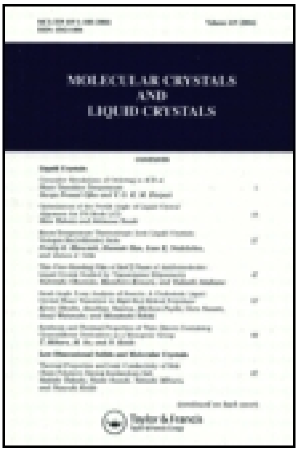

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Solid State Dimerization of a 5-Vinylidene- Cyclopentadiene

Hans Jörg Lindner [a] & Klaus Hafner [a]

[a] Institut für Organische Chemie, Technische Hochschule Darmstadt, Petersenstr. 22, D-64287, Darmstadt

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SOLID STATE DIMERIZATION OF A 5-VINYLIDENE-CYCLOPENTADIENE

HANS JÖRG LINDNER, KLAUS HAFNER
Institut für Organische Chemie, Technische Hochschule Darmstadt,
Petersenstr. 22, D-64287 Darmstadt

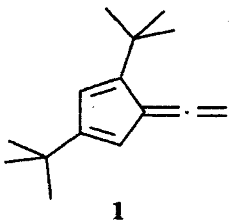
Abstract The kinetically stabilized 1.3-di-t-butyl-5-vinylidenecyclopentadiene (1) dimerizes in a thermal solid state reaction to the tetraquinane derivative 6. A reaction mechanism for this topochemically controlled reaction is proposed on the basis of results of X-ray analyses and semiempirical calculations.

INTRODUCTION

Photochemical dimerizations and polymerizations in organic molecular crystals are well known and studied1). The topochemical principle formulated by Schmidt2) and its extention, the concept of the reaction cavity by Cohen3), have provided a useful conceptional basis for the understanding of these reactions and the development of quantitative models4). Not much is known, however, about thermal dimerizations in the solid state5). The dimerization of 1,3-di-t-butyl-5-vinyliden-cyclopentadiene (1)6) is the first reaction of this kind that is proved to obey the topochemical principle.

PREPARATION AND REACTIONS OF KINETICALLY STABILIZED 5-VINYLIDENECYCLOPENTADIENES

The kinetically stabilized 6-halogenofulvenes 2 are versatile building blocks for the synthesis of non-benzenoid conjugated compounds like 1,3,5,7-tetra-t-butyl-s-indacene (3)7). Methylation of 2 with methyltriflate followed by HCl elimination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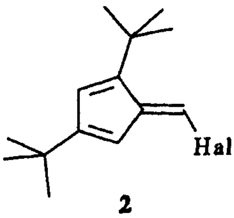

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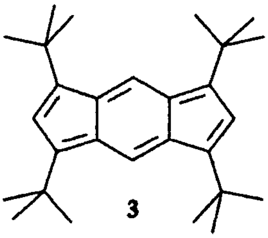
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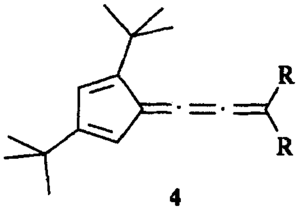
yields the pentafulveneallene 1. In contrast to the highly reactive unsubstituted pentafulveneallene, which was generated by Wentrup$^{8)}$, Hedaya$^{9)}$, and others$^{10)}$ as short-lived intermediate, the allene 1 can be isolated as slowly decomposing yellow crystals (mp. 54°C). Pentafulvenoid cumulenes like 4 and 5 are easily prepared from 1.$^{7,11)}$ The most unexpected reaction, however, is the decomposition of the yellow crystals of 1 to a yellow powder within 2h at room temperature, or within some days at 0°C. From the yellow powder the tetraquinane 6 can be isolated in 50% yield. From 6 the 1,3,5,7-tetra-t-butyldicyclopenta[a,e]pentalene (7) is obtained by dehydration with DDQ$^{6)}$. Studies by Lerch show that the first formed 6a undergoes fast tautomerization to 6b$^{12)}$. In solution, however, even after 36h refluxing in benzene, no dimerization occurs. Only traces of a not characterized trimer are isolated besides 1.$^{12)}$



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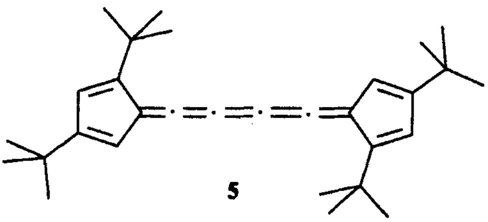

