Chem. Ber. **119**, 1492–1510 (1986)

Thermolabile Hydrocarbons, XXVIII[1,2]

Separation, Structure Analysis, and Thermolysis of a Pair of Stable Rotamers; P-(*R**,*R**)- and M-(*R**,*R**)-D,L-3,4-Di-1-adamantyl-2,2,5,5-tetramethylhexane

Manuela A. Flamm-ter Meer[a], *Hans-Dieter Beckhaus*[a], *Karl Peters*[b], *Hans-Georg von Schnering*[b], *Hans Fritz*[a], and *Christoph Rüchardt**[a]

Institut für Organische Chemie und Biochemie der Universität Freiburg[a],
Albertstr. 21, D-7800 Freiburg i.Br., and

Max-Planck-Institut für Festkörperforschung[b],
Heisenbergstr. 1, D-7000 Stuttgart 80

Received October 21, 1985

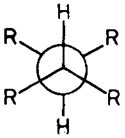
Three diastereomeric hydrocarbons **7** were formed on reaction of 1-adamantyl-1,1-dibromo-2,2-dimethylpropane with magnesium. They were separated by fractional crystallization and identified by ^1H NMR spectroscopy and *X*-ray crystallography as *meso*-**7** and the two rotamers of D,L-**7** mentioned in the title. They are the first examples of simple aliphatic hydrocarbon rotamers, which do not interconvert at room temperature and above. Analogous 1-norbornyl derivatives were also obtained but could not be separated. The kinetics and the products of thermolysis of these hydrocarbons were investigated.

Thermolabile Kohlenwasserstoffe, XXVIII[1,2]

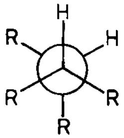
Trennung, Strukturanalyse und Thermolyse eines stabilen Rotamerenpaares; P-(*R,*R**)- und M-(*R**,*R**)-D,L-3,4-Di-1-adamantyl-2,2,5,5-tetramethylhexan**

Aus 1-Adamantyl-1,1-dibrom-2,2-dimethylpropan erhielt man bei der Umsetzung mit Magnesium drei diastereomere Kohlenwasserstoffe **7**, die durch fraktionierte Kristallisation getrennt werden konnten. Sie wurden durch NMR-Spektroskopie und Kristallstrukturanalyse als *meso*-**7** und die rotameren Titelverbindungen **7** erkannt. Es handelt sich um das erste Beispiel bei Raumtemperatur und darüber nicht interkonvertierender, einfacher aliphatischer Kohlenwasserstoff-Rotamere. Die analog hergestellten 1-Norbornylderivate konnten nicht getrennt werden. Die Thermolyse der Verbindungen wurde kinetisch und präparativ studiert.

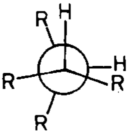
For a bond connecting two tertiary carbons ($C_t - C_t$ systems[2]) in aliphatic hydrocarbons *gauche*-conformations **2** are preferred over *anti*-conformations **1**[2].



1



2

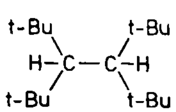


3

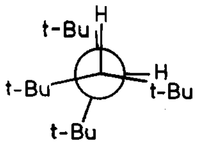
0009–2940/86/0505–1492 $ 02.50/0

2 allows for better reduction of strain by deformation into **3**. Strain arises from the geminal repulsions between R-groups and as a result the gem. R – C – R angles in these systems are increased[2,3]. This type of deformation leads to vicinal repulsions in **1** but much less in **3**. Structures like **3** were recognized clearly from the *X*-ray structure analyses of tetracyclohexylethane[4] as well as *meso*- and D,L-3,4-dicyclohexyl-2,2,5,5-tetramethylhexane[5].

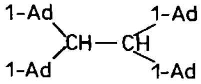
The prototype of a compound presenting the deformed conformation **3** is tetra-*tert*-butylethane **4** (3,4-di-*tert*-butyl-2,2,5,5-tetramethylhexane) which was first prepared by ***Ingold*** and coworkers[6]. Its structure was investigated by NMR[3,6,7] and very thoroughly by force field calculations[3,7,8] and discussed in relation to its strain enthalpy of 66.3 kcal · mol^{-1} as determined from thermochemical data[9]. Due to irregularities in the very weak and low melting crystals of **4** an *X*-ray analysis of its extremely deformed structure **5** was not possible.



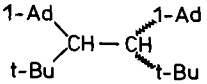
4



5



6



7

1-Ad = 1-adamantyl

From the small ^{1}H NMR coupling constant between the two methine protons in **4** it was concluded that **4** adopts a *gauche*-conformation **5** with a dihedral angle close to 90° between C – H bonds[6,7]. The rotation of one pair of *tert*-butyl groups in **4** is hindered at low temperatures[6] ($\Delta G^{\ddagger}_{\text{rot}}$ = 7 kcal · mol^{-1})[6] but irreversible decomposition via homolytic cleavage of the central C – C bond sets in at about 140 °C[7] i.e. below the temperature required to make the two pairs of *tert*-butyl groups equivalent via rotation around the central $C_t - C_t$ bond. Extensive force field calculations have identified the non-eclipsed *tert*-butyl groups in **5** as having the higher barrier to rotation ($\Delta H^{\ddagger} \approx$ 8 kcal · mol^{-1}[8c]) compared to the eclipsed ones ($\Delta H^{\ddagger} \approx$ 3 kcal · mol^{-1}[10]).

In an attempt to obtain better crystallizing analogues of **4**, which would allow an *X*-ray analysis, we prepared tetraadamantylethane **6** which was, however, too insoluble even for recrystallization.

Therefore, the synthesis of 3,4-di-1-adamantyl-2,2,5,5-tetramethylhexane (**7**) was next attempted, despite the fact that the occurrence of *meso*- and D,L-diastereomers would make the isolation of a pure and homogeneous compound more difficult. An even more complex but also particularly interesting stereochemical situation was expected for **7**, due to hindered rotation around the central $C_t - C_t$ bond (in analogy to **4**, $\Delta G^{\ddagger}_{\text{rot}} \geqslant$ 30 kcal · mol^{-1}). Each configuration should exist as two different conformers. These rotamers can be characterised[11] by the torsional angle Ad – $C_t - C_t$ – Ad (see Fig. 1), which is either positive (i.e. counted clockwise)[11b] in the rotamer P or negative (counterclockwise) in the rotamer M. For *meso*-**7** both rotamers P-(***R***,***S***) and M-(***S***,***R***) are enantiomers, and the mixture is called P-(***R****,***S****) or simply *meso*-**7**. However, each of the two D,L-configurations (***R***,***R***) and (***S***,***S***) consists of two diastereomeric rotamers, e.g. P-(***R***,***R***) and M-(***R***,***R***). Hence D,L-**7** splits into two diastereomeric pairs of enantiomers called P-(***R****,***R****) and M-(***R****,***R****).

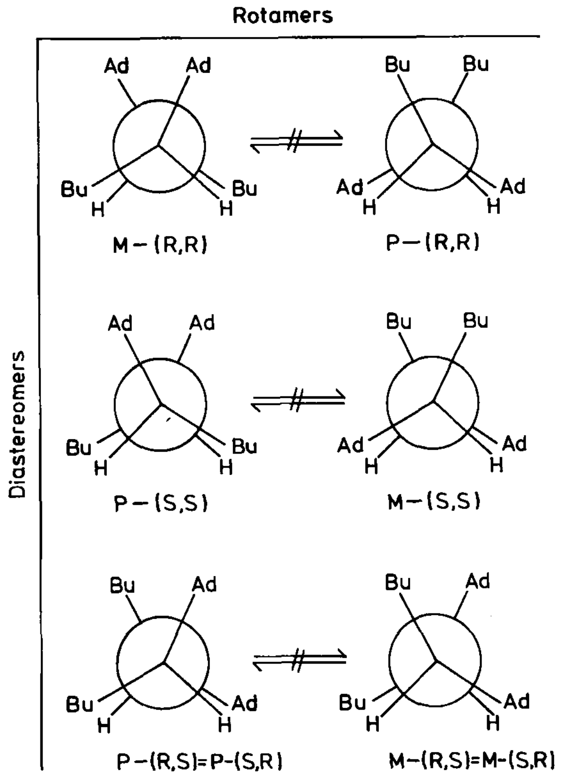
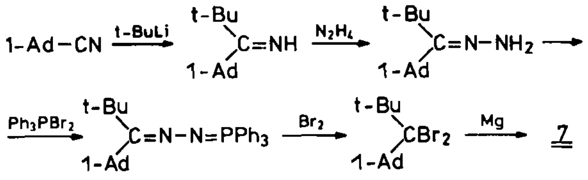


Fig. 1. Newman projections of the stereoisomers of 3,4-di-1-adamantyl-2,2,5,5-tetramethylhexane (7) (see Text)

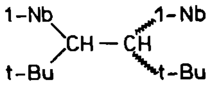
Synthesis of *meso*- and D,L-7

Tetra-*tert*-butylethane **4** has been prepared via the Wurtz coupling reaction of 3-chloro-2,2,4,4-tetramethylpentane with dispersed sodium[6,7], by thermolysis or photolysis of 3-azo-2,2,4,4-tetramethylpentane[10], and by the reaction of 3,3-dibromo-2,2,4,4-tetramethylpentane with magnesium[9]. For the corresponding synthesis of **7** the latter procedure was chosen because it seemed to offer an optimum combination of convenience and yield. The reaction sequence is shown in the scheme. Partly it follows steps which were developed by *Barton*[9,12] and *Maier*[9,13] in another context.

