

ADVANCES IN FREE-RADICAL CHEMISTRY

Volume 6

Edited by

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Advances in free radical chemistry.

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PREFACE

This volume is the first to be produced by the new publishers, Heyden & Son, and in preparing it, the policies followed in the previous volumes in this series have been continued. Since Volume 5 appeared in 1975, free-radical chemistry has advanced rapidly on several fronts, and in this new volume the review literature is brought up to date on several aspects of this branch of chemistry. It is a particular pleasure to welcome an article by Drs R. Kh. Freidlina and A. B. Terent'ev on radical rearrangements, and it is fascinating to observe the progress which has been made in this field since Dr Freidlina herself reviewed it in the first volume of this series. Dr F. Minisci has, in recent years, shown in a series of distinguished papers how polar effects can be used to effect great improvements in synthetic procedures based on free-radical reactions, particularly in respect of their selectivity. The chapter by Dr Minisci and A. Citterio is therefore timely. The contributions of Professor Lord Tedder and Dr J. C. Walton in the field of homolytic halogenation, of Professor J. I. G. Cadogan in solving the historic problems associated with the chemistry of acylarylnitrosamines, and of Dr B. P. Roberts in the free radical chemistry of phosphorus, are well known, and articles from them are therefore most welcome. Literature is covered in this volume generally up to late 1978. As in previous volumes, comprehensive author and subject indexes are provided.

December, 1979

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CONTENTS

Preface	vii
----------------	-----

List of Contributors	ix
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Rearrangement of Short-lived Radicals in the Liquid Phase	1
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R. Kh. Freidlina and A. B. Terent'ev

1. Introduction	1
2. Rearrangement of Radicals Involving Hydrogen Shift	2
3. Rearrangement of Radicals Involving Halogen Shift	15
4. Rearrangement of Radicals Involving Migration of Aryl Groups	32
5. Rearrangement of Radicals Involving Shift of Organoelement Groups	40
6. Radicalotropy	50
7. On the Mechanism and General Patterns of Liquid Phase Rearrangement of Unstable Radicals	53
References	55

Polar Effects in Free-Radical Reactions in Synthetic Chemistry	65
---	----

Francesco Minisci and Attilio Citterio

1. Introduction	65
2. General Concepts	65
3. Free-Radical Aliphatic Substitutions	68
4. Free-Radical Aromatic Substitutions	88
5. Free-Radical Addition to Olefins	115
6. Miscellaneous	125
7. Polar Effects and the Reactivity-Selectivity Relationship	134
References	136

The Halogenation of the Cycloalkanes and their Derivatives	155
---	-----

John M. Tedder and John C. Walton

1. Introduction	155
2. The Formation and Reactivity of the Cycloalkyl Radicals	155
3. The Mechanism of the Halogenation of Cycloalkanes	161
4. The Halogenation of Cyclopropane and its Derivatives	164
5. Directive Effects in the Gas Phase Chlorination of the Substituted Cycloalkanes	169
6. Directive Effects in the Liquid Phase Chlorination of Substituted Cycloalkanes	171
7. Bromination of the Cycloalkanes	173

8. The Stereochemistry of the Halogenation of the Cycloalkanes	175
9. Conclusions	181
References	182

The Mechanistic Role of Radicals, Ions, and Arynes in Reactions of Acylarylnitrosamines 185

J. I. G. Cadogan

1. Introduction	185
2. Reactions of <i>N</i> -Nitrosoacetanilide in Aromatic Solvents	186
3. Reactions of <i>N</i> -Nitrosoacetanilide in Polyhalogenomethanes	214
4. Summary	221
References	221

The Chemistry of Phosphoranyl Radicals 225

Brian P. Roberts

1. Introduction	225
2. Formation of Phosphoranyl Radicals	226
3. Structures of Phosphoranyl Radicals	238
4. Stereochemical Non-Rigidity of Phosphoranyl Radicals	249
5. Fragmentation of Phosphoranyl Radicals	261
6. Reactions of Phosphoranyl Radicals	278
References	284

Author Index 291

Subject Index 315

REARRANGEMENT OF SHORT-LIVED RADICALS IN THE LIQUID PHASE

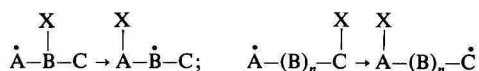
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1. INTRODUCTION

The study of radical rearrangements in the liquid phase is a rapidly developing branch of free radical chemistry, as may be seen from the increased number of review papers on the subject.¹⁻⁹ Nevertheless even in the most recent reviews,^{1,2} the authors claim radical rearrangements to be far less frequent than rearrangements of carbonium ions. As Professor J. M. Tedder pertinently remarked in the Introduction to the monograph,¹ 'The study of free radicals is the Cinderella of organic chemistry', and further: 'In the majority of textbooks on organic chemistry free radical reactions are treated as a special and rather unusual class of reactions despite the fact that in industry and possibly also in nature, one-electron transfers are more common than those involving electron pairs'. No wonder then that radical rearrangements share the fortunes of other topics in radical chemistry. In our view, the ability to rearrange is a general property of radicals, like their ability to recombine, fragment, disproportionate, etc.

