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PLANOID DISTORTIONS IN BRIDGED SPIROCOMPOUNDS

FORMATION OF (ALL-*CIS*)-[5.5.5.5]FENESTRANE IN THE ATTEMPTED SYNTHESIS OF THE (*CIS,CIS,CIS,TRANS*)-ISOMER

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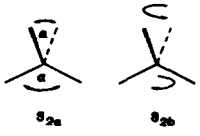
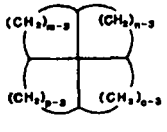
Abstract—Molecular distortions in bridged [4.4]spirononanes and fenestranes are discussed in terms of symmetry deformation coordinates. This analysis reveals that the central, quaternary carbon atom in most of these compounds shows mainly a decrease of the two opposite ring bond angles, whereas the distortions in fenestranes are dominated by an increase of the two opposite bond angles. Dicyclopentadienone **8** serves as the starting material for the preparation of [5.5.5.5]fenestranes. In the key step of the synthesis, the Pd-catalyzed reductive transannular reaction of the enaminonitrile **13** and the ketolactone **17**, (all-*cis*)-[5.5.5.5]fenestrane **6** is formed instead of the (*cis,cis,cis,trans*)-isomer **7**.

The theory of van't Hoff and Le Bel[1] is certainly the most important concept for structural organic chemistry. It was soon realized by Baeyer[2] that considerable deviations from ideal T_d symmetry must have significant energetic consequences. Indeed, strained carbon compounds have played an important rôle for the assessment of relative stability and reactivity ever since. It is remarkable that most of the highly strained hydrocarbons prepared so far contain tertiary or quaternary carbon atoms in a local environment of threefold symmetry.[3] Well-known examples are cubane,[4] tetrakis-t-butyltetrahedrane,[5] dodecahedrane[6] and compounds with inverted carbon like the propellanes.[7]

Strained hydrocarbons containing quaternary carbon atoms in an environment with fourfold rotation–inversion (D_{2d}) or orthorhombic (D_2) symmetry, corresponding to planoid deformations at carbon, are much fewer and have long been neglected.[8] Only recently has planar tetracoordinate carbon received computational[9] and experimental[10] consideration.





1

In order to gain insight into the nature of planoid distortions at carbon, polycyclic compounds containing [4.4]spirononane subunits were analysed systematically in terms of symmetry deformation coordinates.[11] Two modes of distortion from T_d towards D_{2d} or D_2 symmetry have to be considered: (a) increasing or decreasing two opposite bond angles leading to local D_{2d} symmetry (S_{2a} mode); (b) twisting two ligands with respect to the other two, leading to local D_2 symmetry (S_{2b} mode).

The degree of these distortions is specified by a bond angle deformation vector with components S_{2a} (E) and S_{2b} (E).[12] Since there are three fourfold inversion–rotation axes in a tetrahedron, there are six isometric deformations. By appropriate labeling of the bond angles, the corresponding deformation vectors can be confirmed to the space between the positive half of the S_{2a}- and the negative half of the S'_{2a}-axis and therefore any planoid distortion observed in X-ray structures can be represented as shown in the diagram (Fig. 1).

It is apparent that most of the structures included in the diagram show orthorhombic distortions at the spirocentre, i.e. distortions which are intermediate between tetragonal flattening (along $+S_{2a}$) and tetragonal compression (along $-S'_{2a}$). Most of the compounds with local distortions at the spirocentre, which are intermediate between S'_{2b} and S_{2a}, i.e. which are close to pure tetragonal flattering belong to the fenestranes of type **1**, a special class of bridged spirocompounds.

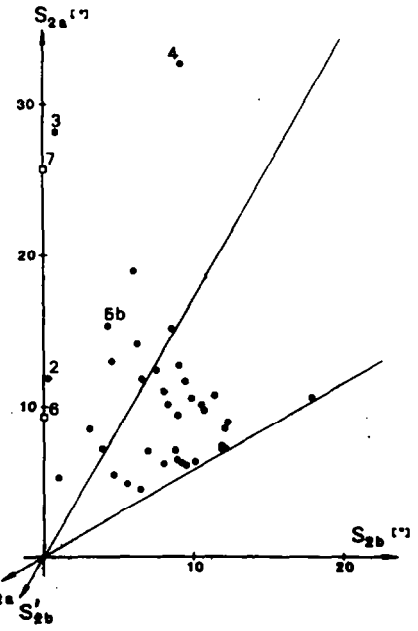
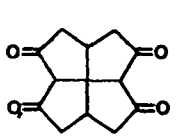


Fig. 1. Symmetry deformation vectors S_{2a} (E) and S_{2b} (E) for the spiro centres in bridged spirocompounds, containing [4.4]spirononane subunits, calculated from crystal structure data.[12] Symmetry deformation vectors of [5.5.5.5]fenestranes, calculated by MNDO, are only given for the two stereoisomers **6** and **7**. For structural identification of the other spirocompounds see Ref. 11.