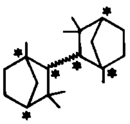


The presence of *meso*-**7** (50%) and of two rotamers of D,L-**7** (28 and 22%, respectively) was recognized from the number of *tert*-butyl signals in the ^1H NMR spectra and their temperature dependence (see below). The separation of *meso*-**7** from the mixture was easily achieved by crystallization from methanol. From a saturated toluene solution of the fine crystalline residue remaining after methanol extraction a small yield of needles separated on standing for 3 – 4 days in an open Erlenmeyer flask. These were isolated. Within further 5 days a complex mixture of needles and platelets precipitated which could be separated manually. The two types of crystalline material were recrystallized separately by slow and controlled cooling of their toluene solutions. The platelets (dec. p. 186 °C) proved to be the P-(R^*,R^*)-, the needles (dec. p. 203 °C) the M-(R^*,R^*)-diastereomer.

2,2,5,5-Tetramethyl-3,4-di-1-norbornylhexane (**8**) was also prepared by the route used for the synthesis of **7**. According to NMR in the oily product one *meso*- and two D,L-diastereomers were again present, which, however, could not be separated. As a further example of this type of $C_t - C_t$ hydrocarbons fenchyl-fenchane **9** was obtained by Wurtz dimerisation of fenchyl chloride with a sodium dispersion. According to gc, the oily product mixture contained only three components. It is possible, and there is NMR evidence[10], that some of the eight possible diastereomers have the same retention time. Only one isomer could be enriched to 95% purity. In agreement with force field calculations no NMR evidence for the existence of stable rotamers was found.



8



9

1-Nb = 1-norbornyl

Spectra and Structures

Correct elementary analyses and (M^+ + 1) peaks in the CI-mass spectra proved the molecular formulas of the diastereomers of **7**. Constitution, configuration, and conformation were determined by NMR and *X*-ray structure analyses. Some significant ^1H and ^{13}C NMR data are recorded in Table 1.

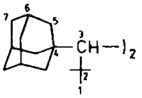
Due to the well-known steric effect[14] the proton signals at the central $C_t - C_t$ bond are shifted about 2.2 ppm downfield, which is much more than in more usual cases[14b]. In **8** the downfield shift is even larger (2.5 ppm). Less significant is the 0.4 ppm downfield shift of the *tert*-butyl protons. Similar downfield shifts are found for the ^{13}C signals of the primary and the quaternary carbons of the *tert*-butyl groups and also for those of the central C_t carbons.

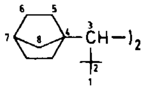
Conformation **5** of tetra-*tert*-butylethane was supported in particular by the observation of two *tert*-butyl signals of the same intensity which did not coalesce at higher temperatures[6,7] and by the coupling constant of 2 Hz between the two methine protons which was obtainable from ^{13}C satellites of the methine protons in the ^1H NMR spectrum[7].

Table 1. ^{13}C and ^{1}H NMR chemicals shifts (δ, ppm) of **4** and the three isomers each of **7** and **8**

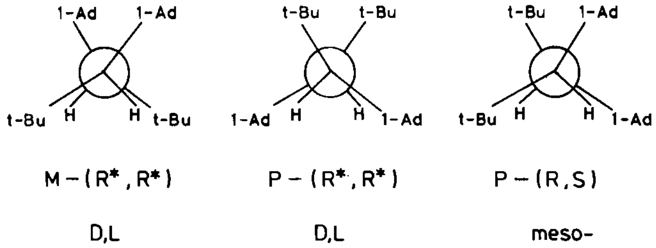
		7			**8**		
	4[a]	P-(*R**,*R**)	M-(*R**,*R**)	P-(*R**,*S**)	M-(*R**, *R**)[b,c]	P-(*R**, *R**)[b,d]	P-(*R**,*S**)
^{13}C NMR							
C-1	35.77 34.36	35.11	–[e,f]	35.60[e] 35.02			
C-2	35.73 38.35	38.69	35.91	36.21 38.61			
C-3	57.06	60.54	56.37	56.85 59.67	58.50	53.64	54.75 56.56
C-4		39.85	40.27	40.40 39.44	56.20	51.69	55.85 51.41
C-5		43.28[e]	43.91	43.98 42.84[c]			
C-6		29.66	30.11	30.22 29.77			
C-7		37.10	37.02	37.05 37.10			
C-8					47.40	45.25	47.23 46.33
^{1}H NMR							
1-H	1.27[e] 1.17	1.20	1.29[e]	1.31[e] 1.19	1.19	1.09	1.17 1.11
3-H	2.26	2.18	2.16	2.20 – 2.10	2.53	2.32	2.50 2.46
5-H		2.17 2.05[e]	1.87 1.94	2.20 – 1.90			
6-H		1.98	1.98	2.20 – 1.90			
7-H		1.70 1.63	1.64	1.75 – 1.60			

[a] Numbering of formula analogous to **7**. – [b] It was not possible to assign further signals in the spectra of the mixture of isomers with certainty. – [c] Main products, assignment of configuration tentative. – [d] Minor product, assignment of configuration tentative. – [e] Hindered rotation. – [f] Broad signal.





Together with the different barriers of rotation of the two types of *tert*-butyl groups and their assignment by force field calculations, mentioned above, the structures of the three diastereomers **7** could be assigned in the following way:



M – (R*, R*) P – (R*, R*) P – (R,S)

D,L D,L meso-

Fig. 2. Newman projections of the diastereomers of **7** (only one of the two enantiomers is shown)

In *meso*- or P-(*R*,*S*)-**7** the two *tert*-butyl and the two 1-adamantyl groups are magnetically non-equivalent. In each D,L-rotamer, on the other hand, like substituents are magnetically equivalent. To the isomer with two *tert*-butyl signals of identical intensity in the ^{1}H NMR spectrum the *meso*-configuration was assigned. The two D,L-rotamers are distinguished by their *tert*-butyl signals differing in their rotational barriers. In the low temperature ^{1}H NMR spectrum of the rotamer crystallizing as platelets, the *tert*-butyl signal, but not the adamantyl signal, showed hindered rotation. To it therefore the P-(R^*,R^*)-D,L-**7** structure was assigned. The M-(R^*,R^*)-D,L-**7** material crystallizing in needles, by contrast, was characterized by dynamic NMR effects for the adamantyl and not for the *tert*-butyl signals.

The ultimate proof of the structures of the two D,L-diastereomers **7** as rotamers was provided by *X*-ray analysis. The two structures were determined by direct methods and refined to $R = 0.046$ and 0.049 for P-(R^*,R^*)- and M-(R^*,R^*)-**7**, respectively. The structure of the former is slightly distorted, that of the latter has C_2-symmetry. Both compounds crystallize as racemates in the space group *C*2/*c*(15). Eight and four molecules are located in the elementary cells of P- and M-**7**, respectively. Details are found in the experimental part. Perspective drawings and Newman projections along the central bonds are shown in Fig. 3 and 4.

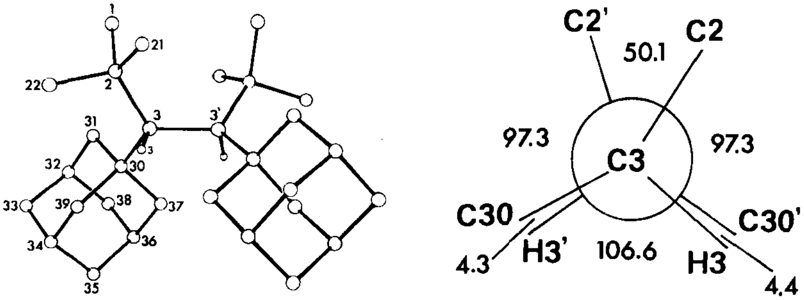


Fig. 3. P-(R^*,R^*)-**7**; stereographic projection of the molecule and numbering of atoms corresponding to Tables 7 and 8 and Newman projection along the C3 – C4 bond and torsional angles from *X*-ray analysis (only the M-(*S*,*S*)-enantiomer is shown)

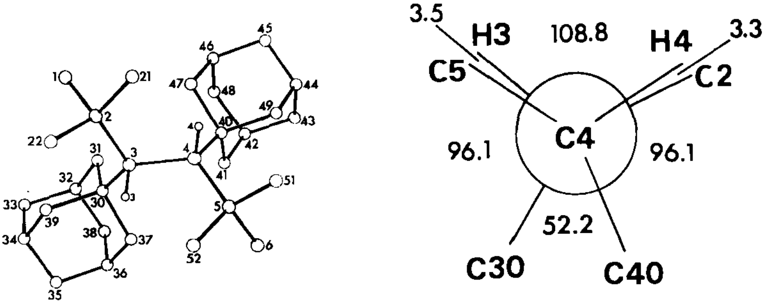


Fig. 4. M-(R^*,R^*)-**7**; stereographic projection of the molecule and numbering of atoms corresponding to Tables 9 and 10 and Newman projection along the C3 – C3' bond and torsional angles from *X*-ray analysis (only the P-(*S*,*S*)-enantiomer is shown)

Selected bond lengths and bond angles are compared with results from force field calculations (see below) using Allingers MM2 force field[15)] in Table 2.

Table 2. Selected bond lengths, bond angles, and strain enthalpies[a,b)] of P-(R*,R*)-7 and M-(R*,R*)-7

		Bond Lengths [pm]		Bond Angles [°]	
	Point Group	C_t-C_t	C_t-C_α(Ad) C_t-C_α(Bu)	$C_t-C_t-C_\alpha$(Ad) $C_t-C_t-C_\alpha$(Bu) C(Ad)$-C_t-$C(Bu)	H_s[a,b)] [kcal·mol^{-1}]
P-(R*,R*)-7 exp.[c)]	C_1[d)]	163.1	159.9/160.3 163.5/162.8	120.6/120.8 113.8/114.1 117.5/117.5	
calcd.[e)]	C_1[d)]	162.1	159.7/160.5 160.8/161.2	119.3/120.9 117.1/118.1 120.1/120.9	73.9[e)]
M-(R*,R*)-7 exp.[c)]	C_2	162.1	162.9 160.0	114.5 120.0 117.2	
calcd.[e)]	C_2	161.5	162.3 159.4	117.9 119.1 120.0	73.3[e)]

[a)] MM2 results[15)]. – [b)] $H_s = \Delta H_f^\circ(g) - \Delta H_f^N(g)$; $\Delta H_f^\circ(g)$ = standard heat of formation obtained from force field calculations[15)]; ΔH_f^N = normal value calculated by *von Schleyer*'s group increment formalism[16)]. – [c)] Maximal standard deviation σ_{CC} = 0.6 pm, σ_{CCC} = 0.4°, σ_{CCCC} = 0.5° (see Fig. 2 and 3). – [d)] Distorted from C_2-symmetry. – [e)] If these values are corrected for the known 7.9 kcal · mol^{-1} strain of each adamantyl group[1)] then H_s = 58.1 and 57.5 kcal · mol^{-1}, respectively.

