

Topics in Current Chemistry

88

Editorial Board: M.J.S. Dewar
K. Hafner E. Heilbronner S. Ito
J.-M. Lehn K. Niedenzu C.W. Rees
K. Schäfer G. Wittig
Managing Editor: F.L. Boschke

C. Rüchardt
Steric Effects
in Free Radical Chemistry

L. Birkofer and O. Stuhl
Silylated Synthons

K. A. Muszkat
The 4a, 4b-Dihydrophenanthrenes

N. T. Anh
Regio- and Stereo-Selectivities
in Some Nucleophilic Reactions



Organic Chemistry
Syntheses and Reactivity

Springer-Verlag Berlin Heidelberg New York

Organic Chemistry
Syntheses and Reactivity



Springer-Verlag
Berlin Heidelberg New York 1980

This series presents critical reviews of the present position and future trends in modern chemical research. It is addressed to all research and industrial chemists who wish to keep abreast of advances in their subject.

As a rule, contributions are specially commissioned. The editors and publishers will, however, always be pleased to receive suggestions and supplementary information. Papers are accepted for "Topics in Current Chemistry" in English.

ISBN 3-540-09817-8 Springer-Verlag Berlin Heidelberg New York
ISBN 0-387-09817-8 Springer-Verlag New York Heidelberg Berlin

Library of Congress Cataloging in Publication Data. Main entry under title: Organic chemistry, syntheses and reactivity. (Topics in current chemistry ; 88) Contents: Rüchardt, C. Steric effects in free radical chemistry. — Birkhofer, L. and Stuhl, O. Silylated synthons. [etc.] 1. Chemistry Organic — Addresses, essays, lectures. I. Rüchardt, Christoph, 1929 — II. Series. QD1.F58. vol. 88. [QD255]540'.8s [547] 79-24429

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically those of translation, reprinting, re-use of illustrations, broadcasting, reproduction by photocopying machine or similar means, and storage in data banks. Under § 54 of the German Copyright Law where copies are made for other than private use, a fee is payable to the publisher, the amount of the fee to be determined by agreement with the publisher.

© by Springer-Verlag Berlin Heidelberg 1980
Printed in Germany

The use of registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Typesetting and printing: Schwetzingen Verlagsdruckerei GmbH, 6830 Schwetzingen. Bookbinding: Konrad Triltsch, Graphischer Betrieb, 8700 Würzburg
2152/3140—543210

Editorial Board:

- | | |
|--------------------------------------|---|
| Prof. Dr. <i>Michael J. S. Dewar</i> | Department of Chemistry, The University of Texas
Austin, TX 78712, USA |
| Prof. Dr. <i>Klaus Hafner</i> | Institut für Organische Chemie der TH
Petersenstraße 15, D-6100 Darmstadt |
| Prof. Dr. <i>Edgar Heilbronner</i> | Physikalisch-Chemisches Institut der Universität
Klingelbergstraße 80, CH-4000 Basel |
| Prof. Dr. <i>Shô Itô</i> | Department of Chemistry, Tohoku University,
Sendai, Japan 980 |
| Prof. Dr. <i>Jean-Marie Lehn</i> | Institut de Chimie, Université de Strasbourg, 1, rue
Blaise Pascal, B. P. 296/R8, F-67008 Strasbourg-Cedex |
| Prof. Dr. <i>Kurt Niedenzu</i> | University of Kentucky, College of Arts and Sciences
Department of Chemistry, Lexington, KY 40506, USA |
| Prof. Dr. <i>Charles W. Rees</i> | Hofmann Professor of Organic Chemistry, Department
of Chemistry, Imperial College of Science and Techno-
logy, South Kensington,
London SW7 2AY, England |
| Prof. Dr. <i>Klaus Schäfer</i> | Institut für Physikalische Chemie der Universität
Im Neuenheimer Feld 253, D-6900 Heidelberg 1 |
| Prof. Dr. <i>Georg Wittig</i> | Institut für Organische Chemie der Universität
Im Neuenheimer Feld 270, D-6900 Heidelberg 1 |

Managing Editor:

