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REARRANGEMENT OF RADICALS IN SOLUTION

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INTRODUCTION

The number of known organic reactions which are accompanied by rearrangement is continuously growing. Such reactions constitute, in a sense, the philosopher's stone for theoretical organic chemistry.

Hückel[1] believes that rearrangements lie outside the scope of structural theory, which cannot explain them or predict their course. Nevertheless, this theory enabled Baker[2] to classify rearrangements (in 1933) on the basis of a combined structural and chemical principle. He distinguishes "diad", "triad", "tetrad", etc. rearrangements, those involving rings, and rings and chains, as well as carbon–carbon, carbon–oxygen, etc. rearrangements, depending on the type of molecule, the nature of the migrating groups, the nature of the rearrangement centres, and the number of atoms in the chain linking two such centres. All the rearrangements discussed by Baker are heterolytic since homolytic rearrangements in solution were not known at that time.

It has been stated that radical rearrangement in solution is impossible or limited in extent. Thus, Dewar[3] suggested that isomerisation of aliphatic radicals did not occur because stable π complexes are not formed. In fact, the absence of rearrangement in the neopentyl residue when sodium reacts with neopentyl chloride has been quoted as proof of the radical mechanism of the Wurtz reaction[4].

Even in recent times some reviews and monographs specifically devoted to the chemistry of radicals either completely neglect the problems of radical rearrangement or regard such rearrangement as a relatively rare phenomenon. Thus, in a symposium dedicated to the memory of M.S. Kharasch, Kutschke and Steacie failed to mention the possibility of rearrangement of free radicals in their list of free-radical reactions in the gas phase. Walling[6] writes: "It seems a safe generalisation that radical rearrangements are less common than those of the corresponding carbonium ions". However, the experimental data accumulated to date show that radical rearrangement occurs widely. Semenov believes rearrangement to be a general property of radicals[7].

Investigations of free radicals in liquid and gas phases have been largely carried out in isolation[5]. Study of free radicals in the gas phase has been mainly confined to the simplest short-lived radicals (methyl, ethyl), and concerned almost exclusively with kinetic problems. Studies in the liquid phase concerned a large number of complex

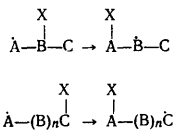
radicals, including stable radicals, and dealt with their structure, their chemical reactions, and new methods for their synthesis. At present, the two fields of study are converging, but the differences between them, both as regards the conditions employed and the approach of the investigators to the problem, still remains very considerable.

This review concerns radical rearrangements in the liquid phase. The general literature on this problem is extremely meagre. We can quote only one small review, in Japanese [8], and a short description of certain problems of radical rearrangement in solution given in the monographs [6,7] quoted above. We shall also consider the structural-chemical principles for classifying rearrangements, designating them as 1,2-, 1,3-, ... 1,5-migration of an atom or group [8]. The numbers denote the mutual disposition of the rearrangement centres.

Among the various factors governing the occurrence of radical rearrangements in solution, the main role appears to be played by the possibility of rearrangement of a less stable radical to one which is more stable under the given conditions [for example, rearrangement of the primary radical $(C_6H_5)_3CCH_2$ to the more stable tertiary radical $(C_6H_5)_2CCH_2C_6H_5$]. Recently, however, examples of rearrangements have been found in which the stabilities of the initial and final radicals do not differ very much (for example, the rearrangement $C_6H_5CH_2^{14}CH_2^{\cdot} \rightarrow \dot{C}H_2^{14}CH_2C_6H_5$), but in these cases the yields of the rearrangement products are small. An important factor in the rearrangement appears to be the ability of the substance the radical stabilises in the reaction to effect chain transfer. The use of less effective chain-transfer agents lengthens the life of the radical and favours rearrangement.

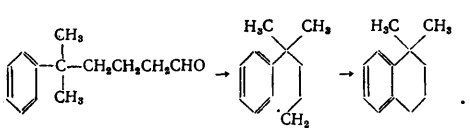
Intramolecular radical rearrangements may be regarded as reactions of the radical with itself. Radical rearrangements may then be divided into three principal groups, according to three types of reactions in which radicals participate.

1. Substitution reactions. These embrace a large number of true rearrangements with migration of various atoms or groups, which may be schematically represented as follows:



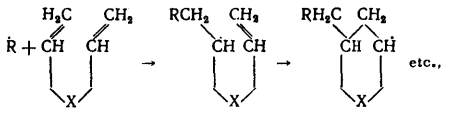
where X is the migrating atom or group.

2. Addition reactions. In our case these will be ring-closure reactions, for example, the formation of tetralin in the peroxide-catalysed decarbonylation of phenyldimethylpentanal [9]:



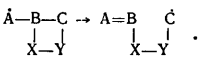
Rearrangements of this type have also been observed in the polymerisation of diene compounds with non-conjugated double bonds, particularly in 1,5- and 1,6-positions (when the formation of 5- and 6-membered rings is possible).

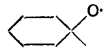
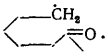
These reactions are important in the synthesis of macromolecular compounds with heterocyclic residues in the chain, for example:



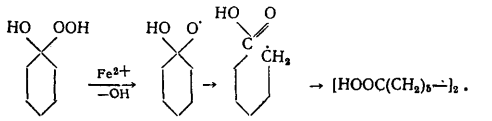
where X = C, N, O, P, Si, Sn. A review of these reactions has been published recently [10].

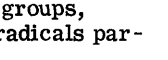
3. Decomposition reactions. This group includes rearrangements with ring rupture as well as some of allylic type. Bond rupture at the β-atom with the formation of a new α,β double bond is characteristic of such rearrangements:



These reactions often take place in radicals with a weakened β,γ-bond; for example, alkoxy radicals with the structure  rearranged to . [11]

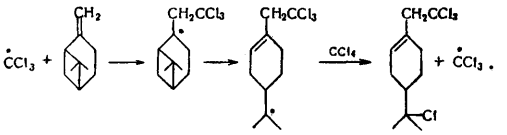
Decomposition of α-hydroxycyclohexyl hydroperoxide in the presence of Fe^{2+} salts results in the formation of α,ω-decanedicarboxylic acid [12]:



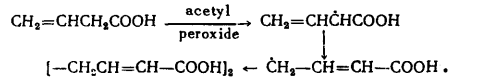
The 5-membered ring in the corresponding hydroxy--radicals opens in the same way [11]; for example, the oxychloride  rearranges to the ω-chloro-derivative

$$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH_2CH_2Cl.$$

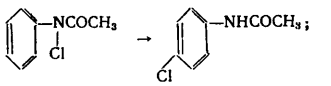
Rearrangements with rupture of a strained ring, for example a 4-membered one, take place even in hydrocarbon radicals. Thus the free-radical addition of carbon tetrachloride and other polyhalogenomethanes to pinene takes place as follows [13]:



Oxidative dimerisation of vinylacetic acid [14] may be quoted as an example of an allylic rearrangement:



It is evident from the above that intermolecular free--radical rearrangements, where there is no true radical rearrangement, are not included here. For example: the rearrangement of chloroacetanilides [15]:



rearrangement of alkoxystyrenes[16], for which the following mechanism has been proposed[17]:

$$CH_2=C(OR)C_6H_5 + \dot{R} \rightarrow RCH_2\dot{C}(OR)C_6H_5 \rightarrow RCH_2C\begin{matrix}O\\ \diagdown\\ C_6H_5\end{matrix} + \dot{R};$$

certain allylic rearrangements:

$$CH_2=CH-CHBrR + Br \rightarrow BrCH_2CH-CHBrR \rightarrow CH_2Br-CH=CHR + Br;$$

etc. Apparently, the free radicals, if they are formed in these reactions, do not undergo rearrangement.

Reactions of types 2 and 3 have been little studied, and this review will deal with rearrangements of type 1, which are accompanied by the migration of hydrogen, chlorine, and aryl and alkyl groups.

I. RADICAL REARRANGEMENTS WITH HYDROGEN MIGRATION

Radical rearrangements with hydrogen transfer are among the most important to be considered. The principal laws governing radical-substitution reactions (for example, radical chlorination), the characteristic features of the ability of individual groups in the molecule to undergo homolytic substitution, and the comparative radical stability series have all been deduced on the assumption that the radical centre, at least in saturated molecules, is not displaced along the molecular chain. However, in a number of studies it has been asserted or assumed that radical rearrangement takes place with migration of a hydrogen atom from an adjacent (1,2-migration) or more distant carbon atom to one bearing an unpaired electron.

A. 1,2-Migration of Hydrogen

Contradictory views have been expressed on the possibility of free-radical rearrangement with 1,2-hydrogen migration. In 1936 the rearrangement of the isopropyl to the n-propyl radical ($CH_3\dot{C}HCH_3 \rightarrow CH_3CH_2\dot{C}H_2$) was described[18]. These data, however, were questioned by Kharasch and his coworkers[19,20], since according to their results alkyl radicals do not isomerise in solution.

1,2-Migration of hydrogen in radicals of the type $RCH_2\dot{C}HCOOH$ was suggested to resolve the contradiction which arose when the action of a chlorine atom[21] and a methyl radical[22] on isobutyric acid was compared. In the first case the substitution was in the β-position (formation of β-chloroisobutyric acid), in the second in the α-position (formation of tetramethylsuccinic acid).

The photochemical reaction between sulphonyl chloride and propionic acid[21] also results in a β-substituted product ($HOSO_2CH_2CH_2COOH$). Kharasch and Brown[21] explained the formation of β-substituted products by rearrangement with 1,2-migration of hydrogen, for example as follows:

$$(CH_3)_2CHCOOH + Cl \rightarrow (CH_3)_2\dot{C}COOH + HCl$$

$$(CH_3)_2\dot{C}COOH \rightarrow \begin{matrix}\dot{C}H_2\\ CH_3\end{matrix}\!\!>\!CH-COOH \xrightarrow{Cl_2} \begin{matrix}ClCH_2\\ CH_3\end{matrix}\!\!>\!CH-COOH + Cl.$$

Later, Brown himself admitted[22] the weakness of this hypothesis and pointed out that the polar character of the attacking atom or radical plays an important role in determining the site of the attack. Consequently, the initial assumption that the chlorine atom and methyl radical must attack at the same site in the molecule is unjustified.

1,2-Rearrangement with hydrogen transfer was postulated to explain the anomalies observed in certain reactions of organomagnesium compounds in the presence of $CoCl_2$. Thus when n-butylmagnesium bromide reacts with γ-chloropropylbenzene in the presence of cobalt chloride, *trans*-β-methylstyrene (and not allylbenzene) and *trans*-2-butene (and not 1-butene) are obtained[23]. The formation of these products was explained by 1,2-migration of hydrogen in the radicals,

$$C_6H_5CH_2CH_2\dot{C}H_2 \rightarrow C_6H_5CH_2\dot{C}HCH_3,$$

$$CH_3CH_2CH_2\dot{C}H_2 \rightarrow CH_3CH_2\dot{C}HCH_3,$$

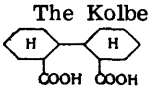
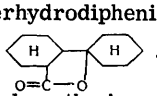
followed by their disproportionation. Slaugh[24], however, believes that the formation of *trans*-β-methylstyrene and *trans*-2-butene is more plausibly explained by the migration of the double bond (rather than 1,2-transfer of hydrogen).

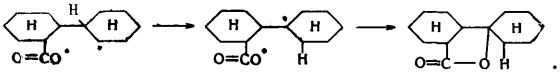
Recently[25] the behaviour of the primary butyl radical under various conditions has been studied in detail. In particular, the reaction between butyl bromide and magnesium in the presence of cobalt bromide was found to yield approximately equal quantities of 1-butene and 2-butene. Since the isomerisation of 1-butene to 2-butene requires more severe conditions, the author explained the formation of 2-butene by the migration of hydrogen in the radical (without specifying from which carbon atom the hydrogen migrates). It should be noted that in the case of both the γ-phenylpropyl and n-butyl radicals the formation of unsaturated compounds with a non-terminal double bond may be explained by 1,3-migration of hydrogen with subsequent disproportionation of the isomerised radicals (see following section).

The decarbonylation of β-phenyl-β-(*p*-methoxyphenyl)-propionaldehyde yielded α-phenyl-α-(*p*-methoxyphenyl)-ethane[26]. The authors suggested that this reaction may involve the 1,2-migration of hydrogen in the radical:

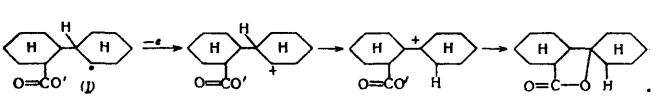
$$p\text{-}CH_3OC_6H_4\!\!>\!\!\begin{matrix}C_6H_5\\ \end{matrix}\!\!CH\dot{C}H_2 \rightarrow p\text{-}CH_3OC_6H_4\!\!>\!\!\begin{matrix}C_6H_5\\ \end{matrix}\!\!\dot{C}-CH_3.$$

Later this hypothesis was checked by Curtin and Cauer[27], who on decarbonylation of β-deutero-β-phenyl-β-(*p*-methoxyphenyl)propionaldehyde obtained only the compound $p\text{-}CH_3OC_6H_4CD(C_6H_5)CH_3$, which indicates the absence of migration of either the aryl group or deuterium.

The Kolbe electrolysis of perhydrodiphenic acids  yields the lactone .[28] The authors[28] suggested that this involves the isomerisation of the radical with 1,2-migration of hydrogen:



It is also possible that the 5-membered lactone may arise due to ionic migration of hydrogen in the carbonium ion formed by the oxidation of the intermediate radical (I):



Thus, although 1,2-migration of hydrogen was postulated in the studies quoted above, its occurrence was not proved. Special investigations were undertaken to settle this question. The most definite results, showing the absence of 1,2-migration of hydrogen in radicals both in the gas and in the liquid phase, were obtained in work with tracer atoms (deuterium, tritium).