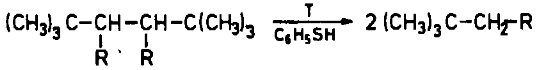
The two structures shown in Fig. 3 and 4 are indeed in excellent agreement with the expectations derived from the force field results for tetra-*tert*-butylethane **4**[7,8c)]. In particular, the small $HC_tC_tC_\alpha$ torsion angles are remarkable. The agreement between the experimental structure parameters and the MM2 results (Table 2) is very good. Bond lengths deviate less than 1.5 pm, bond angles less than 3°. Torsion angles in M-(R*,R*) deviate at most 10° but in P-(R*,R*) up to 28°.

The isolation of the two rotamers of D,L-**7** is, to the best of our knowledge, the first example for the isolation of two pure aliphatic hydrocarbon rotamers. In other examples of isolated rotamers the rotations of sp^3-sp^2 bonds[17)] or of bridgehead bonds of triptycyl derivatives are restricted[18)]. The isolation of pure rotamers of **8** and **9** was not successfully achieved.

Attempts to interconvert the two rotamers at higher temperatures were unsuccessful, because homolytic cleavage of the central C_tC_t bond occurs first (vide supra). Calculations using the driver option of the MM2 program lead to curves for the rotational potentials[10)] very similar to those observed by *Osawa* for **1**[8c)]. The *gauche-anti* interconversions in the diastereomers of D,L-**7** are hindered by barriers of about 40 kcal · mol^{-1} and more, the *gauche-gauche* interconversions by barriers between 45 and 90 kcal · mol^{-1}. For *meso*-**7** the corresponding barriers are 52 and 44 kcal · mol^{-1}, respectively. Also the rotations of the C_tC_q bonds of the *tert*-butyl and 1-adamantyl groups are hindered. For the positions eclipsed to hydrogen the barriers are 5 and 3 kcal · mol^{-1} and for the non-eclipsed groups 16 and 19 kcal · mol^{-1}, respectively. The relative heights of the *tert*-butyl and 1-adamantyl rotational barriers vary from system to system$^{19)}$.

Thermolysis

Tetra-*tert*-butylethane **4** was until now the least stable member of the aliphatic C_t-C_t series$^{3)}$. Despite its high strain enthalpy it followed reasonably well the ΔG^{+} (300 °C) of thermolysis vs. strain H_s (or better "change in strain" D_s) correlations$^{3,20)}$. For these correlations strain enthalpies as obtained from MM2 calculations were used (57.7 kcal · mol^{-1} for **4**)$^{7)}$ and not the more recent experimental value (66.3 kcal · mol^{-1})$^{9,21)}$. In continuation of this work we have investigated the products and the kinetics of the thermal decomposition of the three diastereomers of **7** and of a mixture of the diastereomers of **8**. Some semiquantitative experiments related to the stabilities of **6** and **9** were also performed. In toluene/thiophenol solvent mixtures, **7** and **8** decomposed almost quantitatively into 1-neopentyladamantane (**10**) and 1-neopentylnorbornane (**11**), respectively.



$$(CH_3)_3C-\underset{R}{CH}-\underset{R}{CH}-C(CH_3)_3 \xrightarrow[C_6H_5SH]{T} 2\,(CH_3)_3C-CH_2-R$$

7 R=1-adamantyl **10**

8 R=1-norbornyl **11**

6 decomposed without solvent into a 10:1 mixture of di-1-adamantylmethane and di-1-adamantyl ketone. A clean thermal decomposition via cleavage of the central C_t-C_t bond is, therefore indicated.

The kinetics of decomposition were followed either by Differential Scanning Calorimetry (DSC) as reported previously$^{1)}$ or by following the disappearance of the characteristic *tert*-butyl signals in the ^{1}H NMR spectra of mixtures of P-(R^*,R^*)- and M-(R^*,R^*)-**7**. The results are reported in Table 3 together with strain enthalpies calculated by the MM2 force field method.

A comparison of the new DSC data for **4** with those formerly determined by GC analysis leads to very satisfactory agreement, in particular for ΔG^{+} (300 °C). For **6** (160 ± 5 °C) and **9** (328 °C) only the temperature at which the half time is 1 h can be safely recorded.

As long as the discussion is restricted to the procedure used previously, i.e. the question if a correlation between the free enthalpies of activation ΔG^{+} (300 °C) and the strain enthalpies H_s (or better the changes in strain enthalpy during dissociation D_s) is found, the situation remains rather simple. The three diastereomers of **7** are only little differing by either ΔG^{+}(300 °C) (28.5 ± 1.5 kcal · mol^{-1}) or H_s (57.5 ± 0.6 kcal · mol^{-1}) (see Table 3). The correlations of all known data for this series$^{3)}$ including **7** and **8** are reasonably good:

$$\Delta G^{+}\,(300\,°C) = 66.9 \pm (1.0) - 0.65\,(\pm\,0.04)\,H_s\,[\mathrm{kcal\cdot mol^{-1}}];\; r = -0.975;\quad n = 16$$

and

$$\Delta G^{+}\,(300\,°C) = 66.2\,(\pm\,1.5) - 0.79\,(\pm\,0.07)\,D_s\,[\mathrm{kcal\cdot mol^{-1}}],\ r = -0.97;\quad n = 8$$

They are based on the strain enthalpies H_s obtained from the MM2 calculations and *von Schleyer*'s single conformation increments[16]. The use of ΔG^{+} instead of ΔH^{+} for such correlations has been amply justified previously[20] by the compensation between the temperature function of ΔH^{+} on the one hand and of the $T\Delta S^{+}$ term on the other[22].

Table 3. Rates and activation parameters for the thermal decomposition of **4**, **7**, and **8**

	n[a]	ΔT[b]	Solvent	Method[c]	$\Delta H^{\ddagger} \pm \sigma$[d] [kcal · mol^{-1}]	$\Delta S^{\ddagger} \pm \sigma$[d] [e.u.]	$\Delta G^{\ddagger}$ (300 °C) [kcal · mol^{-1}]	$T(\tau_{1/2} = 1\ \mathrm{h})$[e] [°C]	H_s[f]
4	3	28	mesitylene/ thiophenol (8:2)	DSC	38.2 ± 0.5	15.4 ± 1.3	29.4	144	57.7[7,9]
4[3,7]	7	46	mesitylene	GC	36.4 ± 0.4	11.8 ± 1.0	29.7	141	57.7[7,9]
P-(R^*,R^*)-**7**[g]	4	41	$C_6H_5CD_3$/ thiophenol	NMR	31.7 ± 0.8	7.0 ± 2.2	27.7	109	58.1
M-(R^*,R^*)-**7**[g]	4	41	$C_6H_5CD_3$/ thiophenol	NMR	30.7 ± 1.7	1.4 ± 4.3	29.8	122	57.5
meso-**7**	3	22	9,10-di-hydro-anthracene (1:2)[h]	DSC	37.0 ± 0.3	17.5 ± 0.8	27.0	122	57.1
8[i]	3	49	9,10-di-hydro-anthracene (1:4)[h]	DSC	37.2 ± 0.3	4.4 ± 0.5	34.7	188	43.5 ± 1

[a] n = number of independent rate measurements. – [b] Temperature range of rate measurements in °C. – [c] DSC = Differential Scanning Calorimetry; GC = Gas Chromatography; NMR = ^{1}H NMR of *tert*-butyl signals. – [d] σ = standard deviation. – [e] Temperature at which the half time of decomposition is 1 h. – [f] MM2 strain enthalpy; for definition see footnote [e] and [b] of Table 2; for the compounds **7** and **8** strain enthalpies H_s have been corrected by twice substracting the strain enthalpies of the polycyclic ring systems, i.e. 7.9 and 17.0 kcal · mol^{-1}, respectively. – [g] P-(R^*,R^*) and M-(R^*,R^*) mixtures were used for the kinetic measurements. The integrations of the well separated *tert*-butyl signals served as a quantitative measure of the concentration. – [h] Molar ratio of **7** or **8**: 9,10-dihydroanthracene. – [i] Mixture of *meso*: P-(R^*,R^*): M-(R^*,R^*) = 4:1:2.

According to this analysis the steric effect of 1-adamantyl in **7** as compared to *tert*-butyl in **4** is very similar. Exchanging 1-adamantyl in **7** for 1-norbornyl in **8** leads to a reduction in strain and to an increase in thermal stability of **8** as compared to **4** or **7**. Apparently the small CCC bond angles at the 1-positions of the norbornyl ring are responsible for this. The increase of the slope in going from the H_s- to the D_s-correlation is indicative of residual strain in the radicals formed on thermolysis[20].

On reflection, the situation proves to be somewhat more complex. In particular the larger enthalpy of activation ΔH^{+} and entropy of activation ΔS^{+} for *meso*-**7** as compared to its diastereomers shows that a rather drastic compensation of entropy and enthalpy effects is occurring. Therefore the relative thermal stability of the three diastereomers of **7** is temperature dependent as observed previously for *meso*- and D,L-2,3-di-*tert*-butyl- and 2,3-di-1-adamantylbutanes[3]. A unique interpretation of the entropy effects in this case is not possible at present[23]. That the effect is real and not an artefact due to the different experimental methods used for following the kinetics seems to be safely concluded from the other ΔS^{+} values in Table 3 and elsewhere[20] which do not support a connection between the method applied and the results obtained.

