134. Persistance of the Cyclophane Radical Anions and its Relation to Structure

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(26.IV.82)

Summary

Reactions of $[2_N]$cyclophanes (N = 2,...6) with solvated electrons in 1,2-dimethoxyethane at 193 K have been studied by ESR. and ENDOR. spectroscopy. All but the two most highly bridged cyclophanes (N = 5 and 6) are reduced to paramagnetic species under these conditions. Whereas the radical anions of [2.2]-paracyclophane and $[2_3]$(1,2,4)- and $[2_4]$(1,2,4,5)cyclophanes are sufficiently persistent to be characterized by their hyperfine data, those of the remaining five cyclophanes undergo a rapid cyclization to the radical anions of 4,5,9,10-tetrahydropyrenes. These have been identified as the unsubstituted tetrahydropyrene (from [2.2]-metacyclophane and $[2_3]$(1,2,3)cyclophane), the 2,7-dimethyl-derivative (from $[2_3]$(1,3,5)- and $[2_4]$(1,2,3,5)cyclophanes) and the 1,8-dimethyl-derivative (from $[2_4]$(1,2,3,4)cyclophane). The persistence of the cyclophane radical anions seems to depend on the numbers, n_{meta} and n_{para}, of the *meta*- and *para*-positions of the bridging ethano groups in the two benzene rings. The prerequisite for the radical anion to be persistent is $n_{meta} \leqslant n_{para}$.

Introduction. – In the last few years, all multiply bridged $[2_N]$cyclophanes have been prepared [1]. Their formulae are given below, along with a short-hand notation $N(\mu_1,...\mu_N)$, where N stands for the number of ethano bridges, and $\mu_1,...\mu_N$ specify the bridged centres of the benzene rings [2]. [2.2]Meta- and paracyclophanes, **2**(1,3) and **2**(1,4), respectively, are included in the series, but **2**(1,2) is not, since this dibenzo-1,5-cyclooctadiene can hardly be considered as [2.2]orthocyclophane. For the two highest homologues with five and six ethano bridges, the notations **5**(1,2,3,4,5) and **6**(1,2,3,4,5,6) have been abbreviated to **5** and **6**.

The present paper gives a comprehensive account of the primary and secondary radical anions which are obtained upon reaction of $[2_N]$cyclophanes with solvated

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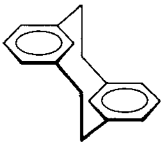
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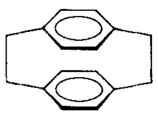
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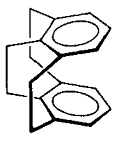
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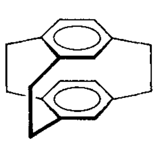
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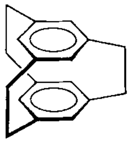
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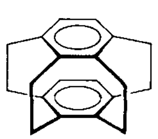
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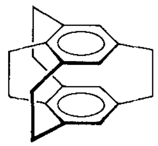
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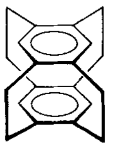
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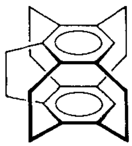
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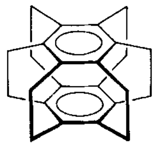
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electrons formed by dissolving potassium metal in 1,2-dimethoxyethane at 193 K [3]. This method of reduction has proved to be more gentle than a direct contact of the solution with the metallic mirror [4a].

Some of the results have been reported previously [4–6].

Results. – *[2.2]Cyclophanes:* **2***(1,3) and* **2***(1,4).* The radical anion, **2**(1,4)$^{\cdot\ominus}$, of [2.2]paracyclophane, which is persistent below 243 K, has been extensively studied by ESR. spectroscopy [5]. On the other hand, the radical anion, **2**(1,3)$^{\cdot\ominus}$, of the isomeric [2.2]metacyclophane is short-lived, since upon reduction of **2**(1,3) merely the ESR. spectrum of a secondary product was observed. This product has been identified [4] [5a] as the well-known [7] radical anion of 4,5,9,10-tetrahydropyrene (**7**).