Brown and Russell[30] chlorinated photochemically 2-deuteroisobutane at -15°. They obtained both t-butyl chloride and isobutyl chloride and, correspondingly, both deuterium chloride and hydrogen chloride, which means that the reaction proceeds *via* two pathways:

$$(CH_3)_2CDCH_3 + Cl_2 \xrightarrow[-15°]{h\nu} \begin{cases} HCl + (CH_3)_2CDC\dot{H}_2 \\ DCl + (CH_3)_2\dot{C}CH_3. \end{cases}$$

The DCl : HCl and t-butyl chloride : isobutyl chloride molar ratios were found to be the same in two experiments, confirming that isomerisation with hydrogen migration, $(CH_3)_2CDC\dot{H}_2 \rightarrow (CH_3)_2\dot{C}CH_2D$ or $(CH_3)_3\dot{C} \rightarrow (CH_3)_2CHC\dot{H}_2$, does not take place, and that the exchange reaction

$$(CH_3)_2CDC\dot{H}_2 + (CH_3)_2CDCH_3 \rightarrow (CH_3)_2CDCH_2D + (CH_3)_2\dot{C}$$

is also absent.

Slaugh[24] studied the behaviour of the 2-phenylethyl radical in the presence of tritium-labelled toluene-ω-thiol. If the primary radical (II) rearranges to the secondary radical (III), the ethylbenzene formed should contain tritium at the "benzyl" atom in the hydrocarbon:

$$\begin{array}{l} C_6H_5CH_2C\dot{H}_2 \xrightarrow{C_6H_5CH_2ST} C_6H_5CH_2CH_2T \\ \text{(II)} \quad \downarrow \\ C_6H_5\dot{C}HCH_3 \xrightarrow{C_6H_5CH_2ST} C_6H_5CHTCH_3. \\ \text{(III)} \end{array}$$

The reaction product was treated with *N*-bromosuccinimide:

$$C_6H_5CHTCH_3 + C_4H_4O_2NBr \rightarrow C_6H_5CHBrCH_3 + C_4H_4O_2NT$$

The activity of the succinimide corresponded to 1.8% rearrangement, but the author believes that it is due to the exchange reaction between the succinimide and the tritium-labelled toluene-ω-thiol.

Kornblum and coworkers[31] studied the possibility of 1,2-migration of hydrogen from carbon to oxygen in the system $H-\overset{|}{C}-\dot{O}$. They investigated the liquid-phase pyrolysis (at 100°) of optically active 2-octyl nitrite and obtained optically active 2-octanol. They believe that the reaction proceeds in a manner analogous to the scheme proposed by Rice[32] for the gas-phase pyrolysis of alkyl nitrite:

$$C_6H_{13}CH(CH_3)ONO \rightarrow C_6H_{13}CH(CH_3)\dot{O} + NO$$
$$C_6H_{13}CH(CH_3)\dot{O} + C_6H_{13}CH(CH_3)ONO \rightarrow C_6H_{13}CH(CH_3)OH + C_6H_{13}\dot{C}(CH_3)ONO$$
$$C_6H_{13}\dot{C}(CH_3)ONO \rightarrow C_6H_{13}C\overset{O}{\diagdown\!\!\diagup}CH_3 + NO.$$

The formation of optically active 2-octanol demonstrates the absence of rearrangement of radical (IV) to radical (V), since this would have resulted in racemisation†:

$$\begin{array}{ll} C_6H_{13}CH\dot{O} & C_6H_{13}\dot{C}-OH \\ \quad | & \quad | \\ \quad CH_3 & \quad CH_3 \\ \text{(IV)} & \text{(V)} \end{array}$$

In another investigation[33] a study was made of the thermal decomposition of an optically active peroxide in the presence of thiophenol at 125°:

$$C_6H_5CH(CH_3)OOC(CH_3)_3 + C_6H_5SH \xrightarrow{125°} C_6H_5CH(CH_3)OH.$$

Optically active phenylmethylmethanol was obtained, which again points to the absence of 1,2-migration of hydrogen in the radical

$$\begin{matrix} H_5C_6 \\ H_3C \end{matrix}\!\!\diagup\!\!\diagdown CH\dot{O}.$$

Proof of the absence of 1,2-migration of hydrogen in radicals may also be derived from many investigations undertaken for the solution of other problems. For example, the homolytic addition of carbon tetrachloride or bromotrichloromethane to olefines of the type $R-CH_2CH=CH_2$ takes place as follows:

$$RCH_2CH=CH_2 + \dot{C}Cl_3 \rightarrow RCH_2\dot{C}HCH_2CCl_3,$$

and even in the case where R = phenyl[34]; the product $RCHXCH_2CH_2CCl_3$ (X = halogen) is not formed, showing that there is no isomerisation of the radical $C_6H_5CH_2.CHCH_2CCl_3$ to the more stable substituted benzyl radical $C_6H_5CHCH_2CH_2CCl_3$.

From the above data, it is evident that up to the present there has not been a single reliable demonstration of 1,2-migration of hydrogen in radicals.

B. MIGRATION OF HYDROGEN TO MORE DISTANT CARBON ATOMS WITH FREE VALENCIES

The migration of hydrogen to a more distant radical centre has been observed in many cases. However, it has often proved impossible to establish unambiguously from which carbon atom the hydrogen migrates.

1,3-Migration of hydrogen. There are few reliable data showing 1,3-migration of hydrogen in a hydrocarbon radical in solution.

Reutov and Shatkina[29] found that the propyl radical formed on thermal decomposition of n-butyryl peroxide (labelled in the α-position) undergoes rearrangement in solution with 1,3-migration of hydrogen:

$$CH_3CH_2\overset{14}{C}H_3 \rightarrow \dot{C}H_2CH_2\overset{14}{C}H_3.$$

The yield of the rearranged product amounts to 4.0 ± 0.5%.

It is possible that in the reactions (mentioned above) between butyl bromide and magnesium in the presence of cobalt halides[25], resulting in a mixture of 1-butene and

† It is possible that the formation of equimolar quantities of 2-octanol and 2-octanone is due to disproportionation of the radicals:

$$2C_6H_{13}\overset{CH_3}{\underset{|}{C}}HO\cdot \rightarrow C_6H_{13}\overset{CH_3}{\underset{|}{C}}HOH + C_6H_{13}COCH_3;$$

however, this does not alter the main conclusion.

2-butene, the formation of 2-butene is due to the 1,3-migration of hydrogen $CH_3CH_2CH_2\dot{C}H_2 = CH_3\dot{C}HCH_2CH_3$ with subsequent disproportionation of the secondary radicals. It seems to us that the behaviour of the phenoxybutyl radical (described in the same paper), which breaks down with the formation of 1-butene, can also be interpreted in terms of a 1,3-migration of hydrogen:

$$C_6H_5OCH_2CH_2CH_2\dot{C}H_2 \rightarrow C_6H_5OCH_2\dot{C}HCH_2CH_3 \rightarrow C_6H_5\dot{O} + CH_2{=}CHCH_2CH_3.$$

1,3-Migration of hydrogen from carbon to nitrogen may take place in the reduction with benzyl radicals of aromatic nitro- and nitroso-compounds to amines[35]. The following reaction scheme has been proposed:

$$ArN{=}O + Ph\dot{C}H_2 \rightarrow Ar\dot{N}OCH_2Ph$$
$$Ar\dot{N}OCH_2Ph \xrightarrow{rearrangement} ArNHO\dot{C}HPh \rightarrow Ar\dot{N}H + PhCHO$$
$$Ar\dot{N}H + Ph\dot{C}H_2 \rightarrow ArNHCH_2Ph \qquad Ar\dot{N}H + Ph\dot{C}H_2 \rightarrow ArNH_2 + Ph\dot{C}H_2.$$

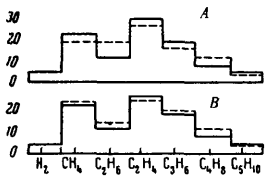
1,5-Migration of hydrogen. Kosiakoff and Rice[36] suggested that the thermal decomposition of higher hydrocarbons results in the formation of long-chain radicals which can isomerise. They suggested, for example, that in the decomposition of n-hexane the primary radical 1-hexyl can isomerise to the secondary radical 2-hexyl:

$$\begin{matrix} CH_2{-}CH_2 \\ | \\ CH_2{-}\dot{C}H_2 \end{matrix} \diagdown CH_2{-}CH_3 \rightleftarrows \begin{matrix} CH_2CH_2 \diagdown \dot{C}H{-}CH_3, \\ | \\ CH_2{-}CH_3 \end{matrix}$$

i.e. with 1,5-migration of hydrogen in the radical. Since the activation energy of such a process is undoubtedly much less than that for decomposition of the radical, equilibrium between the two radicals is probably established. Assuming that at 600° under low pressure n-hexane decomposes according to the scheme:

$$R + C_6H_{14} \rightarrow \begin{cases} CH_3(CH_2)_4\dot{C}H_2 \\ CH_3(CH_2)_3\dot{C}HCH_3 \\ CH_3(CH_2)_2\dot{C}HCH_2CH_3, \end{cases}$$
$$CH_3CH_2CH_2CH_2CH_2\dot{C}H_2 \rightarrow 2C_2H_4 + \dot{C}_2H_5(C_2H_6),$$
$$CH_3CH_2CH_2CH_2\dot{C}HCH_3 \rightarrow C_3H_6 + C_2H_4 + \dot{C}H_3(CH_4),$$
$$CH_3CH_2CH_2\dot{C}HCH_2CH_3 \rightarrow \begin{cases} C_4H_8 + \dot{C}_2H_5(C_2H_6) \\ C_5H_{10} + \dot{C}H_3(CH_4), \end{cases}$$

the authors calculated the yield of the possible products of the thermal decomposition of n-hexane both in the absence and in the presence of free-radical isomerisation with 1,5-migration of hydrogen. The results obtained are clearly shown in the Figure. It is evident that assumption



Thermal decomposition of n-hexane. Continuous line — experimental; broken line — calculated. *A*) Rearrangement not allowed for; *B*) rearrangement allowed for.

of radical isomerisation substantially improves the agreement between the calculated and experimental data. In the case of radicals with longer chains, obtained for example by the cracking of n-octane[36] and n-hexadecane[37], the possibility of the isomerisation of intermediate radicals is even greater and the improvement in the calculated yields becomes still more notable when isomerisation is taken into account.

Grob and Kammüler[38] demonstrated liquid-phase 1,5-migration of hydrogen in a radical. In an attempt to investigate the possible isomerisation of radical (VI) to radical (VII),

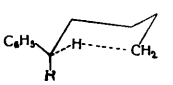
$$\underset{(VI)}{C_6H_5CH_2(CH_2)_3\dot{C}H_2} \rightarrow \underset{(VII)}{C_6H_5\dot{C}H(CH_2)_3CH_3},$$

they studied the pyrolysis of ϵ-phenylcaproyl peroxide at 85° in the presence of dry sand. The following were the products: CO_2, ϵ-phenylcaproic acid, δ-phenylpentyl ether, ϵ-phenylcaproate, n-pentylbenzene, 1,10-diphenyldecane, 5,6-diphenyldecane, and polymeric material. The formation of 5,6-diphenyldecane (yield 4.5%) may be due to the intramolecular rearrangement of radical (VI) to radical (VII) with subsequent recombination of the rearranged radicals. However, the formation of this compound may be interpreted as due to the action of radicals present in the reaction mixture on n-pentylbenzene with subsequent recombination of the 1-phenylpent-1-yl radicals:

$$\dot{R} + C_6H_5CH_2(CH_2)_3CH_3 \rightarrow RH + C_6H_5\dot{C}H(CH_2)_3CH_3,$$
$$2C_6H_5\dot{C}H(CH_2)_3CH_3 \rightarrow [CH_3(CH_2)_3\underset{\displaystyle C_6H_5}{\underset{|}{C}}H{-}]_2.$$

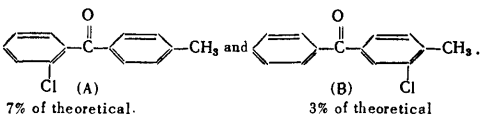
The formation of 5,6-diphenyldecane by the action of radicals (generated in the breakdown of t-butyl peroxide) on n-pentylbenzene is known. Grob and Kammüler quote the following evidence in support of intramolecular rearrangement in this process. When the peroxide is pyrolysed in cumene (at 110°–120°), it might be expected that outside the solvent "cage" the radicals would react with the more reactive cumene and not with n-pentylbenzene the concentration of which in solution is low. Thus the yield of 5,6-diphenyldecane should fall if the compound were formed as a result of the secondary reaction with n-pentylbenzene. Experiment shows that the yield of 5,6-diphenyldecane increases when the reaction is carried out in cumene. The reason for the increase is not clear [possibly it is due to the higher temperature (110°–120°) in cumene (85° without cumene)].

