CHRISTOPH RÜCHARDT

Steric effects in Free Radical Chemistry

Steric Effects in Free Radical Chemistry

Christoph Rüchardt*

Chemisches Laboratorium der Universität Freiburg, Albertstr. 21, D-7800 Freiburg i. Br., Federal Republic of Germany

Dedicated to Professor H. Pommer on the occasion of his 60th birthday.

Table of Contents

I	Introduction	2
II	Steric Effects in Homolytic Decomposition Reactions	3
1	Ring Size Effects	3
2	Group Size Effects	5
3	Further Steric Effects	12
III	Steric Effects in Aliphatic Substitution Reactions	13
IV	Steric Effects in Free Radical Addition Reactions	21
V	Steric Effects in Dimerization and Disproportionation Reactions	26
VI	References	28

* This review is an extended version of an article in „Zeitschrift der Sowjetischen Chemischen Akademie“, 1979, 19, 1079.

I Introduction

Steric effects have been discussed in free radical chemistry ever since the discovery of the first free radical, triphenylmethyl **1** by M. Gomberg in 1900¹⁾. To what extent is the dissociation of its dimer, which was believed to be hexaphenylethane **2**³⁾ till 1968²⁾, determined by electronic stabilization of triphenylmethyl **1**⁴⁾ or by steric strain in its dimer?

The opinion that stabilization of **1** by resonance was decisive, predominated for a long time and mastered the discussion of the relationship between structure and reactivity in free radical chemistry till quite recently⁵⁾: Accordingly selectivity in free radical reactions was assumed to be mainly due to differences in the thermodynamic stability of the radicals taking part in a reaction or a potential competing reaction.

The recognition²⁾ that the α , p-dimer **3** is formed in equilibrium with **1** and not the α , α -dimer **2** was interpreted as a result of the smaller steric strain in **3** than in **2**³⁾. Also the known strong influence of p-substituents on the equilibrium constants between substituted trityl radicals and their dimers⁶⁾ found an obvious explanation in this way. The earlier observation that not only those phenoxy radicals **4** carrying three conjugating phenyl substituents **4** ($\text{R} = \text{C}_6\text{H}_5$)^{7a)} are persistent⁸⁾ but also their

t-butylated counterparts **4** ($\text{R} = \text{t-C}_4\text{H}_9$)^{7b)} pointed to the predominating influence of steric effects. Similar results have been obtained in other classes of persistent radicals^{7c, 8)}. The most convincing evidence for the prime importance of steric effects for the persistence of radicals was provided by the observation of a large series of crowded alkyl radicals like **5–7** over longer periods of time by esr. They do not dimerize for energetic reasons^{9, 10)}.

5 $\text{R} = \text{H}$

6 $\text{R} = \text{C}(\text{CH}_3)_3$

Since these developments became known the importance of steric effects on the reactivity of free radical reactions has also been more clearly recognized and more thoroughly investigated¹¹⁾. Some more important and more recent results along these lines are the topic of this review.

Finally it has to be remarked briefly that the reactivity and selectivity of free radicals is certainly not only determined by steric and bond energy effects or by the thermodynamic stability of these transients. Polar effects are also important, in particular in those reactions which have "early" transition states e.g., the steps of free radical chain reactions¹²⁾. They are either due to dipole interactions in the ground state or to charge polarization at transition states. FMO-theory apparently offers a more modern interpretation of many of these effects¹³⁾.

II Steric Effects in Homolytic Decomposition Reactions

When an alkyl free radical **9** is generated by homolytic cleavage of a C–X bond in its precursor **8**

hybridization at the central C-atom changes simultaneously from sp^3 towards sp^2 ¹⁴⁾. All repulsive forces between the substituents R decrease when the bond angles are increased accordingly. Therefore conformational effects can also influence the ease of generation of alkyl radicals.

1 Ring Size Effects

As a model system for demonstrating conformational effects on the rate of radical generation the determination of the influence of the ring size on the rate of formation of cycloalkyl radicals was chosen. Ring size effects on the rate of generation of cycloalkyl carbenium ions were known from the works of Prelog and Brown¹⁵⁾ and were explained by the I-strain¹⁵⁾ i.e., on conformational grounds. During carbenium ion formation the five-ring system loses conformational strain relative to the six-ring system. Cyclopentyl esters therefore solvolyze faster than their cyclohexyl counterparts. Particularly high rate constants were observed for the medium-ring systems. The large transannular nonbonded interactions are partially relieved on ionization due to the formation of planar or nearly planar carbenium ions¹⁶⁾. When cycloalkyl radicals are generated both effects are also found, in fact the more distinctly, the closer the transition state geometry is approaching the sp^2 -state of the radicals^{5, 12, 17, 18)}.

Table 1. Relative rates of formation of cyclic carbenium ions and free radicals from precursors 10–19^a

n	10	11	12	13	14	15	16	17	18	19
4	2.77	0.03	0.03	0.06	0.297	0.084	0.12	0.23	$1.86 \cdot 10^{-5}$	—
5	124.9	11.5	70.5	2.75	1.18	0.787	0.33	0.47	5.43	0.00
6	≈ 1.00	≈ 1.00	≈ 1.00	≈ 1.00	≈ 1.00	≈ 1.00	≈ 1.00	1.00	≈ 1.00	≈ 1.00
7	108.6	194.0	190	42.8	—	—	1.68	2.27	$2.2 \cdot 10^4$	65
8	285.7	1325	—	187	—	—	2.46	4.27	$3.5 \cdot 10^6$	>4000
9	44.0	—	—	—	—	—	2.05	4.02	—	—
10	17.8	292	—	—	—	—	1.93	3.26	—	—
11	12.0	—	—	—	—	—	1.89	2.77	—	—
12	—	—	—	—	—	—	1.76	1.92	—	—

^a The bonds cleaved in the rate determining step of homolytic decomposition of 11–19 are indicated in the formula.

The five-ring – six-ring effect is larger for the endothermic azo decompositions of 11–13 ($\Delta H^\ddagger \approx 20$ –50 kcal/mol)^{19–21}) than for the decarbonylation of 14 and 15²²) ($\Delta H^\ddagger \approx 9$ –15 kcal/mol)²³). The five membered cyclic hydrocarbon 18 ($\Delta H^\ddagger \approx 50$ kcal/mol)²⁴) also decomposes faster than the six membered. The effect is, however, smaller in this example than for the thermolysis of the corresponding azo compounds 12. This is probably due to the grossly different decomposition temperatures of 18 and 12 and to the overlapping influence of F-strain for 18 (see below). One recognizes from the data in Table 1 that the five-ring – six-ring effect is generally the largest, when α -phenyl- or α -cyano-conjugated radicals are generated. Conjugated radicals require a more strictly planar geometry than unconjugated alkyl radicals¹⁴) (cf. 11–13). The rate of generation of secondary alkyl radicals from 14 or 17 also responds more strongly to ring size effects than the rate of generation of tertiary radicals from 15 and 16²⁵). The formation of secondary radicals is a more endothermic process. The smallest ring size effect and even an inverse five-ring – six-ring effect is observed in the thermolysis reactions of the peresters 16 and 17, although all evidence points to a concerted homolytic fragmentation mechanism for these reactions²⁵). Apparently, at the transition state of this endothermic reaction the peroxide bond is nearly broken, while the stronger C α -CO-bond is stretched only to a relatively small extent. Therefore, hybridization and geometry at C α have hardly changed. This interpretation is supported by the study of α -CH₃O-^{12c}), α -CN-^{12c}) and α -phenyl-substituent effects and by other criteria^{5, 12, 18}).

Exceptional behavior among the reactions of Table 1 is shown by the thermolysis reaction of 18. While the direction of the five-ring – six-ring effect is normal, a particular large rate enhancement (10^4 – 10^6) is found for the thermolysis of the seven and eight membered compounds and an unexpected high thermal stability for the four membered one. Apparently the thermolysis rates of 18 are not only determined by the change in the I-strain but much more by the strong repulsive Van der Waals interactions across the central C-C-bond which are revealed on bond homolysis. A smaller effect of similar nature is recognized in the decomposition rates of *cis*-1-methyl-1-azocycloalkanes 19²⁶). Because of the low activation enthalpies of *cis*-azo decompositions ($\Delta H^\ddagger \approx 10$ –15 kcal/mol)²⁶) the small five-ring – six-ring effect was

11¹⁹⁾ X = CN, toluene, 80°C

12²⁰) $X = C_6H_6$, benzene, 60°C

13¹¹⁾ X = CH₃, benzene, 200°C

$14^{22)} X = H, 125^{\circ}C$ $15^{22)} X = CH_3, 135^\circ C$

16²⁵⁾ X = CH₃, benzene, 80°C

(7²⁵) X = H, ethylbenzene, 110°C

18²⁴⁾ Octane, 220°C

19²⁶⁾ Ethanol, -28°C

expected because the C-N-bonds are stretched much less at transition state than in the *trans*-azo series. The particularly high rates of thermolysis of 19 ($n = 7-8$) most probably are due to the release of Van der Waals repulsive interactions between the *cis*-oriented 1-methyl-cycloalkyl groups.

2 Group Size Effects

The influence of the group size on the rate of generation of alkyl radicals has been investigated for the same reactions as mentioned in Table 1^{12a, 27)}. Most information is available on the thermolysis of t-azoalkanes 20 ($R^1-R^3 = \text{alkyl}$)²⁸⁾.