- | | |
|----------------------------------|---|
| Dr. <i>Friedrich L. Boschke</i> | Springer-Verlag, Postfach 105 280,
D-6900 Heidelberg 1 |
| Springer-Verlag | Postfach 105 280 · D-6900 Heidelberg 1
Telephone (0 62 21) 4 87-1 · Telex 04-61 723
Heidelberger Platz 3 · D-1000 Berlin 33
Telephone (0 30) 82 20 01 · Telex 01-83319 |
| Springer-Verlag
New York Inc. | 175, Fifth Avenue · New York, NY 10010
Telephone 4 77-82 00 |
-

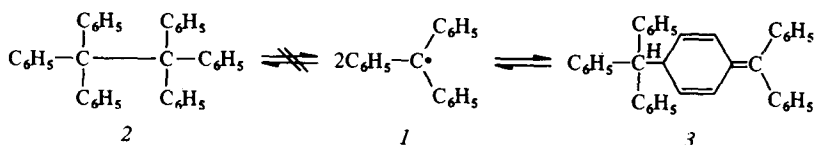
Contents

Steric Effects in Free Radical Chemistry Christoph Rüchardt	1
Silylated Synthons. Facile Organic Reagents of Great Applicability Leonhard Birkofer and Oskar Stuhl	33
The 4a, 4b-Dihydrophenanthrenes Karol A. Muszkat	89
Regio- and Stereo-Selectivities in Some Nucleophilic Reactions Nguyễn T. Anh	145
Author Index Volumes 26–88	163

原书缺页

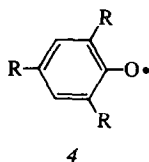
I Introduction

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?

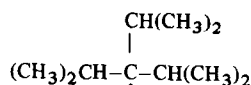
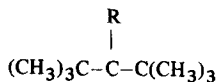


The opinion that stabilization of **1** by resonance was decisive, predominated for a long time and mastered the discussion of the relationship between structure and reactivity in free radical chemistry till quite recently⁵⁾: Accordingly selectivity in free radical reactions was assumed to be mainly 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** ($\text{R} = t\text{-C}_4\text{H}_9$)^{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 $\text{R} = \text{C}(\text{CH}_3)_3$

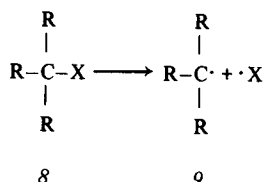
7

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)}.

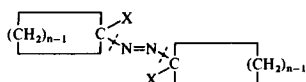
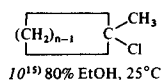
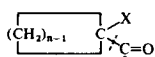
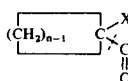
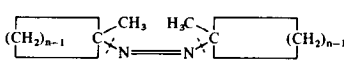
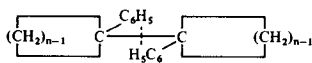
Table 1. Relative rates of formation of cyclic carbenium ions and free radicals from precursors 10–19^a

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	0.009
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}).

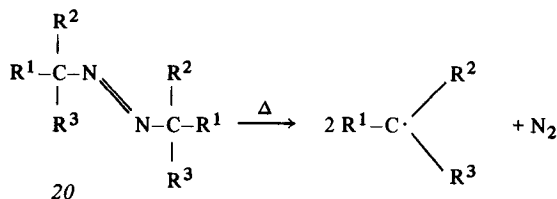
Exceptional behavior among the reactions of Table 1 is shown by the thermolysis reaction of 18. While the direction of the five-ring – six-ring effect is normal, a particular large rate enhancement (10^4 – 10^6) is found for the thermolysis of the seven and eight membered compounds and an unexpected 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°C12²⁰) X = C₆H₅, benzene, 60°C13²¹) X = CH₃, benzene, 200°C14²²) X = H, 125°C15²²) X = CH₃, 135°C16²³) X = CH₃, benzene, 80°C17²⁵) X = H, ethylbenzene, 110°C19²⁶) 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

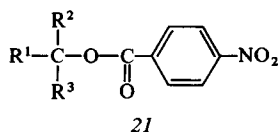
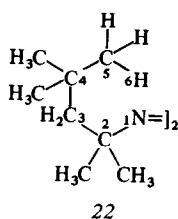


Table 2. Rate Constants k_{rel} and activation parameters for the thermolysis of azoalkanes $R^1R^2R^3C-N=N$ 20 in hydrocarbon solvents