[2$_3$]Cyclophanes: **3***(1,2,3),* **3***(1,2,4) and* **3***(1,3,5).* Of the primary radical anions obtained from these triply bridged cyclophanes, only **3**(1,2,4)$^{\cdot\ominus}$ is sufficiently persistent to be characterized by ESR. and ENDOR. spectroscopy at temperatures below 203 K. The hyperfine data for this radical anion, which have not been reported previously, are listed in *Table 1.*

Table 1. *Proton coupling constants,* $a_{H(ring)}$ *and* $a_{H(methylene)}$ *in mT, for the radical anion of [2$_3$](1,2,4)-cyclophane,* **3***(1,2,4)*[a]) (Solvent/counter-ion as indicated; temperature 213 K (for DMF/Et$_4$N$^{\oplus}$) and 163 K (for MTHF/K$^{\oplus}$). Numbers of protons giving rise to the coupling constants are given in parentheses)

$a_{H(ring)}$[b])		$a_{H(methylene)}$[b])			
DMF/Et$_4$N$^{\oplus}$	MTHF/K$^{\oplus}$	DMF/Et$_4$N$^{\oplus}$	MTHF/K$^{\oplus}$	DMF/Et$_4$N$^{\oplus}$	MTHF/K$^{\oplus}$
0.475 (2)	0.663 (1) 0.289 (1)	0.140 (2)	0.211 (1) 0.145 (1)	0.040 (2)	0.044 (1) 0.029 (1)
0.465 (2)	0.623 (1) 0.241 (1)	0.140 (2)	0.198 (1) 0.122 (1)	<0.020 (2)	0.029 (1) <0.010 (1)
0.330 (2)	0.427 (1) 0.229 (1)	0.040 (2)	0.052 (1) 0.029 (1)	<0.020 (2)	0.018 (1) <0.010 (1)

[a]) Experimental error in the coupling constants: ±0.005 mT. *g*-factor: 2.0029±0.0001. [b]) Tentative assignment.

The ESR. and ENDOR. spectra of **3**(1,2,4)$^{\cdot\ominus}$ in 1,2-dimethoxyethane (DME) are very complex, because they arise from a mixture of a 'free' or loosely associated radical anion and one paired with the counter-ion $K^{\oplus}$. The former has the effective symmetry C_s and should exhibit nine different coupling constants, each from two equivalent protons, whereas for the latter, due to the lower symmetry C_1, 18 coupling constants of non-equivalent protons are expected by analogy with **2**(1,4)$^{\cdot\ominus}$ [5]. The ESR. spectrum of the free radical anion **3**(1,2,4)$^{\cdot\ominus}$ was observed upon electrolytic reduction of the cyclophane in *N,N*-dimethylformamide (DMF) [8] with the use of a special cell constructed in the Basel laboratory (tetraethylammonium perchlorate as the supporting salt). This spectrum (*Fig.*, top) was analyzed in terms of the proton coupling constants given in *Table 1*. Guided by the hyperfine data