Thanks are due to *Deutsche Forschungsgemeinschaft* and to *Fonds der Chemischen Industrie* for financial support and to Dr. *D. Hunkler* and Dr. *J. Wörth* for the NMR and MS measurements.

Experimental Part

The instrumentation for the spectroscopic and chromatographic analyses has been described previously[1].

Synthetic Work

P-(R,S)-, P-(R,R*)-, and M-(R*,R*)-3,4-Di-1-adamantyl-2,2,5,5-tetramethylhexane* (7)

1-(1-Adamantyl)-2,2-dimethyl-1-propanimine[24]: 24.5 g (152 mmol) of 1-cyanoadamantane[25] in 250 ml of dry benzene was added dropwise at 0°C under N_2 to 107.2 ml of a 15% solution of *tert*-butyllithium (167.3 mmol) in pentane. Finally the solution was stirred for 4 h at 25°C and hydrolyzed by the addition of ice water. The aqueous phase was extracted 4 times with petrol ether (30 – 50°C) and the combined organic phases were dried over $MgSO_4$ and concentrated i. vacuo. The solid residue was recrystallized from petrol ether (30 – 50°C). 26.5 g (80%) of a mixture of *syn*- and *anti*-ketimine.

1. Fraction: 19.2 g, m.p. 120 – 125°C; 2. Fraction: 6.8 g, m.p. 155 – 175°C. – IR (KBr): 1595 (C=NH) cm^{-1}. – ^1H NMR (CCl_4/HMDS): δ (ppm) = 1.17 (s; 9H, $C(CH_3)_3$), 1.33 (s; 9H, $C(CH_3)_3$), 1.63 (mc; 12H, adamantyl), 1.87 (mc; 18H, adamantyl), 8.61 (s; =NH) after addition of a drop of CF_3CO_2H.

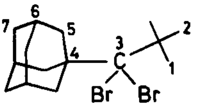
1-(1-Adamantyl)-2,2-dimethyl-1-propanone Hydrazone[26]: A mixture of 26.0 g (119 mmol) of 1-(1-adamantyl-2,2-dimethyl-1-propanimine, 36.0 g (719 mmol) of 100% hydrazine hydrate and 4 drops of 2 N H_2SO_4 was refluxed for 36 h (condenser cooled with ice water). After cooling, the solid residue was taken up with ether and water for hydrolysis. The ether phase and the ether extracts of the aqueous phase were combined, washed neutral, and dried over $MgSO_4$. The solvent was evaporated and the hydrazone recrystallized from hexane. 24 g (86%), m.p. 155°C. – IR (KBr): 3400, 3310, 3240 (NH_2), 1630 (C=N), 1570 (NH_2), 1390 and 1360 ($C(CH_3)_3$) cm^{-1}. – ^1H NMR (CCl_4/HMDS): δ (ppm) = 1.28 (s; 9H, $C(CH_3)_3$), 1.55 (mc; 6H, adamantyl), 1.80 (mc; 9H, adamantyl), 4.98 (s; 2H, NH_2).

$C_{15}H_{26}N_2$ (234.2) Calcd. C 76.85 H 11.19 N 11.96 Found C 76.61 H 11.43 N 11.81

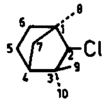
1-(1-Adamantyl)-2,2-dimethyl-1-propanone Triphenylphosphoranylidenehydrazone[26]: All reagents and solvents have to be absolutely dry (P_2O_5). 13.65 g of Br_2 (85.4 mmol) in 100 ml of benzene was dropwise added at 0°C with vigorous stirring to a solution of 22.4 g of triphenylphosphane (85.4 mmol) in 250 ml of benzene. The resulting suspension of dibromotriphenylphosphorane was stirred at room temp. for 30 min, and a solution of 20.0 g of the above hydrazone (85.4 mmol) and 18.8 g of triethylamine (186 mmol) in 30 ml of benzene was added afterwards within 1 h. The temp. was kept below 20°C during this process. After 5 h of continuous stirring, the yellow triethylammonium bromide was removed by filtration and the filtrate was concentrated i. vacuo till yellow crystals of the phosphazene started separating out. They were collected by filtration and recrystallized from $CHCl_3$ by addition of a small amount of petrol ether. 33.6 g (79%); m.p. 188 – 193 °C (dec.). – IR (KBr): 3025 (Ar-H), 1580 (Ar C – C), 1480 (Ar C – C), 1440 (P – Ph), 1385 ($C(CH_3)_3$). – ^1H NMR (CCl_4/HMDS): δ (ppm) = 0.98 (s; 3H, admantyl), 1.48 (mc; 10H, adamantyl), 1.73 (mc; 9H, $C(CH_3)_3$), 2.55 (mc; 2H, adamantyl), 7.27 (mc; 15H, Ph).

$C_{33}H_{39}N_2P$ (494.3) Calcd. C 80.11 H 7.95 N 5.66 Found C 80.21 H 8.13 N 5.64

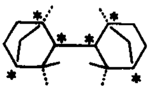
1-(1-Adamantyl)-1,1-dibromo-2,2-dimethylpropane[9,27]: 6.80 g of Br_2 (42.6 mmol) in 90 ml of dry CCl_4 was slowly dropped under N_2 at 0°C into a vigorously stirred solution of 10.6 g (21.3 mmol) of the above phosphazene in 600 ml of dry CCl_4. When the bromine was discoloured stirring was continued for 5 h at 25 °C. The solution was separated from the viscous sticky precipitate and concentrated i. vacuo. The remaining oily residue was purified in a cooled chromatography column over silica gel in methylene chloride solution. 5.8 g (75%), m.p. 98 – 99 °C. – IR (KBr): 690 (C – Br) cm^{-1}. – ^1H NMR (CCl_4, HMDS): δ (ppm) = 1.41 (s; 9H, $C(CH_3)_3$), 1.55 (mc; 6H, adamantyl), 1.93 (mc; 3H, adamantyl), 2.13 (mc; 6H, adamantyl). – ^{13}C NMR ($CDCl_3$, TMS, 25 °C, numbering see formula **12**): δ = 120.21 and 114.12 (s; C-3), 51.42 and 49.95 (s; C-2), 41.57, 41.12 and 40.59 (t; C-5), 36.63, 36.34 and 35.94 (t; C-7), 31.70, 31.16, 30.88, 30.27, 30.13, 29.59 (d; C-6), 29.00. – ^{13}C NMR ([D_8]toluene, 370 K): δ = 113.66 (s; C-3), 51.91 (s; C-2), 41.62 (t; C-5), 36.98 (t; C-7), 32.60 (q; C-1), 30.17 (d; C-6), 30.05 (s, C-4).



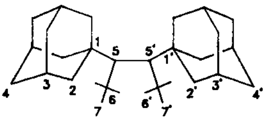
12



13



14



15

The complex splitting pattern of the ^{13}C NMR spectra at 25 °C and the broadness or even absence of *tert*-butyl signals at certain temperatures are due to restricted rotations as previously reported for 3,3-dibromo-2,2,4,4-tetramethylpentane[27].

Hexane Derivative 7: The synthesis followed the procedure used previously for the preparation of tetra-*tert*-butylethane 4[9]. 5.8 g (15.9 mmol) of the above dibromide dissolved in 100 ml of ether (dried over 4 Å molecular sieve) was added dropwise to 627 mg (25.8 mmol) of magnesium turnings in a vacuum dried apparatus under argon in the usual manner. During the addition the solvent started boiling; this was continued by external heating for 36 h. The reaction mixture was hydrolysed with ice water and the aqueous phase extracted several times with ether. The combined ether phases were washed neutral, dried, and concentrated in vacuo. The oily residue was taken up in 100 ml of pentane and the solution was shaken several times with 30 ml portions of conc. H_2SO_4 till the acid became no longer coloured. The pentane phase was again washed neutral, dried, and concentrated in vacuo. 685 mg (21%), containing 49.5% of *meso*-7, 28.2% of P-(R^*,R^*)-7 and 22.3% of M-(R^*,R^*)-7 according to the intensity of *tert*-butyl signals in the ^1H NMR spectrum.

The *meso-diastereomer* was separated with a small amount of boiling methanol from which it was recovered by evaporation of the solvent. It was recrystallized several times from acetone, m.p. 142 – 143 °C (dec.). – ^1H NMR ($CDCl_3$, TMS, numbering according to 15): δ = 2.2 – 2.1 (2 s; 2H, 5-, 5'-H), 2.2 – 1.9 (m; 12H, 2-, 2'-H), 2.2 – 1.9 (m; 6H, 3-, 3'-H), 1.75 – 1.6 (m; 12H, 4-, 4'-H), 1.31 (s; 9H, 7-H), 1.19 (s; 9H, 7'-H). – ^{13}C NMR ($CDCl_3$, TMS): δ = 59.67 (d; C-5), 56.85 (d; C-5'), 43.98 and 42.84 (2 broad; C-2 and C-2'), 40.40 (s; C-1), 39.44 (s; C-1'), 38.61 (s; C-6), 36.26 (s; C-6'), 37.10 (t; C-4), 37.05 (t; C-4'), 35.6 (q; C-7), 30.20 (t; C-3), 29.77 (d; C-3').

$C_{30}H_{50}$ (410.4) Calcd. C 87.72 H 12.28 *meso*-7: Found C 87.58 H 12.42
P-(R^*,R^*)-7: Found C 87.93 H 11.98
M-(R^*,R^*)-7: Found C 87.38 H 12.09

The fine crystalline material remaining after the methanol extraction was recrystallized from toluene in an open Erlenmeyer flask at 16 – 18 °C. Within 3 – 4 days about 20 mg of crystalline needles separated, which was isolated. Within the next 5 – 6 days a mixture of platelets and needles crystallized which was successfully separated using tweezers and a magnifying glass. Both fractions were purified by separate fractional crystallizations from toluene. The solutions were slowly cooled for this purpose by placing them into a well insulated Dewar flask.