It is interesting to compare this with the fact that decomposition of δ-phenylvaleryl peroxide does not result in products derived from 1,4-migration of hydrogen[39]. It is possible that the $C_6H_5(CH_2)_3\dot{C}H_2$ and $C_6H_5(CH_2)_4\dot{C}H_2$ radicals behave differently because in the latter case a conformation favouring rearrangement may be assumed:



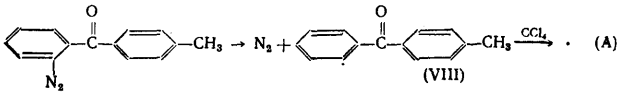
1,5-Migration of a hydrogen atom bound to an aromatic nucleus has been suggested to explain the formation of isomeric products in the decomposition of 2-(4-methylbenzoyl)aryldiazonium salts[40]. The decomposition of aryldiazonium halides of this structure was carried out in

carbon tetrachloride at pH 7.2. Among other products, the following chloro-derivatives were obtained:



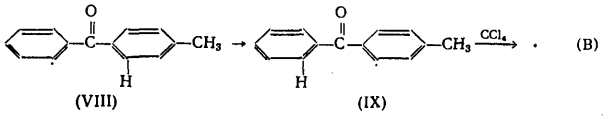
(A) 7% of theoretical. (B) 3% of theoretical

The following reaction has been suggested to explain the formation of chloro-derivative (A):



(A)

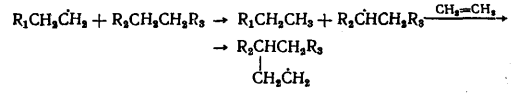
Chloro-derivative (B) was assumed to arise through rearrangement of radical (VIII) to radical (IX) *via* 1,5-migration of hydrogen with subsequent reaction of radical (IX) with carbon tetrachloride:



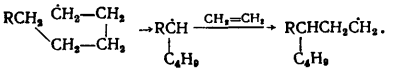
(B)

(VIII) (IX)

It is noteworthy that radical rearrangement with 1,5-migration of hydrogen appears to play a major role in the radical polymerisation of ethylene and other olefines as well as in the polymerisation of dienes and other unsaturated compounds (see, for example, refs. 41 and 42). In recent years data have been obtained suggesting that polyethylene molecules synthesised by radical polymerisation under pressure have side chains. Depending on the reaction conditions, polyethylene with long or short side chains can be obtained. The physicomechanical properties of polyethylene depend to a large extent on the nature of branching in the molecule. It has been suggested[41] that there may be two mechanisms leading to chain branching in the molecule. Long side chains are formed as a result of intermolecular hydrogen transfer:



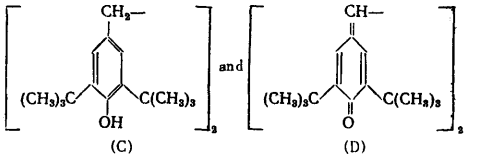
and short side chains are formed *via* intramolecular hydrogen transfer. Assuming that the formation of 5- and 6-membered rings in the transition state is sterically favoured, Roedel[41] suggested that the intramolecular rearrangement is effected mainly by 1,5-migration of hydrogen in the radical:



Study of the infra-red spectra of polyethylene containing short side chains[42] has shown that the number of methyl and ethyl groups in the polyethylene specimens examined was the same. This has been interpreted as showing that pendant methyl side groups are not formed in polyethylene. The short side chains are supposed to arise mainly by 1,5-migration of hydrogen in the radical; 1,3- and 1,4-migrations are also believed to be possible.

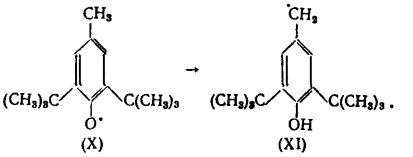
A number of other observations have been interpreted as proof that radicals can isomerise *via* hydrogen transfer from a carbon atom to a non-neighbouring atom with an unpaired electron, but it was impossible to establish from which particular carbon atom the hydrogen migrated.

1,6-Migration of hydrogen from carbon to oxygen in a radical has been invoked to explain the formation of compounds (C) and (D) in the oxidation of 4-methyl-2,6-di-t-butylphenol:



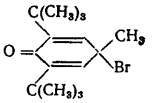
(C) (D)

The formation of these products is supposed to be due to the rearrangement of radical (X) to radical (XI):



(X) (XI)

When the bromo-compound



reacts with mercury, the same compounds, (C) and (D), are formed which confirms the occurrence of this rearrangement.

Thus the ability of radicals to isomerise in solution *via* hydrogen migration to a non-neighbouring atom is now definitely established. However, such isomerisation has been little studied. In particular, the influence of the structure of the radical, the nature of the solvent, the temperature, and other conditions on this reaction is unknown, and no quantitative data characterising the process are available.

The possibility of rearrangement, *via* hydrogen migration, of initially formed radicals must undoubtedly be taken into account in studies on the mechanism of radical substitution, on the reactivity and stability of radicals in solution, and in many other problems.

II. RADICAL REARRANGEMENT WITH CHLORINE MIGRATION. 1,2-MIGRATION OF CHLORINE

Studies on chemical reactions of polychlorohydrocarbons containing the trichloromethyl group have shown that this group is active in homolytic reactions[44]. Thus when $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes are allowed to react with organomagnesium compounds in the presence of cobalt chloride, the CCl_3 group is attacked and compounds with the structure $Cl(CH_2)_nCCl_2CCl_2(CH_2)_nCl$ are formed. The reaction of $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes with copper and nickel takes place similarly. The process apparently goes *via* a stage in which a chlorine atom or a tetrachloroalkane molecule undergoes homolytic scission:

$$\dot{R} + CCl_3(CH_2)_n Cl \rightarrow RCl + \dot{C}Cl_2(CH_2)_nCl,$$

$$2Cl(CH_2)_n\dot{C}Cl_2 \rightarrow Cl(CH_2)_nCCl_2—CCl_2(CH_2)_nCl.$$

It must be emphasised that the removal of a chlorine atom from the trichloromethyl group takes place under

extremely mild conditions. It is possible that the ease of this removal from a CCl_3 group in a polychlorohydrocarbon radical is even greater, by analogy with the greater mobility of hydrogen in hydrocarbon radicals than in the molecules of saturated hydrocarbons[45,46]. The ease of removal of the chlorine atom and the stability of radicals in which a carbon atom with an unpaired electron is bound to two chlorine atoms[47], should favour the rearrangement of radicals of type (A) to radicals of type (B):

$$\underset{(A)}{CCl_3\dot{C}<} \rightarrow \underset{(B)}{\dot{C}Cl_2CCl<}$$

In a number of investigations of this rearrangement the radicals of the above structure were obtained by the homolytic addition of various compounds to olefines containing a polyhalogenomethyl group. The addition of hydrogen bromide, bromotrichloromethane, bromine, and thiophenol to substances with the structure $XCCl_2CY=CH_2$ (where X = Cl, F, H, CH_3; Y = Cl, H, Br, CH_3) has been studied. The results obtained are collected in Tables 1–3.

Table 1 gives some data on the reaction between hydrogen bromide and a number of polyhalogenoalkenes in the presence of benzoyl peroxide or under illumination with ultra-violet light. It is well known that the addition of hydrogen bromide to olefines in the presence of peroxides takes place *via* a chain radical mechanism. The purely homolytic character of the reactions described in Table 1 is emphasised by the fact that in the absence of radical-process initiators there is no reaction between hydrogen bromide and the compounds listed in the table. The chain character of the reaction is confirmed by the fact that addition of negligible quantities of inhibitors brings the reaction to a complete stop. Addition of HBr was carried out by saturating a solution of 0.5 g of benzoyl peroxide in 0.1–0.6 mole of polyhalogenoalkene at 50°–70°. In the general case the reaction results in a mixture of products:

$$\text{(I)}\quad XCCl_2CY{=}CH_2+HBr \xrightarrow{Bz_2O_2} \begin{cases} XCCl_2CHYCH_2Br \\ HCClXCYClCH_2Br & 1 \\ \dot{C}ClX{=}CYCH_2Br & 2 \\ HCClXCYClCH_2Cl & 3 \end{cases}$$

Thus in the case of example 4 in Table 1, where X = Cl and Y = Cl compounds 1′, 2′, and 3′ were obtained:

$$CCl_3CCl{=}CH_2+HBr \xrightarrow{Bz_2O_2} \begin{cases} CHCl_2CCl_2CH_2Br & 1' \\ CCl_2{=}CClCH_2Br & 2' \\ CHCl_2CCl_2CH_2Cl & 3' \end{cases}$$

The following mechanism has been proposed for this process:

$$Bz_2O_2 \rightarrow C_6H_5\dot{}$$

$$C_6H_5\dot{} + HBr \rightarrow C_6H_6 + Br$$

$$CCl_3CCl{=}CH_2 + Br \longrightarrow CCl_3\dot{C}ClCH_2Br \qquad (a)$$

$$\underset{(A)}{CCl_3\dot{C}ClCH_2Br} \xrightarrow{\text{rearrangement}} \underset{(B)}{\dot{C}Cl_2CCl_2CH_2Br} \qquad (b)$$

$$\dot{C}Cl_2CCl_2CH_2Br + HBr \longrightarrow HCCl_2CCl_2CH_2Br + Br \qquad (c)$$

$$\left.\begin{matrix} CCl_3\dot{C}ClCH_2Br \\ \text{or} \\ \dot{C}Cl_2CCl_2CH_2Br \end{matrix}\right\} \longrightarrow CCl_2{=}CClCH_2Br + Cl \qquad (d)$$

$$CCl_3CCl{=}CH_2 + Cl \longrightarrow \underset{(A')}{CCl_3\dot{C}ClCH_2Cl} \qquad (e)$$

$$\underset{(A')}{CCl_3\dot{C}ClCH_2Cl} \xrightarrow{\text{rearrangement}} \underset{(B')}{\dot{C}Cl_2CCl_2CH_2Cl} \qquad (f)$$

$$\dot{C}Cl_2CCl_2CH_2Cl + HBr \longrightarrow HCCl_2CCl_2CH_2Cl + Br \qquad (g)$$

This scheme is analogous to that proposed by Kharasch for the "peroxide effect", but stages (b) and (f) involve the rearrangement of radicals (A) and (A′) to radicals (B) and (B′), and the elimination of a chlorine atom in stage (d) leads to the propagation of a chain reaction [stages (e), (f), and (g)], which is completely analogous to the main process [stages (a), (b), and (c)] resulting from the presence of bromine atoms in the system. Elimination of chlorine, which stabilises the intermediate radicals, is encountered quite frequently in homolytic reactions[48–51].

Introduction of fluorine or hydrogen to a trihalogenomethyl group in unsaturated compounds (Nos. 5 and 7 in Table 1 and No. 3 in Table 3) impedes the rearrangement of radicals and, in addition to the rearranged products, non-rearranged addition products are also formed. Table 2 gives some data on the reaction of bromotrichloromethane, bromine, and mercaptans with 3,3,3-trichloropropene. The

TABLE 1. Addition of hydrogen bromide to polychloroolefines in the presence of benzoyl peroxide or under ultra-violet illumination.

No.	Polychloroolefine	Reaction products (yield, % of theoretical)				% rearrangement**	Reference
		not rearranged	rearranged	rearranged Cl-addition product	unsaturated products		
1	$CCl_3CH{=}CH_2$		$CCl_2H{-}CHCl{-}CH_2Br$ 77			100	52
2*	$CCl_3CH{=}CH_2$		$CHCl_2{-}CHCl{-}CH_2Br$ 88			100	53
3	$CCl_3C(CH_3){=}CH_2$		$CHCl_2{-}C(CH_3)Cl{-}CH_2Br$ 59	$CHCl_2{-}C(CH_3)Cl{-}CH_2Cl$ 11	$CCl_2{=}C(CH_3){-}CH_2Br$ 15	100	54
4	$CCl_3CCl{=}CH_2$		$CHCl_2{-}CCl_2{-}CH_2Br$ 34	$CHCl_2{-}CCl_2{-}CH_2Cl$ 14	$CCl_2{=}CCl{-}CH_2Br$ 15	100	55
5	$CHCl_2{-}CH{=}CH_2$	$CHCl_2{-}CH_2{-}CH_2Br$ 5	$CH_2Cl{-}CHCl{-}CH_2Br$ 46			90	56,57
6	$CH_2CCl_2{-}CH{=}CH_2$		$CH_2CHCl{-}CHCl{-}CH_2Br$ 73			100	57
7*	$CFCl_2{-}CH{=}CH_2$	$CFCl_2CH_2CH_2Br$ 39	$CFClH{-}CClH{-}CH_2Br$ 18			30	53
8	$CHCl_2{-}CCl{=}CH_2$	$CHCl_2{-}CClH{-}CH_2Br$ 30				0	55
9	$CHCl_2{-}C(CH_3){=}CH_2$	$CHCl_2{-}CH(CH_3){-}CH_2Br$ 34	$CH_2Cl{-}C(CH_3)Cl{-}CH_2Br$ ~30		$CHCl{=}C(CH_3){-}CH_2Br$ ~12	~50	57

* Experiments carried out under illumination with ultra-violet light.

** Calculated from the proportions of the addition products.

TABLE 2. Addition of various reagents to 3,3,3-trichloropropene.

No.	Reagent	Initiator	Solvent	Temp., °C	Reaction products (yield, % of theoretical)				Reference
					not rearranged	rearranged	rearranged Cl-addition product	unsaturated	
1	$BrCCl_3$	$(C_6H_5CO)_2O_2$		100		$BrCCl_2CHCl-CH_2Cl$, 18	$BrCCl_2CHCl-CH_2Cl$ 14	$CCl_2=CH-CH_2Cl_2$ 26	52
2	Br_2		CH_3COOH	20	$CCl_2CHBr-CH_2Br$ 80				58
3	Br_2	illumination with incandescent lamp (150 W)	$CHCl_3$		$CCl_2CHBr-CH_2Br$ 70	$CCl_2Br-CHCl-CH_2Br$* 30			58
4	Br_2	$(C_6H_5CO)_2O_2$	CCl_4	80	$CCl_2CHBr-CH_2Br$ 47	$CCl_2Br-CHCl-CH_2Br$* 53			58
5	C_6H_5SH**			115	$CCl_2CH_2CH_2SC_6H_5$ 27				59
6	C_6H_5SH	illumination with incandescent lamp (150 W)		80—90		$CHCl_2CHCl-CH_2SC_6H_5$ 30		$CCl_2=CHCH_2SC_6H_5$ 11	59
7	$C_6H_5CH_2SH$	ditto		110—115		$CHCl_2-CClH-CH_2SCH_2C_6H_5$ 11		$CCl_2=CH-CH_2-S-CH_2C_6H_5$ 39	59
8	$n\text{-}C_6H_{13}SH$	»		110—115				$CCl_2=CHCH_2SC_6H_{13}\text{-}n$ 30	60

* Yield given as a percentage of total products.