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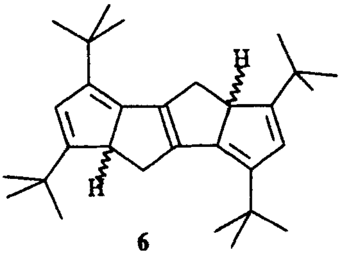

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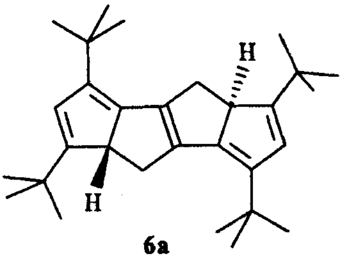
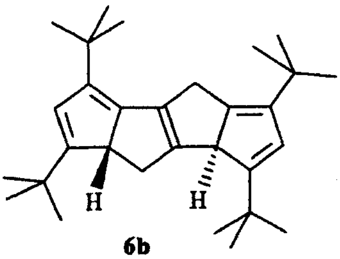
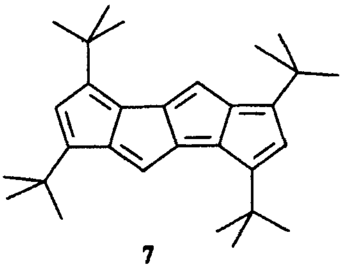


6a



6b



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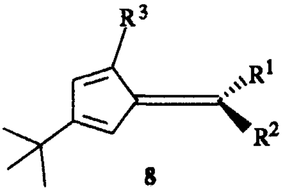
To test if the dimerization is unique to 1, other substituted pentafulvene allenes like 8a to d, 9 and 10a to c were prepared. None of these compounds undergoes dimerization neither in solution nor in the solid state.12) The observed dimerization of 1 is probably due to its special packing pattern in the crystal.



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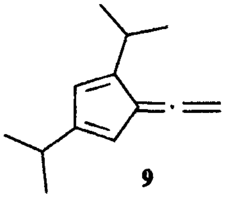

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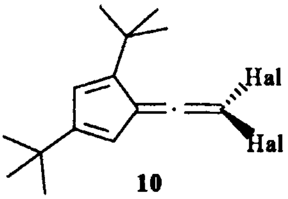

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8	R^1	R^2	R^3
a	H	Me	tBu
b	H	tBu	tBu
c	Me	Me	tBu
d	H	H	H

10	Hal
a	Cl
b	Br
c	I

CRYSTAL STRUCTURE ANALYSIS

Single crystal X-ray analyses of 1 were performed at 138K and at room temperature. The crystallographic data are collected in Table 1. They show a significant extention of the cell constants and an increase of the unit cell volume with increasing temperature. As the single crystals of 1 decompose at room temperature within 2 to 2.5 h, the room temperature data set was obtained by merging the data of overlapping measurements on seven crystals. The structure could be solved with both data sets in the space group $P2_1$. Anisotropic refinement of the 138K structure with the hydrogen atoms on the t-butyl groups geometrically positioned yielded an R value of 0.064. The room temperature structure could not be refined to R smaller than 0.105.13) A disorder of one t-butyl group was resolved by two sets of atomic coordinates. The molecular geometry of 1 derived from both measurements as given in fig. 1 is typical for pentafulvenes and allenes. The packing of the molecules (fig. 2, 138K data), however, is of much interest. The molecules are stacked along the 2_1 axis with the central atoms of the allene moieties close to the screw axis, thus forming a stack of nearly equidistant parallel allenes. The t-butyl groups in the outer regions are packed to rather rigid stacks. The distances between the conjugated systems of two molecules are about 3.6 Å. The arrangement of the atoms allows the motion of the atoms to form the new bonds by small rotations of two adjacent molecules around the axes formed by the two t-butyl groups.

In the difference fourier map calculated from the room temperature data additional electron maxima occured between the allene moieties (fig. 3). These maxima can be explained by assuming the existence of about 10% dimer in the decomposing single crystal. The small motions of the atoms during the reaction can easily be seen in fig. 4, which shows two monomers and the dimer 6 with meso-conformation.