Qualitatively the same reactivity pattern was observed for the decomposition of *sym.* azonitriles **20** ($R^1 = \text{CN}$, R^2 , $R^3 = \text{alkyl}$)²⁹⁾ and several symmetrically and unsymmetrically substituted azo compounds³⁰⁾. A selection of these results is found in Table 2. It is apparent from these data that the thermal stability of **20** decreases as the size of the groups R^1 – R^3 increases. Rüchardt et al. have observed that a linear relationship exists between the thermolysis rates of Table 2 and the S_N1 -solvolysis rates of corresponding *t*-alkyl-*p*-nitrobenzoates **21** in 80% acetone-water^{28d)}. The

Table 2. Rate Constants k_{rel} and activation parameters for the thermolysis of azoalkanes $\text{R}^1\text{R}^2\text{R}^3\text{C}=\text{N}=\text{N}$ 20 in hydrocarbon solvents

R^1	R^2	R^3	$k_{\text{rel.}}$ (180 °C) ^a	$\Delta H^\ddagger$ kcal/mol	$\Delta S^\ddagger$ e. u.
CH_3	CH_3	CH_3	$\equiv 1.00$	43.2 ^b	17.7 ^b
CH_3	CH_3	C_2H_5	1.19	—	—
CH_3	CH_3	1- C_3H_7	[3.3 ^c]	40.7 ^b	14.2 ^b
CH_3	CH_3	1- C_8H_{17}	2.27	—	—
CH_3	CH_3	2- C_3H_7	3.00	—	—
C_2H_5	C_2H_5	C_2H_5	3.65	—	—
CH_3	CH_3	<i>t</i> -But.	5.30	40.9 ^b	16.3 ^b
			[7.7 ^c]		
			[13 ^d]		
CH_3	CH_3	<i>i</i> -But.	7.51	—	—
CH_3	2- C_3H_7	2- C_3H_7	23.0	—	—
CH_3	C_2H_5	<i>t</i> -But.	36.5	—	—
C_2H_5	C_2H_5	<i>t</i> -But.	107	—	—
2- C_3H_7	2- C_3H_7	2- C_3H_7	206	—	—
CH_3	CH_3	neo-Pentyl	247	35.6 ^a	11.9 ^a
			[480 ^c]		
			[1320 ^d]		
CH_3	2- C_3H_7	neo-Pentyl	453	33.8 ^a	9.4 ^a
CH_3	CH_3	neophyl	[706 ^c]	35.0 ^b	11.4 ^b
CH_3	neo-Pentyl	neo-Pentyl	[57000 ^d]	30.0 ^e	5.2 ^e

^a Ref. 28d) ^b Ref. 28c) ^c at 150 ° see Ref. 28c) ^d at 100 °C see Ref. 28a) ^e Ref. 28a)

slope of this correlation is approximately 1. Because both series respond in the same way to group size, steric acceleration by relieve of back strain was proposed as common interpretation²⁸⁾. During homolysis of 20 as well as heterolysis of 21 the repulsive Van der Waals interactions between the side chains R^1-R^3 are continuously reduced because the bond angles between these groups are increased during the change of hybridization from sp^3 towards sp^2 . Interestingly those examples in Table 2 which carry a neopentyl side chain deviate from the observed correlation. It is assumed that the particularly fast thermolyses rates of neopentyl substituted azo compounds like 22 are due to another type of ground state strain which is released on homolysis. It was proposed that due to γ -branching and according to Newman's rule six³¹⁾ heavy Van der Waals repulsions between the methyl hydrogens of the neopentyl groups

and the nitrogen atoms are acting as shown in 22. The same extraordinary rate enhancing effect of neopentyl side chains was observed for the thermolysis rates of azonitriles 20 ($R^1, R^2 = \text{alkyl}, R^3 = \text{CN}$)^{29a} and α -carbomethoxy-azoalkanes 20 ($R^1, R^2 = \text{alkyl}, R^3 = \text{COOCH}_3$)³². For α -phenyl substituted azoalkanes 20 ($R^1, R^2 = \text{alkyl}, R^3 = \text{C}_6\text{H}_5$) the relationship between thermal stability and size of the groups R^1 and R^2 is more complex, apparently because the resonance stabilization of the developing radical center at the transition state 23 decreases with increas-

23

ing group size³³). This could be partly due to steric hindrance of resonance³⁴). In addition, however, the transition state 23 is probably reached earlier on the reaction coordinate when the group size of R^1 and R^2 is increased. According to the Hammond principle¹⁷) this means less C-N-bond stretching and less radical character in 23. For symmetrical azo compounds 20 ($R^1, R^2 = \text{alkyl}, R^3 = \text{alkyl}, \text{CN}, \text{COOCH}_3, \text{C}_6\text{H}_5$) there is good evidence that both C-N-bonds are cleaved more or less simultaneously in the rate determining step³⁵). This is not generally so for unsymmetrical azo compounds $R^1\text{N}_2R^2$ ³⁶).

In comparison with the decomposition of *trans*-azoalkanes 20 a much larger group size effect has been found for the thermolysis rates of a few *cis*-azoalkanes 24. Due to the repulsion of the free electron pairs on the two nitrogen atoms and due to steric interaction between the *cis* oriented alkyl groups *cis* azoalkanes 24 decom-

24

Table 3. Steric acceleration of thermolysis of *trans*-azoalkanes 20 (180 °C, ethylbenzene) and *cis*-azoalkanes 24 (−28 °C, ethanol)

R^1	R^2	R^3	$k_{\text{rel}}(20)$	$k_{\text{rel}}(24)^{37)}$
CH ₃	CH ₃	CH ₃	≡1.00	≡1.00 ^a
CH ₃	CH ₃	C ₂ H ₅	1.19	4.4
CH ₃	CH ₃	i-C ₃ H ₇	3.00	64
CH ₃	CH ₃	i-C ₄ H ₉	7.51	153
CH ₃	C ₂ H ₅	C ₂ H ₅	1.87	37
C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	3.65	1428
CH ₃	CH ₃	t-C ₄ H ₉	5.30	>1600

^a $k_1 = 0.615 \cdot 10^{-4} \text{ s}^{-1}$

pose at much lower temperatures into radicals^{35c, 37)}. Although the transition state of this much less endothermic reaction should be located earlier on the reaction coordinate than for the thermolysis of 20^{12a, 17)}, rates are subject to larger steric acceleration. In addition to the relief of back strain, front strain between the to groups $R^1 R^2 R^3 C$ also becomes important (cf. Table 3).

The rates of homolytic fragmentation of peroxyesters 25 are also enhanced when the size of the side chains $R^1 - R^3 = \text{alkyl}$ is increased. This is shown for several examples in Table 4. The rate enhancing effect is smaller than for the azoalkane thermolyses

discussed above. Taking into account, however, the multiplicative back strain effect in both alkyl parts of azoalkanes, then the effect of steric acceleration becomes comparable for the thermolysis of 20 and 25. The different temperature of these two thermolyses reactions may partly be responsible for this. The data of the two series even show a linear correlation with the slope ~ 1 on a logarithmic scale^{38b)}. Again only the neopentyl substituted compounds deviate from this correlation as discussed previously.

It is somewhat contradictory and not yet fully understood why the back strain effect on the rate of perester decompositions is so large. We had reasoned before from the discussion of conformational effects that the C_α -CO-bond of 25 is only stretched to a small extent at transition state. From an analysis of bond energies^{5, 18)} it becomes questionable if the homolysis of C-N-bonds (as in 20) and C-C-bonds (as in 25) is likely to be directly comparable^{5, 12a, 18)}. In addition the extent of C_α -CO-cleavage at the transition state of fragmentation of 25 may well be itself dependent on the

Table 4. Steric acceleration of thermolysis of peroxyesters 25 in ethylbenzene at 60 °C³⁸⁾

R^1	R^2	R^3	$k_1(\text{rel})$ (60 °C)	$\Delta H^\ddagger$ kcal/mol	$\Delta S^\ddagger$ e.u.
CH ₃	CH ₃	CH ₃	$\equiv 1.00$	28.3	5.3
CH ₃	CH ₃	C ₂ H ₅	1.29		
CH ₃	CH ₃	1-C ₈ H ₁₆	1.73		
CH ₃	CH ₃	(CH ₃) ₂ CHCH ₂	2.30		
C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	3.19		
C ₂ H ₅	C ₂ H ₅	2-C ₃ H ₇	6.50		
CH ₃	CH ₃	(CH ₃) ₃ C	3.4	27.2	4.6
CH ₃	CH ₃	(CH ₃) ₃ CCH ₂	2.6	26.5	2.0
2-C ₃ H ₇	2-C ₃ H ₇	2-C ₃ H ₇	32	26.6	6.7

size of the groups $R^1 - R^3$ in 25. This is indicated e.g., by the small steric acceleration observed when the rates of decomposition of a series of peresters 25 ($R^1, R^2 = \text{alkyl}, R^3 = C_6H_5$) with alkyl side chains of different bulk are compared³³⁾.

Table 5. Thermal decomposition of hydrocarbons $R^1R^2R^3C-CR^1R^2R^3$. Temperature T for $t_{1/2} = 1$ h, free enthalpy of activation $\Delta G^\ddagger$ at 300 °C and strain enthalpy E_S^a

No.	R^1	R^2	R^3	$T(^{\circ}C)$ ($t_{1/2} = 1$ h)	$\Delta G^\ddagger(300^{\circ}C)$ [kcal/mol]	E_S^a [Kcal/mol]	Ref.
1	CH ₃	CH ₃	CH ₃	490	60.5	7.8	39b, 42)
2	CH ₃	CH ₃	C ₂ H ₅	420	55.3	14.9	43, 45)
3	CH ₃	CH ₃	1-C ₃ H ₇	411	53.6	14.8	44)
4	CH ₃	CH ₃	1-C ₄ H ₉	412	53.9	14.5	44)
5	CH ₃	CH ₃	i-C ₄ H ₉	384	51.9	18.7	45)
6	CH ₃	CH ₃	2-C ₃ H ₇	329	46.4	26.3	45)
7	CH ₃	CH ₃	(CH ₃) ₃ CCH ₂	321	46.3	27.8	45)
8	CH ₃	CH ₃	c-C ₆ H ₁₁	315	45.8	32.1	43, 45)
9	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	285	43.1	42.4	43, 45)
10	CH ₃	C ₂ H ₅	c-C ₆ H ₁₁	250	39.6	44.3	43, 45)
11	CH ₃	CH ₃	t-C ₄ H ₉	195	33.7	51.8	45)
12	CH ₃	CH ₃	H	565	68	2.0	46)
13	C ₆ H ₁₁	C ₆ H ₁₁	H	384	52.1	22.8	45, 47)
14	C ₆ H ₁₁	t-C ₄ H ₉	H(D, L)	329	46.7	32.6	45, 48)
15	C ₆ H ₁₁	t-C ₄ H ₉	H(meso)	285	42.6	38.5	45, 48)
16	t-C ₄ H ₉	t-C ₄ H ₉	H	141	29.6	62.7	45, 49)
17	CH ₃	H	H	590	69	0	50)
18	H	H	H	695	79	0	51)
19	2.2.4.4 Tetramethylpentane ^b			502	63.9	6.4	45)
20	2.2.3.4.4 Pentamethylpentane ^b			415	55.8	15.1	45)
21	2.2.3.3.4.4 Hexamethylpentane ^b			350	48.8	24.9	45)
22 ^c	CH ₃	C ₆ H ₅	H	365	50.0	2.8	41)
23 ^c	C ₂ H ₅	C ₆ H ₅	H	363	49.7	4.0	41)
24 ^c	i-C ₃ H ₇	C ₆ H ₅	H	335	47.4	7.6	41)
25 ^c	t-C ₄ H ₉	C ₆ H ₅	H	289	42.1	21.4	41)
26 ^d	t-C ₄ H ₉	C ₆ H ₅	H	303	44.6	18.5	41)
27 ^e	t-C ₅ H ₄	C ₆ H ₅	H	259	40.3	24.6 ^e	41)

^a Difference in heat of formation as calculated by the force fields according to Ref.³⁹⁾ (for 1–21) and Ref.⁴⁰⁾ (Set B) for 22–27 and the hypothetical heat of formation of the unstrained molecules^{39b, 41)}.