P-(R,R*)-7*: Platelets, m.p. 186 °C (dec.). – ^{1}H NMR ($CDCl_3$, TMS; numbering according to **15**): δ = 2.18 (s; 2H, 5-H), 2.17 and 2.05 (m; 12H, 2-H), 1.98 (m; 6H, 3-H), 1.70 and 1.63 (m; 12H, 4-H), 120 (s; 18H, 7-H). – ^{13}C NMR (CCl_4, $CDCl_3$, TMS): δ = 60.54 (d; C-5), 43.28 (t; C-2), 39.85 (s; C-1), 38.69 (s; C-6), 37.10 (t; C-4), 35.11 (q; C-7), 29.66 (d; C-3).

M-(R,R*)-7*: Needles, m.p. 203 °C (dec.). – ^{1}H NMR ($CDCl_3$, TMS, numbering according to **15**): δ = 2.16 (s; 2H, 5-H), 1.98 (m; 6H, 3-H), 1.94 and 1.87 (m; 12H, 2-H), 1.64 (m; 12H, 4-H), 1.29 (s; 18H, H-7). – ^{13}C NMR (CCl_4, $CDCl_3$, TMS): δ = 56.37 (d; C-5), 43.91 (t; C-2), 40.27 (s; C-1), 37.02 (t; C-4), 35.91 (s; C-6), 30.11 (d; C-3).

2,2,5,5-Tetramethyl-3,4-di-1-norbornylhexane (**8**): Starting with 1-norbornanecarboxylic acid[28,29], which was transformed via the acyl chloride[29] into the amide (m.p. 230 °C), 1-cyanonorbornane[30,31] was prepared. It was used as starting material for the same series of reactions which was used for the preparation of **7**. Only the yields and physical properties of the intermediates are, therefore, recorded.

2,2-Dimethyl-1-(1-norbornyl)-1-propanimin: 81% yield, b.p. 110 °C/12 Torr. – IR (film): 1610 (C=NH) cm^{-1}. – ^{1}H NMR (CCl_4, HMDS): δ = 2.31 – 1.16 (m; 11H, norbornyl), 1.09 (s; 9H, C_4H_9).

2,2-Dimethyl-1-(1-norbornyl)-1-propanone Hydrazone: 62% yield, m.p. 107 °C. – ^{1}H NMR ($CDCl_3$, TMS): δ = 4.9 (broad; 2H, NH_2), 2.27 – 1.13 (m; 11H, norbornyl), 1.05 (s; 9H, $C(CH_3)_3$). – IR (KBr): 3385 and 3310 (NH_2 free), 3240 (NH_2 associated), 1640 (C=N), 1580 (NH), 1390 and 1360 ($C(CH_3)_3$) cm^{-1}.

$C_{12}H_{22}N_2$ (194.2) Calcd. C 74.16 H 11.42 N 14.42 Found C 74.34 H 11.62 N 14.43

2,2-Dimethyl-1-(1-norbornyl)-1-propanone Triphenylphosphoranylidenehydrazone: 75% yield, m.p. 175 – 180 °C (dec.). – ^{1}H NMR ($CDCl_3$, TMS): δ = 7.70 – 7.08 (m; 15H, C_6H_5), 3.05 – 1.00 (m; 11H, norbornyl), 1.43 and 1.00 (s; 9H, C_4H_9). – IR (KBr): 3070 and 3050 (Ar C – H), 1590 (Ar C – C), 1480 (Ar C – C), 1440 (P – Ph), 1387 and 1360 (C_4H_9) cm^{-1}.

$C_{30}H_{35}N_2P$ (454.3) Calcd. C 79.25 H 7.76 N 6.16 Found C 79.00 H 7.60 N 6.07

1,1-Dibromo-2,2-dimethyl-1-(1-norbornyl)propane: 84% yield, m.p. 40 – 41 °C. – IR (KBr): 1395 and 1365 (C_4H_9), 712 (CBr) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 2.28 – 1.43 (m; 11H, norbornyl), 1.38 (s; 9H, C_4H_9).

2,2,5,5-Tetramethyl-3,4-di-1-norbornylhexane (**8**): After treating the pentane solution, obtained from 9.0 g of the above dibromide and 1.1 g of magnesium turnings, with conc. H_2SO_4 the raw product was subjected to a kugelrohr distillation i. vacuo. 2,2-Dimethyl-1-(1-norbornyl)-propane distilled over at a bath temperature of 80 °C and the mixture of dimers **8** at 150 °C. **8** was further purified by chromatography over silica gel in CH_2Cl_2 but could not be separated into the diastereomers, despite extensive attempts. 1.5 g (33%) colourless oily liquid remained which, according to NMR, consisted of 47% of *meso*-**8** and 53% of the two D,L-**8** rotamers in a 2:1 ratio. – ^{1}H NMR ($CDCl_3$, TMS): δ = 2.53 (s; 2H, CH – CH (DL-g1)), 2.50 (s; 1H, CH (*meso*), 2.46 (s; 1H, CH (*meso*)), 2.32 (s; 2H, CH – CH (DL-g2)), 2.15 – 1.23 (m; 22H, norbornyl), 1.19 (s; 18H, $C(CH_3)_3$ (DL-g1)), 117 (s; 9H, $C(CH_3)_3$ (*meso*)), 1.11 (s; 9H, $C(CH_3)_3$ (*meso*)), 1.09 (s; 18H, $C(CH_3)_3$ (DL-g2)). – ^{13}C NMR ($CDCl_3$, TMS): δ = 58.50 (d; C-1 and C-2, DL-g1), 56.56 and

54.75 (2 d; C-1 and C-2, *meso*), 53.64 (d; C-1 and C-2, DL-g2), 56.20 (s; C-1′, DL-g1), 55.85 and 51.41 (2 s; C-1′, *meso*), 51.69 (s; C-1′, DL-g2), 47.40 (t; C-7′, DL-g1), 47.23 and 46.33 (2 t; C-7′, *meso*), 45.25 (t; C-7′, DL-g2), 42.13 (t), 41.34 (t), 39.85 (t), 39.17 (t), 38.01 (s), 35.50 (s), 35.16 (d?), 34.29 (d?), 34.36 (d?), 34.25, 34.12 (q?), 34.02 (q?), 33.92 (q?), 33.86, 33.75 (q?), 33.21 (d?), 32.88 (t), 31.80 (t), 31.75 (t), 31.11 (t), 30.92 (t), 30.92 (t), 30.73 (t), 30.56 (t), 30.50 (t).

$C_{24}H_{42}$ (330.3) Calcd. C 87.20 H 12.80 Found C 87.14 H 12.41

1,1,2,2-Tetra-1-adamantylethane (**6**): Di-1-adamantyl ketone[32] and di-1-adamantylmethanol[33] were prepared following lit. procedures. From the latter with $SOCl_2$ a 66% yield of di-1-adamantylmethyl chloride[33a] was obtained, which was used for a Wurtz reaction.

1.0 g (43 mmol) of a freshly cut piece of sodium was melted by heating it in 100 ml of absol. decane under N_2 to 130°C (bath). It was then finally dispersed at this temperature with a Ultra Turrax stirring device (20000 turns/min) for 10 min. After cooling the decane was exchanged for pentane by repeated decantation under N_2. To the stirred sodium dispersion a saturated solution of 600 ml (1.88 mmol) of di-1-adamantylmethyl chloride in 12 ml of absol. pentane was injected in portions through a septum seal, the temp. in the solution being kept below 25°C. Then stirring was continued till the reaction had ended and additional pentane was added before the mixture was cautiously hydrolysed with cooling under a stream of N_2. Besides the organic and the aqueous phase 100 mg (19%) of an insoluble residue was isolated, which was dried for further purification. It could not be sublimed but instead small amounts of di-1-adamantyl ketone and di-1-adamantylmethane sublimed as thermal decomposition products of **6** at 180°C. The compound was insoluble in all tested solvents including THF, chloronaphthalene, HMPT, and CH_2Cl_2; m.p. 210°C (dec.). – IR (KBr): 1015 cm^{-1}. – MS (70 eV, 160°C): *m/z* = 566 (4.2%, M^+), 565 (2, $M^+ - 1$), 564 (4, $M^+ - 2$), 432 (19.1), 431 (22.1), 429 (7.1), 297 (23.7), 296 (21.6), 295 (24.5), 285 (48.1), 284 (48.0), 283 (51.9), 282 (83.9), 217 (32.6), 216 (97.9), 215 (11.9), 168 (9.1), 149 (7.1), 148 (9.3), 147 (96.7), 146 (63.4), 136 (98), 135 (100%).

Fenchyl-fenchane **9**: Fenchyl chloride was prepared from fenchol in analogy to a procedure for the preparation of geranyl chloride[34]. The raw product was freed from the alcohol by chromatography over silica gel (coated with 10 weight % of water) in pentane. α-Fenchene was removed at 20 Torr/20°C. Yield of fenchyl chloride: 20%. A small sample of this material, which was 92% pure, was twice crystallized from pentane at −70°C. GC-Retention: Carbowax 20% 2 m 110°C: 3.3 min, 90°C: 6.5 min. – ^{13}C NMR ($CDCl_3$/TMS, numbering see formula **13**): δ = 79.79 (d; C-2), 50.65 (s; C-1), 49.42 (d; C-4), 44.45 (s; C-3), 41.29 (t; C-7), 35.67 (t; C-6), 27.57, 26.53 (q; C-9, 10), 25.52 (t; C-5), 19.52 (q; C-8).