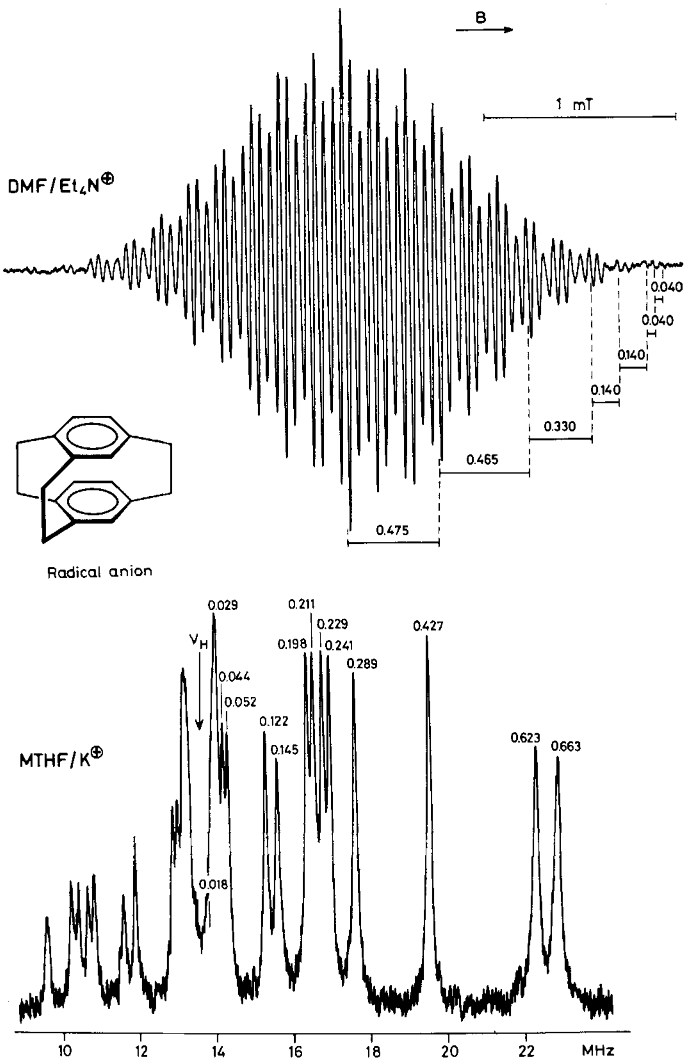


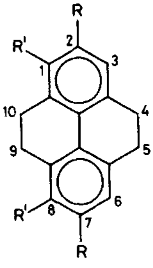
Figure. *ESR.* (top) *and ENDOR.* (bottom) *spectra of the radical anion of* $[2_3]$*(1,2,4)cyclophane,* **3***(1,2,4)* (Solvent/counter-ion as indicated. Temperature 213 K (top) and 163 K (bottom). The numbers indicate proton coupling constants in mT) for **2**(1,4)$^{\ominus\cdot}$ [5] and **4**(1,2,4,5)$^{\ominus\cdot}$ [6], the three largest values have tentatively been assigned to the ring protons. The ESR. spectrum of **3**(1,2,4)$^{\ominus\cdot}$ paired with K$^{\oplus}$ was obtained by reduction of the cyclophane with potassium in 2-methyltetrahydrofuran (MTHF). As a consequence of the large number of overlapping lines, which stem from the 18 non-equivalent protons, this spectrum is poorly resolved and not suitable for a reliable analysis. The pertinent coupling constants have been provided by the corresponding proton ENDOR. spectrum (*Fig.*, bottom). In *Table 1*, they are arranged pairwise in such a way that the average of each pair of values nearly matches one of the nine coupling constants found for the free radical anion in DMF.

Reduction of **3**(1,2,3) and **3**(1,3,5) led to **7**$^{\ominus\cdot}$ and the radical anion of 2,7-dimethyl-4,5,9,10-tetrahydropyrene (**8**), respectively. The previous identification of the secondary product from **3**(1,3,5) as **8**$^{\ominus\cdot}$ [4] has been confirmed in the present work by synthesis of **8** [9] and reduction of this compound to its radical anion. The spectra resulting therefrom are the same as those observed on starting from **3**(1,3,5).

[2$_4$]Cyclophanes: **4***(1,2,3,4),* **4** *(1,2,3,5) and* **4** *(1,2,4,5).* The ESR. and ENDOR. spectra of **4**(1,2,4,5)$^{\ominus\cdot}$, the most persistent of the radical anions of all [2$_N$]cyclophanes, can be conveniently studied up to room temperature and have recently been described [6]. The radical anions of the two remaining quadruply bridged cyclophanes, **4**(1,2,3,4) and **4**(1,2,3,5), are short-lived and yielded only spectra of secondary products. While **4**(1,2,3,5) was converted to **8**$^{\ominus\cdot}$, reduction of **4**(1,2,3,4) afforded a hitherto not observed ESR. spectrum which is attributed to the radical anion of 1,8-dimethyl-4,5,9,10-tetrahydropyrene (**9**). The proton coupling constants determined from this spectrum are given in *Table 2* where they are compared with the corresponding data for **7**$^{\ominus\cdot}$ and **8**$^{\ominus\cdot}$.

[2$_5$]- and [2$_6$]cyclophanes, **5** *and* **6**. The two most highly bridged [2$_N$]cyclophanes **5** and **6** ('superphane') were not reduced by solvated electrons ($e^{\ominus}_{solv}$) in DME. Neither a change in the blue color due to $e^{\ominus}_{solv}$ nor ESR. signals other than that of

Table 2. *Proton coupling constants,* a_{H_μ} *in mT, for the radical anion of 4,5,9,10-tetrahydropyrene* (**7**) and *its 2,7- and 1,8-dimethyl derivatives,* **8** *and* **9**, *respectively*[a]) (Solvent: DME, counter-ion: K$^{\oplus}$, temperature 193 K)