These results indicate that the dimerization of 1 is a typical solid state reaction obeying the topochemical postulate of Schmidt.[1]

TABLE 1 Crystallographic data of 1

		room temp.	138 K
formula		$C_{15}H_{22}$	$C_{15}H_{22}$
space group		$P2_1$ (no.4)	$P2_1$ (no.4)
Lattice constants [Å]	a	10.65 (1)	10.509 (6)
	b	7.10 (1)	7.067 (6)
	c	9.32 (1)	9.153 (2)
	ß	92.74 (5)	92.63 (3)
V [Å^3]		704.1	679.12
Z		2	2
D_c [gcm^{-3}]		0.954	0.989
Diffractometer		STOE-Stadi2	Enraf-Nonius CAD4
λ [Å]		1.5418 (CuKα)	0.7107 (MoKα)
μ [smm^{-1}]		0.33	0.03
2θ max [°]		110	44
data collection		±h +k +l	±h +k +l
reflection measured		855	871
independent obs. refl.		538	774
n in $\lvert F \rvert \geq n\sigma_F$		4	4
number of parameters		138	171
R		0.105	0.064
R^2_W		0.310	0.181
(disp./σ)$_{max}$		0.74	0.96
residual elec.density [eÅ^{-3}]		+0.29/-0.34	+0.20/-0.23