The present work covers the period 1965 to 1977. Earlier papers are only included when essential to arguing. Like our previous review,⁵ this one is limited to rearrangements proper involving intraradical shifts of atoms or groups of atoms, which may schematically be written as



During the past years much work has been done on rearrangements of familiar types; on the other hand, more or less conclusive evidence has been presented of certain novel rearrangement processes such as reversible radical isomerization which we call radicalotropy, rearrangements of organoelement radicals involving shifts of R_3Si - and R_3Ge -groups, 1,5 and 1,6 H-shifts in vinyl radicals, 1,2 Cl-shifts in monochlorohydrocarbon radicals, 1,2 Cl-shifts in polymerization of polyhalopropylenes. The field of telomerization reactions involving 1,3 and 1,5 H-shifts and of reactions involving 1,2 Br- and RS-group shifts has been broadened essentially. The section 'Unusual Rearrangements' (p. 11) includes data on

rearrangements of more stable radicals into less stable ones. Important results deepening our understanding of the phenomenon have been obtained during the period in question. Thus, the radical mechanism has been proved rigorously for a large number of reactions involving radical rearrangements by the ESR and ESR spin trapping techniques. The EPR data on 1,2 Cl-shift is discussed in a separate section. Many important results have been obtained in the studies of rearrangements of optically active compounds and of labelled compounds.

2. REARRANGEMENT OF RADICALS INVOLVING HYDROGEN SHIFT

Among rearrangements of various types, those involving hydrogen shifts hold a prominent position which depends not only on their diversity and frequency of occurrence but, in the first place, on their significance for understanding of various important processes such as radical substitution, oxidation, reduction, addition, telomerization and polymerization of olefinic compounds, etc. Data on isomerization of alkyl radicals in the gas phase is given in the review.¹⁰ Rearrangements of biradicals via 1,2 migration of hydrogen or methyl groups have been described;¹¹ these reactions are not considered here. The mechanism of liquid-phase reactions involving H-shift in monoradicals, of course, differs from that of the aforementioned processes and of rearrangements involving transfer of atoms or groups bearing lone pairs or having vacant *d*-orbitals or π -bonds. This may, in particular, be seen from the fact that 1,2 H-shifts (supposing transitions of this type are possible after all) go only with difficulty. H-Shift rearrangements are known which proceed by migration of hydrogen from carbon to non-adjacent carbon, oxygen, or nitrogen atoms bearing unpaired electrons and from one heteroatom to another. The literature data on H-shifts in radicals is summarized in Table 1. Below, we shall only briefly touch on the most interesting points.

2.1. 1,2, 1,3, and 1,4 Hydrogen Shift

Only few examples of rearrangements of these types involving hydrogen transfer from one carbon atom to another or across chains containing heteroatoms are known. These are included in Table 1 under Nos 1–19. The most typical processes are those involving 1,5 or, less frequently, 1,6 H-shifts (see below). It should be noted that the possibility of 1,2 H-shift in the liquid phase has not been proved rigorously thus far.^{2,5}

This transition has been claimed to be symmetry forbidden¹² in agreement with the Woodward-Hoffman rules. According to Dewar and Kirschner,¹³ however, the latter are inapplicable to radical reactions. There seems to be no theoretical objection to the possibility of 1,2 H-shift in radicals, so works suggesting this mechanism do appear from time to time (Table 1, Nos 1, 2). The authors themselves, however, note that their interpretations lack unambiguity.^{14,15}

Only during the last few years, a significant number of reactions have been shown to follow the 1,3 H-shift mechanism. These are, in particular,

TABLE 1
Rearrangement of radicals involving hydrogen shift




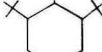
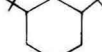
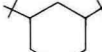
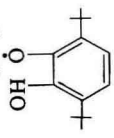
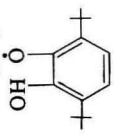
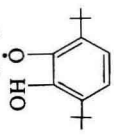
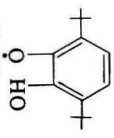