** Reaction carried out in the presence of sulphur as inhibitor of the homolytic process.

first of these compounds add to trichloropropene solely by a chain radical mechanism. The addition of bromine to 3,3,3-trichloropropene may be heterolytic when the reaction is carried out in a polar solvent (acetic acid) and in the absence of initiators (No.2 in Table 2). Under these conditions a non-rearranged addition product with the structure $CCl_3CHBrCH_2Br$ is formed. When the reaction is carried out in a non-polar solvent under illumination (No.3 in Table 2) or in the presence of benzoyl peroxide (No. 4 in Table 2), a mixture of rearranged ($BrCCl_2CHClCH_2Br$) and non-rearranged compounds is formed.

In exactly the same way the addition of thiophenol to trichloropropene can be effected by both a heterolytic (in the presence of sulphur as an inhibitor of the homolytic process, No.5 in Table 2) and a homolytic (No. 6 in Table 2) mechanism. In the first case a non-rearranged product with the structure $CCl_3CH_2CH_2SC_6H_5$ is formed, and in the second a rearranged product and an unsaturated compound ($HCCl_2CHClCH_2SC_6H_5$ and $CCl_2=CHCH_2SC_6H_5$). The last is obtained in a slight yield. When thiophenol is replaced by toluene-ω-thiol (No. 7 in Table 2) or n-hexanethiol (No. 8 in Table 2), the principal products are $CCl_2=CHCH_2SCH_2C_6H_5$ and $CCl_2=CHCH_2SC_6H_{13}$ respectively. It is interesting that in these reactions the chlorine eliminated instead of being bound to the trichloropropene reacts with toluene-ω-thiol and n-hexanethiol to form hydrogen chloride.

A number of factors affect the chemical behaviour of the radicals in solution; this is reflected particularly in the relative yields of products 1,2, and 3 (scheme I) and those of the non-rearranged products. The most important of these factors are the relative stabilities of the initial and rearranged radicals, the relative rates of their reaction with the chain-transfer agent (HBr, Br_2, C_6H_5SH), etc. Comparison of the results of the reactions (Tables 1 and 2) leads to certain conclusions on the relation between the structure of the radical and its ability to rearrange with 1,2-migration of chlorine.

The reactions listed in Table 1 were carried out under comparable conditions with the same chain-transfer agent — hydrogen bromide. The results obtained show that rearrangement leads to the formation of more stable radicals. For example, the reaction of 2,3,3-trichloroprop-1-ene (No. 8 in Table 1) with hydrogen bromide takes place without rearrangement, since, in conformity with the general rule, the initial secondary radicals $CHCl_2\dot{C}ClCH_2Br$ are more stable than the primary radicals $\dot{C}HClCCl_2CH_2Br$, which would be formed as a result of rearrangement. Radicals in which the unpaired electron is associated with the group $\dot{C}Cl_2-\overset{|}{C}-$ are more stable than secondary radicals of the type $-\overset{|}{C}-\dot{C}H-\overset{|}{C}-$ or $-\overset{|}{C}-\dot{C}Cl-\overset{|}{C}-$, and also more stable than tertiary radicals. Accordingly, radicals (A), (B), and (C) rearrange to (A'), (B'), and (C') (Nos. 1, 3, and 4 in Table 1).

$$\underset{(A)}{CCl_3\dot{C}HCH_2Br} \rightarrow \underset{(A')}{\dot{C}Cl_2CHClCH_2Br},$$

$$\underset{(B)}{CCl_3\dot{C}ClCH_2Br} \rightarrow \underset{(B')}{\dot{C}Cl_2CCl_2CH_2Br},$$

$$\underset{(C)}{CCl_3\dot{C}(CH_3)-CH_2Br} \rightarrow \underset{(C')}{\dot{C}Cl_2CCl(CH_3)CH_2Br}.$$

Primary radicals bound to chlorine are somewhat more stable than secondary radicals bound to hydrogen; thus radicals (D) rearrange to (D'):

$$\underset{(D)}{CHCl_2\dot{C}HCH_2Br} \rightarrow \underset{(D')}{\dot{C}HClCHClCH_2Br}. \qquad \text{(No. 5, Table 1)}$$

It is therefore readily seen why the secondary radical (E) rearranges to the more stable secondary radical (E'):

$$\underset{(E)}{CH_3CCl_2\dot{C}HCH_2Br} \rightarrow \underset{(E')}{CH_3\dot{C}ClCHClCH_2Br}. \qquad \text{(No. 6, Table 1)}$$

Reactions of 3,3,3-trichloropropene with various substances which can function as chain-transfer agents are compared in Table 2. Examination of the data shows that, in all cases where the reaction is carried out in the presence of radical initiators (Nos.1, 3, 4, 6, and 7), the initial radicals $CCl_3\dot{C}HCH_2Y$ (Y = CCl_3, Br, C_6H_5S) rearrange to the more stable radicals $\dot{C}Cl_2CHClCH_2Y$. The different chain-transfer agents resulted merely in a change of the relative yields of products of types 1, 2, and 3 (scheme I, p. 7). This also confirms that the main factor determining the occurrence of rearrangement is the greater stability of the rearranged radical.

In some of the cases investigated, "normal" addition products were obtained together with the rearranged products:

(1) $CCl_3CH=CH_2 + Br_2 \rightarrow CCl_3CHBrCH_2Br$ (No. 4, Table 2)
$BrCCl_2CHClCH_2Br$,

(2) $CFCl_2CH=CH_2 + HBr \rightarrow CFCl_2CH_2CH_2Br$ (No. 7, Table 1)
$HCFClCHClCH_2Br$,

(3) $CFCl_2CBr=CH_2 + HBr \rightarrow CFCl_2CHBrCH_2Br$ (No. 3, Table 3)
$CFCl=CClCH_2Br$,

(4) $CHCl_2-CH=CH_2 + HBr \rightarrow CHCl_2-CH_2CH_2Br$ (No. 5, Table 1)
$CH_2Cl-CHCl-CH_2Br$,

(5) $CHCl_2-C(CH_3)=CH_2 + HBr \rightarrow CHCl_2-C(CH_3)H-CH_2Br$ (No. 9, Table 1)
$CH_2Cl-CCl(CH_3)-CH_2Br$.

In all cases except the first, the formation of non-rearranged products by simultaneous heterolytic addition reactions is eliminated from consideration since these reactions do not occur in the absence of benzoyl peroxide and illumination. Furthermore, addition of traces of inhibitors suppresses the formation of both the rearranged and non-rearranged products. It is possible that the initial radicals $CFCl_2\dot{C}HCH_2Br$, $CFCl_2\dot{C}BrCH_2Br$, $CHCl_2\dot{C}HCH_2Br$, and $CHCl_2\dot{C}(CH_3)CH_2Br$, and the corresponding rearranged radicals $\dot{C}FClCHClCH_2Br$, $\dot{C}FClCBrClCH_2Br$, $\dot{C}HClCHClCH_2Br$, and $\dot{C}HClCCl(CH_3)CH_2Br$ have comparable lifetimes, which results in a mixture of rearranged and non-rearranged products.

During studies of 1,2-migration of chlorine in radicals the interesting homolytic transformation of 3,3,3-trichloro-2-bromoprop-1-ene to the isomeric 1,1,2-trichloro-3-bromoprop-1-ene was investigated[61] (No. 1 in Table 3). The compound ($CCl_3CBr=CH_2$) isomerises on standing after an induction period (over 1–2 days) or on illumination (without heating) with a mercury-vapour lamp (over several minutes):

$$CCl_3CBr=CH_2 \rightarrow CCl_2=CClCH_2Br.$$

The radical chain mechanism of this rearrangement has been demonstrated by the following observations. The rearrangement is initiated by illumination of the substance with ultra-violet light and is inhibited by the addition of small quantities of such inhibitors as hydroquinone and dimethylaniline. The homolytic isomerisation of this compound differs from the heterolytic anionotropic isomerisation, which is of the allylic type:

$$CCl_3CBr=CH_2 \xrightarrow{h\nu} CCl_2=CClCH_2Br$$
$$CCl_3CBr=CH_2 \xrightarrow{SbCl_5} CCl_2=CBrCH_2Cl.$$

The following scheme has been proposed for the homolytic isomerisation.

(III)
$$Br + CCl_3CBr=CH_2 \xrightarrow{a} CCl_3\dot{C}BrCH_2Br$$
$$\uparrow \qquad\qquad\qquad\qquad b \downarrow$$
$$Br + CCl_2=CClCH_2Br \xleftarrow{c} \dot{C}Cl_2CBrClCH_2Br.$$

The results of other studies on isomerisation of this type are given in Table 3.

Compounds of the type $XCCl_2CBr=CH_2$ (where X = CH_3, F) can also isomerise on illumination with ultra-violet light or on heating with benzoyl peroxide:

$$XCCl_2CBr=CH_2 \rightarrow XCCl=CClCH_2Br.$$

3,3-Dichloro-2-bromobut-1-ene (No. 2, Table 3) isomerises heterolytically under the action of $SbCl_5$ with the formation of the allylic isomer 1,3-dichloro-2-bromobut-2-ene, whereas on illumination with ultra-violet light it

TABLE 3. Homolytic isomerisation of compounds of the type $XCCl_2CBr=CH_2$.

No.	Polyhalogenoalkene	$SbCl_5$-catalysed anionotropic isomerisation	Homolytic isomerisation	Interaction with various reagents: reagent	products: unsaturated	products: addition products	yield, % of theoretical	% rearrangement	Reference
1	$CCl_3CBr=CH^*_2$	$CCl_2=CBr-CH_2Cl$	$CCl_2=CCl-CH_2Br$**	C_6H_5SH	$CCl_2=CCl-CH_2SC_6H_5$	–	55	100	61
				C_6H_5SH	$CCl_2=CCl-CH_2SC_6H_5$	–	30	100	60
				C_6H_5SH+S	–	$CCl_2CHBr-CH_2SC_6H_5$	38	0	
2	$CH_3CCl_2CBr=CH^*_2$	$CH_3CCl=CBr-CH_2Cl$	$CH_3CCl=CCl-CH_2Br$**	HBr+ $+(C_6H_5CO_2)_2$	$CH_3CCl=CCl-CH_2Br$	–	90	100	62
3	$CFCl_2-CBr=CH^*_2$		$CFCl=CCl-CH_2Br$*** + dimer* (C)	HBr (u.v. light)	$CFCl=CCl-CH_2Br$ (A)	$CFCl_2-CHBr-CH_2Br$+ (B) +dimer* (C)	78 (B); 3 (A); 9 (C);	4****	63
				heating with $(C_6H_5CO_2)_2$	$CFCl=CClCH_2Br$ (A)	dimer* (C)	46 (A); 49 (C);	100****	

* After an induction period Nos.1 and 2 undergo homolytic isomerisation to $CClX=CCl-CH_2Br$ (X = Cl, CH_3); on standing No.3 is converted to dimer (C) with the structure $CH_2Br-CBr(CFCl_2)-CH_2-CCl=CFCl$; on interaction with dialkylamines Nos.1, 2, and 3 form amines with the structure $CXCl=CBr-CH_2NR_2$(X = Cl, F, CH_3).

** Illumination with ultra-violet light.

*** Heating or illumination with ultra-violet light.

**** Yield of dimers not taken into account.

isomerises homolytically to 2,3-dichloro-1-bromobut-2--ene. Ultra-violet light causes the homolytic isomerisation of 3-fluoro-3,3-dichloro-2-bromoprop-1-ene (No. 3 in Table 3) to 1-fluoro-1,2-dichloro-3-bromoprop-1-ene, a dimer which probably has the structure $CH_2BrCBr(CFCl_2)-CH_2CCl=CClF$ being formed at the same time.

Such isomerisation of compounds of the type $XCCl_2CBr=CH_2$ is due to the fact that radicals with the bond system $-\overset{|}{C}-\overset{|}{C}-Br$ readily split off the bromine atom, then becoming stabilised by rearrangement to unsaturated compounds [reaction *c*, scheme (III)]. Thus compounds with the structure $XCCl_2CBr=CH_2$ (where X = Cl, CH_3) do not undergo homolytic addition, even of extremely effective chain-transfer agents such as hydrogen bromide and thiophenol (Nos. 1 and 2 in Table 3); in all cases the initially formed radicals of the type $XCCl_2\dot{C}BrCH_2Y$ (where X = Cl, CH_3; Y = Br, C_6H_5S) isomerise to $X\dot{C}ClCClBrCH_2Y$ which become stabilised by splitting off bromine and rearranging to unsaturated compounds of the type $XCCl=CClCH_2Y$. Only when hydrogen bromide is added to 3-fluoro-3,3--dichloro-2-bromoprop-1-ene under ultra-violet illumination (No. 3 in Table 3) is a saturated addition product ($CFCl_2CHBrCH_2Br$) obtained together with the unsaturated compound ($CFCl=CClCH_2Br$). The former, however, is formed from the non-rearranged radical, and the rearranged radical is stabilised solely by eliminating bromine and undergoing conversion to an unsaturated compound:

$$CFCl_2CBr=CH_2 + Br \rightarrow CFCl_2\dot{C}BrCH_2Br \quad (F)$$

(IV)
$$CFCl_2\dot{C}BrCH_2Br \xrightarrow{heat} \dot{C}FClCClBrCH_2Br \quad (F')$$
$$\downarrow HBr \qquad\qquad \downarrow$$
$$CFCl_2CHBrCH_2Br + Br \qquad CFCl=CClCH_2Br + Br.$$

1,2-Migration of chlorine is observed also in other reactions. Thus Urry and Eiszner[64] obtained a 60% yield of tetra(chloromethyl)methane in the reaction between diazomethane and carbon tetrachloride under illumination. The reaction must be based on a radical chain mechanism, since it is very slow in the dark, becomes faster on illumination, and is inhibited by diphenylamine. In stages (1), (2) and (3) [scheme (V)] the mechanism proposed for the formation of tetrachloromethylmethane involves rearrangement with migration of a chlorine atom from the trichloromethyl group (and then from the dichloromethyl and monochloromethyl groups) to a neighbouring carbon atom with an unpaired electron.