^b a statistical correction $k_1 = k_{\text{exp}}/2$ was introduced because this molecule has two equivalent bonds which can be cleaved on thermolysis.

^c meso-diastereomer

^d racem.diastereomer

^e experimental value from heat of combustion

As previously pointed out in the discussion of ring size effects on bond homolyses the largest steric acceleration by bulky substituents is expected for the thermal cleavage of C-C-bonds in tetra- or hexasubstituted ethanes 26. In comparison to azoal-

26

kanes the N₂-group separating the two alkyl fragments is missing in 26. Therefore much stronger front strain interaction across the central C-C-bond is expected in 26 than was found between the alkyl groups in 20 or 24. This is verified by the results in Table 5. The temperature at which the hydrocarbons recorded in the table decompose with a half time $t_{1/2} = 1$ h varies between 695 °C for ethane and 141 °C for sym. tetra-*t*-butylethane. The difference in free enthalpy of activation is almost 50 kcal/mol in this series! It has been shown that this extremely large rate effect is due to steric acceleration. When the rate constants were correlated with the Taft-Hancock steric substituent constants E_s^c ⁸²⁾ for the halves of the molecules 26 two separate linear correlations were found: one for the compounds 1–11 in Table 5⁴³⁾ in which the central C-C-bond connects two quaternary centers, the second correlation line is followed by the rate data of a large group of compounds⁵²⁾ with a central C-C-bond between two tertiary carbons e.g., the compounds 12–16 in Table 5. This separation into two separate correlations is due to differences in structure. The C_T–C_T compounds 12–16 have a gauche ground state conformation which allows for much larger angle deformations in order to escape the building up of ground state strain than anticonformations^{47–49)}.

It was all the more satisfying to find a linear correlation (Fig. 1) between the thermal stability of most aliphatic compounds of Table 5 as expressed by $t_{1/2} = 1$ h or by $\Delta G^\ddagger$ (300 °C), and their ground state strain. The strain energies were obtained by force field calculations^{39, 40, 51)} and confirmed for a selected number of examples by the determination of heats of combustion^{48, 49, 52, 53)}. This proves that C-C-bond strengths of branched alkanes are mainly influenced by Van der Waals repulsions acting in the ground state of hydrocarbons which are released on bond dissociation. The exponential increase of bond strength for those hydrocarbons 26 with particularly small strain energies (no. 12 and 17–19 in Table 5) is still unexplained⁵⁾. The correlation of Fig. 1 allows the prediction of thermal stabilities of many aliphatic hydrocarbons by force field calculations. It is particularly interesting to note that the diastereomeric compounds no. 14 and 15 of Table 5 have distinctly different stabilities. This was explained on conformational grounds⁴⁸⁾. Another interesting phenomenon is the observation that the slope of the correlation for the aliphatic compounds in Fig. 1 is not –1 but –0.6 as shown by the equation derived from Fig. 1.

$$\Delta G^\ddagger (300^\circ\text{C}) = -0.6 E_s + 65.6 \text{ kcal/mol.}$$

Fig. 1. Correlation between Thermal Stability and Ground State Strain E_s for hydrocarbons 26 (results from Table 5)

This suggests that at the transition state of this homolytic cleavage reaction 40% of the ground state strain is still present. Under the reasonable assumption that the radicals, which are the cleavage products, are more or less strain-free^{10b,49)}, this means that the recombination of bulky alkyl radicals has an activation barrier of corresponding magnitude. A bond dissociation enthalpy $D_H \sim 76$ kcal/mol is calculated for the C-C-bonds in almost unstrained branched aliphatic hydrocarbons by this correlation in good agreement with the literature value for the central bond of 2,3-dimethyl butane⁴⁵⁾.

A corresponding correlation is obtained for the rate constants of α,α' -phenyl substituted alkanes 26 ($R^1 = C_6H_5$, $R^2 = H$, $R^3 = \text{alkyl}$) (see Fig. 1)⁴¹. It has, however, a different slope and a different axis intercept. When both correlations are extrapolated to $E_{Sp} = 0$, a difference of about 16 kcal/mol in $\Delta G^\ddagger$ is found. This value is not unexpected because in the decomposition of α,α' -phenyl substituted ethanes (Table 5, no. 22–27) resonance stabilized secondary benzyl radicals are formed. From Fig. 1 therefore a resonance energy of about 8 kcal/mol for a secondary benzyl radical is deduced. This is of the expected order of magnitude⁵⁴.

What is the reason for the smaller slope of this correlation?

$$\Delta G^\ddagger (300^\circ \text{C}) = 51 - 0.41 E_{Sp} [\text{kcal/mol}]$$

Two factors are probably contributing: On increasing the strain by increasing the group R^3 in 26 benzyl type radicals are generated which could deviate from planarity and therefore suffer from steric hindrance of resonance³⁴. Alternatively, the more strained 26 is, the more the transition state of dissociation of 26 will be shifted in the direction of the hydrocarbon. Its radical character will decrease accordingly and therefore also the size of the resonance effect on the rates⁴¹.

It has to be pointed out, however, that these considerations suffer somewhat from the fact that up to now it was necessary to calculate the strain energies of the phenyl substituted alkanes by a different force field⁴⁰ than those of the alkanes³⁹.

3 Further Steric Effects

When 2-norbornyl type radicals are generated from exo/endo isomeric precursors differences in rate are generally observed. The higher rate of decomposition of the exo-isomer is usually explained on steric grounds^{12, 18}. This phenomenon is demonstrated by the following examples:

$$k_{\text{exo(Azo)}}/k_{\text{endo}} = 116 (200^\circ \text{C})^{18)}$$

$$k_{\text{exo(Azo)}}/k_{\text{endo}} = 68 (200^\circ \text{C})^{18)}$$

$$k_{\text{exo(Azo)}}/k_{\text{endo}} = 99 (200^\circ \text{C})^{55)}$$

$$k_{\text{exo}}(\text{CO}_2\text{OtBut})/k_{\text{endo}} = 6.4 \text{ (80 } ^\circ\text{C)}^{18, 55}$$

$$k_{\text{exo}}(\text{CO}_2\text{OtBut})/k_{\text{endo}} = 4.1 \text{ (80 } ^\circ\text{C)}^{18, 56}$$

$$k_{\text{exo}}(\text{CO}_2\text{OtBut})/k_{\text{endo}} = 2.9 \text{ (80 } ^\circ\text{C)}^{55}$$

The torsional effect as proposed by Schleyer⁵⁷⁾ and steric hindrance of the departing group according to Brown⁵⁷⁾ both have been discussed as interpretations of these reactivity series.

The rate of homolytic decomposition of bi- and polycyclic bridgehead azo compounds^{18, 58)} and peroxyesters^{18, 59)} decreases with increasing strain of the polycyclic system, because internal ring strain increases further on dissociation. This view is supported by the observation of a linear correlation between the rates of radical generation and the change in strain energy on dissociation as estimated by force field calculations according to Schleyer^{58, 59)}. For the perester decomposition again a polar effect probably is superimposed.

III Steric Effects in Aliphatic Substitution Reactions

When alkyl radicals take part in atom transfer reactions as acceptors

or as donors

a change in hybridization between the sp^2 and the sp^3 state of the central carbon atom is involved, even though the transition states of these reactions are usually found to be placed early on the reaction coordinates^{5, 12, 18)}. Because of the different steric interactions of substituents at the central carbon atom and because of the different shielding of the reaction center by these groups in the two hybridization states, steric effects on reactivity are expected in addition to electronic¹³⁾ and polar effects¹³⁾.

A conformational effect was detected for the H-transfer reactions from cycloalkanes to a series of attacking radicals. The data of Table 6 show that cyclopentane is generally a better H-donor than cyclohexane. The rate ratio is generally largest for the least reactive radicals because the change in hybridization at transition state

Table 6. Relative Rates of H-transfer from cyclopentane (k_5) and cyclohexane (k_6) to radicals $X\cdot$.⁶⁰⁾

$X\cdot$	$Cl\cdot$ $CCl_4, 0^\circ C$	$t\text{-}BuO\cdot$ $CCl_4, 0^\circ C$	$C_6H_5\cdot$ $CH_3CN, 75^\circ C$	$\cdot CCl_3$ $BrCCl_3\text{-}CCl_4, 75^\circ C$	$Br\cdot$ $CH_3CN, 75^\circ C$
k_5/k_6	1.0	1.0	2.8	4.0	3.1

has progressed to the farthest extent in these cases. Increased reactivity is also observed for cycloalkanes of the medium-ring size ($C_8\text{--}C_{10}$)⁶⁰⁾.