No.	Reagents, reaction conditions	Structure of radicals			Type of migration	Ref.
		Unrearranged	Rearranged			
1. 1,2-, 1,3-, 1,4-Hydrogen shift						
1	$(\text{CH}_3)_2\text{CHCH}_2\text{Br}$, $h\nu$, -196°C	$(\text{CH}_3)_2\text{CH}\dot{\text{C}}\text{H}_2$	$(\text{CH}_3)_2\dot{\text{C}}\text{CH}_3$		1,2 C-C	14
2	$(\text{CH}_3)_2\text{CHCH}_2\text{Br}$, C_6H_5	$(\text{CH}_3)_2\text{CH}\dot{\text{C}}\text{HCH}_2$	$(\text{CH}_3)_2\dot{\text{C}}\text{CH}_3$		1,2 C-C	15
3	$\text{C}_6\text{H}_5\text{NO}$, $\text{C}_6\text{H}_5\text{NHOH}$	$\text{C}_6\text{H}_5\text{NHO}$	$\text{C}_6\text{H}_5\text{NOH}$		1,2 N-O	16
4	(a) $\text{V}(\text{O})(\text{OCH}_3)$ (hinokali) (b) $\text{CH}_3\text{CH}_2\text{OOH}$, Ti^{III}	$\text{RCH}_2\dot{\text{O}}$ ($\text{R} = \text{H}, \text{CH}_3$)	$\text{R}\dot{\text{C}}\text{HOH}$		1,2 C-O	17a
5	$[\text{RCO}_2]_2$, $\text{R} = \text{CH}_3\text{CH}_2\text{CD}_2$ $\text{R} = o\text{-CH}_3\text{C}_6\text{H}_4$	$\text{CH}_3\text{CH}_2\dot{\text{C}}\text{D}_2$ $o\text{-CH}_3\text{C}_6\text{H}_4\dot{\text{C}}\text{H}_2$	$\dot{\text{C}}\text{H}_2\text{CH}_2\text{CD}_2\text{H}$ $\text{C}_6\text{H}_5\dot{\text{C}}\text{H}_2$		1,3 C-C	17b
6	$\text{BrCH}_2(\text{CH}_2)_2\text{CO}_2\text{CH}_3$, $(\text{C}_2\text{H}_5)_3\text{SiH}$, RO	$\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$	$\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCO}_2\text{CH}_3$		1,3 C-C	18, 19
7	$\text{CH}_2\text{XCO}_2\text{R}$, $\text{CH}_2=\text{CHCH}_3$, $\text{R}'\dot{\text{O}}$	$\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{CH}(\text{X})\text{CO}_2\text{R}$	$\text{CH}_3\text{CH}_2\text{CH}_2\dot{\text{C}}(\text{X})\text{CO}_2\text{R}$		1,3 C-C	20
8	CH_2Cl_2 , $\text{CH}_2=\text{CH}_2$, $\text{R}\dot{\text{O}}$	$\text{CHCl}_2\text{CH}_2\dot{\text{C}}\text{H}_2$	$\dot{\text{C}}\text{Cl}_2\text{CH}_2\text{CH}_3$		1,3 C-C	21
9	 , $\text{HO}_2\text{CC}\equiv\text{CCO}_2\text{H}$, $\text{H}\dot{\text{O}}$				1,3 C-C	24
10	$\text{CH}_3\text{COCH}=\text{CHCO}_2\text{C}_2\text{H}_5$, $\text{C}_6\text{H}_5\dot{\text{C}}\text{H}_2$	$\text{CH}_3\text{CO}\dot{\text{C}}\text{HCHCO}_2\text{C}_2\text{H}_5$	$\dot{\text{C}}\text{HC}_6\text{H}_5$		1,3 C-C	25
11	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{H}$, $\text{RC}_6\text{H}_4\text{CH}_3$, DTBP, 300°	$\text{RC}_6\text{H}_4\text{CH}_2\text{CH}_2\dot{\text{C}}(\text{CH}_3)\text{CO}_2\text{H}$	$\text{RC}_6\text{H}_4\dot{\text{C}}\text{HCH}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{H}$		1,3 C-C	26
12	$\text{R}'\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{R})\text{OOH}$	$\text{R}'\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{R})\text{O}\dot{\text{O}}$	$\text{R}'\text{CH}_2\text{CH}_2\text{CH}_2\dot{\text{C}}(\text{R})\text{OOH}$		1,3 C-O	4
13	$\text{HO}_2\text{CC}\equiv\text{CCO}_2\text{H}$, $\text{H}\dot{\text{O}}$	$\text{HOC}(\text{CO}_2\text{H})=\dot{\text{C}}\text{CO}_2\text{H}$	$\text{O}=\text{C}(\text{CO}_2\text{H})\dot{\text{C}}\text{HCO}_2\text{H}$		1,3 O-C	24
14	ArNO , $\text{C}_6\text{H}_5\dot{\text{C}}\text{H}_2$	$\text{Ar}\dot{\text{N}}\text{OCH}_2\text{C}_6\text{H}_5$	$\text{ArNHO}\dot{\text{C}}\text{H}_2\text{C}_6\text{H}_5$		1,3 C-N	27
15	 , Br , $(\text{CH}_3)_3\text{Sn}$				1,4 C-C	28