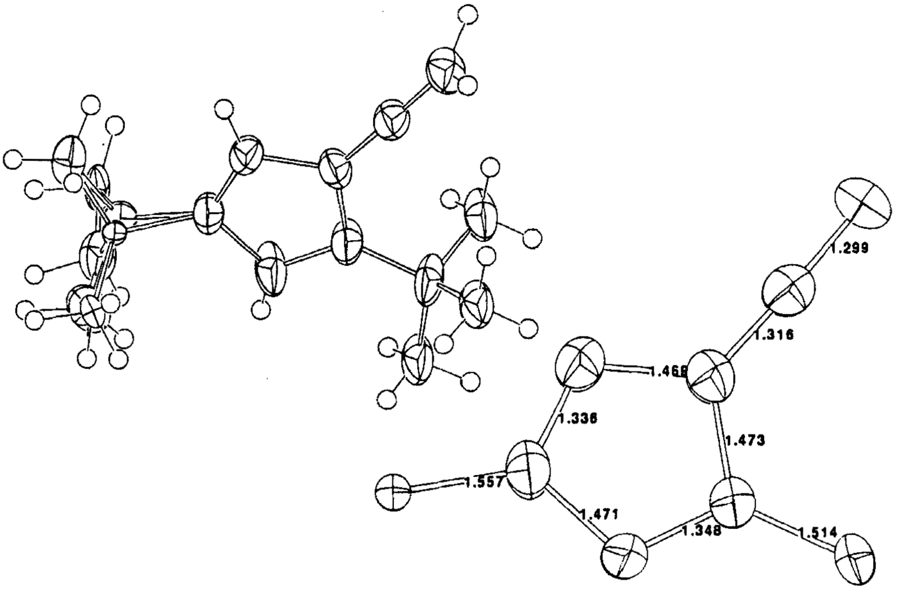


FIGURE 1: Molecular geometry of 1, view along b-axis

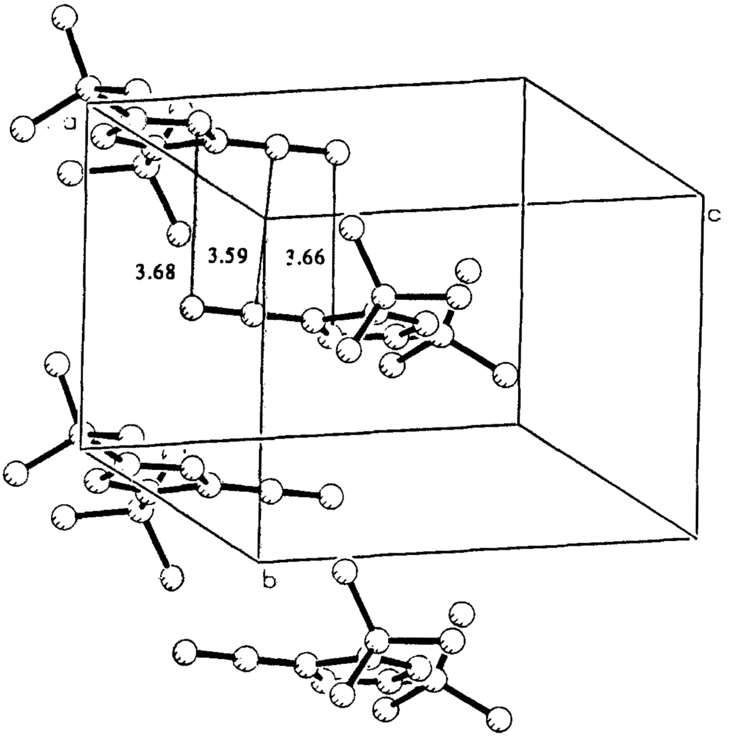


FIGURE 2: Crystal packing of 1, the stacking along the b-axis

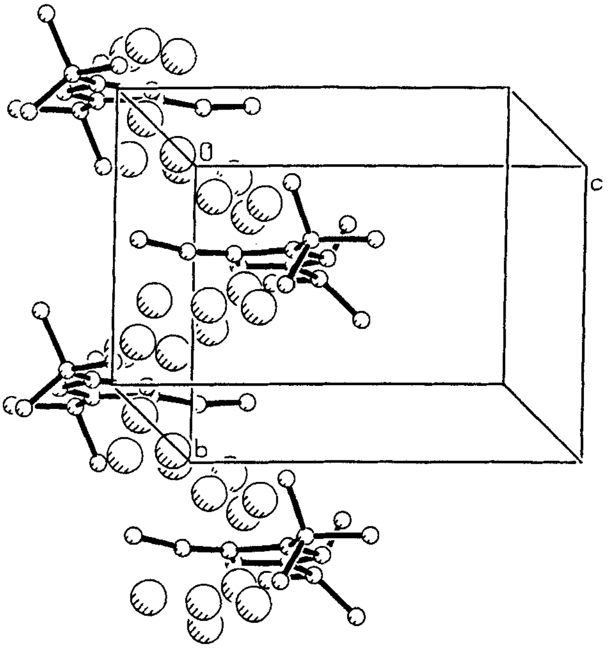


FIGURE 3: Stacking of 1 along the b-axis with maxima of residual electron densities between the pentafulvene allene molecules (room temperature measurement)