The well known difference in reactivity in transfer reactions of primary, secondary and tertiary hydrogens is most probably neither due to steric acceleration nor to a difference in electronic stability of primary, secondary and tertiary radicals^{5, 12, 18)}. This latter interpretation was favored in the literature until quite recently⁵⁾ because H-transfer reactivity of primary, secondary, and tertiary hydrogens decreases parallel with an increase in the C-H-bond dissociation energy. The suggestion that the drastic change in C-H bond energies is due to a ground state effect^{5, 12)} was recently supported by McKean⁶¹⁾, who observed an interesting correlation between bond dissociation energies and infrared stretching frequencies ν_{CH} for a large group of compounds. Hydrogen bound to carbon atoms which carry good conjugating groups like phenyl or CN deviate distinctly from this correlation. Using the PMO-theory Boldt et al.^{13c)} recently recognized fairly good correlations between activation energies of some H-transfer reactions and the superdelocalizabilities $S_r^{(R)}$ ^{13a, b)}. They point out that the principle of maximum overlap, using MINDO-3 data, may serve well in predicting relative rates of H-transfer reactions. Apparently the C-H bond energies are directly related to $S_r^{(R)}$.

Bartlett et al.⁶²⁾ on the other hand have found that mainly exo-2-norbornyl halides 28 are obtained from 2-norbornyl radicals 27 and halogen transfer agents. The product ratio of exo-halide 28 and endo-isomer 29 was largest for large halogen transfer agents XY. XY apparently approaches 27 preferentially from the less shielded exo-side. The torsional effect⁵⁷⁾ discussed before is probably also of importance. Similar results were obtained more recently for the transfer of hydroxy groups from peracids to 27⁶³⁾.

Table 7. Relative rates of H-transfer from the 2-position (k_2) and the 1-position (k_1) of adamantane to attacking radicals $X\cdot$ 65, 66)

$X\cdot$	$Cl\cdot$	$Br\cdot$	$\cdot CCl_3$	$\begin{array}{c} O \quad O \\ \quad \\ [CH_3-C-C-CH_3]^* \end{array}$	$C_2H_5O-CO-\dot{N}Cl$
k_1/k_2	2-6	9	24	∞	∞

The well known decreased reactivity of hydrogen bound to the bridgehead position of small polycyclic hydrocarbons in transfer reactions is in accord with the steric bridgehead effect⁶⁴⁾ discussed above. Although this position usually is shielded to a comparatively low extent an increase in internal strain is expected on bond dissociation. The 2-position of adamantane is more shielded than the 1-position. The ratio of products obtained by radical attack at the 1-position (k_1) and the 2-position (k_2) therefore increases with the size of the attacking radical species^{64, 65)} as shown by the data of Table 7. Steric hindrance of H-transfer has also been observed in autoxidation reactions. An example is the decreasing reactivity of hydrogens in benzyl position towards attacking cumylperoxy radicals⁶⁷⁾ with increasing size of R. In other

cases, however, steric acceleration of H-transfer due to relief of back strain was postulated as in the bromination of a series of dibenzo-bicyclooctanes⁶⁸⁾. For example

the compound with $R = CH_3$ is more reactive than the corresponding compound with $R = H$ because the steric interaction between *vic.* eclipsed methyl groups decreases in the process of H-transfer. Steric hindrance to H-transfer becomes more pronounced, the bulkier the attacking radical is. This has been favorably used in preparative free radical halogenations for increasing selectivity⁶⁹⁾. The best known examples are the chlorinations with N-chloramines in sulfuric acid. Aminium radical cations $R_2NH^{+\cdot}$ are the H-transfer agents in these reactions⁷⁰⁾ and their size can be systematically changed by ranging the groups R. An example is the chlorination of isopentane⁷¹⁾:

R	Relative rate of <i>prim.</i> , <i>sec.</i> , and <i>tert.</i> hydrogens ^a		
CH ₃	0.32	0.93	≡1
i-C ₃ H ₇	0.25	0.70	≡1
neo-C ₅ H ₁₁	0.71	2.70	≡1
t-C ₄ H ₉	1.70	6.00	≡1

^a statistically corrected.

In the product determining chain transfer step⁷⁰⁾

of di-*tert.*-butylaminium radical cation the secondary hydrogen is more reactive than the primary and both exceed the reactivity of the tertiary hydrogen, quite in contrast to the usual reactivity order in other hydrogen transfer reactions⁵⁾. For the same reason an unusual product composition of heptylchlorides is obtained in the chlorination of n-heptane using N-chlor-diisobutylamine in H₂SO₄ as chlorinating agent.

1.3 69.4 22.9 11.3 isomer distribution of chloroheptanes (%)

The high yield of 2-chloroheptane is again due to the least steric shielding of the methylene group in the 2-position from attack by the bulky diisobutyl aminium radical cation. This may be partly due to coiling of the alkane chain in the polar reaction medium. 99% 1-chloroadamantane is obtained by this procedure from adamantane and N-chloro dimethylamine. As the attacking radical has a positive charge this reaction also strongly responds to polar effects. Thus n-alkane derivatives carrying

Product distribution of chlorinations with N-chloro-diisopropylamine

CH ₃ —CH ₂ —CH ₂ —CH ₂ —CH ₂ —CH ₂ —X	X				
4 85 10 1 — —	—O—COCH ₃				
6 90 2 2 — —	—OH				
4 83 11 1 — 1	—OCH ₃				
7 90 3	—COOCH ₃				

electronegative substituents in the 1-position are chlorinated with high selectivity in the ω -1-position⁷⁰⁾. Similar principles have been used with particular advantage for the selective halogenation of steroids. The bulky reagents

allow in many instances a selective substitution of the most easily accessible 9- α - or 14- α -hydrogens, thus opening synthetic routes to the corticosteroids⁷⁴⁾ and cardenolids⁷³⁾. Similar selective hydroxylations⁷⁵⁾ and fluorinations⁷⁶⁾ of steroids have been disclosed which probably also are free radical reactions⁷⁴⁾. A Completely different highly successful approach for selective free radical substitutions in the steroid field based on intramolecular H-transfer was introduced by the Barton Reaction and widely extended since⁷⁷⁾. The key idea was that 1.5-hydrogen transfer⁷⁸⁾ is for steric reasons by far the preferred intramolecular mode of transfer. This principle has been elegantly extended in recent years by R. Breslow⁷³⁾ to "template directed" reactions in which the reagent, e.g., the aryl iodine dichloride moiety, is bound to the steroid substrate *via* alkyl chains of different chain length. A particular advantage has been worked out in the so-called "relay mechanism" in which the substrate bound reagent — e.g., aryl iodine dichloride — is generated *in situ* by an external reagent — e.g., SO_2Cl_2 — and a substrate bound precursor of the reagent — e.g., aryl iodine⁷³⁾. All these reactions will not be discussed in more detail in this review.

An investigation of the competing halogen transfer from BrCCl_3 and CCl_4 ^{5, 79)} has shown that steric effects are also of importance in atom transfer reactions to alkyl and aryl radicals. Giese⁸⁰⁾ investigated very carefully the temperature depen-

pendence of the selectivity κ of this reaction for a large series of alkyl and aryl radicals. Linear Eyring plots of $\log \kappa$ vs. $1/T$ were obtained over a large temperature range (0°C – 130°C). Two types of radicals had to be distinguished according to this plot, however, because two separate sheafs of straight correlation lines with intersecting points (isoselective temperature) in the range of $60 \pm 20^\circ\text{C}$ and $50 \pm 10^\circ\text{C}$, respectively, were observed. The two types of radicals were classified as π -radicals and σ -radicals, respectively⁸⁰⁾, but probably a more operational distinction as "flexible" (π) and "nonflexible" (σ) may be preferable⁸¹⁾. Above and below the isoselective temperature the selectivity series are reversed. There exists therefore no simple structure selectivity relationship. In contrast, however, the scale of differences in activation enthalpies $\Delta H_{\text{Cl}}^\ddagger - \Delta H_{\text{Br}}^\ddagger$ of the two competing halogen transfer reactions

is independent of temperature. A good linear correlation is obtained, when $\Delta H_{Cl}^\ddagger - \Delta H_{Br}^\ddagger$ is plotted vs. the steric substituent constants $E_s^{c(82)}$ as shown in Fig. 2 for a series of alkyl radicals.

$$\frac{\Delta \Delta_R^\ddagger}{\Delta \Delta H_{CH_3}^\ddagger} = \delta E_s^c$$

With increasing steric shielding of the radical center $\Delta H_{Cl}^\ddagger - \Delta H_{Br}^\ddagger$ also increases. This steric effect is explained by the difference in X-CCl₃ bond strengths which dominates to a greater extent the selectivity ($\Delta H_{Cl}^\ddagger - \Delta H_{Br}^\ddagger$) the later the transition state is reached on the reaction coordinate i.e., the more bulky the attacking alkyl radical is.

Because E_s^c -constants for complex groups are obtainable at present only by an empirical procedure⁸²⁾ a corresponding analysis is not possible for aryl-, vinyl-, and other nonflexible σ -type radicals. This difficulty was overcome recently by the development of a new set of steric substituent parameters $\mathcal{S}_f$ for front strain phenomena. These constants are defined as the difference in heat of formation for the hydrocarbons 30 and 31. The heats of formation are calculated for this purpose by

Fig. 2. Linear free enthalpy relationship between the difference in enthalpy of activation for the halogen transfer from CCl₄ and BrCCl₃ to alkyl radicals and the steric substituent parameters of alkyl radicals⁸³⁾

30

31

molecular mechanics⁸⁴⁾. The plot of Fig. 3 shows that flexible and nonflexible radicals again give two separate correlation lines with $\mathcal{S}_f$ parameters⁸⁵⁾. The nonflexible σ -type radicals have the same geometry as the group R has in the model compounds 30 and 31 used for the computation of $\mathcal{S}_f$. The planar flexible π -type

Fig. 3. Correlation of $\Delta H_{Cl}^{\ddagger} - \Delta H_{Br}^{\ddagger}$ [for the halogen transfer from CCl₄ and BrCCl₃ to radicals] and the steric substituent constants $\mathcal{S}_f$ ^{84, 85)}

No.	Radical	No.	Radical
1	CH ₃	8	CH ₃ C(C ₂ H ₅) ₂
2	1-C ₆ H ₁₃	9	CH ₂ =CH
3	c-C ₆ H ₁₁	10	c-C ₃ H ₅
4	2-Bicyclo[2.2.2]octyl	11	C ₆ H ₅
5	2-C ₈ H ₁₇	12	7-Norbornyl
6	C ₄ H ₉ C(CH ₃) ₂ -CH ₂	13	o-t-C ₄ H ₉ -C ₆ H ₄
7	C ₈ H ₁₇ C(CH ₃) ₂		

radicals on the other hand exert a larger front strain effect towards a reaction partner than predicted from the interaction of its bent analogue structure in **30** and **31**. Therefore the slope of the correlation for the flexible radicals in Fig. 3 is larger than for the nonflexible. This phenomenon supports the assumption of a planar geometry for the flexible π -type alkyl radicals¹⁴). In addition it stresses the importance of steric effects on free radical substitution reactions. Recently, in a similar analysis for bridgehead free radicals it was shown that $\Delta H_{\text{Cl}}^\ddagger - \Delta H_{\text{Br}}^\ddagger$ decreases with increasing internal strain of the polycyclic ring systems, although the front strain of these bridgehead radicals increases⁸⁶). The position of the transition states on the reaction coordinate for halogen transfer to bridgehead radicals is apparently mainly determined by the change in i-strain and not so much by f-strain as expected.