TABLE 1—continued

No.	Reagents, reaction conditions	Structure of radicals		Type of migration	Ref.
		Unrearranged	Rearranged		
16	$\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ (C_2H_5) ₃ SiH, R $\dot{\text{O}}$	$\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$	$\text{CH}_3\text{CH}_2\text{CH}_2\dot{\text{C}}\text{HCO}_2\text{CH}_3$	1,4 C—C	21
17	$\text{CCl}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ Fe(CO) ₅ , i-C ₄ H ₉ OH	$\dot{\text{C}}\text{Cl}_2(\text{CH}_2)_2\text{CH}_2(\text{CH}_2)_3\text{Cl}$	$\text{CHCl}_2(\text{CH}_2)_2\dot{\text{C}}\text{H}(\text{CH}_2)_3\text{Cl}$	1,4 C—C	29
18	$\text{R}'\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{R})\text{OOH}$	$\text{R}'\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2\text{CH}(\text{R})\text{O}\dot{\text{O}}$ 	$\text{R}'\text{CH}_2\text{CH}_2\dot{\text{C}}\text{HCH}(\text{R})\text{OOH}$	1,4 C—O	4
19	 +, PbO ₂			1,4 O—O	30
2. 1,5- and 1,6-Hydrogen shift in C-centred radicals					
20	$[\text{C}_6\text{H}_5(\text{CH}_2)_3\text{CO}_2]_2$	$\text{C}_6\text{H}_5\dot{\text{C}}\text{H}_2(\text{CH}_2)_3\dot{\text{C}}\text{H}_2$	$\text{C}_6\text{H}_5\dot{\text{C}}\text{H}(\text{CH}_2)_3\text{CH}_3$	1,5 C—C	31
21	$\text{RCH}_2(\text{CH}_2)_4\text{CH}_2\text{CO}_2\text{H}$ R = CH ₃ —C ₇ H ₁₅	$\text{RCH}_2(\text{CH}_2)_4\dot{\text{C}}\text{H}_2$	$\text{RCH}_2\dot{\text{C}}\text{H}(\text{CH}_2)_3\text{CH}_3$	1,5 C—C	32–34
22	$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{COOH}$, S ₂ O ₈ ²⁻ , Ag ⁺ , Cu ^{II}	$\text{CH}_3(\text{CH}_2)_3\dot{\text{C}}\text{H}_2$	$\text{RCH}(\text{CH}_2)_4\text{CH}_3$	1,6 C—C	35
23	$[\text{C}_6\text{H}_5\text{CCH}_2(\text{CH}_2)_3\text{CH}_2\text{CO}_2]_2$	$\text{CH}_3\text{O}_2\text{CCH}_2(\text{CH}_2)_3\dot{\text{C}}\text{H}_2$	$\text{CH}_3\text{O}_2\dot{\text{C}}\text{H}(\text{CH}_2)_3\text{CH}_3$	1,5 C—C	36
24	$\text{BrCH}_2(\text{CH}_2)_4\text{CH}=\text{CH}_2$, (C_4H_9) ₃ Sn	$\dot{\text{C}}\text{H}_2(\text{CH}_2)_4\text{CH}=\text{CH}_2$	$\text{CH}_3(\text{CH}_2)_3\dot{\text{C}}\text{HCH}=\text{CH}_2$	1,5 C—C	37
25	$\text{BrCH}_2(\text{CH}_2)_3\text{CH}_2\text{CO}_2\text{CH}_3$, (C ₂ H ₅) ₃ SiH, R $\dot{\text{O}}$	$\dot{\text{C}}\text{H}_2(\text{CH}_2)_3\text{CH}_2\text{CO}_2\text{CH}_3$	$\text{CH}_3(\text{CH}_2)_3\dot{\text{C}}\text{HCO}_2\text{CH}_3$	1,5 C—C	21
26	$\text{BrCH}_2(\text{CH}_2)_3\text{CH}_2\text{CO}_2\text{CH}_3$, (C ₂ H ₅) ₃ SiH, R $\dot{\text{O}}$	$\dot{\text{C}}\text{H}_2(\text{CH}_2)_3\text{CH}_2\text{CO}_2\text{CH}_3$	$\text{CH}_3(\text{CH}_2)_3\dot{\text{C}}\text{HCO}_2\text{CH}_3$	1,6 C—C	21
27	 , CH ₂ =CH ₂ , R $\dot{\text{O}}$			1,5 C—C	38, 8
28	$\text{RCH}_2\text{CO}_2\text{R}'$, CH ₂ =CH ₂ , R'' $\dot{\text{O}}$, [γ - ⁶⁰ Co] R = H, CH ₃ , C ₂ H ₅ , C ₄ H ₉ , CN, CO ₂ R', Cl R' = H, CH ₃	$\text{RCH}_2\text{CH}_2\dot{\text{C}}\text{H}(\text{R})\text{CO}_2\text{R}'$	$\text{H}(\text{CH}_2\text{CH}_2)_2\dot{\text{C}}\text{RCO}_2\text{R}'$	1,5 C—C	8, 39, 40a, b
29	RCH_2CN , CH ₂ =CH ₂ , R'' $\dot{\text{O}}$, [γ - ⁶⁰ Co]	$\text{RCH}_2\text{CH}_2\dot{\text{C}}\text{H}(\text{R})\text{CN}$	$\text{H}(\text{CH}_2\text{CH}_2)_2\dot{\text{C}}(\text{R})\text{CN}$	1,5 C—C	8