(V)
$$\dot{C}Cl_3 + CH_2N_2 \rightarrow CCl_3\dot{C}H_2 + N_2,$$
$$CCl_3\dot{C}H_2 \rightarrow \dot{C}Cl_2-CH_2Cl, \quad (1)$$
$$\dot{C}Cl_2-CH_2Cl + CH_2N_2 \rightarrow CH_2CCl_2-\dot{C}HCl + N_2,$$

$$\dot{C}H_2CCl_2-CH_2Cl \rightarrow CH_2Cl-\dot{C}Cl-CH_2Cl, \quad (2)$$

$$CH_2Cl-\dot{C}Cl-CH_2Cl + CH_2N_2 \rightarrow CH_2Cl-\underset{\displaystyle CH_2}{\overset{|}{C}}Cl-CH_2Cl + N_2,$$

$$CH_2Cl-\underset{\displaystyle \dot{C}H_2}{\overset{|}{C}}Cl-CH_2Cl \rightarrow CH_2Cl-\underset{\displaystyle CH_2Cl}{\overset{|}{\dot{C}}}-CH_2Cl, \quad (3)$$

$$CH_2Cl-\underset{\displaystyle CH_2Cl}{\overset{|}{\dot{C}}}-CH_2Cl + CH_2N_2 \rightarrow CH_2ClCl-\underset{\displaystyle CH_2Cl}{\overset{|}{\underset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2Cl + N_2,$$

$$CH_2Cl-\underset{\displaystyle CH_2Cl}{\overset{|}{\underset{\displaystyle \dot{C}H_2}{\overset{|}{C}}}}-CH_2Cl + CCl_4 \rightarrow (CH_2Cl)_4C + \dot{C}Cl_3.$$

It might be supposed that in the reaction between diazomethane and carbon tetrachloride the C–Cl bond is ruptured and the biradical $\cdot CH_2$ "inserted", which should also result in the formation of tetra(chloromethyl)methane. However, since CH_3CCl_3 and CH_2ClCCl_3 do not react with diazomethane under these conditions, this hypothesis was rejected.

Diazomethane reacts similarly with bromotrichloromethane, chloroform, and methyl trichloroacetate[64]. Methyl diazoacetate reacts with chloroform, carbon tetrachloride, and bromotrichloromethane with the formation of rearranged products[65]:

$$CHN_2COOCH_3 + XCCl_3 \rightarrow \underset{(G)}{CCl_3CHCOOCH_3} + (X)\ (X = H, Cl, Br),$$

(VI)
$$CCl_3-\dot{C}HCOOCH_3 \rightarrow \dot{C}Cl_2CHCl-COOCH_3$$
$$(G) \qquad\qquad (G')$$

$$\dot{C}Cl_2-CHCl-COOCH_3 \;(G') \begin{cases} \xrightarrow{XCCl_3} CCl_2X-CHCl-COOCH_3 + \dot{C}Cl_3 & (X = H, Br) \\ \xrightarrow{-H} CCl_2=CCl-COOCH_3 & (X = Cl, Br). \end{cases}$$

It must be emphasised that although the secondary radical (G) in scheme (VI) is stabilised by the neighbouring methoxycarbonyl group, it is nevertheless less stable than the (G′) radical which contains the $\dot{C}Cl_2$ group.

Reaction between olefines and sulphonyl chloride in the presence of t-butyl peroxide proceeds as follows[66]:

$$RCH=CH_2 + SO_2Cl_2 \begin{cases} \longrightarrow RCHClCH_2Cl \\ \longrightarrow (RCHClCH_2)_2SO_2. \end{cases}$$

The authors suggested that the reaction involves rearrangement of the radicals with 1,3-migration of chlorine from sulphur to carbon:

$$RCH=CH_2 + \dot{S}O_2Cl \rightarrow R-\dot{C}HCH_2SO_2Cl$$
$$\searrow \text{ rearrangement}$$
$$RCHClCH_2SO_2CH_2\dot{C}HR \xleftarrow{RCH=CH_2} RCHClCH_2\dot{S}O_2$$
$$\downarrow SO_2Cl_2$$
$$(RCHClCH_2)_2SO_2 + \dot{S}O_2Cl.$$

Assuming that rearrangement of polyhalogenoalkyl radicals results in the formation of more stable radicals, the following table of relative stabilities has been set up:

$$CCl_3\dot{C}H_2 < \dot{C}Cl_2CH_2Cl\ [64]$$
$$CH_2ClCCl_2\dot{C}H_2 < CH_2ClC\dot{C}lCH_2Cl\ [64]$$
$$(CH_2Cl)_2CCl\dot{C}H_2 < (CH_2Cl)_2C\dot{C}H_2Cl\ [64]$$
$$\dot{C}HClCCl_2CH_2Br < CHCl_2C\dot{C}lCH_2Br\ [55]$$
$$CCl_3\dot{C}HCH_2X < \dot{C}Cl_2CHClCH_2X\ (X=Cl\ [52],\ Br\ [52],\ CCl_3\ [53],\ SC_6H_5\ [50])$$
$$CCl_3\dot{C}HCOOCH_3 < \dot{C}Cl_2CHClCOOCH_3\ [65]$$
$$CCl_3\dot{C}ClCH_2Br < \dot{C}Cl_2CCl_2CH_2Br\ [55]$$
$$CCl_3\dot{C}BrCH_2Y < \dot{C}Cl_2CClBrCH_2Y\ (Y=Br\ [58],\ SC_6H_5\ [60])$$
$$CH_3CCl_2\dot{C}HCH_2Br < CH_3C\dot{C}lCHClCH_2Br\ [57]$$
$$CCl_3\dot{C}(CH_3)CH_2Br < \dot{C}Cl_2CCl(CH_3)CH_2Br\ [64]$$
$$CHCl_2\dot{C}HCH_2Br \leqslant \dot{C}HClCHClCH_2Br\ [56,57]\ddagger$$
$$CHCl_2\dot{C}(CH_3)CH_2Br < \dot{C}HClC(CH_3)Cl-CH_2Br\ [57]\ddagger$$
$$CFCl_2\dot{C}HCH_2Br \leqslant \dot{C}FClCHClCH_2Br\ [63]\ddagger$$
$$CFCl_2\dot{C}BrCH_2Br \leqslant \dot{C}FClCClBrCH_2Br\ [63]\ddagger$$

‡ Under the given conditions these radicals have comparable life-times. Sufficient data for an actual estimate of their stabilities are not available, but it appears that the stabilities of radicals in the left-hand column are less than or close to the stabilities of those in the right-hand column.

From this table, the radicals can be arranged in the following series with respect to their stability:

$$R\dot{C}H_2 < R_2\dot{C}H < R_3\dot{C} \leqslant R\dot{C}HCl < R_2\dot{C}Cl < R\dot{C}Cl_2,$$

where R are polyhaloalkyl radicals. The agreement between the left-hand side of this stability series and the related series for hydrocarbon radicals (primary < secondary < tertiary) emphasises the correctness of the hypothesis that the principal factor governing the occurrence of rearrangement is the formation of radicals which are more stable under the given conditions.

The available experimental evidence shows that the rearrangement involves intramolecular migration of a chlorine atom. For example, in the homolytic addition of HBr to 3,3,3-trichloropropene the process may be represented by scheme (A):

(A)
$$\begin{array}{ccc} Br + CCl_3CH{=}CH_2 & \longrightarrow & CCl_3\dot{C}HCH_2Br \\ \uparrow & & \downarrow \text{rearrangement} \\ Br + HCCl_2CHClCH_2Br & \xleftarrow{HBr} & \dot{C}Cl_2CHClCH_2Br. \\ & (III) & \end{array}$$

An alternative possibility is the migration of a chlorine atom to the reaction point and its subsequent addition to the double bond with the formation of a rearranged radical, as in scheme (B):

(B)
$$\begin{array}{ccccc} Br + CCl_3CH{=}CH_2 & \rightarrow & CCl_3\dot{C}HCH_2Br & \longrightarrow & CCl_2{=}CHCH_2Br + Cl \\ \uparrow & (I) & & & \downarrow \quad (II) \\ Br + HCCl_2CHClCH_2Br & \xleftarrow{HBr} & & & \dot{C}Cl_2CHClCH_2Br. \\ (III) & & & & \end{array}$$

However, the chlorine atom is known to add on very much more readily to compounds of type (I) than to those of type (II) and consequently process (B) cannot explain the observed preferential formation of the rearranged compound (III).

The fact that in a number of cases rearrangement does not yield any product which could be ascribed to intermolecular migration of chlorine constitutes the principal proof that the migration of the chlorine atom is intramolecular. Some examples of rearrangements of this type, which result in almost quantitative yields of a single product, are given below:

$$CCl_3CBr{=}CH_2 \xrightarrow{h\nu} CCl_2{=}CClCH_2Br,$$
$$CH_3CCl_2CBr{=}CH_2 \xrightarrow[HBr]{Bz_2O_2} CH_3CCl{=}CClCH_2Br,$$
$$CCl_3CH{=}CH_2 + HBr \xrightarrow{Bz_2O_2} HCCl_2CHClCH_2Br.$$

In addition to intramolecular migration of chlorine, intermolecular migration is also possible in a number of cases. This always leads to the formation of side products, as for example in scheme (C) which describes the homolytic addition of thiols to 3,3,3-trichloropropene with the formation of the rearranged compounds (V) (pathway *a*, *b*, *c*) and the unsaturated compounds (IV) plus hydrogen chloride (pathway *a*, *d*, *e*):

(C)
$$\begin{array}{ccccc} \dot{S}R + CCl_3CH{=}CH_2 & \xrightarrow{a} & CCl_3\dot{C}HCH_2SR & \xrightarrow{d} & CCl_2{=}CH{-}CH_2SR + Cl \\ & & & & (IV) \\ & & \downarrow b \text{ rearrangement} & & Cl + HSR \xrightarrow{e} HCl + \dot{S}R \\ \dot{S}R + HCCl_2CHClCH_2SR & \xleftarrow[c]{HSR} & \dot{C}Cl_2CHClCH_2SR. & & \\ (V) & & & & \end{array}$$

III. RADICAL REARRANGEMENTS WITH MIGRATION OF ARYL GROUPS

A. 1,2-Migration of Aryl Groups

A number of free-radical rearrangements involving 1,2-migration of aryl groups are known. The first such rearrangement, for the neophyl radical, was described by Urry and Kharasch[67] in 1944. They found that when phenylmagnesium bromide is allowed to react with 1-chloro-2-phenyl-2-methylpropane(neophyl chloride) in the presence of cobalt chloride, hydrocarbons (I)–(IV) are formed in 55% yield, which corresponds to 50% rearrangement. The following scheme was proposed:

$$C_6H_5MgBr + CoCl_2 \rightarrow C_6H_5CoCl + MgBrCl,$$
$$2C_6H_5CoCl \rightarrow C_6H_5C_6H_5 + 2CoCl^{\cdot},$$
$$C_6H_5C(CH_3)_2CH_2Cl + CoCl^{\cdot} \rightarrow C_6H_5C(CH_3)_2\dot{C}H_2 + CoCl_2,$$
$$C_6H_5C(CH_3)_2\dot{C}H_2 \xrightarrow{ether} \underset{(I)}{C_6H_5C(CH_3)_2CH_3},$$
$$C_6H_5C(CH_3)_2\dot{C}H_2 \xrightarrow{rearrangement} \dot{C}(CH_3)_2CH_2C_6H_5,$$

$$C_6H_5CH_2\dot{C}(CH_3)_2 \rightarrow \begin{cases} CH_3 \\ | \\ C_6H_5CH_2C{=}CH_2 \quad (II) \\ + \\ C_6H_5CH_2CH(CH_3)_2 \quad (III) \end{cases} \qquad C_6H_5CH_2\dot{C}(CH_3)_2 \rightarrow \begin{cases} CH_3 \\ | \\ C_6H_5CH{=}C{-}CH_3 \quad (IV) \\ + \\ III. \end{cases}$$

An analogous rearrangement takes place in the decarbonylation of β-phenylisovaleraldehyde catalysed by di-t-butyl peroxide, which results in approximately identical yields of t-butylbenzene and isobutylbenzene[68]. Seubold[69] studied the effect of dilution and temperature on the rearrangement in this reaction. He found that the ratio of the reaction products (isobutylbenzene : t-butylbenzene) to a large extent depends on the concentration of the aldehyde and only little on the temperature (see Table 4).