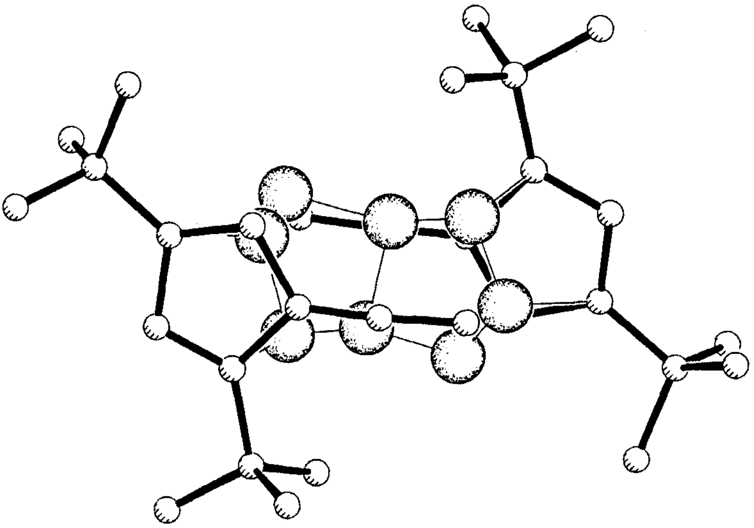


FIGURE 4: Superposition of two pentafulvene allene molecules and the dimer

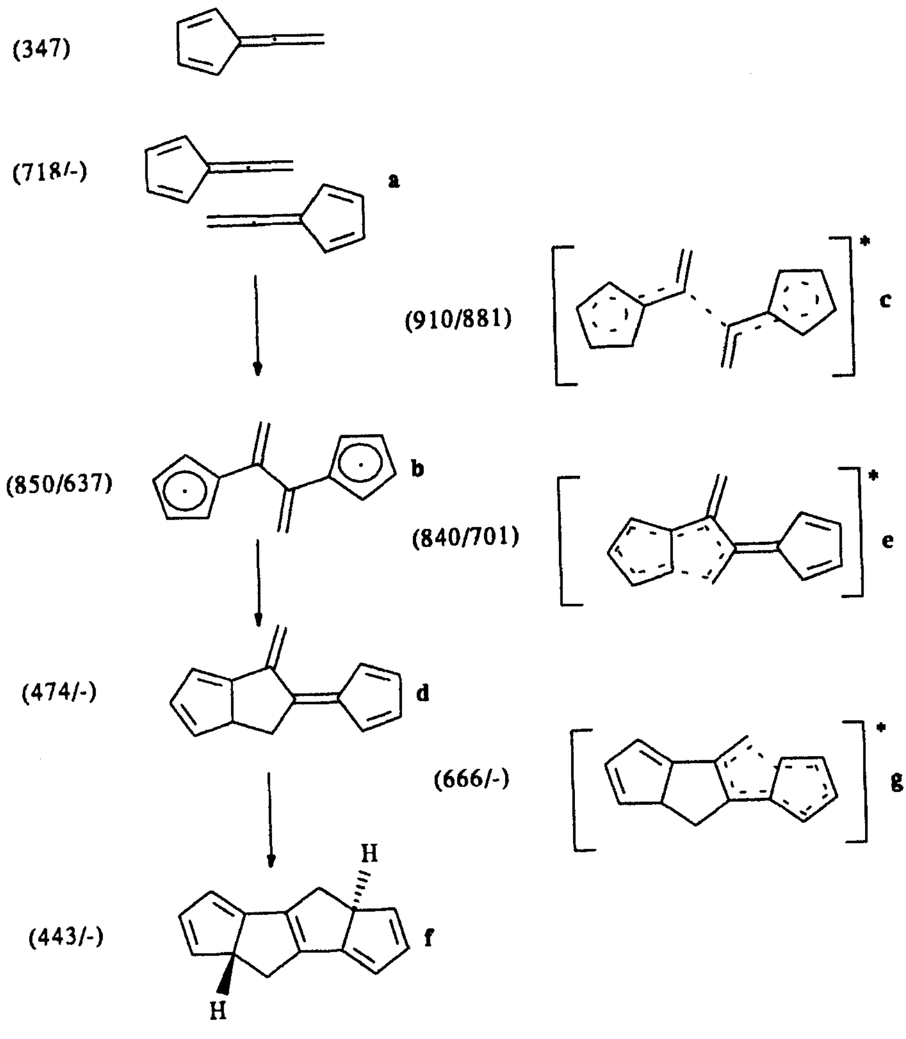
To compare the crystal packing of 1 with those of pentafulvene allenes, which show no tendency for dimerization in the solid state, X-ray analyses of 8c and 10a to 10c were performed. In none of these crystal structures a stacking of the allenes suitable for a dimerization was observed.[12,14]

THE MECHANISM OF THE DIMERIZATION OF 1

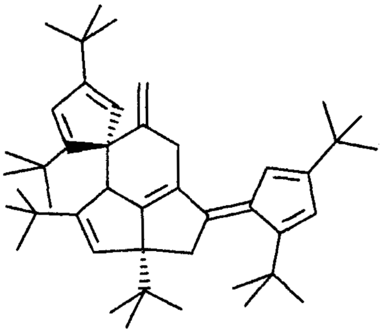
The results presented so far clearly indicate the importance of the molecular arrangement in the crystal for the dimerization of 1. The mutual orientation of the reacting sites of the molecules forced by the crystal packing apparently opens a reaction channel which is very unfavourable in solution. A possible mechanism for the dimerization is postulated on the basis of the results of semiempirical MNDO calculations[15] of the dimerization of two unsubstituted pentafulvene allenes, which are compiled in Table 2. The formation of the complex of two pentafulvene allenes with the orientation found in the crystal a has a heat of formation about 25 kJ/mol higher than that of the isolated molecules. The fixation of the complex lowers the entropy of the system by 100 J/Mol K, a value comparable with the activation entropy of a cycloaddition. The dimerization starts with the approximation of the two sp centers of the allene moieties and formation of the biradical b. The calculated heats of formation for b give strong evidence for a diradical species. In the transition state c for this step the distance between the bond forming atoms is 2.1 Å. The following step to a closed shell dihydropentalene intermediate d is extremely exothermic and proceeds via a biradicaloid transition state e. A final 8π electron cyclization gives the tetraquinane derivative f with a transition state 9 expected for an allowed electrocyclic reaction. This reaction sequence is only accessible, however, if the biradical b is restricted to an extended conformation. Without restrictions which in the solid state dimerization of 1 are introduced by the crystal packing, the biradical b adopts a more stable conformation with a torsion angle near 0° for the newly formed σ-bond, which could react to other products. An ESR signal, too weak for interpretation, observed at a reacting crystal of 1 by Sustmann[16], may be the radical intermediate in the solid state dimerization. Diradicals as intermediates of allene dimerizations have been observed by Roth et al.[17] and postulated by Toda et al.[18].