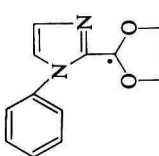
30	RCH_2OH , $\text{CH}_2=\text{CH}_2$, $\text{R}^{\cdot}\dot{\text{O}}$	$\text{H}(\text{CH}_2\text{CH}_2)_2\dot{\text{C}}(\text{R})\text{OH}$	1,5 C-C	8
31	RCOCH_3 , $\text{CH}_2=\text{CH}_2$, $\text{R}^{\cdot}\dot{\text{O}}$, [Mn(OCOCH ₃) ₃ , $\gamma\text{-}^{60}\text{Co}$]	$\text{RCOCH}(\text{CH}_2\text{CH}_2)_2\text{H}$	1,5 C-C	8, 41a, b
32	HCOOCH_3 , $\text{CH}_2=\text{CH}_2$, $\text{R}^{\cdot}\dot{\text{O}}$, [$\gamma\text{-}^{60}\text{Co}$]	$\text{CH}_3(\text{CH}_2\text{CH}_2)_2\dot{\text{C}}\text{HCO}_2\text{CH}_3$	1,6 C-C	8
33	RCH_2X , $\text{CF}_2=\text{CFY}$, $\text{R}^{\cdot}\dot{\text{O}}$; X = Alk, OH; Y = F, Cl	$\text{R}\dot{\text{C}}\text{X}(\text{CF}_2\text{CFY})_2\text{H}$	1,5 C-C	42a, b
34	$\text{CH}_2\text{XCO}_2\text{R}$, $\text{CH}_2=\text{CH}-\text{CH}_3$, $\text{R}^{\cdot}\dot{\text{O}}$, X = H, Cl, CH ₃	$\text{H}[\text{CH}(\text{CH}_3)\text{CH}_2]_2\dot{\text{C}}\text{XCO}_2\text{R}$	1,5 C-C	8
35	$\text{CH}_2\text{ClCO}_2\text{R}$, $(\text{CH}_3)_2\text{C}=\text{CH}_2$, $\text{R}^{\cdot}\dot{\text{O}}$	$\text{H}[(\text{CH}_3)_2\text{CCH}_2]_2\dot{\text{C}}\text{ClCO}_2\text{R}$	1,5 C-C	43
36	$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_3$, $(\text{CH}_3)_2\dot{\text{N}}$	$(\text{CH}_3)_2\dot{\text{N}}(\text{CH}_2)_3\dot{\text{C}}\text{HC}_2\text{H}_5$	1,5 C-C	44
37	$\text{CH}_3\text{CH}=\text{CHCO}_2\text{CH}_3$, $\text{R}^{\cdot}\dot{\text{O}}$	$\dot{\text{C}}\text{H}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_3$	1,6 C-C	45
38	$\text{CCl}_3(\text{CH}_2)_3\text{CH}_2\text{Cl}$, $\text{Fe}(\text{CO})_5$, $i\text{-C}_3\text{H}_7\text{OH}$	$\text{CHCl}_2(\text{CH}_2)_3\dot{\text{C}}\text{HCH}_2\text{CH}_2\text{Cl}$	1,5 C-C	29
39	$\text{CCl}_3(\text{CH}_2)_3\text{CH}_3$, $\text{Fe}(\text{CO})_5$, $i\text{-C}_3\text{H}_7\text{OH}$	$\text{CHCl}_2(\text{CH}_2)_4\dot{\text{C}}\text{HCH}_2\text{Cl}$	1,6 C-C	46
40	$\text{CCl}_3(\text{CH}_2)_3\text{CH}_2\text{Cl}$, $\text{Fe}(\text{CO})_5$, $i\text{-C}_3\text{H}_7\text{OH}[\text{CH}_2\text{OH}, \text{HCON}(\text{CH}_3)_2]$	$\text{CHCl}_2(\text{CH}_2)_3\dot{\text{C}}\text{HCH}_2\text{CH}_3$	1,5 C-C	47
41	$\text{CCl}_3\text{CH}_2\text{CH}_2\text{Cl}$, $\text{CH}_2=\text{CCl}_2$, $\text{Fe}(\text{CO})_5$, $i\text{-C}_3\text{H}_7\text{OH}$	$\text{CHCl}_2\text{CH}_2\text{CCl}_2\text{CH}_2\dot{\text{C}}\text{HCl}$	1,5 C-C	48
42	$\text{CCl}_2=\text{CH}(\text{CH}_2)_2\text{CH}_2\text{Cl}$, CCl_4 , $\text{R}^{\cdot}\dot{\text{O}}$	$\text{H}(\text{CCl}_2\text{CH}_2)_2\text{CCl}_2\dot{\text{C}}\text{HCH}_2\text{Cl}$	1,6 C-C	49
43	$o\text{-}(\text{RCH}_2)_2\text{NC}(\text{O})\text{C}_6\text{H}_4\text{N}_2\text{X}$; Cu_2Cl_2	$\text{CHCl}_2\text{CH}(\text{CCl}_3)(\text{CH}_2)_2\dot{\text{C}}\text{HCl}$	1,5 C-C	50
44	$o\text{-RC}_6\text{H}_4\text{XC}_6\text{H}_4\text{N}_2^+$, Ti^{III} , X = O, CH ₃ , R = H, COO ⁻	$\text{C}_6\text{H}_4\text{C}(\text{O})\text{N}(\text{CH}_2\text{R})\dot{\text{C}}\text{HR}$ $o\text{-RCHCH}_2\text{XC}_6\text{H}_5$	1,5 C-C	51
45	$o\text{-NH}_2\text{C}_6\text{H}_4\text{-N} \begin{array}{c} \diagup \text{N} \\ \diagdown \end{array} \begin{array}{c} \diagup \text{O} \\ \diagdown \end{array} \text{HNO}_2$		1,5 C-C	52
46	$\text{CH}\equiv\text{C}(\text{CH}_2)_3\text{CH}_2\text{R}$, CCl_4X , X = H, Cl, Br; R = H, CH ₃ , C ₂ H ₅	$\text{CCl}_3\text{CH}=\text{CH}(\text{CH}_2)_3\dot{\text{C}}\text{HR}$	1,5 C-C	53, 54
47	$\text{R}^{\cdot}\text{R}^{\cdot}\text{R}^{\cdot}\text{CHCO}_2\text{C}(\text{CH}_3)_2\text{C}\equiv\text{CH}$, CCl_4	$\text{R}^{\cdot}\text{R}^{\cdot}\text{R}^{\cdot}\dot{\text{C}}\text{CO}_2\text{C}(\text{CH}_3)_2\text{CH}=\text{CHCCl}_3$	1,5 C-C	55