9: 6.0 g (210 mmol) of a sodium suspension and 9.64 g of fenchyl chloride (92% pure) was reacted at −40°C by the same procedure as used for tetraadamantylethane. The pentane extracts after hydrolysis were concentrated and α-fenchene and fenchane were removed in vacuo. In the oily residue (513 mg, 26%) three isomers (85:14:1 ratio) of fenchyl-fenchane were detected by GC (1% carbowax, 2 m, 100°C). Fraction 2 was enriched to 95% purity by crystallization from methanol, fraction 1 to 90% using methanol/ether (1:1 to 15) as solvent.

Fraction 1: m.p. 75−78°C. – ^{13}C NMR ($CDCl_3$, TMS): δ = 56.35 (d), 48.80 (d), 46.78 (s), 45.58 (t), 45.58 (s), 44.03 (t), 27.57 (q), 26.92 (q), 24.03 (t), 21.71 (q).

Fraction 2: m.p. 99−102°C. – ^{13}C NMR ($CDCl_3$, TMS): δ = 53.91 (d), 49.92 (s), 49.70 (d), 49.39 (t), 41.67 (s), 32.73 (q), 28.52 (t), 27.70 (t), 26.52 (q), 24.20 (q). – MS (70 eV): *m/z* = 274 (1.41%, M^+), 193 (9.0), 192 (5.5), 191 (5.9), 145 (6.0), 137 (62.7), 136 (7.0), 135 (9.8), 123 (40.6), 122 (22.1), 121 (17.3), 109 (22.0), 107 (15.1), 95 (27.2), 93 (12.3), 91 (9.1), 83 (20.0), 82 (12.6), 81 (100), 80 (24.9), 79 (13.5), 77 (7.6), 69 (33.5), 67 (19.1), 57 (10.1), 55 (25.1), 53 (8.6).

$C_{20}H_{34}$ (274.3) Calcd. C 87.50 H 12.50 Found C 87.64 H 12.52

Fenchyl-fenchane incorporates 6 chiral centers (**14**). Because the bridgehead position must have *R,S* or *S,R*-configuration, 8 diastereomers are expected. By inspection of its formula[35] three groups are recognized consisting of 1) two *meso*-forms, 2) two D,L-forms, and 3) four diastereomers with *exo-endo*-connection of the two ring systems. The three fractions isolated possibly are still mixtures which cannot be separated by GC.

Thermolysis

Quantitative product analyses were performed as described previously[1]. The results are recorded in Table 4.

Table 4. Quantitative and qualitative product analyses for the thermolyses of **6** – **8**

	T/t[a]	Solvent	GC[b]	Product	mol/mol Educt	Identification
7[c]	120/10	toluene/ thiophenol	A	1-neopentyl-adamantane	1.95	^1H NMR; MS: m/z 206 (2%, M^+), 149 (4%, 1-ad-CH_2^+); *135* (100% ad^+)
8[d]	210/2	toluene/ thiophenol	A	1-neopentyl-norbornane	1.97	independent synthesis
6	100/120	none	B	di-1-adamantyl-methane : di-1-adamantyl ketone 10:1	–	independent synthesis

[a] Thermolyse temperature (°C) and time (h). – [b] A = 25 m SE 30 capillary; B = 2 m 5% SE 30 steel column. – [c] Mixture of D,L-**7** rotamers. – [d] Mixture of diastereomers of **8**.

Independant Syntheses of Product Samples

1-Neopentylnorbornane = 1-(2,2-Dimethylpropyl)norbornane was obtained as a side product of the dimerisation to **8** in 11% yield and separated by Kugelrohr distillation i. vacuo. – IR (film): 1390 and 1360 ($C(CH_3)_3$) cm^{-1}. – ^1H NMR ($CDCl_3$, TMS): δ = 2.25 – 1.16 (m; 13H), norbornyl and CH_2), 1.03 (s; 9H, $C(CH_3)_3$).

Di-1-adamantylmethane was obtained as a side product of the Wurtz synthesis of **6** in 52% yield, m.p. 170.0°C (Lit.[33a] 171 – 177°C). – IR (KBr): 850, 990, 1100 cm^{-1}. – ^1H NMR (CCl_4, TMS): δ = 1.5 – 2.0 (m).

Table 5. Kinetics of the thermolysis of P-(R^*,R^*)-**7** and M-(R^*,R^*)-**7** in [D_8]toluene/thiophenol

	T [°C]	$10^4 \cdot k_1$ [s^{-1}] ± σ	$t_{1/2}$ [h]
P-(R^*,R^*)-**7**	78.0	0.501 ± 0.008	38.40
	90.0	2.08 ± 0.01	9.24
	110.0	30.4 ± 0.1	0.63
	118.8	58.1 ± 0.8	0.33
M-(R^*,R^*)-**7**	78.0	0.081 ± 0.016	239
	90.0	0.60 ± 0.02	32.3
	110.0	7.08 ± 0.03	2.72
	118.8	13.8 ± 0.03	1.40

Kinetik

The DSC-method has been described previously in detail[1]. For the kinetic analysis by NMR the following procedure was used: 3 mg of a mixture of the D,L-7 rotamers were weighed into a thickwalled NMR tube and about 12 mg of thiophenol was added. Then 0.1 ml of [D$_8$]toluene was condensed into the tube. The samples were carefully degassed by repeated freeze and thaw cycles under evacuation and aerating with pure N_2. The sealed tubes were subjected for definite periods to an oil bath kept at constant temp. (± 0.1 °C), cooled quickly, and the concentration was determined via the *tert*-butyl signals in the ^{1}H NMR spectra. The aromatic protons in the solution served as standard. After suitable correction for the time taken for thermal equilibration of the samples, good first order kinetics were obtained, which were analysed with the program kinetik 80[36]. The results are recorded in Table 5.

Table 6. *X*-Ray operations and results

Compound	P-(*R**,*R**)-7	M-(*R**,*R**)-7
Crystal size, mm	0.7 × 1.15 × 0.35	0.5 × 1.2 × 0.4
Measured Intensities	4432	2124
Observed Reflections	4256	2027
Structure Factors of direct Phase Determination	427	424
R_{aniso}	0.046	0.049
Space Group (no.)	*C*2/*c* (15)	*C*2/*c* (15)
a, pm	1862.4(15)	1900.3(8)
b, pm	1505.9(12)	990.4(5)
c, pm	1838.0(15)	1342.0(4)
β, deg	109.01(6)	104.27(3)
Z	8	4
Calcd. Density, g · cm^{-3}	1.119	1.114

Table 7. Positional and thermal (pm^2 × 10^{-1}) parameters of P-(*R**,*R**)-7[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	9372(1)	5808(2)	6316(2)	51(1)	47(1)	64(1)	-17(1)	7(1)	-3(1)
C(2)	9783(1)	7107(2)	6183(1)	37(1)	50(1)	37(1)	-11(1)	5(1)	-1(1)
C(3)	9757(1)	8376(2)	6911(1)	28(1)	38(1)	27(1)	-1(1)	5(1)	-2(1)
C(21)	588(1)	6744(2)	6285(2)	44(1)	63(1)	53(1)	-22(1)	12(1)	5(1)
C(22)	9507(1)	7497(2)	5036(1)	53(1)	80(1)	36(1)	-18(1)	9(1)	-0(1)
C(30)	8988(1)	9177(2)	6738(1)	29(1)	38(1)	29(1)	2(1)	4(1)	0(1)
C(31)	8290(1)	8311(2)	6459(1)	34(1)	45(1)	40(1)	2(1)	6(1)	-3(1)
C(32)	7598(1)	9175(2)	6234(2)	29(1)	58(1)	56(1)	4(1)	3(1)	-4(1)
C(33)	7589(1)	117(2)	5331(2)	39(1)	67(1)	48(1)	6(1)	-6(1)	7(1)
C(34)	8247(1)	1048(2)	5612(2)	46(1)	54(1)	53(1)	20(1)	-1(1)	4(1)
C(35)	8216(1)	1882(2)	6554(2)	50(1)	47(1)	87(2)	1(1)	-6(1)	13(1)
C(36)	8234(1)	921(2)	7449(2)	48(1)	63(1)	51(1)	-12(1)	2(1)	20(1)
C(37)	8930(1)	64(2)	7671(1)	38(1)	48(1)	39(1)	-5(1)	2(1)	8(1)
C(38)	7573(1)	4(2)	7186(2)	42(1)	79(2)	58(1)	7(1)	15(1)	19(1)
C(39)	8944(1)	206(2)	5845(1)	38(1)	50(1)	41(1)	12(1)	4(1)	-3(1)

[a] U_{ij} is defined for $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^*)]$; the standard deviations are given in parentheses.