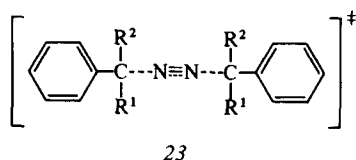
R^1	R^2	R^3	$k_{\text{rel.}}$ (180 °C) ^a	ΔH^\ddagger kcal/mol	ΔS^\ddagger e. u.
CH ₃	CH ₃	CH ₃	$\equiv 1.00$	43.2 ^b	17.7 ^b
CH ₃	CH ₃	C ₂ H ₅	1.19	—	—
CH ₃	CH ₃	1-C ₃ H ₇	[3.3 ^c]	40.7 ^b	14.2 ^b
CH ₃	CH ₃	1-C ₈ H ₁₇	2.27	—	—
CH ₃	CH ₃	2-C ₃ H ₇	3.00	—	—
C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	3.65	—	—
CH ₃	CH ₃	<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 ₃ H ₇	2-C ₃ H ₇	23.0	—	—
CH ₃	C ₂ H ₅	<i>t</i> .But.	36.5	—	—
C ₂ H ₅	C ₂ H ₅	<i>t</i> .But.	107	—	—
2-C ₃ H ₇	2-C ₃ H ₇	2-C ₃ H ₇	206	—	—
CH ₃	CH ₃	neo-Pentyl	247	35.6 ^a	11.9 ^a
			[480 ^c] [1320 ^d]		
CH ₃	2-C ₃ H 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-



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 $R^1\text{N}_2\text{R}^2$ 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-

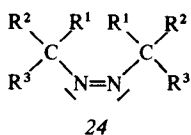


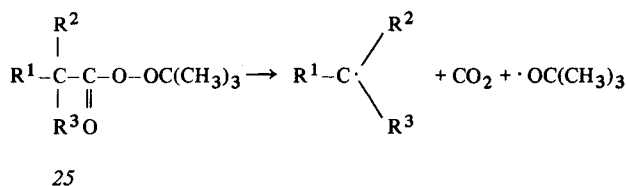
Table 3. Steric acceleration of thermolysis of *trans*-azoalkanes 20 (180 °C, ethylbenzene) and *cis*-azoalkanes 24 (-28 °C, ethanol)

R^1	R^2	R^3	$k_{\text{rel}}(20)$	$k_{\text{rel}}(24)^{37)}$
CH_3	CH_3	CH_3	≈ 1.00	$\approx 1.00^a$
CH_3	CH_3	C_2H_5	1.19	4.4
CH_3	CH_3	$i\text{-C}_3\text{H}_7$	3.00	64
CH_3	CH_3	$i\text{-C}_4\text{H}_9$	7.51	153
CH_3	C_2H_5	C_2H_5	1.87	37
C_2H_5	C_2H_5	C_2H_5	3.65	1428
CH_3	CH_3	$t\text{-C}_4\text{H}_9$	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 R¹R²R³C also becomes important (cf. Table 3).

The rates of homolytic fragmentation of peroxyesters 25 are also enhanced when the size of the side chains R¹–R³ = 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 (rel) (60 °C)	ΔH [‡] kcal/mol	ΔS [‡] e.u.
CH ₃	CH ₃	CH ₃	≡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 ΔG^\ddagger at 300 °C and strain enthalpy E_S^a

No.	R^1	R^2	R^3	$T[^\circ\text{C}]$ ($t_{1/2} = 1$ h)	$\Delta G^\ddagger(300^\circ\text{C})$ [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>i</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	<i>o</i> -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	<i>o</i> -C ₆ H ₁₁	250	39.6	44.3	43, 45)
11	CH ₃	CH ₃	<i>t</i> -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	<i>t</i> -C ₄ H ₉	H(D, L)	329	46.7	32.6	45, 48)
15	C ₆ H ₁₁	<i>t</i> -C ₄ H ₉	H(meso)	285	42.6	38.5	45, 48)
16	<i>t</i> -C ₄ H ₉	<i>t</i> -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>i</i> -C ₃ H ₇	C ₆ H ₅	H	335	47.4	7.6	41)
25 ^c	<i>t</i> -C ₄ H ₉	C ₆ H ₅	H	289	42.1	21.4	41)
26 ^d	<i>t</i> -C ₄ H ₉	C ₆ H ₅	H	303	44.6	18.5	41)
27 ^c	<i>t</i> -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)}.