Typical examples for structures containing spiro carbon atoms in a planoid environment are given by the fenestranes **2–4**.†[13] The diterpene laurene **5a** also has a fenestrane skeleton and is to the best of our knowledge the only natural product in this special class of spiro compounds. As revealed by the X-ray structure of the bromo derivative **5b** the local structure of the spiro carbon atom in this bridged spiro compound shows also significant planoid distortions.[15] When MNDO-results of the six stereoisomers‡ of [5.5.5.5]fenestrane, amongst them **6** and **7** were analysed in the same way, it



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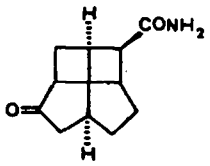

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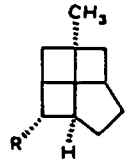
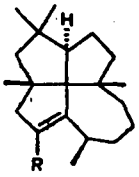
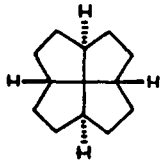


4 R = CONH-p-C_6H_4Br



5a R = H

5b R = Br



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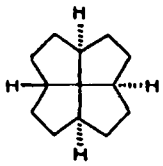


7

became apparent that the local geometry at the spiro centre corresponds to increasing angle opening ($\alpha > 109.47°$), leading to planoid distortions along the $+S_{2a}$-axis.[11] Because of these specific structural features, fenestranes with small rings and stereoisomers thereof are of particular interest. Here we describe our attempts to prepare (*cis,cis,cis,trans*)-[5.5.5.5]-fenestrane **7**, which however led to the all-*cis*-isomer **6**.

Synthesis of **6**

In the course of our first synthesis of a bridged all-*cis*-[5.5.5.5]fenestrane,[10a,b] it became clear that stereoisomers of fenestranes would be of special interest.

Making use of the symmetry of [5.5.5.5]fenestrane and in consideration of the strain to be expected for compounds like **6** and **7** and the option to prepare stereoisomers from a common precursor, a trans-annular carbene insertion in an appropriately functionalized cyclooctane was anticipated as the key step in our syntheses.

Following our earlier procedure,[16] the tricyclic compound **10** was prepared via **9** from the readily available enone **8**. Subsequent hydrogenation of **10**, formation of the ketal with methanol, oxidation with ruthenium tetroxide and esterification with methanol gave the diesterketal **11**. Because the Dieckmann reaction in the closely related compound **18** gave not more than 5% of the intramolecular condensation product,[14d] the diester **11** was transformed into the dinitrile **13** via the corresponding diamide, followed by dehydration. Ziegler–Thorpe cyclization gave a mixture of enaminonitriles in over 60% yield. Because of its subsequent transformation into the ketolactone **14**, it has not been determined whether **13** or its regioisomer was formed in excess.

With the successful synthesis of the enaminonitrile **13** the carbon skeleton required for the formation of (*cis,cis,cis,trans*)-[5.5.5.5]fenestrane **7** had been obtained, the overall yield for the reaction sequence **8** → **13** was 11%.

The remaining steps for the formation of the fenestrane, shaped according to our earlier results obtained with the synthesis of (all-*cis*)-[5.5.5.5]fenestrane,[10a,b] required the hydrolysis of the enaminonitrile **13**, and transformation of the corresponding ketone **14** into the carbene appropriate for transannular insertion. When the enaminonitrile **13** was hydrolyzed under acidic conditions, an intermediate was isolated, from which the ketolactone **14** could be obtained by oxidation only in moderate yield. This result is surprising in view of the efficient hydrolysis reported for the enaminonitrile obtained from 1,9-nonanedinitrile.[17]