Table 8. Bond lengths (pm) and angles (deg) for P-(R^*,R^*)-7 (standard deviations in parentheses)

C(1) - C(2)	153.8(3)	C(3) - C(30)	162.9(2)	C(32) - C(33)	152.6(3)	C(34) - C(39)	153.0(3)
C(2) - C(3)	160.0(2)	C(30) - C(31)	154.7(2)	C(32) - C(38)	152.9(3)	C(35) - C(36)	152.6(3)
C(2) - C(21)	154.4(3)	C(30) - C(37)	155.5(2)	C(33) - C(34)	152.5(3)	C(36) - C(37)	153.8(3)
C(2) - C(22)	154.8(2)	C(30) - C(39)	155.9(2)	C(34) - C(35)	152.3(3)	C(36) - C(38)	151.8(3)
C(3) - C(3')	162.1(3(	C(31) - C(32)	153.4(2)				

C(1) - C(2) - C(3)	119.5(2)	C(3) - C(30) - C(31)	116.8(1)	C(32) - C(33) - C(34)	109.0(1)
C(1) - C(2) - C(21)	108.3(2)	C(3) - C(30) - C(37)	113.6(1)	C(33) - C(34) - C(35)	109.6(2)
C(1) - C(2) - C(22)	105.5(1)	C(3) - C(30) - C(39)	107.8(1)	C(33) - C(34) - C(39)	109.7(2)
C(3) - C(2) - C(21)	107.9(1)	C(31) - C(30) - C(37)	106.3(1)	C(35) - C(34) - C(39)	109.5(1)
C(3) - C(2) - C(22)	111.0(1)	C(31) - C(30) - C(39)	107.2(1)	C(34) - C(35) - C(36)	108.5(2)
C(21) - C(2) - C(22)	103.4(2)	C(37) - C(30) - C(39)	104.4(1)	C(35) - C(36) - C(37)	110.3(2)
C(2) - C(3) - C(3')	120.0(1)	C(30) - C(31) - C(32)	112.4(1)	C(35) - C(36) - C(38)	109.5(2)
C(2) - C(3) - C(30)	117.2(1)	C(31) - C(32) - C(33)	109.9(2)	C(37) - C(36) - C(38)	109.7(2)
C(3') - C(3) - C(30)	114.5(1)	C(31) - C(32) - C(38)	109.6(1)	C(30) - C(37) - C(36)	112.6(1)
		C(33) - C(32) - C(38)	109.8(2)	C(32) - C(38) - C(36)	108.7(2)
				C(30) - C(39) - C(34)	113.2(2)

Table 9. Positional and thermal ($pm^2 \times 10^{-1}$) parameters of M-(R^*,R^*)-7 (U_{ij} as in Table 7; standard deviations in parentheses)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	911(1)	5457(1)	1962(1)	46(1)	47(1)	55(1)	4(1)	21(1)	14(1)
C(2)	1529(1)	4854(1)	2498(1)	37(1)	39(1)	37(1)	0(1)	15(1)	3(1)
C(3)	1968(1)	4182(1)	2086(1)	29(1)	27(1)	30(1)	3(1)	9(1)	1(1)
C(4)	2849(1)	4456(1)	2220(1)	29(1)	27(1)	28(1)	1(1)	8(1)	-1(1)
C(5)	3466(1)	3732(1)	2713(1)	31(1)	37(1)	34(1)	8(1)	7(1)	2(1)
C(6)	3883(1)	3184(1)	2272(1)	40(1)	46(1)	52(1)	11(1)	15(1)	12(1)
C(21)	2065(1)	5477(1)	3101(1)	55(1)	51(1)	46(1)	-12(1)	24(1)	-1(1)
C(22)	1148(1)	4301(1)	2983(1)	48(1)	56(1)	46(1)	2(1)	26(1)	2(1)
C(30)	1469(1)	3700(1)	1307(1)	30(1)	30(1)	33(1)	1(1)	8(1)	-4(1)
C(31)	1150(1)	4255(1)	562(1)	34(1)	39(1)	36(1)	4(1)	5(1)	-5(1)
C(32)	711(1)	3677(1)	-131(1)	48(1)	55(1)	36(1)	2(1)	0(1)	-12(1)
C(33)	30(1)	3248(1)	20(1)	42(1)	69(1)	55(1)	-5(1)	-2(1)	-17(1)
C(34)	326(1)	2661(1)	734(1)	43(1)	54(1)	60(1)	-3(1)	12(1)	-23(1)
C(35)	832(1)	1932(1)	596(1)	62(1)	44(1)	65(1)	-11(1)	12(1)	-22(1)
C(36)	1511(1)	2366(1)	447(1)	53(1)	40(1)	51(1)	-13(1)	15(1)	-10(1)
C(37)	1946(1)	2927(1)	1150(1)	38(1)	30(1)	40(1)	-2(1)	10(1)	-4(1)
C(38)	1232(1)	2958(1)	-266(1)	61(1)	62(1)	40(1)	-14(1)	13(1)	-18(1)
C(39)	768(1)	3234(1)	1428(1)	36(1)	43(1)	45(1)	3(1)	13(1)	-10(1)
C(40)	3069(1)	5024(1)	1589(1)	31(1)	27(1)	28(1)	1(1)	9(1)	-2(1)
C(41)	3099(1)	4560(1)	848(1)	37(1)	30(1)	33(1)	-2(1)	13(1)	-3(1)
C(42)	3283(1)	5219(1)	293(1)	46(1)	41(1)	32(1)	-0(1)	17(1)	-5(1)
C(43)	4064(1)	5631(1)	677(1)	43(1)	49(1)	47(1)	7(1)	21(1)	-7(1)
C(44)	4054(1)	6123(1)	1402(1)	40(1)	45(1)	43(1)	2(1)	11(1)	-18(1)
C(45)	3466(1)	6865(1)	1179(1)	62(1)	33(1)	50(1)	1(1)	22(1)	-14(1)
C(46)	2687(1)	6453(1)	792(1)	48(1)	31(1)	43(1)	8(1)	16(1)	2(1)
C(47)	2506(1)	5813(1)	1359(1)	38(1)	28(1)	35(1)	1(1)	13(1)	-0(1)
C(48)	2682(1)	5950(1)	72(1)	49(1)	44(1)	35(1)	10(1)	12(1)	-3(1)
C(49)	3861(1)	5466(1)	1952(1)	36(1)	38(1)	34(1)	0(1)	8(1)	-8(1)
C(51)	4074(1)	4215(1)	3374(1)	43(1)	57(1)	38(1)	9(1)	-1(1)	-3(1)
C(52)	3132(1)	3052(1)	3141(1)	42(1)	47(1)	43(1)	19(1)	9(1)	4(1)

Table 10. Bond lengths (pm) and angles (deg) for M-(R^*,R^*)-7 (standard deviations in parentheses)

C(1) - C(2)	154.3(2)	C(5) - C(6)	153.4(3)	C(33) - C(34)	152.9(3)	C(41) - C(42)	153.9(2)
C(2) - C(3)	163.5(2)	C(5) - C(51)	154.6(2)	C(34) - C(35)	152.1(3)	C(42) - C(43)	152.6(2)
C(2) - C(21)	154.4(2)	C(5) - C(52)	154.1(2)	C(34) - C(39)	153.8(2)	C(42) - C(48)	152.7(2)
C(2) - C(22)	154.9(3)	C(30) - C(31)	154.8(2)	C(35) - C(36)	152.6(3)	C(43) - C(44)	153.0(3)
C(3) - C(4)	163.1(2)	C(30) - C(37)	154.8(2)	C(36) - C(37)	153.5(2)	C(44) - C(45)	152.5(2)
C(3) - C(30)	160.3(2)	C(31) - C(32)	154.0(2)	C(36) - C(38)	152.9(2)	C(44) - C(49)	153.8(2)
C(4) - C(5)	162.8(2)	C(32) - C(33)	152.8(3)	C(40) - C(41)	154.8(2)	C(45) - C(46)	152.4(2)
C(4) - C(40)	159.9(2)	C(32) - C(38)	152.6(3)	C(40) - C(47)	154.8(2)	C(46) - C(47)	153.5(2)
						C(46) - C(48)	152.2(2)

C(1) - C(2) - C(3)	116.7(1)	C(3) - C(30) - C(39)	110.2(1)	C(4) - C(40) - C(47)	107.4(1)
C(1) - C(2) - C(21)	105.9(1)	C(31) - C(30) - C(37)	108.6(1)	C(4) - C(40) - C(49)	110.4(1)
C(1) - C(2) - C(22)	107.4(1)	C(31) - C(30) - C(39)	105.7(1)	C(41) - C(40) - C(47)	108.8(1)
C(3) - C(2) - C(21)	113.9(1)	C(37) - C(30) - C(39)	104.2(1)	C(41) - C(40) - C(49)	105.6(1)
C(3) - C(2) - C(22)	109.0(1)	C(30) - C(31) - C(32)	112.0(1)	C(47) - C(40) - C(49)	104.6(1)
C(21) - C(2) - C(22)	103.0(1)	C(31) - C(32) - C(33)	109.7(2)	C(40) - C(41) - C(42)	111.8(1)
C(2) - C(3) - C(4)	113.8(1)	C(31) - C(32) - C(38)	109.9(1)	C(41) - C(42) - C(43)	109.9(1)
C(2) - C(3) - C(30)	117.5(1)	C(33) - C(32) - C(38)	109.8(2)	C(41) - C(42) - C(48)	109.8(1)
C(4) - C(3) - C(30)	120.8(1)	C(32) - C(33) - C(34)	108.2(1)	C(43) - C(42) - C(48)	109.6(1)
C(3) - C(4) - C(5)	114.1(1)	C(33) - C(34) - C(35)	110.1(2)	C(42) - C(43) - C(44)	108.6(2)
C(3) - C(4) - C(40)	120.6(1)	C(33) - C(34) - C(39)	109.5(1)	C(43) - C(44) - C(45)	109.4(1)
C(5) - C(4) - C(40)	117.5(1)	C(35) - C(34) - C(39)	110.5(1)	C(43) - C(44) - C(49)	109.4(1)
C(4) - C(5) - C(6)	116.9(1)	C(34) - C(35) - C(36)	108.4(1)	C(45) - C(44) - C(49)	110.2(2)
C(4) - C(5) - C(51)	109.0(1)	C(35) - C(36) - C(37)	109.0(2)	C(44) - C(45) - C(46)	108.6(1)
C(4) - C(5) - C(52)	113.5(1)	C(35) - C(36) - C(38)	109.5(1)	C(45) - C(46) - C(47)	108.9(1)
C(6) - C(5) - C(51)	107.5(1)	C(37) - C(36) - C(38)	109.9(1)	C(45) - C(46) - C(48)	110.1(2)
C(6) - C(5) - C(52)	105.7(1)	C(30) - C(37) - C(36)	113.2(1)	C(47) - C(46) - C(48)	109.7(1)
C(51) - C(5) - C(52)	103.1(1)	C(32) - C(38) - C(36)	109.3(2)	C(40) - C(47) - C(46)	112.9(1)
C(3) - C(30) - C(31)	119.3(1)	C(30) - C(39) - C(34)	112.4(1)	C(42) - C(48) - C(46)	109.3(1)
C(3) - C(30) - C(37)	107.8(1)	C(4) - C(40) - C(41)	119.2(1)	C(40) - C(49) - C(44)	112.7(1)

*X-Ray Results and Operations*37)

The orientation matrix and the cell parameters were determined from transparent colourless crystals of given dimensions on a SYNTEX-P3 four circle diffractometer. Measurement of intensities: ω scan, 1° range, Mo-K_α, 2Θ maximum = 55°. The structures were solved by direct-phase determination. Positional and thermal parameters could be refined by anisotropic least-squares cycles to the given *R* values. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements.