7 R=R'=H
8 R=Me, R'=H
9 R=H, R'=Me

Radical anion	**7**$^{\ominus\cdot}$	**8**$^{\ominus\cdot}$ b)	**9**$^{\ominus\cdot}$
$\mu = 1,3,6,8$	0.032	0.042	0.015c) 0.075d)
$\mu = 4,5,9,10$	0.381e) 0.079f)	0.398e) 0.083f)	0.465g)
$\mu = 2,7$	0.568	0.615h)	0.550

a) Experimental error in the coupling constants: ±0.003 mT; *g*-factor for all three radical anions: 2.0026±0.0001. b) Due to an error in calibration, the values given in a previous paper [4a] for this radical anion were slightly too large. c) Ring protons in the positions (μ=) 3 and 6. d) Protons of the two methyl groups in the positions (μ=) 1 and 8. e) Protons in the *axial* positions. f) Protons in the *equatorial* positions. g) Sum of the coupling constants of the *axial* and *equatorial* protons. (Due to the inversion of the ethano groups on the hyperfine time-scale and the resulting 'alternating' line-widths, only this value could be determined. Moreover, the slight non-equivalence of the protons in the 4,5- and 9,10-ethano-groups, expected on symmetry grounds, was not detected.) h) Protons of the two methyl groups in the positions (μ=)2 and 7.

$e^{\ominus}_{\text{solv}}$ were observed. Even a prolonged contact of the solution with the K-mirror did not lead to the radical anions $\mathbf{5}^{\ominus\cdot}$ and $\mathbf{6}^{\ominus\cdot}$.

The results for the reduction of the ten [2_N]cyclophanes are summarized in *Table 3.*

Table 3. *Products of the reduction of [2_N]cyclophanes*

Cyclophane	Primary radical anion	Secondary product, identified as the radical anion of	Class
2(1,3)	Short-lived[a])	tetrahydropyrene **7**	I
2(1,4)	Persistent up to 243 K	–[b])	II
3(1,2,3)	Short-lived[a])	tetrahydropyrene **7**	I
3(1,2,4)	Persistent up to 203 K	–[b])	II
3(1,3,5)	Short-lived[a])	2,7-dimethyltetrahydropyrene **8**	I
4(1,2,3,4)	Short-lived[a])	1,8-dimethyltetrahydropyrene **9**	I
4(1,2,3,5)	Short-lived[a])	2,7-dimethyltetrahydropyrene **8**	I
4(1,2,4,5)	Persistent up to 303 K	–[b])	II
5	Not formed[a])	–[c])	III
6	Not formed[a])	–[c])	III

[a]) Spectra of primary radical anions not observed. [b]) Spectra of secondary radical anions not observed. [c]) Only the ESR. signal of $e^{\ominus}_{\text{solv}}$ observed.

Discussion. – *Thermodynamic and kinetic stabilities.* As indicated in *Table 3,* the [2_N]cyclophanes fall into three classes with respect to their behavior in and upon reaction with solvated electrons $C + e^{\ominus}_{\text{solv}} \rightleftharpoons C^{\ominus\cdot}{}_{\text{solv}}$ (C = Cyclophane).

These classes consist of the following compounds: I: **2**(1,3), **3**(1,2,3), **3**(1,3,5), **4**(1,2,3,4) and **4**(1,2,3,5); II: **2**(1,4), **3**(1,2,4) and **4**(1,2,4,5); III: **5** and **6**.

The cyclophanes of classes I and II are reduced by $e^{\ominus}_{\text{solv}}$ in DME, so that the equilibrium of the reaction is shifted considerably to the right. The radical anions generated by this reaction in solution must thus be considered as thermodynamically stable relative to the neutral compounds and solvated electrons. By contrast, the cyclophanes of class III do not react to a measurable extent with $e^{\ominus}_{\text{solv}}$ in DME, and the equilibrium of the reaction essentially favors the left-hand side[1]). The radical anions of these cyclophanes therefore lack thermodynamic stability under the experimental conditions.

The compounds classified as I and II differ in the kinetic stability (persistence) of their radical anions. Whereas the radical anions of cyclophanes of class II are sufficiently persistent to be characterized by ESR. and ENDOR. spectroscopy, only secondary products are identified for the cyclophanes of class I. It is tempting to relate the differing persistence of the radical anions in these two classes to structural features. *Table 4* indicates the numbers of pairs of ethano bridges which occur in the *ortho-*, *meta-* and *para*-positions of the benzene rings in the various [2_N]cyclophanes with N = 2, 3 and 4. A common feature of the class I is $n_{meta} > n_{para}$. Obviously, ethano bridges in the *para*-positions render the radical anions of the cyclophanes more persistent, whereas an opposite effect is exerted by the *meta*-positioned

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[1]) The resistance of **5** and **6** to reduction might be due to their low electron affinity and/or to the poor solvation of the bulky anions $\mathbf{5}^{\ominus\cdot}$ and $\mathbf{6}^{\ominus\cdot}$.