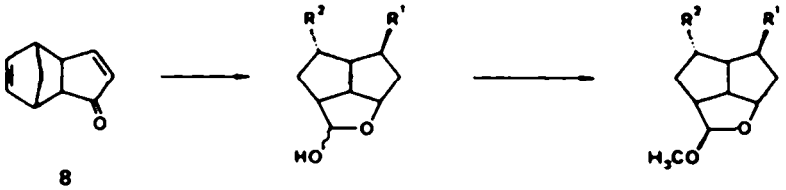
The moderate yield is not due to the oxidation step, because it did not increase when **13** was transformed into ketoacetal **17**. Similarly, it had been observed that the enaminonitrile, prepared from **19**, could only be hydrolyzed in moderate yield under other conditions.[14d] This reluctance of efficient hydrolysis in these two closely related cases might be due to the

† For syntheses of fenestranes see: Refs 10*a,b* and 14*a–e* ([5.5.5.5]fenestrane); Refs 13*b* and 14*f,g* ([5.5.5.4]fenestrane and [5.5.4.4]fenestrane); and Ref. 14*h* ([5.4.4.4]fenestrane).

‡ The six stereoisomers of [5.5.5.5]fenestrane are defined by *cis* or *trans* ring fusion of the bicyclo[3.3.0]octane subunits. According to IUPAC nomenclature, the (all-*cis*)-isomer **6** is *cis - transoid - cis - transoid - cis - transoid - cis - transoid* - tetracyclo[5.5.1.$0^{4,12}$.$0^{10,13}$]tridecane; the "*c,c,c,t*"-isomer **7** is *cis - transoid - cis - transoid - cis - transoid - trans - cisoid* - tetracyclo[4.4.1.$0^{4,13}$.$0^{10,13}$]tridecane. The formulae of the fenestranes **2–7** represents Fischer projections for the configuration of the central carbon atom.

restricted conformational flexibility imposed onto the cycloöctane ring by the annulated ring system.

The ketolactone **14** obtained was subsequently transformed into the corresponding 2,4,6-tri(isopropyl)phenyl-sulfonylhydrazone **15**. Photolysis of the potassium salt of **15** gave instead of the desired fenestrane the olefin **16** (or its regioisomer) as the major component. The dominant formation of olefins in this and in a related case[14d] is in contrast to the corresponding reactivity found in **23**,[10b] where transannular insertion leads preferentially to the



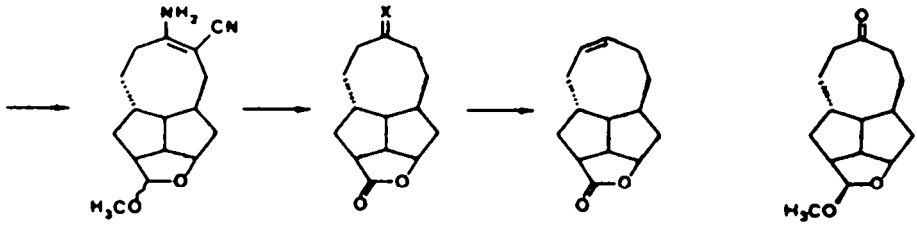
8

9 $R^1 = (CH_2)_3OCH_2C_6H_5$, $R^2 = CHO$

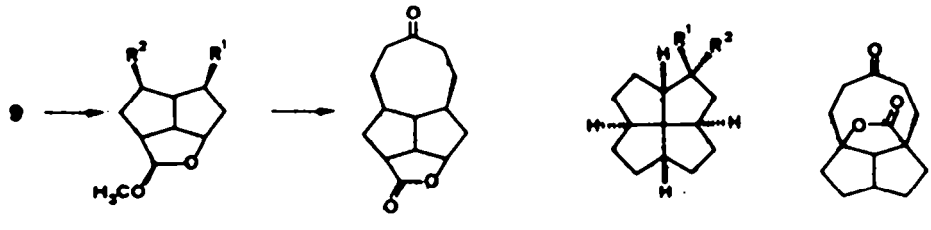
10 $R^1 = (CH_2)_3OCH_2C_6H_5$, $R^2 = CH{=}CHCOOC_2H_5$