TABLE 1—continued

No.	Reagents, reaction conditions	Structure of radicals		Type of migration	Ref.
		Unrearranged	Rearranged		
48	$\text{HO}_2\text{CC}\equiv\text{CCO}_2\text{H}; (\text{C}_2\text{H}_5)_2\text{O}; \dot{\text{O}}\text{H}$		$\text{CH}_3\text{CH}_2\text{OCH}(\text{CH}_3)\text{C}(\text{CO}_2\text{H})=\dot{\text{C}}\text{CO}_2\text{H}$	$\text{CH}_3\dot{\text{C}}\text{HOCH}(\text{CH}_3)\text{C}(\text{CO}_2\text{H})=\text{CHCO}_2\text{H}$	24
49	$\text{HO}_2\text{CC}\equiv\text{CCO}_2\text{H}; \text{CH}_2(\text{OCH}_3)_2; \dot{\text{O}}\text{H}$		$\text{CH}_3\text{OCH}_2\text{OCH}_2\text{C}(\text{CO}_2\text{H})=\dot{\text{C}}\text{CO}_2\text{H}$	$\text{CH}_3\text{O}\dot{\text{C}}\text{HOCH}_2\text{C}(\text{CO}_2\text{H})=\text{CHCO}_2\text{H}$	24
			$\text{CH}_3\text{OCH}(\text{OCH}_3)\text{C}(\text{CO}_2\text{H})=\dot{\text{C}}\text{CO}_2\text{H}$	$\dot{\text{C}}\text{H}_2\text{OCH}(\text{OCH}_3)\text{C}(\text{CO}_2\text{H})=\text{CHCO}_2\text{H}$	
50	$\text{H}_2\text{O}; \text{HO}_2\text{CC}\equiv\text{CCO}_2\text{H}; \dot{\text{O}}\text{H}$			$\text{O}=\text{CHCH}_2\text{CH}_2\dot{\text{C}}\text{HC}(\text{CO}_2\text{H})=\text{CHCO}_2\text{H}$	24
51	$(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}=\text{CH}_2$, 		unidentified		56
52	$\text{CCl}_4, \text{CCl}_3\text{Br}, (\text{C}_n\text{F}_{2n+1})\dot{\text{I}}$		$\text{CCl}_3, (\text{C}_n\text{F}_{2n+1})$		57-59
53	$\text{NC}_6\text{H}_{11}, \text{Fe}^{\text{II}}$		$\text{CH}_3(\text{CH}_2)_3\dot{\text{C}}\text{HCONHC}_6\text{H}_{11}$		60
54	$\text{R}\dot{\text{O}}$				61
55	$(\text{CH}_2)_n\text{CH}_2=\text{CH}_2, \text{R}\dot{\text{O}}$ $n = 0, 1, 2$				62

3. 1,5- and 1,6-Hydrogen shift in O-centred radicals

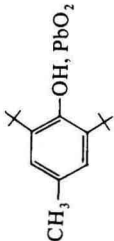
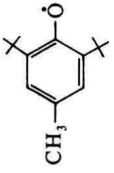
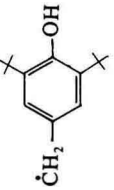
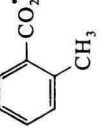
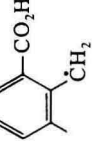






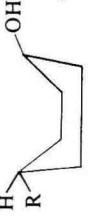
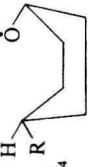
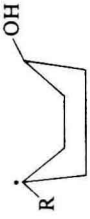

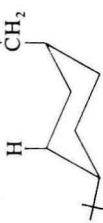
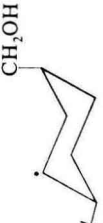


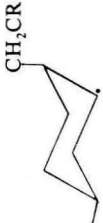
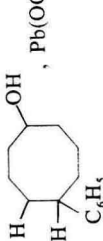
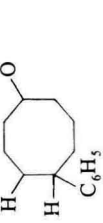
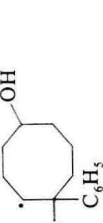
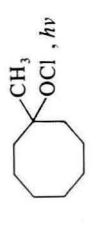
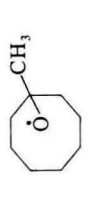
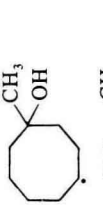