Table 4. *Numbers, n, of the* ortho-, meta- *and* para-*positions of the ethano bridging groups in the benzene rings of* [2_N]*cyclophanes* ($N = 2, 3, 4$)

Cyclophane of Class I	n_{ortho}	n_{meta}	n_{para}	Cyclophane of Class II	n_{ortho}	n_{meta}	n_{para}
2(1,3)	0	1	0	**2**(1,4)	0	0	1
3(1,2,3)	2	1	0	**3**(1,2,4)	1	1	1
3(1,3,5)	0	3	0	**4**(1,2,4,5)	2	2	2
4(1,2,3,4)	3	2	1				
4(1,2,3,5)	2	3	1				

bridges. The simplest and most illustrative examples in this respect are the persistent radical anion **2**(1,4)$^{\dot{\ominus}}$ of [2.2]paracyclophane and the transient isomeric radical anion **2**(1,3)$^{\dot{\ominus}}$ of [2.2]metacyclophane. Moreover, the bridging groups in the *para*-positions seem to be more effective in enhancing the persistence than their *meta*-positioned counterparts in lowering it. This statement is suggested by the order of increasing persistence, **3**(1,2,4)$^{\dot{\ominus}}$ < **2**(1,4)$^{\dot{\ominus}}$ < **4**(1,2,4,5)$^{\dot{\ominus}}$, for class II (*Table 3*), *i.e.*, **4**(1,2,4,5)$^{\dot{\ominus}}$ is the most persistent, owing to the largest number n_{para} and despite an equal number n_{meta}. As for the bridging groups in the *ortho*-positions, there is no straightforward relationship between n_{ortho} and the persistence of the radical anions.

Conversions into secondary radical anions. These conversions, which were observed for the cyclophanes of class I, are formulated below.

$$\mathbf{2}(1,3)^{\dot{\ominus}} \xrightarrow{-2\,H} \mathbf{7}^{\dot{\ominus}} \xleftarrow{-(CH_2)_2} \mathbf{3}(1,2,3)^{\dot{\ominus}}$$

$$\mathbf{3}(1,3,5)^{\dot{\ominus}} \xrightarrow[+2\,H]{-2\,H^{2)}} \mathbf{8}^{\dot{\ominus}} \xleftarrow[+2\,H]{-(CH_2)_2} \mathbf{4}(1,2,3,5)^{\dot{\ominus}}$$

$$\mathbf{9}^{\dot{\ominus}} \xleftarrow[+2\,H]{-(CH_2)_2} \mathbf{4}(1,2,3,4)^{\dot{\ominus}}$$

Cyclization of **2**(1,3)$^{\dot{\ominus}}$ to **7**$^{\dot{\ominus}}$, with a concomitant loss of two H-atoms, is not unexpected, since in an analogous reaction, induced by UV. irradiation, [2.2]metacyclophane **2**(1,3) is converted into 4,5,9,10-tetrahydropyrene (**7**) [10]. It is known in many cases that radical ions react in a way similar to the excited states (see, *e.g.*, [4] and [11]), due to single occupancies of the frontier orbitals. For **2**(1,3) and its radical anion, the cyclization is favored by the *anti*-conformation of the benzene rings. It is therefore surprising to find that conversion to **7**$^{\dot{\ominus}}$ also readily occurs for **3**(1,2,3)$^{\dot{\ominus}}$, although the ethano bridging of the 2-positions forces the benzene rings to adopt the *syn*-conformation (*cf.* formulae and *Table 2*). Actually, this bridging group, which would hinder the cyclization, is eliminated on passing from **3**(1,2,3)$^{\dot{\ominus}}$ to **7**$^{\dot{\ominus}}$.

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[2] Whereas formation of a C,C-bond between the two benzene rings requires an elimination of two H-atoms, conversion of the two methylene groups into methyl substituents implies an acquisition of two such atoms.