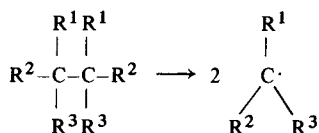
^b a statistical correction $k_1 = k_{\text{exp.}}/2$ was introduced because this molecule has two equivalent bonds which can be cleaved on thermolysis.

^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 $t_{1/2} = 1\text{h}$ 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 $t_{1/2} = 1\text{h}$ or by ΔG^\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.

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

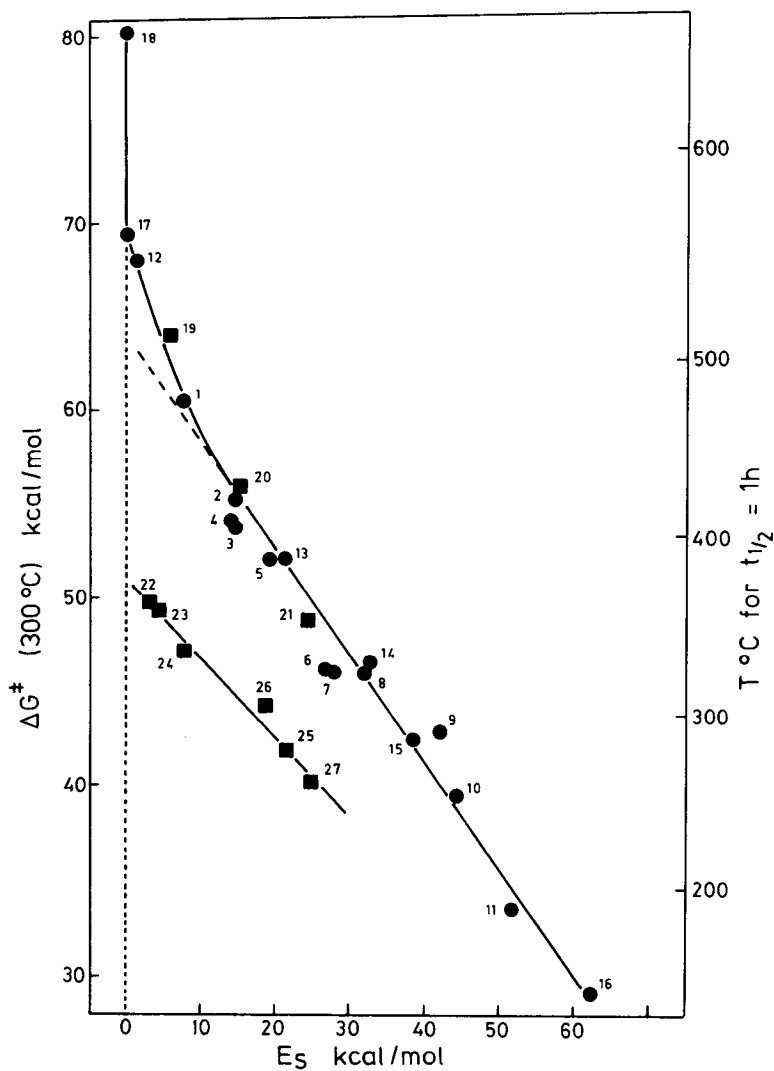


Fig. 1. Correlation between Thermal Stability and Ground State Strain E_s for hydrocarbons 26 (results from Table 5)

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 ΔG^\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?

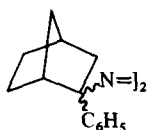
$$\Delta G^\ddagger (300^\circ\text{C}) = 51 - 0.41 E_{Sp} [\text{kcal/mol}]$$

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.

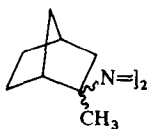
It has to be pointed out, however, that these considerations suffer somewhat from the fact that up to now it was necessary to calculate the strain energies of the phenyl substituted alkanes by a different force field⁴⁰ than those of the alkanes³⁹.

3 Further Steric Effects

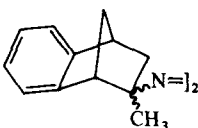
When 2-norbornyl type radicals are generated from exo/endo isomeric precursors differences in rate are generally observed. The higher rate of decomposition of the exo-isomer is usually explained on steric grounds^{12, 18}. This phenomenon is demonstrated by the following examples:



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



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



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