Force Field Calculations

The calculations were performed using the MM2-program15a) on the SPERRY-UNIVAC 1108 at the Rechenzentrum of the University of Freiburg. The original15b) MM2-force field for alkanes is used throghout this work (cf. lit.21b)) to calculate structures and ΔH_f^0. The strain enthalpy is derived therefrom by *von R. Schleyer*'s scheme16). The rotational itinerary has been explored by using the simple driver method15a).

Force field calculations of 7 are somewhat laborious, because of the difficulty in reaching the global minimum. Due to strong nonbonded repulsion several local minima exist, which differ slightly in energy but belong to the same type of conformation.

CAS Registry Numbers

6: 100084-05-7 / **7** (isomer 1): 100083-98-5 / **7** (isomer 2): 100164-05-4/**7** (isomer 3): 100164-06-5/ **8** (isomer 1): 100084-03-5 / **8** (isomer 2): 100084-04-6 / **9**: 3294-53-9 / **11**: 100084-06-8 / **12**: 100083-97-4 / AdCN 23074-42-2 / Ph_3PBr_2 1034-39-5 / $(Ad)_2CH_2$ 54781-15-6 / $(Ad)_2CHCl$ 54781-14-5 / $Br_2C(tBu)(Nb)$ 100084-02-4 / $HN=C(tBu)(Nb)$ 100083-99-6 / $H_2NN=C(Ad)(tBu)$ 89375-83-7 / $H_2NN=C(tBu)(Ad)$ 100084-00-2 / *anti*-$HN=C(Ad)(tBu)$ 100083-95-2 / *syn*-$HN=C(Ad)(tBu)$ 100083-94-1 / $Ph_3P=NN=C(Ad)(tBu)$ 100083-96-3 / $Ph_3P=NN=C(tBu)(Nb)$ 100084-01-3 / fenchyl chloride 90976-73-1

[1] Part XXVII: *M. A. Flamm-ter Meer, H.-D. Beckhaus, K. Peters, H.-G. v. Schnering,* and *C. Rüchardt,* Chem. Ber. **118**, 4665 (1985).

[2] Preliminary report: *C. Rüchardt* and *H.-D. Beckhaus,* Angew. Chem. **97**, 531 (1985); Angew. Chem., Int. Ed. Engl. **24**, 529 (1985).

[3] *G. Hellmann, S. Hellmann, H.-D. Beckhaus,* and *C. Rüchardt,* Chem. Ber. **115**, 3364 (1982).

[4] *S. G. Baxter, H. Fritz, G. Hellmann, B. Kitschke, H. J. Lindner, K. Mislow, C. Rüchardt,* and *S. Weiner,* J. Am. Chem. Soc. **101**, 4493 (1979).

[5] *H.-D. Beckhaus, G. Hellmann, C. Rüchardt, B. Kitschke, H. J. Lindner,* and *H. J. Fritz,* Chem. Ber. **111**, 3764 (1978).

[6] [6a] *G. D. Mendenhall, D. Griller, D. Lindsay, T. T. Tidwell,* and *K. U. Ingold,* J. Am. Chem. Soc. **96**, 2441 (1974). – [6b] *S. Braunstein, J. Dunogues, D. Lindsay,* and *K. U. Ingold,* J. Am. Chem. Soc. **99**, 2073 (1977).

[7] *H.-D. Beckhaus, G. Hellmann,* and *C. Rüchardt,* Chem. Ber. **111**, 72 (1978).

[8] [8a] *E. Osawa* and *H. Musso,* Top. Stereochem. **5**, 118 (1982). – [8b] *E. Osawa* and *H. Musso,* Angew. Chem. **95**, 1 (1983); Angew. Chem., Int. Ed. Engl. **22**, 1 (1984). – [8c] *E. Osawa, H. Shirahama,* and *T. Matsumoto,* J. Am. Chem. Soc. **101**, 4824 (1979).

[9] *M. A. Flamm-ter Meer, H.-D. Beckhaus,* and *C. Rüchardt,* Thermochem. Acta **80**, 81 (1984).

[10] *M. A. Flamm-ter Meer,* Dissertation, Univ. Freiburg 1984.

[11] [11a] *V. Prelog* and *G. Helmchen,* Angew. Chem. **94**, 614 (1982); Angew. Chem., Int. Ed. Engl. **21**, 567 (1982). – [11b] A torsional angle between two groups is called positive, if the group in front must be rotated in a clockwise direction to eclipse the same group at the back.

[12] *T. G. Back, D. H. R. Barton, M. R. Britten-Kelly,* and *F. S. Guziec,* J. Chem. Soc., Perkin Trans 1 **1976**, 2079.

[13] *H.-O. Kalinowski, E. Röcker,* and *G. Maier,* Org. Magn. Reson. **21**, 64 (1983).

[14] [14a] *D. H. Williams* and *J. Fleming,* Spektroskopische Methoden zur Strukturaufklärung organischer Verbindungen, Thieme Verlag, Stuttgart **1979**. – [14b] *E. Pretsch, T. Clerc, J. Seibl,* and *W. Simon,* Tabellen zur Strukturaufklärung organischer Verbindungen, Springer Verlag, Berlin 1976.

[15] [15a] *N. L. Allinger* and *Y. H. Yuh,* QCPE-program no. 395 (1980). – [15b] *N. L. Allinger,* J. Am. Chem. Soc. **99**, 8127 (1977).

[16] *P. v. R. Schleyer, J. E. Williams,* and *K. R. Blanchard,* J. Am. Chem. Soc. **99**, 2377 (1970).

[17] Cf. *J. F. Lomas* and *J.-E. Dubois,* J. Org. Chem. **41**, 3033 (1976); *J. S. Lomas, P. K. Luong,* and *J.-E. Dubois,* ibid. **42**, 3394 (1977); *S. Murata, S. Kanno, Y. Tanabe, M. Nakamura,* and *M. Oki,* Bull. Chem. Soc. Jpn. **57**, 525 (1984).

[18] *M. Oki,* Angew. Chem. **88**, 67 (1976); Angew. Chem., Int. Ed. Engl. **15**, 87 (1976); Top. Stereochem. **14**, 1 (1983).

[19] *J. E. Anderson, H. Pearson,* and *D. I. Rawson,* J. Am. Chem. Soc. **107**, 1446 (1985).

[20] For a review see *C. Rüchardt* and *H.-D. Beckhaus,* Top. Curr. Chem. **130**, 1 (1986).

[21] [21a] The MM2-force field[15b] as well as *Osawa*'s version MM2′[21b] tend to underestimate the strain in crowded alkanes like **4** and **7** (cf. lit.[9]). Preliminary results show a way to improve the method by changing the van der Waals potentials. Simultaneously this improves the capability to calculate the heights of barriers to rotation (cf. lit.[21b]). Note, that this failure of the MM2-results does not influence the quality of the correlation between thermal stability and strain enthalpy in a significant way. Only the slope increases by about 10% compared to correlations using experimentally determined strain values[20]. – [21b] *C. Jaime* and *E. Osawa,* Tetrahedron **39**, 2769 (1983).

[22] *S. W. Benson,* Thermochemical Kinetics, 2nd ed., p. 21 – 23; J. Wiley, New York 1976.

[23] Cf. lit.[10] for a more tentative interpretation.

[24] Following the general procedure of *G. D. Mendenhall* and *K. U. Ingold,* J. Am. Chem. Soc. **95**, 2963 (1973).

[25] [25a] *J. A. Krynitsky* and *H. W. Carhart,* Org. Synth., Coll. Vol. IV, 136 (1963). – [25b] *J. H. Wieringa, H. Wynberg,* and *J. Strating,* Tetrahedron Lett. **1972**, 2071.

[26] Following the general procedure given in lit.[12].

[27] *H.-O. Kalinowski, E. Röcker,* and *G. Maier,* Org. Magn. Reson. **21**, 64 (1983).

[28] *P. Yates* and *P. Eaton,* J. Am. Chem. Soc. **81**, 2767 (1959).

[29] *V. Golzke, F. Groeger, A. Oberlinner,* and *C. Rüchardt,* Nouv. J. Chem. **2**, 169 (1978).

[30] *M. Meier,* Diplomarbeit, Univ. Freiburg 1983.

[31] *G. Range,* Dissertation, Univ. Freiburg 1979.

[32] [32a] *J. H. Wieringa, H. Wynberg,* and *J. Strating,* Tetrahedron Lett. **1972**, 207. – [32b] *J. P. Mazaleyrat,* Can. J. Chem. **56**, 2731 (1978). – [32c] *H.-D. Hartzler,* J. Am. Chem. Soc. **93**, 4572 (1971).

[33] [33a] *J. H. Wieringa, H. Wynberg,* and *J. Strating,* Tetrahedron **30**, 3053 (1974). – [33b] Organikum, 13. ed., p. 549, VEB Deutscher Verlag der Wissenschaften, Berlin 1974.

[34] *R. D. Rieke, S. E. Bales, P. M. Hudnall,* and *G. S. Poindexter,* Org. Synth. **59**, 85.

[35] For detail see Lit.[10], p. 27.

[36] Dissertation *W. Barbe,* Univ. Freiburg 1981.

[37] Further details of the structure determination are deposited at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2 (West Germany). These data are available with quotation of the registry number CSD 51541, the authors, and the reference to this publication.

[241/85]