The dependence of the extent of rearrangement on the concentration suggests that the rearrangement involves the formation of a free neophyl radical with subsequent migration of the phenyl group, resulting in the formation of the phenylisobutyl radical:

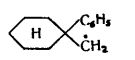
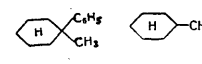
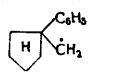
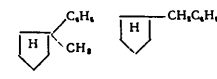
$$R_1\dot{C}O \xrightarrow{k_1} \dot{R}_1 + CO,$$
$$\dot{R}_1 + R_1CHO \xrightarrow{k_2} R_1H + R_1\dot{C}O,$$
$$\dot{R}_1 \xrightarrow[k_3]{rearrangement} \dot{R}_2,$$
$$\dot{R}_2 + R_1CHO \xrightarrow{k_4} R_2H + R_1\dot{C}O,$$
$$\frac{(R_2H)}{(R_1H)} \simeq \frac{d(R_2H)}{d(R_1H)} = \frac{k_3}{k_2(R_1CHO)}.$$

Another possibility, by analogy with heterolytic rearrangements, is that the phenyl group participates in the reaction

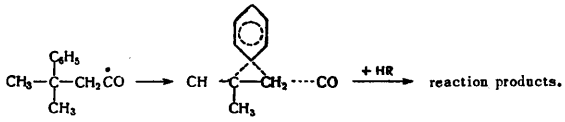
TABLE 4.

Temp., °C	Molar concn. of aldehyde in chlorobenzene	% rearrangement
130	6.4	51
130	1	80
130, 150	without solvent	57±3
170	ditto	63±3

TABLE 5. Decarbonylation of aldehydes (RCHO) on heating to 130°–150°.

No.	R	Migrating group	Temperature, °C	Products (overall yield, %)	% rearrangement	Reference
1	$C_6H_5C(CH_3)_2CH_2$	C_6H_5	130	$C_6H_5C(CH_3)_2CH_3$, $C_6H_5CH_2CH(CH_3)_2$ 71	57±3	68,69
2	$CH_3C_6H_4C(CH_3)_2CH_2$	p-$CH_3C_6H_4$	130	$CH_3C_6H_4C(CH_3)_2CH_3$, $CH_3C_6H_4CH_2CH(CH_3)_2$, $CH_3C_6H_4CH_2C(CH_3)=CH_2$, $CH_3C_6H_4CH=C(CH_3)_2$ 55	48–49	78
3	$(C_6H_5)_2C(CH_3)CH_2$	C_6H_5		$[C_6H_5CH_2C(CH_3)C_6H_5]_2$ 34	100	26
4	$(C_6H_5)_2C(CH_3)CH_2$	C_6H_5	140	$(C_6H_5)_2CHCH_2C_6H_5$, $(C_6H_5)_2C=CHC_6H_5$ 24.3	96	27
5	$(C_6H_5)_2C(CH_3)CH$	C_6H_5		$(C_6H_5)_2CHCH(CH_3)C_6H_5$, $(C_6H_5)_2C=C(CH_3)C_6H_5$ 33	100	26
6	p-$NO_2C_6H_4C(C_6H_5)_2CH_2$	p-$NO_2C_6H_4$	140	p-$NO_2C_6H_4CH=C(C_6H_5)_2$ unidentified p-nitrophenyl-hydrocarbon 4	80	27
7		C_6H_5	140	 47	89	70,79
8		C_6H_5	140	 74	63	70,79
9	$CH_3OC_6H_4CD(C_6H_5)CH_3$	C_6H_5 or $CH_3OC_6H_4$	140	$CH_3OC_6H_4CD(C_6H_5)CH_3$ 45–50	0	27
10	$C_6H_5{}^{14}CH_2CH_3$	C_6H_5	145–150 (in chlorobenzene)	$C_6H_5{}^{14}CH_2{}^{(14)}CH_3$, $C_6H_5{}^{14}CH{}^{(14)}CH_2$ 67.8	3.3±0.1	24
11	$C_6H_5CH_2C(CH_3)_2CH_3$	C_6H_5		$C_6H_5CH_2CH(CH_3)_2$	0	78

through a bridge-type transition state, for example as follows:



Here the proportion of the reaction product should not depend on the concentration of the hydrogen donor, in this case aldehyde. It is noteworthy that the 1,1-dimethyl-2--phenylethyl radical obtained by the decarbonylation of the corresponding aldehyde does not rearrange to the neophyl radical (No. 11 in Table 5).

Later[9,24,70] it was shown that the extent of rearrangement during the decarbonylation of aldehydes decreases on addition of a hydrogen donor, for example, toluene-ω-thiol or thiophenol, to the reaction mixture. Such a reaction may be represented as follows:

$$RSH + \dot{A} \rightarrow R\dot{S} + AH,$$
$$R\dot{S} + R_1CHO \rightarrow RSH + R_1\dot{C}O,$$
$$R_1\dot{C}O \rightarrow \dot{R}_1 + CO,$$
$$\dot{R}_1 \xrightarrow{RSH} R_1H + R\dot{S}$$
$$\dot{R}_1 \xrightarrow{\text{rearrangement}} \dot{R}_2,$$
$$\dot{R}_2 + RSH \rightarrow R_2H + R\dot{S},$$

where R = C_6H_5, $C_6H_5CH_2$.

The chain transfer constants for mercaptans are known to be much higher than for aldehydes[71,72], *i.e.* mercaptans are better hydrogen donors in free-radical reactions than aldehydes. This confirms the data obtained by Slaugh[24], who found that the side chain of the ethylbenzene obtained in the decarbonylation of 3-phenylpropionaldehyde in the presence of tritium-labelled toluene-ω-thiol contained tritium. Thus addition of the mercaptan shortens the life

of the radical so that the latter does not have time to undergo rearrangement. Seubold[69] explains the absence of rearrangement in the peroxide-catalysed chlorination of t-butylbenzene[73] by the fact that the rate of the reaction of the neophyl radical with chlorine is higher than the rate of the rearrangement.

The small temperature dependence of the relative yields of the reaction products shows that the activation energy for the rearrangement and for the removal of hydrogen from the aldehyde are approximately the same. For the latter process, $E = 7-8$ kcal mole^{-1}§. Seubold[69] also quotes the heat of migration of the phenyl group in the neophyl radical:

$$\dot{H} + C_6H_5C(CH_3)_2\dot{C}H_2 \rightarrow C_6H_5C(CH_3)_2CH_3 + 95.5 \text{ kcal mole}^{-1}$$

(it is assumed that this quantity is the same as in neopentane),

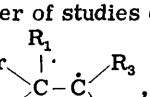
$$C_6H_5CH_2CH(CH_3)_2 \rightarrow C_6H_5CH_2\dot{C}(CH_3)_2 + \dot{H} - 86.5 \text{ kcal mole}^{-1}$$

(as in isobutane),

$$\frac{C_6H_5C(CH_3)_2CH_3 \rightarrow C_6H_5CH_2CH(CH_3)_2 - 0.3 \text{ kcal mole}^{-1},}{C_6H_5C(CH_3)_2\dot{C}H_2 \rightarrow C_6H_5CH_2\dot{C}(CH_3)_2 + 8.7 \text{ kcal mole}^{-1}.}$$

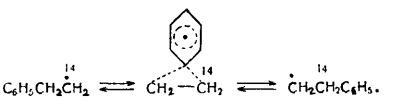
Apart from the above examples, the rearrangement of the neophyl radical was also observed in the decomposition of β-phenylisovaleryl peroxide[74], when bromine was allowed to react with the silver salt of β-phenylisovaleric acid. Here, however, contradictory results were obtained: Berr[75] and Wilt[76] state that there is no rearrangement in the reaction, whereas Smith and Sellas[77] found the extent of rearrangement to be 52%. In general, the extent of rearrangement should depend on the relative rate of the rearrangement of the radical with respect to the rates of the competing reactions (substitution, disproportionation, etc.). The dependence of the extent of rearrangement on the rates of the competing reactions is particularly evident (as described above) in the case of the neophyl radical (dependence on the hydrogen donor concentration, absence of rearrangement in the chlorination of t-butylbenzene, etc.).

From a comparison of the extent of rearrangement in a series of similar reactions, assuming that the rates of the competing reactions change little within a given series, the qualitative dependence of the rate of isomerisation on the structure of the radicals can be determined.

A number of studies on the rearrangement of radicals of the type , where R_1 and R_2 = H, CH_3, Ar, and R_3 and R_4 = H, Alk are summarised in Tables 5 and 6. Great care must be exercised in comparing radicals which were obtained in different reactions and consequently had different lifetimes. Even in a series of similar reactions, as for example in the decarbonylation of aldehydes, the radicals formed in the intermediate stage are stabilised at different rates and sometimes even by different pathways because of the differences in the structure of the aldehydes and their transfer constants. For instance, in the decarbonylation of phenylisovaleraldehyde (No. 1 in Table 5) the radicals react by removing a hydrogen atom from the aldehyde, whereas in the decarbonylation of β,β-diphenylbutyraldehyde (No. 3 in Table 5) the radicals dimerise; under these conditions triphenylethyl radicals (No. 4 in Table 5) are stabilised mainly by disproportionation.

Rearrangement depends markedly on the degree of substitution at the β-carbon atom, the quantity of rearranged products increasing with increase in the number of substituents. This increase may be due to a number of factors: steric strain in the initial radical, the tendency to form a more stable radical (the rearrangement of a primary to a secondary or tertiary radical), etc. (*cf.* Nos. 1, 10, and 11 in Table 5 and 1, 2, and 3 in Table 6).

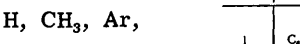
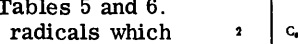
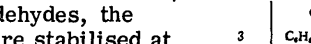
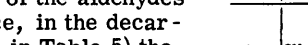
In the case of the phenylethyl radical (No. 10 in Table 5 and No. 1 in Table 6) structural factors favouring rearrangement are lacking. Here rearrangement may be effected by the formation of a bridge-type transition state, in which the unpaired electron is delocalised over the benzene ring:



As a result, 50% rearrangement might be expected. However, in practice this equilibrium is not attained and the yields of rearranged products prove to be much lower. Thus when [2-^{14}C]-3-phenylpropionaldehyde is decarbonylated, rearrangement takes place to the extent of only a few per cent. As with the neophyl radical, the rearrangement depends on dilution and on the addition of mercaptan, which is interpreted as proof that the reaction goes *via* the free [^{14}C]-2-phenylethyl radical. In this case the extent of rearrangement increases with the temperature. Thus, unlike the case of the neophyl radical, the activation energy for the migration of the phenyl group in the phenylethyl radical is somewhat higher than the energy required for the removal of a hydrogen atom from the aldehyde.

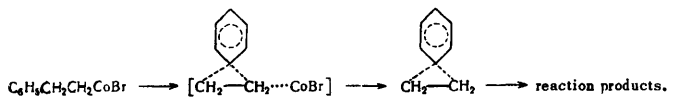
The appreciable rearrangement in the reaction of 2-phenylethyl bromide with magnesium in the presence of cobalt bromide (No. 1 in Table 6) may be explained by the

TABLE 6. Rearrangements in Grignard reactions in the presence of cobalt salts.

No.	R	Reaction	Products (overall yield, %)	% rearrangement	Reference
1		RBr+Mg+CoBr$_2$	 44	19—20	80
2		RBr+Mg+CoBr$_2$	 17	40	80
3		RCl+C$_6$H$_5$MgBr+CoCl$_2$	 55	50	67
4		RCl+C$_6$H$_5$MgBr+CoCl$_2$	 54.6	36	78

§ Signs of the heats have been changed throughout to conform with English notation (Ed. of Translation).

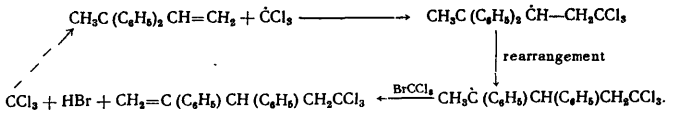
long lifetime of the radical in this reaction. It is also possible that decomposition of phenylethylcobalt halide proceeds in step with the rearrangement, for example [80]:



The question of the formation of non-classical transition states may be resolved by studying the stereospecificity of group migration.

The rearrangement is also considerably influenced by the nature of the substituent at the β-carbon atom. Curtin and coworkers [26,27] studied the decarbonylation of a number of aryl-substituted aldehydes (Nos. 3, 4, 5, 6, and 9 in Table 5). Their results show that when the methyl groups of the neophyl radical are replaced by phenyl groups, the capacity of the radicals to undergo rearrangement increases. Thus, in the decarbonylation of β,β-diphenylbutyraldehyde, β,β,β-triphenylpropionaldehyde, and β,β,β-triphenyl-α--methylpropionaldehyde, only rearranged products were obtained. Rearrangement of the β,β,β-triphenylethyl radical was also observed in the thermal decomposition of $(C_6H_5)_3CCH_2CN{=}NCCH_2C(C_6H_5)_3$, resulting in the formation of β,β,α-triphenylethane and triphenylethylene in approximately equal amounts [81].

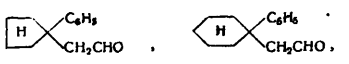
A rearrangement was also found to occur [82] in the peroxide--catalysed addition of butyraldehyde to 3,3-diphenylbut-1--ene, the reaction yielding 2,3-diphenyloctan-4-one. A similar rearrangement was observed [83] in the reaction of this diphenylbutene with bromotrichloromethane in the presence of benzoyl peroxide:



It is interesting that in the homolytic addition of butane thiol or thiolacetic acid to the same diphenylbutene there is no migration of the phenyl group.

The presence of the p-methoxyphenyl group in α-phenyl--α-(p-methoxyphenyl)ethyl radical (No. 9 in Table 5) suppresses rearrangement, the only product of the reaction being α-phenyl-α-(p-methoxyphenyl)ethane.

Very few data are available on the effect of other substituents. Wilt and Philip [70,79] studied the effect on the rearrangement of the incorporation of the cyclopentyl and cyclohexyl rings in the aldehyde molecule. They found that, in the t-butyl peroxide catalysed decarbonylation of aldehydes with structures



the size of the ring appreciably influences the extent of rearrangement (Nos. 7 and 8 in Table 5). The effect of temperature and mercaptans is shown in Table 7. The marked influence of toluene-ω-thiol on the rearrangement

TABLE 7.