The cyclization is likewise not prevented by the introduction of an ethano bridge in the benzene 5-positions of **2** (1,3) to yield **3**(1,3,5). It is achieved by the cleavage of the C,C-bond in one of the three equivalent bridging groups in **3**(1,3,5)$^{\dot{\ominus}}$, the two methylene moieties of this group appearing as methyl substituents in the radical anion of 2,7-dimethyl-4,5,9,10-tetrahydropyrene (**8**) thus formed2).

As in **3**(1,2,3)$^{\dot{\ominus}}$, elimination of the bridging group in the 2-position occurs in **4**(1,2,3,4)$^{\dot{\ominus}}$ and **4**(1,2,3,5)$^{\dot{\ominus}}$ which are also bridged at three consecutive benzene C-atoms. Thereby, **4**(1,2,3,5)$^{\dot{\ominus}}$ cyclizes to **8**$^{\dot{\ominus}}$, while **4**(1,2,3,4)$^{\dot{\ominus}}$ affords the radical anion of 1,8-dimethyl-4,5,9,10-tetrahydropyrene (**9**). Thus, the bridging group in either the 5- and 4-position, respectively, is again transformed into two methyl substituents.

It is noteworthy that the conversion of **3**(1,3,4)$^{\dot{\ominus}}$≡**3**(1,2,4)$^{\dot{\ominus}}$ to **9**$^{\dot{\ominus}}$ is missing. As stated above, the cyclophane **3**(1,2,4) falls into class II, since it is reduced to a relatively persistent radical anion which does not give rise to an observable paramagnetic product upon its decay.

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*. Financial assistance by *Ciba-Geigy SA*, *Sandoz SA* and *Hoffmann-La Roche & Cie. SA* is likewise acknowledged. We also thank Dr. *P. Fürderer* for taking the ESR. and ENDOR. spectra of 3(1,2,4)$^{\dot{\ominus}}$ in MTHF.

REFERENCES

[1] a) *B. Neuenschwander & V. Boekelheide*, Isr. J. Chem. *20*, 288 (1980); b) *S. Trampe, H. Hopf & K. Menke*, Chem. Ber. *110*, 371 (1977); c) *J. Kleinschroth & H. Hopf*, Angew. Chem. *91*, 336 (1979); Angew. Chem. Int. Ed. *18*, 329 (1979); d) *W. Gilb, K. Menke & H. Hopf*, Angew. Chem. *89*, 177 (1977); Angew. Chem. Int. Ed. *16*, 191 (1977); e) *R. Gray & V. Boekelheide*, J. Am. Chem. Soc. *101*, 2128 (1979); f) *P.F.T. Schirch & V. Boekelheide*, ibid. *101*, 3125 (1979); g) *Y. Sekine, M. Brown & V. Boekelheide*, ibid. *101*, 3126 (1979).

[2] *B. Kovač, M. Mohraz, E. Heilbronner, V. Boekelheide & H. Hopf*, J. Am. Chem. Soc. *102*, 4314 (1980).

[3] *F. Gerson, G. Moshuk & M. Schwyzer*, Helv. Chim. Acta *54*, 361 (1971).

[4] a) *Ch. Elschenbroich, F. Gerson & V. Boekelheide*, Helv. Chim. Acta *58*, 1245 (1975); b) *Ch. Elschenbroich, F. Gerson & J.A. Reiss*, J. Am. Chem. Soc. *99*, 60 (1977).

[5] a) *F. Gerson & W.B. Martin, jr.*, J. Am. Chem. Soc. *91*, 1883 (1969); b) *F. Gerson, W.B. Martin, jr. & Ch. Wydler*, Helv. Chim. Acta *59*, 1365 (1976).

[6] *F. Gerson, J. Lopez & V. Boekelheide*, J. Chem. Soc., Perkin Trans. II *1981*, 1298.

[7] *M. Iwaizumi & T. Isobe*, Bull. Chem. Soc. Jpn. *38*, 1547 (1965).

[8] *H. Ohya-Nishiguchi*, Bull. Chem. Soc. Jpn. *52*, 2064 (1979).

[9] *N.L. Allinger, B.J. Gorden, Shin-En Hu & R.A. Ford*, J. Org. Chem. *32*, 2272 (1965).

[10] *T. Sato, E. Yamada, Y. Okamura, T. Amada & K. Hata*, Bull. Chem. Soc. Jpn. *38*, 1049 (1965).

[11] *P. Fürderer, F. Gerson & A. Krebs*, Helv. Chim. Acta *60*, 1226 (1977).