11 $R^1 = R^2 = (CH_2)_2COOCH_3$

12 $R^1 = R^2 = (CH_2)_2CN$



13 **14** X = O; **15** X = N-NHTrisyl **16** **17**



18 $R^1 = R^2 = (CH_2)_2COOCH_3$ **19** $R^1 = R^2 = (CH_2)_2CN$ **20** **21** $R^1 = CH_3$, $R^2 = H$ **22** $R^1 = H$, $R^2 = CH_3$ **23**

desired derivative of (all-*cis*)-[5.5.5.5]fenestrane **6**. Eventually we submitted the ketolactone **14** to the same reaction conditions by which the isomeric ketolactone **20** had been transformed into (all-*cis*)-[5.5.5.5]fenestrane **6**.[14d] Thus, treatment of **14** with Pd and some H_2 at high temperature gave a [5.5.5.5]fenestrane as the major product. Since we had to take into account extensive hydrogen exchange under these conditions,[18] (all-*cis*)-[5.5.5.5]fenestrane **6** might have been formed instead of **7**.

From GC comparison of the product isolated with an authentic sample of **6** under a variety of conditions it was concluded that the [5.5.5.5]fenestrane obtained from ketolactone **14** is indeed the more stable[10b] all-*cis*-isomer **6**. When the enaminonitrile **13** itself was submitted to the same reaction conditions (all-*cis*)-[5.5.5.5]fenestrane was again isolated. In this case two additional products could be identified as methyl-substituted fenestranes. It is very likely that both of these isomers, formulated as **21** and **22**, are derivatives of (all-*cis*)-[5.5.5.5]fenestrane **6**, although it cannot yet be excluded that one of the isomers might be a derivative of **7**.

At any rate, the reductive transannular insertion catalyzed by Pd in the presence of H_2 provided a high temperature method for the formation of (all-*cis*)-[5.5.5.5]fenestrane **6**. Whether the (*cis,cis,cis,trans*)-

stereoisomer 7 can be prepared from 14 or 17 by other methods remains to be demonstrated.

CONCLUSIONS

In a systematic search for organic compounds with strong planoid distortions, it has been found that fenestranes with small rings show unique structural features. A key step in syntheses of [5.5.5.5]fenestrane is the transannular reaction in a cyclooctane substructure. This reaction can be induced in appropriate starting materials by Pd, which in the presence of H_2 and high temperature acts as a catalyst.

From the study of fenestranes and other model compounds with carbon atoms in a highly distorted, planoid environment presently underway in our and other laboratories[10,13,14] a more precise view of the relationship between structure, strain and reactivity will arise. It is hoped that systematic structure analysis by diffraction, force field or quantum-mechanical methods[19] of strained compounds with distortions of two-, four- and threefold symmetry will eventually lead to a more general picture of strain and its origin in four coordinate carbon compounds.

EXPERIMENTAL

General remarks.[16,20] IR spectra were measured in $CHCl_3$ on Perkin–Elmer 457 or 782 instruments; only the strongest and structurally characteristic signals are reported. NMR spectra were obtained in $CDCl_3$ using Varian EM 360, EM-360L, Bruker WP80 and AM400 and Varian XL 100 (^{13}C) instruments; heavily overlapping signals are reported as "stack". GC coupled mass spectra were recorded on a Varian Mat 44S instrument. For capillary GC a Carlo–Erba Fractovap 2450 instrument was used. If not stated otherwise, columns of 20 m length with SE 54, chemically bonded, were used as stationary phase. We would like to thank Dr Bigler, Dr Kamber and Mr Strähl for many NMR measurements, and Mr Gfeller for GC–MS analyses.

Dimethyl - 6 - exo - *methoxy* - 5 - *oxa*[5.2.1.$0^{4,10}$]*decan* - 2 - exo,9 - endo - *diproprionate* (**11**)