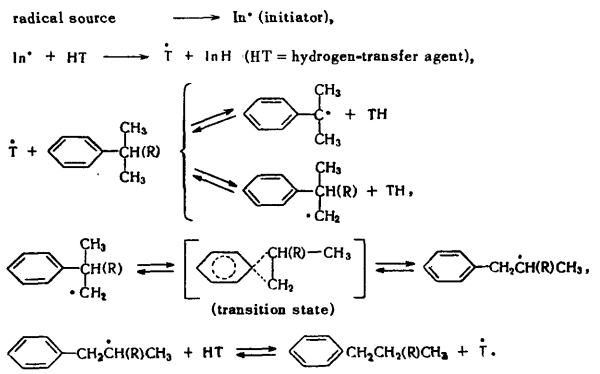
R	% rearrangement at various temperatures			
	140°	190°	132° (in chlorobenzene)	160° (20 mole % toluene-ω-thiol)
1-Phenylcyclopentyl	63	71	92	3
1-Phenylcyclohexyl	89	91	94	50

was interpreted by the authors as a confirmation of the free-radical mechanism, the following radicals participating in the reaction:



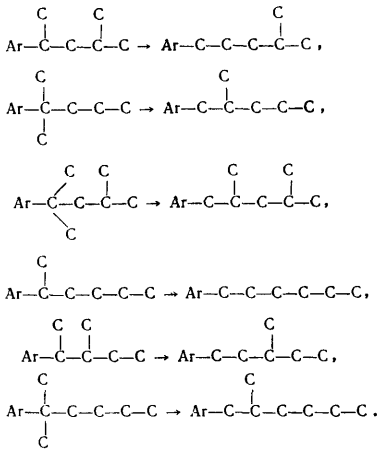
The percentage rearrangement was calculated from the proportions of the hydrocarbons formed, which were obtained in 64–74% yield in the case of the cyclopentyl derivative, and in 21–47% in the case of the cyclohexyl derivative.

The concept of 1,2-migration of the phenyl group was used to explain the isomerisation of certain alkylbenzenes during pyrolysis at high pressure [84,85]. When isopropylbenzene, p-isopropyltoluene, and s-butylbenzene were passed through a heated copper tube (816 atm, 479°–528°), n-propylbenzene, p-n-propyltoluene, and n-butylbenzene (the last in small yield) were obtained respectively, as well as other products [85]. Quite recently Slaugh and Raley [85] found that when these alkylbenzenes are pyrolysed in an autoclave in the presence of effective chain-transfer agents, the yields of the rearranged alkylbenzenes increase. Chain-transfer agents such as C_6H_5SH, H_2S, etc. are either introduced directly or are formed as a result of pyrolysis of halogen- or sulphur-containing promoters. The authors believe the best promoters to be organic bromo-derivatives. The following mechanism was proposed for this isomerisation:

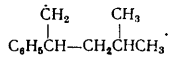


The relatively difficult removal of a hydrogen atom from the β-position in isopropylbenzene appears to be facilitated by the removal of the resulting radical from the equilibrium system by the 1,2-migration of the phenyl group followed by further reactions of the isomeric radical.

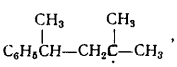
Similar isomerisations with 1,2-migration of the aryl group were also observed in the thermal alkylation (410–420 atm, 400°–485°) of alkylbenzene with olefines[86-88], in the following systems:



For example, alkylation of ethylbenzene with isobutene[86] yielded 2-methyl-4-phenylpentane and 1-phenyl-4-methylpentane, the formation of which is explained by the migration of the phenyl group in the radical



The latter may arise either as a result of 1,4-migration of hydrogen in the radical intermediate formed during the alkylation,



or by the removal of hydrogen from the α-methyl group in 2-methyl-4-phenylpentane (*cf.* isomerisation of alkylbenzenes).

B. Radical Rearrangements with 1,2-Migration of Aryl Groups from Carbon to Oxygen

According to thermochemical calculations, rearrangement of alkoxy radicals ($R_3C-\dot{O}$) with migration of substituents to oxygen should be accompanied by a gain in energy[89]. However, in practice such rearrangements are observed only in radicals containing three aryl groups: $Ar_3C-\dot{O} \rightarrow Ar_2\dot{C}-OAr$. Kharasch *et al.*[90] concluded that the formation of the diphenyl ether of benzopinacol in the thermal decomposition of triphenylmethyl peroxide[91] and triphenylmethyl hyponitrite[92], and in the decomposition of triphenylmethyl hydroperoxide in the presence of ferrous salts, goes *via* the rearrangement of the free radical:

$$(C_6H_5)_3C-\dot{O} \rightarrow (C_6H_5)_2\dot{C}-OC_6H_5 \rightarrow \text{dimer.}$$

Direct confirmation of the formation of free radicals when hydroperoxides are decomposed in the presence of ferrous salts was obtained by Kharasch and his coworkers[93] in the reactions of t-butoxy and α-cumyloxy radicals. In the presence of butadiene, products expected for a reaction between radicals and an olefine were obtained:

$$ROOH + Fe^{2+} \rightarrow R\dot{O} + FeOH^{2+},$$
$$R\dot{O} + CH_2{=}CH{-}CH{=}CH_2 \rightarrow (ROC_4H_6)^{\cdot};$$
$$2\,(ROC_4H_6)^{\cdot} \rightarrow (ROCH_2CH{=}CHCH_2{-})_2,$$
$$2\,(ROC_4H_6)^{\cdot} \rightarrow ROCH_2CH{=}CHCH_2CH\,(CH{=}CH_2)\,CH_2OR.$$

To determine the relative capacity of aryl groups for migration, Kharasch and his coworkers[94] studied the thermal decomposition of t-butyltriarylmethyl peroxides in cumene solution. The following reaction scheme was proposed:

$$(C_6H_5)_3COOC(CH_3)_3 \rightarrow (C_6H_5)_3C\dot{O} + (CH_3)_3C\dot{O},$$
$$(CH_3)_3C\dot{O} + C_9H_6C(CH_3)_2H \rightarrow C_6H_5(CH_3)_2\dot{C},$$
$$[\text{and also } CH_4 + (CH_3)_2CO \text{ or } (CH_3)_3COH],$$
$$2\,(C_6H_5)_3C\dot{O} \rightarrow 2C_6H_5O(C_6H_5)_2\dot{C} \rightarrow [C_6H_5O(C_6H_5)_2C{-}]_2,$$
$$[C_6H_5O(C_6H_5)_2C{-}]_2 + C_6H_5(CH_3)_2\dot{C} \rightarrow C_6H_5O(C_6H_5)_2C{-}C(CH_3)_2C_6H_5 +$$
$$+ C_6H_5O(C_6H_5)_2\dot{C}.$$

The extent of rearrangement was determined by the hydrolysis of the reaction product with subsequent estimation of the phenols. Before hydrolysis the product contained only slight quantities of phenols. The rearrangements of the radicals $ArC(C_6H_5)_2\dot{O}$ (where Ar = p-$CH_3C_6H_4$, α-naphthyl, p-biphenylyl) were investigated in this way, and the capacity for migration of the groups in the given compounds was assessed from the proportions of the aryloxy derivatives. The mobilities of the phenyl and tolyl radicals proved to be approximately the same. The rate of migration of the α-naphthyl and p-biphenylyl groups is six times greater than that of the phenyl group.

Attempts were also made to compare the capacities for migration of p-nitrophenyl and phenyl groups. The following compounds were obtained in the thermal decomposition of nitrophenyldiphenylmethyl hydroperoxide[95]: phenol, p-nitrophenol, p-nitrobenzophenone, p-nitrophenyldiphenylmethanol, and biphenyl. The large quantity of p-nitrophenol and the absence of benzophenone suggest that the rate of migration of the nitrophenyl group is high compared with that of the phenyl group, but the mechanism of the reaction remains obscure. The results obtained in the thermal decomposition of t-butyl p-nitrophenyldiphenylmethyl peroxide are no more definite[94]:

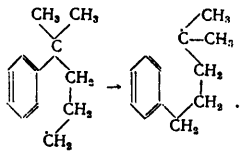
$$p\text{-}NO_2C_6H_4C(C_6H_5)_2{-}O{-}O{-}\ t\text{-}C_4H_9.$$

The results obtained in studies on carbon–carbon rearrangements lead to analogous conclusions about the capacity for migration of certain aryl groups. For example, the proportions of the rearranged and non-rearranged products in the decarbonylation of phenylisovaleraldehyde and p-tolylisovaleraldehyde (Nos. 1 and 2 in Table 5) are similar; this is also the case in the reactions of neophyl chloride and p-methylneophyl chloride with a Grignard reagent in the presence of cobalt chloride (Nos. 3 and 4 in Table 6). It is therefore concluded that the capacities of the phenyl and p-tolyl groups for 1,2-migration are the same. In the decarbonylation of β,β-diphenyl-β-p-nitrophenylpropionaldehyde (No. 6 in Table 5) α-p-nitrophenyl-β,β-diphenylethylene was obtained in 3.3% yield, which constituted approximately 80% of the nitrohydrocarbon monomer fraction. The authors therefore suggested that the p-nitrophenyl group migrates more readily than the phenyl group.

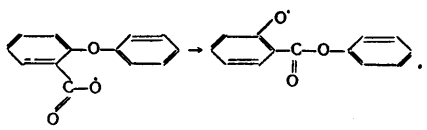
C. Migration of Aryl Groups to a More Distant Radical Centre

There are indications that migration of the phenyl group in free radicals to more distant atoms may be possible.

Winstein *et al.*[9] observed the 1,4-rearrangement in the peroxide-catalysed decarbonylation of 5-methyl-5-phenylhexanal:

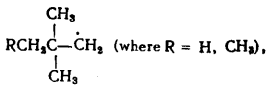


The rearrangement was inferred from the presence of 2-methyl-5-phenylpentane [$C_6H_5CH_2CH_2CH_2CH(CH_3)CH_3$]. In the thermal decomposition of 2-phenoxybenzoyl peroxide[96] phenyl salicylate was obtained, the formation of which the authors explained by the migration of the phenyl group in the free radical:

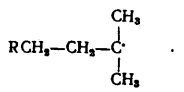


IV. RADICAL REARRANGEMENTS WITH MIGRATION OF ALKYL GROUPS

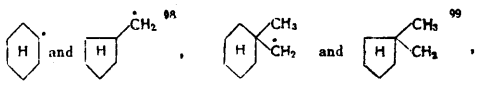
In contrast to carbonium ions in which migration of alkyl groups is frequently observed, hydrocarbon radicals in solution are very stable to such rearrangement. Thus neopentyl[97] and neohexyl[78,98] radicals,



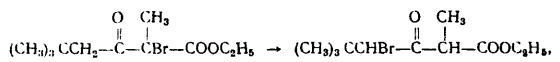
obtained in various ways, do not rearrange to t-pentyl and t-hexyl radicals:



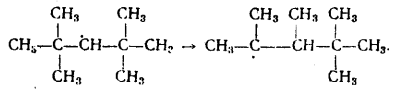
Radicals with the structures



formed in the peroxide-catalysed decomposition of the corresponding aldehydes, also do not undergo isomerisation in which there is a change in the carbon framework. In fact, the absence of migration of the methyl group in the isomerisation of the α-bromoacetoacetic ester[100] containing the neopentyl group,

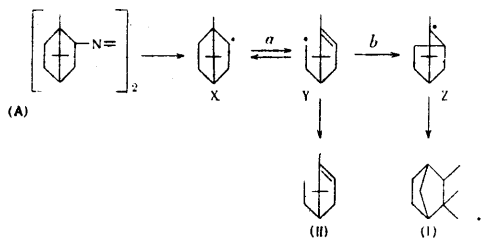


is quoted as proof that the reaction may proceed by a radical mechanism. However, the products obtained in the bromination of 2,2,4,4-tetramethylpentane under ultraviolet illumination (200°) and in the reaction of 3-chloro-2,2,4,4-tetramethylpentane with a Grignard reagent in the presence of $CoBr_2$ are explained by postulating the rearrangement of the initially formed secondary radical to the tertiary radical[101]:

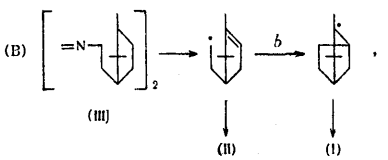


In this case the rearrangement may be due to the structure of the radical in which the methyl groups screen the carbon atom with a free valency; the lifetime of the radical is thereby increased and hence the probability of the rearrangement. It is not impossible, however, that the change in the carbon framework in the above example may be due to a number of other factors, unrelated to homolytic migration of the methyl group (for example, ionic isomerisation of the reaction products).

Isomerisation of alkyl radicals involving rupture of the C–C bond requires considerable activation energy. This is apparently the reason for the low probability of such isomerisation in the liquid phase (at a moderate temperature). At higher reaction temperatures, the migration of alkyl groups becomes more probable. Thus, in the peroxide catalysed decomposition of  at 140°–150°, the bornyl radical formed does not undergo a rearrangement involving rupture of the C–C bond[102]. If, however, the bornyl radical comes from 2,2′-bisazocamphane, the decomposition of which requires temperatures up to 255°–290° (in hexadecane), then homolytic rearrangement (of the Wagner–Meerwein type) of the radical does occur[102]. In addition to disproportionation products of the initially formed bornyl radical, , isocamphane (I) (mixture of stereoisomers) and trimethylethylcyclopentene (II) were isolated in the reaction. The authors explain their formation by the following scheme:

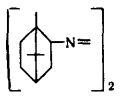


Here the molar ratio (I) : (II) = 0.035 : (> 0.01). To obtain experimental confirmation of this hypothesis, the authors studied the decomposition of the azo-compound (III) under the same conditions and again isolated compounds (I) and (II), the formation of which was represented as follows:

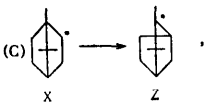


the molar ratio being (I) : (II) = 0.5 : 2.1.