Szeimies recently published an impressive example of a steric effect on a $S_{\text{R}}2$ reaction at carbon for the addition of thiols to the central bond of bicyclo[1.1.0]-systems⁸⁷). From the radical chain addition of thiophenol to **32** the stereoisomeric cyclobutanes **33a** and **33b** are obtained exclusively in 56% yield. The thiylradical

attacks the central C-C-bond in **32** preferentially at the less hindered carbon, generating **34**, although this radical is less stabilized than **35** which would be generated by reversed regioselectivity of thiyl attack on **32**. Steric effects are also known for $S_{\text{R}}2$ -

substitution at heteroelements. When *t*-butoxy radicals attack di-*n*-butyl-*t*-butyl tinchloride a *n*-butyl group is expelled preferentially because it is the smaller ligand which prefers an apical position from which the leaving group usually departs from the addition complex⁸⁸).

IV Steric Effects in Free Radical Addition Reactions

The recognition of anti-Markownikoff orientation when HBr was added to alkenes in the presence of traces of peroxides or air lead to the discovery of the large and important class of free radical addition reactions to unsaturated systems⁸⁹⁾. The anti-Markownikoff orientation of these reactions i.e., the preference of initial radical at-

tack at the less substituted carbon atom of the unsaturated system was interpreted for a long time by the stabilizing influence of α -substituents and in particular of α -alkyl groups at a radical center. As an alternative interpretation, the smaller steric repulsions during radical attack, a double bond at the less substituted end has been discussed⁹⁰⁾. Since the analysis of a large series of bond energies of primary, secondary and tertiary alkyl derivatives had lead to the conclusion that alkyl radicals are not particularly stabilized by α -alkyl substituents⁵⁾, the steric interpretation began to enjoy greater popularity¹⁸⁾. This was supported by the results of intramolecular radical additions leading to cyclization. The homoallylic radical 36 or the 5-hexenyl

radical 38 cyclize exclusively or at least with high preference to the primary radicals 37 and 40, respectively, and not or much slower to the secondary radicals 35 or 39. This was no longer explainable on energetic grounds and a stereoelectronic interpretation was given. During cyclization bond formation by radical attack occurs preferentially at the end of the double bond which is more accessible on steric grounds^{78,91}).

Because the addition steps are generally fast and consequently exothermic chain steps, their transition states should occur early on the reaction coordinate and therefore resemble the starting alkene. This was recently confirmed by *ab initio* calculations for the attack at ethylene⁹²) by methyl radicals and fluorene atoms. The relative stability of the adduct radicals therefore should have little influence on reactivity^{12a}). The analysis of reactivity and regioselectivity for radical addition reactions, however, is even more complex, because polar effects seem to have an important influence. It has been known for some time that electronegative radicals $X\cdot$ prefer to react with ordinary alkenes⁹³) while nucleophilic alkyl or acyl radicals rather attack electron deficient olefins e.g., cyano or carbonyl substituted olefins^{94,95}). The best known example for this behavior is copolymerization⁹⁶). This view was supported by different MO-calculation procedures^{92,97}) and in particular by the successful FMO-treatment of the regioselectivity and relative reactivity of additions of radicals to a series of alkenes^{13a,98}). An excellent review of most of the more recent experimental data and their interpretation was published recently by Tedder and Walton⁹³).

Many examples of the influence of steric effects on reactivity and regioselectivity in free radical additions are known. The anti-Markownikoff regioselectivity apparently is smaller than originally assumed^{5, 18, 93, 99}) and frequently dependent on the size of the attacking radical¹⁰⁰) as shown by the following data¹⁰¹):

1 2 $\text{CH}_3-\text{CH}=\text{CH}-\text{R}$		Relative Reactivity for attack at C_1/C_2	
	$\text{R} \backslash \text{X}\cdot$	$n\text{-C}_4\text{H}_9\text{S}\cdot$	$t\text{-C}_4\text{H}_9\text{S}\cdot$
	$\text{C}_2\text{H}_5\cdot$	1.08	1.10
	$2\text{-C}_3\text{H}_7\cdot$	1.30	2.55
	$t\text{-C}_4\text{H}_9\cdot$	1.91	>100:1

Particularly striking is the deactivation of the rate of radical addition by methyl groups at the center of primary attack as shown by the following data¹⁰²):

Relative rates of attack of alkenes by $\text{CF}_3\cdot$ -radicals

$\text{CH}_2=\text{CH}_2$	$\text{CH}_2=\text{CHCH}_3$	$\text{CH}_2=\text{C}(\text{CH}_3)_2$	$\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2$
↑	↑ ↑	↑ ↑	↑
≡1.0	2.3 0.2	6.0 0.5	2.80

While β -methyl groups exert a slight rate enhancing effect for attack by CF_3 -radicals, α -methyl groups reduce it. The small changes in relative rate make it particularly difficult to propose a unique interpretation⁹³⁾ for these and similar results, because high regioselectivity and low substrate selectivity cannot both be explained on the same energetic grounds e.g., by the different thermodynamic stability of primary, secondary and tertiary radicals¹⁰³⁾. This is even more contrasting for radicals other than CF_3 . Ethylene and isobutene have comparable methyl affinities which are 5–10 times higher than those of *cis*- and *trans*-butene^{18, 104)}. Cyclopropyl radicals attack ethylene even three times faster than isobutene¹⁰⁵⁾. Similar trends have been observed in detailed investigations of halogenated alkenes⁹³⁾.

A further interesting example of a steric effect was recently published¹⁰⁶⁾. The sterically shielded 2.2.6.6-tetramethyl piperidinium radical cation adds to cyclohexene by almost three powers of ten slower than the piperidinium radical cation itself¹⁰⁷⁾.

The combined influences of polar and steric effects and of the strength of the newly formed bond⁹³⁾ was also recognized in the reaction of α,β -unsaturated carbonyl compounds and similar electron deficient alkenes⁹⁵⁾ with organomercurials and NaBH_4 . For the addition of alkyl radicals to substituted styrenes, ρ assumed a

small positive value which was, however, dependent on temperature. For the ρ -values of a series of alkyl radicals an isoselective temperature at 90 °C was noted¹⁰⁸⁾. For the addition of alkyl radicals of different size to maleic anhydride **46** and methyl-maleic anhydride **41**, steric effects on the regioselectivity and stereoselectivity became apparent besides polar effects^{99, 103)}. The regioselectivity series **44**: **45** is in accord with an explanation by the steric effect in the addition step. The competition constants $k_{\text{H}}/k_{\text{CH}_3}$ for the reaction of an alkyl radical with **41** and **46**, respectively, likewise show the influence of a steric effect, but a polar effect as described by the FMO-description could hardly be distinguished. The more nucleophilic attacking radical e.g., *t*-butyl, is the more reactive and likewise the more selective¹⁰⁹⁾. Finally stereoselectivity in the formation of *cis*- and *trans*-**44** shows that in the second chain step, H-transfer from the less hindered side is preferred, although in this way the less stable *cis*-**44** is formed in preference to *trans*-**44**. It has been known for a long time that norbornene is also attacked by radicals from the *exo*-side^{89, 110)} with great preference.

$R\cdot$	44:45	<i>cis</i> -44: <i>trans</i> -44	k_H/k_{CH_3} ($-10^\circ C$)
$(CH_3)_3C\cdot$	99:1	92: 8	13.6
$\alpha\text{-C}_6\text{H}_{11}\cdot$	97:3	89:11	9.8
$1\text{-C}_6\text{H}_{13}\cdot$	97:3	62:38	6.5
$CH_3\cdot$	98:2	43:57	—

The first step of a free radical aromatic substitution, the formation of the σ -complex, is also an addition step. The o,m,p-product ratio therefore also responds to steric effects. This is shown for the free radical phenylation and dimethylamination of toluene and *t*-butylbenzene in Table 8. The larger the substituent on the aromatic system and the bulkier the attacking radical, the more p-substitution product is obtained at the expense of o-substitution. In the phenylation reaction the yield of m-product also increases in contrast to the dimethylamination reaction. The substitution pattern of this latter reaction is, in addition to the steric effect, governed heavily by polar effects because a radical cation is the attacking species¹¹³.

Table 8. Steric substituent effects in free radical aromatic substitutions

R·	Toluene			t.-Butylbenzene		
	%o	%m	%p	%o	%m	%p
C ₆ H ₅ · ¹¹¹⁾	63	21	16	24	49	27
(CH ₃) ₂ NH ⁺ · ¹¹²⁾	5.6	22.6	71.8	0	14.6	85.4

Even more pronounced steric effects have been observed for the free radical alkylation of protonated N-heterocyclic bases by the procedure of Minisci^{69, b, d)}. Quinoline is attacked selectively in the 2- and 4-position by nucleophilic alkyl radicals in sulfuric acid. The largest radicals, *t*.-butyl, react exclusively in the 2-position because of steric hindrance by the peri-hydrogen when attack occurs at the 4-position.

