140°C), it was found that an increase of temperature leads to a sharp increase of the yield of the rearrangement product (almost by a factor of 20 for acetone diphenyl mercaptole). Instead of the expected formation of $CH_3CH(SC_4H_9)CH_2SC_6H_5$ (via an elimination–addition mechanism), in the isomerisation of $CH_3C(SC_6H_5)_2CH_3$ in the presence of 20 mole % $CH_3C(SC_4H_9) = CH_2$ the process was found to be inhibited and the unsaturated sulphide was fully consumed in side reactions. The study of the rearrangement of mixed ketone mercaptoles (acetone butyl phenyl and butyl *p*-tolyl mercaptole) initiated by t-butyl peroxide showed [111] that, together with symmetrisation, there is a rearrangement of both symmetrical and mixed mercaptoles; in the latter case the rearrangement proceeds mainly as a result of the migration of the arylthio-group.

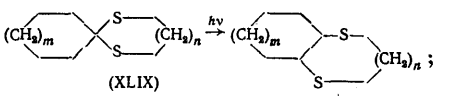
In the isomerisation of 2-butanone and 2-hexanone dibutyl mercaptoles under the influence of t-butyl peroxide at 140°C the butylthio-group migrates in two directions—to the neighbouring methyl and methylene carbon atoms [105]. In both examples [Scheme (12), R = CH_3 or C_3H_7] the 1,2-bis-sulphides $C_4H_9SCH_2CH(SC_4H_9)CH_2R$ are formed preferentially, i.e. the migration proceeds to a large extent towards the carbon of the methyl group.

The study of the isomerisation of butanone diphenyl mercaptole by EPR in the presence of 2-methyl-2-nitrosopropane as the spin trapping agent made it possible to detect the spin-adducts of the initial radical $CH_3C(SC_6H_5)_2.\dot{C}HCH_3$ and the rearranged radical $CH_3\dot{C}(SC_6H_5)CHCH_3$. [112]
SC_6H_5

It is noteworthy that the migration of the RS group to a radical centre more remote than a neighbouring centre has not so far been observed.

For the mercaptoles of cyclic ketones, the yield of the rearrangement products is influenced significantly by the ring size [107]. Thus the yield of 1,2-bis(butylthio)cycloalkane is twice as high for a six-membered ring as for a five-membered ring. This rearrangement proceeds solely on heating with t-butyl peroxide. On the other hand, thermolysis yields mainly 1-butylthiocyclohex-1-ene and butanethiol. The absence of rearrangement products on thermolysis and ultraviolet irradiation shows that the reverse addition of butanethiol to the unsaturated compound does not occur under the given conditions, which rules out an elimination–addition mechanism.

The study of the photochemical isomerisation of cyclic ketone mercaptoles (XLIX, *a* = *d*) showed that the possibility of isomerisation depends significantly on the ring size [113]:



(XLIX)

(a) $m = 1$, $n = 0$; (b) $m = n = 0$, (c) $m = n = 1$, (d) $m = 0$, $n = 1$. (13)

In the reaction involving ethylene mercaptoles (XLIX, *a* and *b*) the main process is the splitting off of ethylene sulphide with formation of cyclic thiones. The propylene mercaptoles (XLIX, *c* and *d*) undergo a kind of isomerisation under these conditions with transfer of one of the geminal sulphur atoms to a neighbouring carbon atom [Scheme (13)]. It has been suggested that the reaction proceeds in this case via an elimination–addition mechanism. However, the usual intermolecular transfer is naturally ruled out.

The study of the rearrangement of radicals has come to be a permanent and very important topic in the modern chemistry of free radicals. The possibility of rearrangements must be reckoned with in studies on new reactions and also in industrial radical processes such as chlorination, oxidation, reduction, polymerisation, telomerisation, and many other processes.

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