Finally, high pressure experiments of Klärner[19] must be mentioned. As expected, he found the dimer 6 after exposing crystalline 1 to a pressure of 10 kbar. From a 2 m solution of 1 in pentane (room temperature, 11.4 kbar, 68h) he isolated the trimer 11, the structure of which was determined by X-ray analysis[14]. From a

TABLE 2: Proposed reaction path of the dimerization from results of MNDO calculations; values given: Δ Hf (RHF/CI) [kJ mol^{-1}]



0.2 m solution of 1 (80°C, 8.5 kbar, 17h) he obtained 11 as well as 6. These results can be explained by postulating the formation of the biradical 12, which either reacts in the way described above or undergoes a conformational change and reacts to the dihydropentane 13. Diels-Alder reaction of 13 with 1 then yields the trimer 11.



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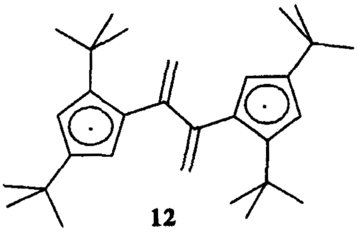

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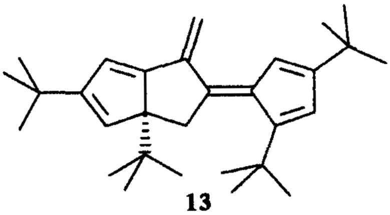

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CONCLUSION

Results of experimental and theoretical investigations of the solid state dimerization of 1 give a clear picture of the reaction and its topochemical control. Further work is necessary to obtain a deeper further insight into the reaction pathway by fast X-ray diffraction methods and calculations including effects of the crystal environment.

ACKNOWLEDGEMENT

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REFERENCES

1. R. Perrin and R. Lamartine in Structure and Properties of Molecular Crystals, edited by M. Pierrot (Elsevier, Amsterdam, 1990), Chap. 2, pp 107-160.
2. G.M.C. Schmidt, Pure Appl. Chem., 27, 647 (1971) and earlier papers.
3. M.D. Cohen, Angew. Chem. Int. Ed. Engl., 14, 386 (1975).
4. T. Luty and C.J. Eckhardt, J. Am. Chem. Soc., 117, 2411 (1995).
5. G. Wegner, Pure Appl. Chem., 49, 443 (1977); for a nontopochemical reaction see T. Machiguchi, T. Hasegawa, and S. Itoh, J. Am. Chem. Soc., 111, 1920 (1989).
6. B. Stowasser and K. Hafner, Angew. Chem. Int. Ed. Engl., 25, 466 (1986).
7. K. Hafner, Pure Appl. Chem., 62, 531 (1990).
8. R.W. Hoffmann, I.H. Loof, and C. Wentrup, Liebigs Ann. Chem., 1980, 1198, and earlier papers.
9. E. Hedaya and M.E. Kent, J. Am. Chem. Soc., 92, 2149 (11970).
10. R.G. Bergmann, Acc. Chem. Res., 6, 25 (1973) and lit. cited in ref. 7.
11. N. Nimmerfroh, Dissertation TH Darmstadt, 1989.
12. A. Lerch, Dissertation TH Darmstadt, 1992.
13. SHELXL-93, G.M. Sheldrick, Universität Göttingen, Germany, 1993.
14. H.J. Lindner and J. Richter, unpublished results.
15. M.J.S. Dewar and W. Thiel, J. Am. Chem. Soc., 99, 4899 (1977) J.J.P. Stewart, J. Computer-Aided Molecular Design, 4, 1 (1990).
16. R. Sustmann, private communication.
17. W.R. Roth, M. Heiber, G. Erker, Angew. Chem. Int. Ed. Engl. 12, 508 (1973); ; W.R. Roth, M. Biermann, G. Erker, and K. Jelich, Chem. Ber., 113, 586 (1980).
18. T. Toda, N. Shinazaki, and T. Mukai, Chem. Lett., 1979, 171; Tetrahedron Lett., 1980, 4001; Angew. Chem. Int. Ed. Engl., 26, 335 (1987).
19. F.G. Klärner, private communication.