R·	% 2-alkylquinoline	% 4-alkylquinoline
CH ₃ ·	23	25 ^a
1-C ₃ H ₇ ·	28	36 ^a
2-C ₃ H ₇ ·	13	26 ^a
<i>t</i> -C ₄ H ₉ ·	100	0

^a besides 2,4-dinitroquinoline.

Steric effects, although clearly recognized, introduce relatively small rate retardations or increases in selectivity in all these examples, probably because the transition states of all these addition reactions are rather loose ones, i.e., they occur early on the reaction coordinate when the distances between the radical and the substrates are still rather large^{92, 93, 97)}. An extreme example of a free radical reaction which does not respond heavily to steric effects, is the S_{RN}1-substitution reaction of Kornblum¹¹⁴⁾ by which bonds between two quaternary carbons can be formed with great ease and in good yield, as is shown by one of many published examples¹¹⁴⁾. The decisive step

in the chain reaction is the attack of a *p*-nitrobenzyl radical at the carbanion center generating a new aromatic radical anion. The rate of this new type of reaction is apparently extremely high and therefore does not respond strongly to steric effects

The unusual persistence of many highly branched alkyl radicals^{9, 10)} mentioned in the introduction proves that radical dimerizations can be hindered or even suppressed by the steric effect of bulky groups. For the dimerization of di-*tert*-butylmethyl e.g., an activation barrier of about 20 kcal/mol was estimated⁴⁹⁾. Most examples of persistent alkyl radicals, as e.g., 5 and 6, have no β -hydrogens which are the prerequisite for disproportionation to occur. Triisopropylmethyl 7, however, is also persistent although β -elimination of hydrogen should lead to destruction of this radical in the course of disproportionation with another radical. It is presumed⁹⁾ that 7 has a conformation 47 in which the β -hydrogens are arranged in the nodal plane of the SOMO. Therefore, H-transfer to an attacking radical and formation of a double bond cannot be a synchronous process. Very recently, however, Berndt et al.^{10b)} have

reported that trineopentylmethyl **48** and a few other neopentyl substituted methyl radicals also show remarkable persistence. It was not reported whether their decay is a unimolecular or bimolecular process.

In general, the rate ratio of the disproportionation k_d and dimerisation k_c increases with the bulk or size of the radicals concerned¹¹⁷⁾. For simple alkyl radicals even a

Fig. 4. Relation between the statistical corrected ratio of rates of disproportionation and dimerization of alkyl radicals and their E_s^c -constants⁴³⁾ $\lg \frac{k_d}{k_c} \cdot \frac{1}{n_{\beta H}} = -0.48 E_s^c - 1.73$ ($r = 0.9901$)
 $n_{\beta H}$ = number of β -H-atoms in the radical

linear relation between $\lg k_d/k_c$ (statistically corrected) and Taft's steric substituent constants E_s^c was found⁴³⁾ (see Fig. 4). The interpretation of this steric effect is a more subtle problem than recognized on first sight. Schuh and Fischer¹¹⁸⁾ have shown by an investigation of the influence of temperature and solvent viscosity on the termination constant, as well as k_d and k_c , for *t*-butyl radicals that this effect cannot be explained simply by the greater steric hindrance of approach of the two radicals for dimerization than for disproportionation. The termination constant $2k_t$ of the self reaction of *t*-butyl radicals is diffusion controlled and requires no activation. Observed large solvent and temperature dependences of k_d/k_c were ascribed to anisotropic reorientation motions of the radicals during their encounter in the solvent cage. This may also be the reason for the low probability of recombination of 2-cyano-2-propyl radicals as deduced from CIDNP-experiments¹¹⁹⁾.

Recently, an interesting example of stereoselective radical dimerization was described which awaits explanation. It was found that radical 49 ($X = p\text{-Cl}$; $R = t\text{-butyl}$) dimerizes diastereoselectively¹²⁰⁾ to the more stable *D, L*-diastereomer in contrast to other radicals 49 with smaller side chains R . It has not been clearly decided so far

X·	R	Yield ratio D, L: meso
H	CH ₃	1:1
H	C ₂ H ₅	1:1
Cl	t-C ₄ H ₉	1.66:1

whether the dimerization of this rather bulky radical is an activated process or a diffusion controlled one, and whether diastereoselectivity is due to a difference in free activation enthalpy for the two possible dimerization modes or due to anisotropic orientation motions as discussed by Schuh and Fischer¹¹⁸). The temperature dependence of the diastereoselectivity of this dimerization was found to be quite small. The influence of solvent¹¹⁸) is actively being investigated at present at the author's laboratory.

Acknowledgements. It is a pleasure to thank my coworkers whose names are mentioned in the references and in particular to Dr. Beckhaus for excellent collaboration and important contributions to our own work reported in this review. We are also indebted to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and BASF AG for financial support of our work.

VI References

1. For a stimulating discussion on historical developments see: a) McBride, J. M.: *Tetrahedron* **30**, 2009 (1974), b) Walling, C.: *Organic Free Radicals*. W. A. Pryor (ed.). ACS symposium Series 69, p. 3 (1978)
2. Lankamp, H., Nauta, W. T., McLean, C.: *Tetrahedron Lett.* **1968**, 249; Staab, H. A., Brettschneider, H., Brunner, H.: *Chem. Ber.* **103**, 1101 (1970); Volz, H., Lotsch, W., Schnell, H. W.: *Tetrahedron* **26**, 5343 (1970)
3. Force Field Calculations of **2** were recently published by Hounshell, W. D., et al.: *J. Am. Chem. Soc.* **99**, 1916 (1977); for an x-ray analysis of the first isolated derivative of **2** see Stein, W., Winter, W., Rieker, A.: *Angew. Chem.* **90**, 737 (1978); *Angew. Chem. Int. Ed. Engl.* **17**, 692 (1978). The unusually short central C-C-bond length is in conflict with the low thermal stability of this compound and with the known long C-C-bonds in other crowded hydrocarbons e.g., Destro, R., Pilati, T., Simonetta, M.: *J. Am. Chem. Soc.* **100**, 6509 (1978)
4. Stolle, F. V. D., Rozantsev, E. G.: *Russ. Chem. Rev.* **42**, 1011 (1973); Kessler, H., Moosmayer, A., Rieker, A.: *Tetrahedron* **25**, 287 (1969); Stein, M., Rieker, A.: *Tetrahedron Lett.* **1975**, 2123
5. Rüchardt, C.: *Angew. Chem.* **82**, 845 (1970); *Angew. Chem. Int. Ed. Engl.* **9**, 830 (1970)
6. Ballester, M. in *Free Radicals in Solution*, p. 123, London: Butterworths 1967; *Pure and Appl. Chem.* **15**, 123 (1967)

- 7a. Dimroth, K., Kalk, F., Neubauer, G.: *Chem. Ber.* **90**, 2058 (1957); b. Müller, E., Ley, K.: *Z. Naturforsch.* **8b**, 694 (1953); Cook, C. D.: *J. Org. Chem.* **18**, 261 (1953); c. Buchachenko, A. L., *Stable Radicals*, New York: Consultants Bureau 1965; Forrester, A. R., Hay, J. M., Thompson, R. H., *Organic Chemistry of Stable Free Radicals*, New York, London: Academic Press 1968
8. For a discussion concerning the difference between thermodynamic stability of radicals and their kinetic persistence e.g., due to steric effects see Ref.⁹⁾
9. Griller, D., Ingold, K. U.: *Acc. Chem. Res.* **9**, 13 (1976)
10. For further examples of persistent nonconjugated crowded radicals see e.g., a. Schreiner, K., Berndt, A.: *Tetrahedron Lett.* **1973**, 3411; b. Schlüter, K., Berndt, A.: *Tetrahedron Lett.* **1979**, 929; c. Mendenhall, G. D., Griller, D., Ingold, K. U.: *Chem. in Britain* **10**, 248 (1974); d. Mendenhall, G. D.: *Sci. Prog. Oxford* **65**, 1 (1978)
11. For an early pioneer work see Ziegler, K.: *Angew. Chem.* **61**, 168 (1949)
- 12a. Rüchardt, C., *Mechanismen radikalischer Reaktionen*, Forschungsbericht des Landes Nordrhein-Westfalen Nr. 2471, Westdeutscher Verlag, Opladen 1975; Rüchardt, C., *Topics Curr. Chem.* **6**, 251 (1966); Russ. Translation: *Uspekhi Khim.* XXXVII, 1402 (1968); b. Davies, W. H., Glenton, J. H., Pryor, W. A.: *J. Org. Chem.* **42**, 7 (1977), c. Rüchardt, C., Mayer-Ruthardt, J.: *Chem. Ber.* **104**, 593 (1971); Rüchardt, C., Pantke, R.: *Chem. Ber.* **106**, 2542 (1973)
- 13a. Fleming, Ian, *Frontier Orbitals and Organic Chemical Reactions* p. 182, London: Wiley 1976; b. Fukui, K., *Theory of Orientation and Stereoselection*, p. 47ff. Heidelberg-New York: Springer 1975; c. Bartels, H., Eichel, W., Riemenschneider, K., Boldt, P.: *J. Am. Chem. Soc.* **100**, 7740 (1978); d. Giese, B. und Meixner, J., *Angew. Chem.* **91**, 167 (1979); *Angew. Chem. Int. Ed. Engl.* **18**, 154 (1979)
14. Although many spectroscopic and chemical investigations of alkyl free radicals have been interpreted by a planar geometry, several more recent results point to a slightly pyramidal arrangement of the bonds at the central C-atom of some alkyl radicals. c.f. Kaplan L., *Free Radicals*, Kochi, J. K., (ed.), Vol. 2, p. 361, 1st edition, New York: Wiley 1973; Fort, R. C., Schleyer, P. v. R.: *Adv. in Alicyclic Chem.* **1**, 284 (1966); Beckwith, A. L. J., *MTP International Review of Science*, Vol. **10**, 1 (1973); Wood, D. E. et al.: *J. Am. Chem. Soc.* **94**, 6241 (1972); Symons, M. C. R.: *Tetrahedron Lett.* **1973**, 207; Lisle, J. B., Williams, L. F., Wood, D. E.: *J. Am. Chem. Soc.* **98**, 227 (1976); Krusic, P. J., Meakin, P.: *J. Am. Chem. Soc.* **98**, 228 (1976); Krusic, P. J., Bingham, R. C.: *J. Am. Chem. Soc.* **98**, 230 (1976); Bonazzola, L., Leray, N., Roncin, J.: *J. Am. Chem. Soc.* **99**, 8348 (1977); McBride, J. M.: *J. Am. Chem. Soc.* **99**, 6760 (1977); Claxton, T. A., Platt, E., Symons, M. C. R.: *Molecular Phys.* **32**, 1321 (1976); Dyke, J. et al.: *Phys. Sci.* **16**, 197 (1977); C.A. **89**, 107103 (1978); Griller, D. et al.: *J. Am. Chem. Soc.* **100**, 6750, (1978). Giese, B., Beckhaus, H. D., *Angew. Chem.* **90**, 635 (1978); *Angew. Chem. Int. Ed. Engl.* **17**, 594 (1978). In any case, all results point to much weaker force constants of out of plane deformations for free radicals than for carbenium ions. Bulky substituents seem to increase the tendency for a planar geometry of a radical center as e.g., in 2,2-di-*t*-butyl cyclopropyl radicals; cf. Malatesta, V., Forrest, D., Ingold, K. U.: *J. Am. Chem. Soc.* **100**, 7073 (1978)
15. c.f. Eliel, E. L., *Stereochemistry of Carbon Compounds*, 1st edition, p. 267 ff. New York: McGraw-Hill Book Co. 1962, Eliel, E. L. in Newman, M. S., *Steric Effects in Organic Chemistry*, p. 212ff. New York: Wiley 1965
16. The geometry at the transition states of the ionisation is close to the sp^2 -state of the carbenium ion: cf. Arnett, E. M., Petro, C.: *J. Am. Chem. Soc.* **100**, 2563 (1978)
17. cf. Hammond, G. S.: *J. Am. Chem. Soc.* **77**, 334 (1955)
18. Rüchardt, C. et al.: *Structure Reactivity-Relationships in the Chemistry of Aliphatic Free Radicals*. XXIII. Internat. Congr. Pure and Appl. Chemistry, Vol. **4**, p. 223. Special Lectures, London: Butterworths 1971
19. Overberger, C. G. et al.: *J. Am. Chem. Soc.* **75**, 2078 (1953)
20. Bonnekessel, J., Rüchardt, C.: *Chem. Ber.* **106**, 2890 (1973)
21. Hinz, J., Rüchardt, C.: *Liebigs Ann. Chem.* **765**, 94 (1972)
22. Applequist, D. E., Klug, J. H.: *J. Org. Chem.* **43**, 1729 (1978)