A C–C bond is ruptured in stage *a*, *b* and a new one formed. However, in the decomposition of 2,2′-bisazocamphane,

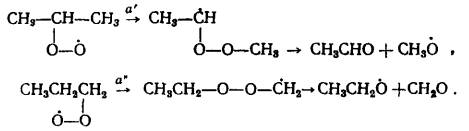


there is also the possibility that the bornyl radical may rearrange as follows:



i.e. radical X rearranges to Z, omitting the stage in which radical Y is formed [scheme (A)]. Otherwise the ratio (I) : (II) in reactions (A) and (B) should be the same.

The probability of such rearrangements becomes greater in the gas phase (at a high temperature)[7,9]. Thus, according to Semenov and his coworkers[7], the appearance of formaldehyde and acetaldehyde in the gas-phase oxidation of propane is due to isomerisation with C–C bond rupture of the normal and branched-chain peroxy radicals formed in the oxidation. The scheme proposed by Semenov and his coworkers includes migration of an alkyl group in stages *a′* and *a″*:



1. W. Hückel, "Theoretical Principles of Organic Chemistry" (Translated into Russian), Vol. 1, Inostr. Lit., Moscow, 1958.
2. J. W. Baker, "Tautomerism" (Translated into Russian), ONTI, 1937.
3. M. J. S. Dewar, "The Electronic Theory of Organic Chemistry", Oxford, 1949, p. 263.
4. G. Dupont, R. Dulou, and G. Clement, Bull. Soc. chim. France, 1056, 1115 (1950).
5. K. O. Kutschke and E. W. R. Steacie, "Vistas in Free-Radical Chemistry", Pergamon, London, 1959, p. 162.
6. C. Walling, "Free Radicals in Solution", Wilen, New York, 1957, p. 267.
7. N. N. Semenov, "O Nekotorykh Problemakh Khimicheskoi Kinetiki i Reaktsionnoi Sposobnosti" (Some Problems of Chemical Kinetics and Reactivity), Izd. Akad. Nauk SSSR, Moscow, 1958.
8. M. Okawa, Kagaku (Kyoto), 10, No. 1, 39 (1955).
9. S. Winstein, R. Heck, S. Lapporte, and R. Baird, Experientia, 12, 138 (1956).
10. G. S. Kolesnikov and S. L. Davydova, Uspekhi Khim., 29, 1474 (1960) [Russ. Chem. Rev., 679 (1960)].
11. P. Gray and A. Williams, Chem. Rev., 59, 239 (1959).
12. N. Brown, M. J. Hartig, M. J. Roedel, A. W. Anderson, and C. E. Schweitzer, J. Amer. Chem. Soc., 77, 1756 (1955).
13. D. M. Oldroyd, G. S. Fischer, and L. A. Goldblatt, J. Amer. Chem. Soc., 72, 2407 (1950).
14. K. Mathur and R. Thakur, J. Chem. Soc., 3231 (1956).
15. C. C. Beard, J. R. B. Boocock, and W. J. Hickinbotton, J. Chem. Soc., 520 (1960).
16. L. Claisen, Ber., 29, 2931 (1896).
17. K. B. Wiberg and B. I. Rowland, J. Amer. Chem. Soc., 77, 1159 (1955).
18. H. H. Glazebrook and T. G. Pearson, J. Chem. Soc., 1777 (1936).
19. M. S. Kharasch, S. S. Kane, and H. C. Brown, J. Amer. Chem. Soc., 63, 526 (1941).
20. M. S. Kharasch, S. S. Kane, and H. C. Brown, J. Amer. Chem. Soc., 64, 1621 (1942).
21. M. S. Kharasch and H. C. Brown, J. Amer. Chem. Soc., 62, 925 (1940).
22. H. C. Brown, "Vistas in Free-Radical Chemistry", Pergamon, London, 1959, p. 207.
23. M. S. Kharasch, F. L. Lambert, and W. H. Urry, J. Org. Chem., 10, 298 (1945).
24. L. H. Slaugh, J. Amer. Chem. Soc., 81, 2262 (1959).
25. W. Smith, J. Org. Chem., 23, 509 (1958).
26. D. Y. Curtin and M. J. Hurwitz, J. Amer. Chem. Soc., 74, 5381 (1952).
27. D. Y. Curtin and G. C. Cauer, J. Org. Chem., 25, 880 (1960).
28. C. G. Overberger and P. Kabasakalian, J. Amer. Chem. Soc., 79, 3182 (1957).
29. O. A. Reutov and T. I. Shatkina, Dokl. Akad. Nauk SSSR, 133, 381 (1960).
30. H. C. Brown and G. A. Russell, J. Amer. Chem. Soc., 74, 3995 (1952).
31. N. Kornblum and E. P. Oliveto, J. Amer. Chem. Soc., 71, 226 (1949).
32. F. O. Rice and E. L. Rodowskas, J. Amer. Chem. Soc., 57, 350 (1935).
33. N. Kornblum and H. E. de la Mare, J. Amer. Chem. Soc., 74, 3079 (1952).
34. R. Durand-Dran, Ann. Chim., 4, 43 (1959).
35. R. A. Jackson and W. A. Waters, J. Chem. Soc., 1653 (1960).
36. A. Kossiakoff and F. Rice, J. Amer. Chem. Soc., 65, 590 (1943).
37. H. H. Voge and G. M. Good, J. Amer. Chem. Soc., 71, 593 (1949).
38. C. A. Grob and H. Kammüller, Helv. Chim. Acta, 40, 2139 (1957).
39. D. F. de Tar and C. Weis, J. Amer. Chem. Soc., 78, 4296 (1956).
40. D. F. de Tar and D. I. Relyea, J. Amer. Chem. Soc., 78, 4302 (1956).
41. M. J. Roedel, J. Amer. Chem. Soc., 75, 6110 (1953).
42. W. M. D. Bryant and R. C. Voter, J. Amer. Chem. Soc., 75, 6113 (1953).
43. C. D. Cook, N. G. Nash, and H. R. Flanagan, J. Amer. Chem. Soc., 77, 1783 (1955).
44. A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, Dokl. Akad. Nauk SSSR, 96, 87 (1954).
45. D. N. Kursanov and V. V. Voevodskii, Uspekhi Khim., 23, 641 (1954).
46. C. Walling, "Free Radicals in Solution", Wiley, New York, 1957, p. 53.
47. Kh. S. Bagdasar'yan, Zhur. Fiz. Khim., 23, 1375 (1949).
48. L. Schmerling and J. P. West, J. Amer. Chem. Soc., 71, 2015 (1949).
49. L. Schmerling and J. P. West, J. Amer. Chem. Soc., 75, 6216 (1953).
50. M. S. Kharasch and M. Sage, J. Org. Chem., 14, 537 (1949).
51. K. E. Wilzbach, F. R. Mayo, and R. Van Meter, J. Amer. Chem. Soc., 70, 4069 (1948).
52. A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, Dokl. Akad. Nauk SSSR, 81, 199 (1951).

53. V. N. Kost, T. T. Sidorova, R. Kh. Freidlina, and A. N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 132, 606 (1960).
54. A. N. Nesmeyanov, R. Kh. Freidlina, and A. B. Belyavskii, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1028 (1959).
55. R. Kh. Freidlina, V. N. Kost, M. Ya. Khorlina, and A. N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 128, 316 (1959).
56. R. Kh. Freidlina, M. Ya. Khorlina, and A. N. Nesmeyanov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 658 (1960).
57. R. Kh. Freidlina, V. N. Kost, M. Ya. Khorlina, and A. N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 137, 341 (1961).
58. A. N. Nesmeyanov, R. Kh. Freidlina, and V. N. Kost, Dokl. Akad. Nauk SSSR, 113, 828 (1957); Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1205 (1958).
59. A. N. Nesmeyanov, R. Kh. Freidlina, R. G. Petrova, and A. B. Terent'ev, Dokl. Akad. Nauk SSSR, 127, 575 (1959).
60. A. N. Nesmeyanov, R. Kh. Freidlina, A. B. Terent'ev, and R. G. Petrova, Dokl. Akad. Nauk SSSR, 138, 859 (1961).
61. A. N. Nesmeyanov, R. Kh. Freidlina, and V. N. Kost, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1199 (1958).
62. M. Ya. Khorlina and V. N. Kost, Dokl. Akad. Nauk SSSR, 137, 1133 (1961).
63. R. Kh. Freidlina, V. N. Kost, T. T. Vasil'eva, and A. N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 137, 1385 (1961).
64. W. H. Urry and J. R. Eiszner, J. Amer. Chem. Soc., 74, 5822 (1952).
65. W. H. Urry and J. W. Wilt, J. Amer. Chem. Soc., 76, 2594 (1954).
66. M. S. Kharasch and A. F. Zavist, J. Amer. Chem. Soc., 73, 964 (1951).
67. W. H. Urry and M. S. Kharasch, J. Amer. Chem. Soc., 66, 1438 (1944).
68. S. Winstein and F. H. Seubold, J. Amer. Chem. Soc., 69, 2916 (1947).
69. F. H. Seubold, J. Amer. Chem. Soc., 75, 2532 (1953).
70. J. W. Wilt and H. Philip, J. Org. Chem., 24, 441 (1959).
71. C. Walling, J. Amer. Chem. Soc., 70, 2561 (1948).
72. R. A. Gregg, D. M. Alderman, and F. Mayo, J. Amer. Chem. Soc., 70, 3740 (1948).
73. M. S. Kharasch and H. C. Brown, J. Amer. Chem. Soc., 61, 2142 (1939).
74. L. Kent, Unpublished work, quoted in ref. 9.
75. C. Berr, Thesis, University of California, Los Angeles, 1952.
76. J. Wilt, J. Amer. Chem. Soc., 77, 6397 (1955).
77. W. Smith and J. Sellas, Trans. Kentucky Acad. Sci., 16, 72 (1955).
78. W. Urry and N. Nicolaides, J. Amer. Chem. Soc., 74, 5163 (1952).
79. J. W. Wilt and H. Philip, J. Org. Chem., 25, 891 (1960).
80. W. B. Smith and J. D. Anderson, J. Amer. Chem. Soc., 82, 656 (1960).
81. D. Y. Curtin and T. C. Miller, J. Org. Chem., 25, 885 (1960).
82. J. Weinstock and S. Lewis, J. Amer. Chem. Soc., 79, 6243 (1957).
83. R. Kh. Freidlina, G. T. Martirosyan, and A. N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 137, 1129 (1961).
84. V. N. Ipatieff, B. Kvetinskas, E. E. Meisinger, and H. Pines, J. Amer. Chem. Soc., 75, 3323 (1953).
85. L. H. Slaugh and J. H. Raley, J. Amer. Chem. Soc., 82, 1259 (1960).
86. H. Pines and J. T. Arrigo, J. Amer. Chem. Soc., 79, 4958 (1957).
87. H. Pines and C. N. Pillai, J. Amer. Chem. Soc., 81, 3629 (1959).
88. V. N. Ipatieff, H. Pines, and B. Kvetinskas, U. S. P. 2758140 (1956); Chem. Abs., 51, 16532 (1957).
89. P. Gray and A. Williams, Chem. Rev., 59, 261 (1959).
90. M. S. Kharasch, A. Fono, and W. Nudenberg, J. Org. Chem., 15, 763 (1950).
91. H. Wieland, Ber., 44, 2553 (1911).
92. M. A. Spielman, J. Amer. Chem. Soc., 57, 1117 (1935).
93. M. S. Kharasch, F. S. Arimoto, and W. Nudenberg, J. Org. Chem., 16, 1556 (1951).
94. M. S. Kharasch, A. C. Poshkus, A. Fono, and W. Nudenberg, J. Org. Chem., 16, 1458 (1951).
95. P. D. Bartlett and J. D. Cotman, J. Amer. Chem. Soc., 72, 3095 (1950).
96. D. de Tar and A. Hlynsky, J. Amer. Chem. Soc., 77, 4411 (1955).
97. F. C. Whitmore, A. H. Popkin, H. I. Bernstein, and J. P. Wilkins, J. Amer. Chem. Soc., 63, 124 (1941).
98. F. H. Seubold, J. Amer. Chem. Soc., 76, 3732 (1954).
99. M. A. Muhs, Thesis, quoted by H. Breederveld and E. C. Kooyman, Rec. Trav. chim., 76, 305 (1957).
100. E. Reid and R. Fortenbaugh, J. Org. Chem., 16, 33 (1951).
101. M. S. Kharasch, Yu Cheng Liu, and W. Nudenberg. J. Org. Chem., 19, 1150 (1954).
102. J. A. Berson, C. J. Olsen, and J. S. Walia, J. Amer. Chem. Soc., 82, 5000 (1960).

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THE STEREOCHEMISTRY AND MECHANISM OF DEHYDRATION OF CYCLOHEXANE DERIVATIVES

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INTRODUCTION

Since van't Hoff formulated the principles of the stereochemistry of tetravalent carbon, the attention of chemists has constantly been attracted to problems connected with the steric course of the fundamental chemical reactions, such as addition, elimination, and replacement, and with the differences in reactivity between geometric isomers. From a formal examination of the tetrahedral models of van't Hoff, it appeared natural that in substitution the entering atoms or group of atoms should occupy the same position as the leaving group, and that addition and elimination reactions should proceed most readily when the entering or leaving groups are as close as possible. This