A soln of 10 g (0.025 mol) **10**[16] in 125 ml monoglyme–water (3:2) was hydrogenated with 10% Pd–C to give an oil, which was refluxed in MeOH with a trace of *p*-toluenesulfonic acid. Subsequent oxidation with 0.7 g (3.11 mmol) $RuCl_3 \cdot xH_2O$ and 12.9 g (60.3 mmol) sodium periodate in water gave an acid, which after acid-catalyzed esterification with MeOH and purification by medium pressure chromatography (t-butylmethylether–hexane, 3:2) yielded 6.02 g **11** (71%, purity 90%) as a yellowish oil. An analytically pure sample—containing 2.3% of the 2-*exo*,9-*exo*-isomer **18**[16d]—was obtained by HPLC (t-butylmethylether–hexane, 1:1). R_f (ether) 0.52; cap. GC (220°) 6.9 min; IR: 2960, 1732, 1440, 1095, 1062; ^{1}H-NMR: 0.75–2.77 (stack, 16H), 2.87–3.38 (stack with s at 3.25, 4H), 3.65 (s, 6H), 4.41 (dd, J = 6, 5 Hz, 1H), 4.66 (s, 1H); ^{13}C-NMR: 25.3 t, 30.3 t, 32.4 t, 33.1 t, 33.8 t, 37.5 t, 39.1 t, 43.7 d, 49.6 d, 50.8 q (2C), 52.5 d, 53.2 d, 53.3 q, 82.2 d, 109.1 d, 172.8 s, 172.9 s; MS 340 (M^+, 2), 309, 277, 248, 220, 216, 206, 153, 133, 121, 119, 105, 93, 92, 91. (Found: C, 63.50; H, 8.37. Calc for $C_8H_{28}O_6$: C, 63.51; H, 8.29%.)

6 - exo - *Methoxy* - 5 - *oxa*[5.2.1.$0^{4,10}$]*decan* - 2 - exo,9 - endo - *dipropionitrile* (**12**)

A mixture of 3.0 g (8.82 mmol) **11** and 1.5 g (88.2 mmol) ammonia in 1.3 g MeOH was heated in a pressure bomb to 160° for 18 h. The highly insoluble diamide was dehydrated in a mixture of 120 ml $CHCl_3$, 0.2 g benzyltriethylammonium chloride and 20 g of 50% NaOH aq.[21] Flash chromatography with subsequent medium pressure chromatography gave 1.04 g (3.78 mmol, 43%, purity 95%) **12** as a colourless oil, which slowly crystallized upon refrigeration. An analytically pure sample was obtained by crystallization from CH_2Cl_2–pentane, m.p. 89–90°. R_f (ether) 0.23; cap. GC (220°) 7.26 min; IR: 2960, 2938, 2250 w, 1095, 1093, 995. ^{1}H-NMR: 0.66–2.86 (stack, 16H), 2.86–3.46 (stack with s at 3.23, 4H), 4.42 (dd, J = 7, 4 Hz, 1H), 4.66 (s, 1H); MS 274 (M^+, 1), 243, 174, 160, 133, 132, 120, 91, 79. (Found: C, 69.86; H, 8.11; N, 10.08. Calc for $C_{16}H_{22}O_2N_2$: C, 70.04; H, 8.08; N, 10.21.)

rel - (1*S*,3*S*,5*R*,6*R*,8*S*,14*R*,15*S*) - 4 - *Oxa* - 5 - *methoxy* - 11 - *amino* - *tetracyclo*[6.5.1.$0^{3,6}$.$0^{14,15}$]*pentadec* - 11 - *ene* - 12 - *carbonitrile* (**13**) *or its regioisomer*

A soln of 8.8 g (54.7 mmol) hexamethyl-disilazane in 500 ml of THF was treated with 54.7 mmol BuLi at 0°. After heating to reflux a soln of 3.0 g (10.94 mmol) of **12** in 200 ml THF was added during 22 h. After heating for 1.5 h, the turbid, brown soln was worked up. Extraction with CH_2Cl_2 gave a crude oil, which was flash chromatographed with ether–CH_2Cl_2 (1:1). A colourless product **13** (1.91 g, 6.98 mmol, 63%) was obtained by crystallization from THF–pentane, m.p. 179–181°. R_f (ether) 0.30; IR: 3510, 3410, 2180, 1635, 1600; MS 274 (M^+), no higher peaks. According to the ^{1}H- and ^{13}C-NMR data, this compound contains two other isomers.

rel - (1*S*,3*S*,5*R*,6*R*,8*S*,14*R*,15*S*) - 4 - *Oxa* - 5 - *methoxy* - *tetracyclo*[6.5.1.1^{3,6}.$0^{14,15}$]*pentadecan* - 11 - *one* (**17**)