23. Schuh, H., et al.: *Helv. Chim. Acta* 57, 2011 (1974)
24. Beckhaus, H. D., Schoch, J., Rüchardt, C.: *Chem. Ber.* 109, 1369 (1976)
- 25a. Lorenz, P., Rüchardt, C., Schacht, E.: *Chem. Ber.* 109, 1369 (1976); b. The thermal decomposition of cycloalkanecarboxylates and their α -methyl- and α -phenyl derivatives was recently reinvestigated very carefully by Wolf, R. A., Migliore, M. J., Fuery, P. H., Gagnier, P. R., Sabeta, J. C., Trocino, R. J.: *J. Am. Chem. Soc.* 100, 7867 (1978); Their results are in perfect agreement with the interpretation given earlier^{25a)} although a slightly modified interpretation is offered, see also Nelsen, S. F., Peacock, V. E., and Kesse, C. R. *J. Am. Chem. Soc.* 100, 7017 (1978)
26. Schulz, A., Nguyen-Tran-Giac, Rüchardt, C.: *Tetrahedron Lett.* 1977, 845
27. Tidwell, T. T.: *Tetrahedron* 34, 1855 (1978), see also Ziebarth, M. and Neumann, W. P. *Liebigs Ann. Chem.* 1978, 1765
- 28a. Bandlish, B. K. et al.: *J. Am. Chem. Soc.* 97, 5856 (1975); b. Garner, A. W. et al.: *J. Am. Chem. Soc.* 97, 7377 (1975); c. Prochazka, M.: *Collect. Czechoslov. Chem. Commun.* 41, 1557, (1976); d. Duismann, W. et al.: *Liebigs Ann. Chem.* 1976, 1820; Nguyen-Tran-Giac, Rüchardt, C.: *Chem. Ber.* 110, 1095 (1977)
- 29a. Overberger, C. G., et al.; *J. Am. Chem. Soc.* 76, 6185 (1954); b. Overberger, C. G., DiGiulio, A. V. *J. Am. Chem. Soc.* 81, 2154 (1959); c. Lim, D.: *Collect. Czechoslov. Chem. Commun.* 33, 1122 (1968)
- 30a. Overberger, C. G., DiGiulio, A. V.: *J. Am. Chem. Soc.* 81, 1194 (1959); b. Prochazka, M., Rejmanova, P., Ryba, O.: *Collect. Czechoslov. Chem. Commun.* 39, 2404 (1974); c. Prochazka, M., Ryba, O., Lim, D.: *Collect. Czechoslov. Chem. Commun.* 36, 2640, 3650 (1971); d. Kovacic, P. et al.: *J. Org. Chem.* 34, 3312 (1969); e. Gohen, S. G., Groszos, S. J., Sparrow, D. B.: *J. Am. Chem. Soc.* 72, 3947 (1950); f. Brooks, B. W., Dainton, F. S., Ivin, K. I.: *Trans. Farad. Soc.* 61, 1437 (1965)
31. Newman, M. S.: in *Steric Effects in Organic Chemistry* 1st edition, p. 206, New York: Wiley 1956
32. Prochazka, M.: *Collect. Czechoslov. Chem. Commun.* 42, 2394 (1977)
33. Duismann, W., Rüchardt, C.: *Chem. Ber.* 106, 1083 (1973)
34. Schreiner, K., Berndt, A.: *Angew. Chem.* 87, 285 (1975) *Angew. Chem. Int. Ed. Engl.* 14, 366 (1975)
- 35a. Koenig, T.: in *Free Radicals*, Kochi, J. K. (ed.) 1st edition, Vol. 1, p. 113, New York: Wiley Interscience 1973; b. Hinz, J., Oberlinner, A., Rüchardt, C.: *Tetrahedron Lett.* 1973, 1975; c. Engel, P. S., Bishop, D. J.: *J. Am. Chem. Soc.* 97, 6754 (1975); d. Koga, G., Anselme, J. P. in *The Chemistry of the Hydrazo, Azo and Azoxy Groups*, Patai, S. (ed.), Vol. 2, 1st edition, p. 861, New York: Interscience 1975
36. cf. Green, J. G., Porter, N. A.: *J. Am. Chem. Soc.* 99, 1264 (1977), Suehiro, T., et al.: *Bull. Chem. Soc. Jap.* 50, 3325 (1977). Porter, N. A., Dubay, G. R., Green, J. G.: *J. Am. Chem. Soc.* 100, 920 (1978); Pryor, W. A., Smith, K.: *J. Am. Chem. Soc.* 89, 1741 (1967)
37. Schulz, A., Rüchardt, C.: *Tetrahedron Lett.* 1977, 849
- 38a. Ernst, J. A., Thankachan, C., Tidwell, T. T.: *J. Org. Chem.* 39, 3614 (1974); b. Duismann, W., Rüchardt, C.: *Liebigs Ann. Chem.* 1976, 1834
- 39a. Engler, E. M., Andose, J. D., Schleyer, P. v. R.: *J. Am. Chem. Soc.* 95, 8005 (1973); b. Schleyer, P. v. R., Williams, J. B., Blanchard, K. R.: *J. Am. Chem. Soc.* 92, 2377 (1970)
40. Andose, J., Mislow, K.: *J. Am. Chem. Soc.* 96, 2168 (1974)
41. Hellmann, G., Beckhaus, H. D., Rüchardt, C.: *Chem. Ber.* 1979 in print
42. Tsang, W.: *J. Chem. Phys.* 44, 4283 (1966)
43. Beckhaus, H. D., Rüchardt, C.: *Chem. Ber.* 110, 878 (1977)
44. Rüchardt, C., Winiker, R.: unpublished
45. Rüchardt, C. et al.: *Angew. Chem.* 89, 913 (1977); *Angew. Chem. Int. Ed. Engl.* 16, 875 (1977)
46. Tsang, W.: *J. Chem. Phys.* 43, 352 (1965)
47. Baxter, S. G. et al.: *J. Am. Chem. Soc.* submitted
48. Beckhaus, H. D., Hellmann, G., Rüchardt, C.: *Chem. Ber.* 111, 3764 (1978)
49. Beckhaus, H. D., Hellmann, G., Rüchardt, C.: *Chem. Ber.* 111, 72 (1978)