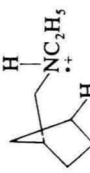
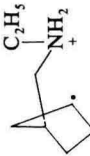
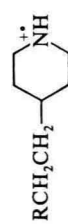
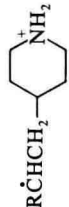
56	$RCH_2CH_2(CH_2)_2C(CH_3)_2OCl$, $R = H$ $R = CH_3, C_6H_5$	$CH_3CH_2(CH_2)_2C(CH_3)_2\dot{O}$ $RCH_2CH_2(CH_2)_2C(CH_3)_2\dot{O}$	$CH_3\dot{C}H(CH_2)_2C(CH_3)_2OH$ $RCH_2\dot{C}H(CH_2)_2C(CH_3)_2OH$ $R\dot{C}HCH_2(CH_2)_2C(CH_3)_2OH$ $R\dot{C}H(CH_2)_2CH_2OH$ $R'\dot{C}H(CH_2)_2CH(OH)R''$	1,5 C-O 1,5 C-O 1,6 C-O 1,5 C-O 1,5 C-O	63 64, 65 66, 67
57	$RCH_2(CH_2)_2CH_2ONO$, $h\nu$	$RCH_2(CH_2)_2CH_2\dot{O}$	$RCH_2(CH_2)_2CH_2\dot{O}$		
58	$R'CH_2CH_2CH_2CH(OH)R''$, $Pb(OCOCH_3)_4$	$R'CH_2(CH_2)_2CH(\dot{O})R''$	$CH_3CH_2(CH_2)_2C(CH_3)_2\dot{O}$		
59	$CH_3CH_2(CH_2)_2C(CH_3)_2OOH$, Cu^I, Fe^{II}				68
60	$CH_3CH_2(CH_2)_2CO_2H, Cl_2, HCl, h\nu$	$CH_3CH_2(CH_2)_2C(\dot{O})=O^+$	$CH_3\dot{C}H(CH_2)_2C(=OH)^+$	1,5 C-O	69
61				1,6 C-O	70, 71
62	$[o-CH_3C_6H_4CO_2]_2$			1,5 C-O	20
63				1,5 C-O	72
64				1,5 C-O	73
65				1,5 C-O	74

TABLE 1—continued

No.	Reagents, reaction conditions	Structure of radicals		Type of migration	Ref.
		Unrearranged	Rearranged		
66	 CH_2OH <i>cis</i> , $\text{Pb}(\text{OCOCH}_3)_4$	 CH_2OH <i>cis</i> , $\text{Pb}(\text{OCOCH}_3)_4$	 CH_2OH	1,5 C—O	67, 75
67	 $\text{CH}_2\text{CR}'\text{R}''\text{OH}$	 $\text{CH}_2\text{CR}'\text{R}''\text{OH}$	 $\text{CH}_2\text{CR}'\text{R}''\text{OH}$	1,5 C—O	75
68	 OH , $\text{Pb}(\text{OCOCH}_3)_4$ $\text{R}'\text{R}'' = \text{H}, \text{CH}_3, \text{Pb}(\text{OCOCH}_3)_4$	 OH , $\text{Pb}(\text{OCOCH}_3)_4$	 OH , $\text{Pb}(\text{OCOCH}_3)_4$	1,5 C—O	76
69	 CH_3 , OCl , $h\nu$	 CH_3	 CH_3	1,6 C—O	77
70	$\text{HC}\equiv\text{CCO}_2\text{H}$, HO	$\text{HOCH}=\text{C}(\text{CO}_2\text{H})\text{CH}=\dot{\text{C}}\text{CO}_2\text{H}$ $\text{HOC}(\text{CO}_2\text{H})=\text{CHCH}=\dot{\text{C}}\text{CO}_2\text{H}$	$\dot{\text{O}}\text{CH}=\text{C}(\text{CO}_2\text{H})\text{CH}=\text{CHCO}_2\text{H}$ $\dot{\text{O}}\text{C}(\text{CO}_2\text{H})=\text{CHCH}=\text{CHCO}_2\text{H}$	1,5 O—C 1,5 O—C	24
71	 $\text{CH}(\text{R})\text{OH}$, $\text{R}'\text{O}$, $h\nu$	$\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}=\text{C}(\text{R})\text{OH}$	$\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HC}(\text{R})=\text{O}$	1,5 O—C	78, 79

4. 1,5- and 1,6-Hydrogen shift in N-centred radicals

72	$[(CH_3)_3CN(OH)]_2CO, PbO_2$	$(CH_3)_3CN(\dot{O})CON(OH)C(CH_3)_3$	$(CH_3)_3CN(OH)CON(\dot{O})C(CH_3)_3$	1,5 O→O	80
73	$RCH_2CH_2(CH_2)_3N(R')Cl,$ $H_2SO_4, CH_3COOH, R = H$ $R = CH_3, C_6H_5$	$CH_3CH_2(CH_2)_3\dot{N}HR'$ $RCH_2CH_2(CH_2)_3\dot{N}HR'$	$CH_3\dot{C}H(CH_2)_3NH_2R'$ $RCH_2\dot{C}H(CH_2)_3NH_2R'$ $R\dot{C}HCH_2(CH_2)_3NH_2R'$	1,5 C-N 1,5 C-N 1,6 C-N	81, 82, 83
74				1,5 C-N	84, 85
75	$(C_4H_9)_2NCl,$ $H_2SO_4, h\nu$	$CH_3(CH_2)_3\dot{N}HC_4H_9$	$\dot{C}H_2(CH_2)_3NH_2C_4H_9$	1,5 C-N	86
76	RCH_2CH_2- $N-Cl, H^+, h\nu$ $R = H, CH_3$		$RCH_2\dot{C}H-$ 	1,5 C-N 1,6 C-N	87
77	$(C_4H_9)_3\dot{N}-O^-, Fe^{II}$	$(C_4H_9)_2\dot{N}CH_2CH_2CH_2CH_3$	$(C_4H_9)_2\dot{N}CH_2CH_2CH_2\dot{C}H_2$	1,5 C-N	88
78	$RCH_2CH_2CH_2CH_2C(O)N(C)R',$ $h\nu$	$RCH_2CH_2CH_2CH_2C(O)\dot{N}R'$	$RCH_2\dot{C}HCH_2CH_2C(O)NHR'$ $R\dot{C}HCH_2CH_2CH_2C(O)NHR'$	1,5 C-N 1,6 C-N	82 89, 90
79	$RCH_2C(O)NBnR', h\nu$ $R = CH_3CH_2CH_2, R' = H, C(CH_3)_3,$ $R = C(CH_3)_3, R' = C(CH_3)_3CH_2C(CH_3)_2$	$CH_3CH_2CH_2CH_2C(O)\dot{N}R'$ $(CH_3)_3CCH_2C(O)\dot{N}$ $(CH_3)_3CCH_2CH_2C(O)\dot{N}$	$CH_3\dot{C}HCH_2CH_2C(O)NHR'$ $(CH_3)_3CCH_2C(O)-NH$ $\dot{C}H_2(CH_3)_2CCH_2(CH_3)_2C-NH$	1,5 C-N 1,5 C-N	89 91
80	$RCH_2CH_2(CH_2)_2SO_2N(C)R',$ $h\nu$	$RCH_2CH_2(CH_2)_2SO_2\dot{N}R'$	$RCH_2\dot{C}H(CH_2)_2SO_2NHR'$ $R\dot{C}HCH_2(CH_2)_2SO_2NHR'$	1,5 C-N 1,6 C-N	82, 92
81	$RCH_2(CH_2)_nOP(O)N(C)R', n = 1, 2, h\nu$	$RCH_2(CH_2)_nOP(O)\dot{N}R'$	$R\dot{C}H(CH_2)_nOP(O)NHR'$	1,5 (n = 1) 1,6 (n = 2) C-N	93
82	$o-HOC_6H_4C(R)=NOH, h\nu$	$o-HOC_6H_4C(R)=\dot{N}$	$o-\dot{O}C_6H_4C(R)=NH$	1,5 O-N	94

telomerization⁸ (Table 1, Nos 7, 8), addition to the triple bond $C\equiv C^{24}$ proceeding via vinyl radical intermediates (Nos 9, 13), addition to the double bond^{25,26} followed by fragmentation of rearranged radicals (Nos 10, 11).

Quite recently, the first works on reversible 1,2 and 1,4 H-shifts (Nos 3, 19) have appeared (for details, see Section 6, 'Radicalotropy').

Examples of 1,4 H-shift, which goes to only a negligible extent, still remain exceedingly scarce^{4,28,29} (Nos 15–18).

2.2. 1,5 and 1,6 H-Shifts in C-Centred Radicals

Hydrogen shifts to the fifth and sixth carbon atoms are the best studied paths of radical isomerization. Table 1 provides many examples (Nos 20–55) of quite varied types of chemical reactions involving 1,5 and 1,6 H-shifts.

During recent years, the problem has been studied systematically, using series of radicals of a given sort, in order to determine the extent of rearrangement as depending on various factors (chain length of radicals, competition of chain transfer, rates of competing processes, differences in radical stabilities, etc.).

Hydrogen shift in long-chain radicals

The extent to which rearrangement occurs was studied as depending on the distance between the radical centre and the carbon atom donating hydrogen for the series of radicals.²¹



(Table 1, Nos 6, 16, 25, 26)

Spin-adducts of both unrearranged $(CH_3O_2CCH_2(CH_2)_nCH_2N(\dot{O})Ar)$ and rearranged $CH_3(CH_2)_nCH(CO_2CH_3)N(\dot{O})Ar$ radicals [$Ar = (CH_3)_3C_6H_2$] were identified in the presence of nitrosodurene as spin trap. The ESR signals from the adducts of the 1,3-, 1,4-, 1,5-, and 1,6- rearranged radicals had the intensity ratio 0.03:0.10:1:0.25.

The hydrocarbon radicals $RCH_2CH_2(CH_2)_3\dot{C}H_2$ ($R = CH_3$ to C_7H_{15}) rearrange by both 1,5- and 1,6-mechanisms (Table 1, No. 21), the product ratio depending strongly on the radical R chain length. The relative yield of the rearrangement products (1,5- + 1,6-) varies only insignificantly in going from $R = CH_3$ to $R = C_3H_7$. Further elongation of R (from C_4H_9 to C_7H_{15}), however, leads to an almost twofold decrease of the extent of rearrangement.³²⁻³⁴ With radicals $C_{11}-C_{13}$ ($R = C_5H_{11}$ to C_7H_{15}), the analytical data suggest the occurrence of 1,10 and 1,11 H-shifts, though an alternative explanation (successive 1,5 and 1,6 H-shifts in radical **1**) is also possible:³²⁻³⁴