50. Berces, T., Seres, L., Manta, F.: *Acta Chim. Acad. Sci. Hung.* **71**, 31 (1973)
51. Burcat, A. et al.: *Int. J. Chem. Kinetics* **5**, 345 (1973)
52. Dissertation Hellmann, G., Univ. Freiburg 1977
53. Diplomarbeit Kratt, G., Univ. Freiburg 1976
54. Stein, S. E., Golden, D. M.: *J. Org. Chem.* **42**, 839 (1977)
55. Dissertation Dempewolf, E., Univ. Freiburg 1977
56. Bartlett, P. D., McBride, M. J.: *J. Am. Chem. Soc.* **87**, 1727 (1965)
57. Sargent, G. D.: in G. Olah, Schleyer, P. v. R., *Carbonium Ions III*, New York: Wiley-Interscience 1972, 1099
58. Goltzke, V. et al.: *Nouv. J. Chim.* **2**, 169 (1978)
59. Dissertation Goltzke, V., Univ. Freiburg 1977; s. a. Heine, H. G. et al.: *J. Org. Chem.* **41**, 1907 (1976) for the corresponding photochemical formation of bridgehead radicals
60. Bunce, N. J., Hadley, M.: *J. Org. Chem.* **39**, 2271 (1974)
61. McKean, D. C.: *Chem. Soc. Rev.* **7**, 399 (1978)
62. Bartlett, P. D. et al.: *Acc. Chem. Res.* **3**, 177 (1970)
63. Gruselle, M., Lefort, D.: *Tetrahedron* **32**, 2719 (1976)
64. Fort, R. C., Schleyer, P. v. R.: *Adv. in Alicyclic Chem.* **1**, 284 (1966); Koch, V. R., Gleicher, G. J.: *J. Am. Chem. Soc.* **93**, 1657 (1971)
65. Tabushi, I., Kojo, S., Fukunishi, K.: *J. Org. Chem.* **43**, 2370 (1978)
66. Mazur, Y., Cohen, Z.: *Angew. Chem.* **90**, 289 (1978); *Angew. Chem. Int. Ed. Engl.* **17**, 281 (1978)
67. Opeida, I. A., Timokhin, V. I.: *Ukr. Khim. Zh.* **44**, 187 (1978); *C. A.* **88**, 189609 (1978); Koshel, G. N. et al.: *Zh. Org. Khim. (USSR)* **14**, 534 (1978)
68. Cristol, S. J. et al.: *J. Org. Chem.* **41**, 1919 (1976)
69. Russell, G., *Free Radicals*, Kochi, J. K. (ed.) Vol. 1, p. 312 1st edition, New York: Wiley 1973; s. a. Breslow, R. et al.: *J. Am. Chem. Soc.* **94**, 3276 (1972)
- 70a. Deno, N. C.: in *Methods in Free Radical Chemistry* (E. S. Huyser) Vol. 3, New York: Dekker 1972; Deno, N. C., Pohl, D. G.: *J. Org. Chem.* **40**, 380 (1975); *J. Am. Chem. Soc.* **96**, 6680 (1974); b. Minisci, F.: *Synthesis* 1973, 1; c. Bernardi, R., Galli, R., Minisci, F.: *J. Chem. Soc. B*, 1968, 324; d. Minisci, F.: *Topics Curr. Chem.* **62**, 1 (1976); e. Johnson, R. A., Green, F. D.: *J. Org. Chem.* **40**, 2192 (1975)
71. Deno, N., Fishbein, R., Wyckoff, J. C.: *J. Am. Chem. Soc.* **93**, 2065 (1971)
72. Breslow, R. et al.: *J. Am. Chem. Soc.* **94**, 3277 (1972)
73. Breslow, R.: *Chem. Soc. Rev.* **1**, 553 (1972); Breslow, R. et al.: *J. Am. Chem. Soc.* **100**, 1213 (1978)
74. Breslow, R. et al.: *J. Am. Chem. Soc.* **99**, 905 (1977)
75. Rotman, A., Mazur, Y.: *J. Am. Chem. Soc.* **94**, 6228 (1972); Mazur, Y.: *Pure Appl. Chem.* **41**, 145 (1975)
76. Barton, D. H. R. et al.: *J. Am. Chem. Soc.* **98**, 3036 (1976)
77. Akhtar, M.: *Adv. Photochemistry* **2**, 263 (1964); Mihailovic, M. L., Cekovic, Z.: *Synthesis* 1970, 209; Kalvoda, J., Heusler, K.: *Synthesis* 1971, 501; Heusler, K.: *Heterocycles* **3**, 1035 (1975); Hesse, R. H., *Adv. Free Rad. Chem.* **3**, 83 (1969)
78. Wilt, J. W.: in Kochi, J. K., *Free Radicals*, Vol. 1, p. 333, New York: Wiley 1973
79. Herwig, K., Lorenz, P., Rüchardt, C.: *Chem. Ber.* **108**, 1421 (1975)
80. Giese, B.: *Angew. Chem.* **88**, 159, 161, 723 (1976); *Angew. Chem. Int. Ed. Engl.* **15**, 173, 174, 688 (1976)
81. Private communication of Prof. Giese, Darmstadt
82. Fujita, T., Takayama, C., Nakajima, M.: *J. Org. Chem.* **38**, 1623 (1973)
83. Giese, B.: *Angew. Chem.* **89**, 162 (1977); *Angew. Chem. Chem. Int. Ed. Engl.* **16**, 125 (1977)
84. Beckhaus, H. D.: *Angew. Chem.* **90**, 633 (1978); *Angew. Chem. Int. Ed. Engl.* **17**, 592 (1978)
85. Giese, B., Beckhaus, H. D.: *Angew. Chem.* **90**, 635 (1978) *Angew. Chem. Int. Ed. Engl.* **17**, 594 (1978)
86. Giese, B., Stellmach, J.: *Tetrahedron Lett.* 1979, 857
87. Szeimies, G. et al.: *Chem. Ber.* **111**, 1922 (1978); Dietz, P., Szeimies, G., *Chem. Ber.* **111**, 1923 (1978)

88. Davies, A. G. et al.: *J. Organometal. Chem.* **118**, 289 (1976)
89. For a summary see Davies, D. I. in *MTP International Review of Science*, Vol. **10**, p. 49, London, Butterworths 1973; Abell, P. I., *Free Radicals*, Kochi, J. K. (ed.) Vol. **2**, p. 63, New York: Wiley 1973
90. Walling, C.: *Free Radicals in Solution*, New York: Wiley 1957. For a recent MINDO/3 study supporting this interpretation see Dewar, M. J. S. and Olivella, S., *J. Am. Chem. Soc.* **100**, 5290 (1978)
91. Summaries at Beckwith, A. L. J., *Essays in Free Radical Chemistry* Norman, R. O. C. ed. Chemical Society, Special Publ. **1970**, 239; Julia, M.: *Pure and Appl. Chem.* **15**, 167 (1967); Nonhebel, D. C., Walton, J. C.: *Free Radical Chemistry*, p. 533ff. Cambridge: University Press 1974
92. Clark, D. T., Scanlan, J. W., Walton, J. C.: *Chem. Phys. Lett.* **55**, 102 (1978)
93. Tedder, J. M., Walton, J. C.: *Acc. Chem. Research* **9**, 183 (1976)
94. Brown, H. C.: *Organic Synthesis via Boranes*, New York: Wiley 1975; Davies, D. I., Parrott, J. M., *Free Radicals in Organic Synthesis*, Berlin-Heidelberg-New York: Springer 1978
95. Giese, B., Meister, J.: *Chem. Ber.* **110**, 2588 (1977)
96. Jenkins, A. D.: *Adv. in Free Radical Chem.* **2**, 139 (1967)
97. Bonacic-Koutecky, V., Koutecky, J., Salem, L.: *J. Am. Chem. Soc.* **99**, 842 (1977)
98. Riemenschneider, K. et al.: *Tetrahedron Lett.* **1979**, 185; Riemenschneider, K. et al.: *Tetrahedron Lett.* **1979**, 189
99. Giese, B., Meixner, J.: *Tetrahedron Lett.* **1977**, 2779 and Ref.⁸⁾
100. Capka, M., Chvalovsky, V.: *Collect. Czechoslov. Chem. Commun.* **33**, 2872 (1968)
101. Dissertation Müller, H. J.: Univ. Freiburg 1977
102. Low, H. C., Tedder, J. M., Walton, J. C.: *Int. J. Chem. Kinet.* **10**, 325 (1978)
103. Giese, B., Zwick, W.: *Angew. Chem.* **90**, 62 (1978); *Angew. Chem. Int. Ed. Engl.* **17**, 66 (1978)
104. Szwarc, M., Binks, J. H.: *Theoretical Organic Chemistry Kekule Symposium 1958*, p. 262, London: Butterworths 1958
105. Stefani, A. P., Chuang, L. Y. Y., Todd, H. E.: *J. Am. Chem. Soc.* **92**, 4168 (1970)
106. Yip, R. W. et al.: *J. Phys. Chem.* **82**, 1194 (1978)
107. Cessna, A. J. et al.: *J. Am. Chem. Soc.* **99**, 4044 (1977)
108. Giese, B., Meister, J.: *Angew. Chem.* **89**, 178 (1977); *Angew. Chem. Int. Ed. Engl.* **16**, 178 (1977)
109. Caronna, T. et al.: *Tetrahedron* **33**, 793 (1977); Citterio, A. et al.: *J. Am. Chem. Soc.* **99**, 7960 (1977)
110. Giese, B., Jay, K.: *Chem. Ber.* **110**, 1364 (1977)
111. Perkins, M. J.: *Free Radicals*, Kochi, J. K. (ed.), Vol. **2**, p. 231, 1st edition, New York: Wiley 1973
112. Minisci, F.: *Topics Curr. Chem.* Vol. **62**, Heidelberg: Springer 1970, p. 3; Sosnovsky, G., Rawlinson, D. J., *Adv. Free Radical Chem.* **4**, 203 (1972)
113. Chow, Y. L. et al.: *Chem. Rev.* **78**, 243 (1978)
114. Kornblum, N.: *Angew. Chem.* **87**, 797 (1975), *Angew. Chem. Int. Ed. Engl.* **14**, 734 (1975); Kornblum, N.: *Pure and Appl. Chem.* **4**, 81 (1971); Kornblum, N.: *J. Am. Chem. Soc.* **100**, 289 (1978)
115. Bunnett, J. F.: *J. Chem. Educ.* **51**, 313 (1974); Bunnett, J. F.: *Acc. Chem. Research* **11**, 431 (1978)
116. Norris, R. K., Randler, D.: *Austr. J. Chem.* **29**, 2621 (1976)
117. Gibian, M. J., Corley, R. C.: *Chem. Rev.* **73**, 441 (1973); Stein, S. E., Rabinovitch, B. S.: *Int. J. Chem. Kinetics* **7**, 531 (1975)
118. Schuh, H. H., Fischer, H.: *Helv. Chim. Acta* **61**, 2130, 2463 (1978)
119. Pershin, A. D. et al.: *Collect. Czechoslov. Chem. Commun.* **43**, 1349 (1978)
120. Eichin, K. H. et al.: *Angew. Chem.* **90**, 987 (1978); *Angew. Chem. Int. Ed. Engl.* **17**, 934 (1978)