A soln of 0.40 g (1.46 mmol) **13** in 6 ml Ac_2O and 0.5 ml AcOH was refluxed under Ar for 2 h. After addition of 6 ml AcOH, 2 ml water and 4 ml of (85%) phosphoric acid, the mixture was refluxed for 22 h. The mixture was extracted with CH_2Cl_2 and washed with 2 N NaOH. The crude product was refluxed in 10 ml MeOH in the presence of 0.02 g *p*-toluenesulfonic acid for 4 h and eventually extracted with CH_2Cl_2. Purification by flash chromatography with t-butylmethylether and low pressure chromatography[22] (with t-butylmethylether–hexane, 2:1) gave 0.081 g (0.34 mmol, 23%) **17** as white crystals of 90% purity. According to GC-MS and ^{13}C-NMR analysis the by-product is 5-desmethoxy-17. M.p. 131–132°. R_f (t-butylmethylether–hexane, 1:1) 0.27; cap. GC (180°) 10.1 min (by-product at 6.6 min); IR: 3007, 2953, 2920, 1695, 1100, 1082, 1075, 1060, 982; ^{1}H-NMR: 0.72–1.70 (stack, ~3H), 1.70–2.95 (stack, ~13H), 2.95–3.80 (stack with s at 3.37, 4H), 4.38 (dd, J = 6, 5 Hz, 1H), 4.67 (s, 1H); ^{13}C-NMR: 25.7 t, 34.2 t, 36.8 t, 38.51 d, 38.51 t, 41.7 t, 44.8 d, 45.4 t, 49.3 d, 50.9 d, 53.7, 55.5, 82.3 d, 109.4 d, 216.3 s; MS 250 (M^+, 10), 219, 190, 172, 162, 136, 132, 131, 119, 118, 117, 105, 93, 92, 91, 80, 79. (Found: C, 72.22; H, 8.94. Calc for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86%.)

rel - (1*S*,3*S*,6*R*,8*S*,14*R*,15*S*) - 4 - *Oxa* - *tetracyclo* - [6.5.1.1^{3,6}.$0^{14,15}$]*pentadecan* - 5,11 - *dione* (**14**)

At reflux temp 0.795 g (2.9 mmol) of crude **13** was dissolved in 18 ml glacial AcOH. After 30 min 7 ml (85%) phosphoric acid was added and reflux continued for 15 h. The hydrolysis products were extracted into CH_2Cl_2 and freed from acid with a soln of K_2CO_3. The crude product was stirred in 30 ml acetone containing 1 ml 1 M perchloric acid and oxidized with Jones reagent at 0°. After work-up, chromatography (ether–CH_2Cl_2, 1:1) and further purification by HPLC (t-butylmethylether) gave 0.069 g (0.29 mmol, 10%) **14** as white crystals, m.p. 150–152°. R_f (t-butylmethylether) 0.22; IR: 1760, 1748, 1700, 1200, 1180; ^{1}H-NMR: 1.15–2.63 (stack, 14H), 2.63–3.68 (stack, 3H), 4.78 (dd, J = 6.6, 5.4 Hz, 1H); MS 234 (M^+), 216, 206, 205, 177, 176, 134, 133, 131, 117, 105, 94, 93, 92, 91, 79. (Found: C, 71.92; H, 7.85. Calc for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74%.)

Photolysis of the potassium salt of rel - (1*R*,3*S*,6*R*,8*S*,14*R*,15*S*) - 4 - *oxa* - *tetracyclo*[6.5.1.1^{3,6}.$0^{14,15}$]*pentadecan* - 5,11 - *dione* - 1 - (2,4,6 - *triisopropylphenylsulfonyl*)*hydrazone* (**15**)

Hydrazone **15**, prepared from 0.065 g (0.27 mmol) pure **14**

and 0.084 g (0.28 mmol) 2,4,6-triisopropylphenylsulfonylhydrazide in CH_2Cl_2 according to Ref. 23 was deprotonated in a quartz cuvette with 0.012 g (0.295 mmol) KH in THF under Ar. After 10 min the clear, yellowish soln was irradiated with a 125 W high pressure lamp. After work up, the crude material was analysed by GC. Besides triisopropylbenzene and **14** four products were detected, which were separated off by chromatography with ether as eluent (0.025 g of material) and analysed by GC-MS (SE 54, 20 m, 200°) [product ratio (retention times in min): 3 (6.9) : 4 (7.3) : 77 (7.6) : 13 (8.1)] and by NMR spectra. Major component **16** (or its regioisomer): MS 218 (M^+), 190, 173, 144, 131, 117, 105, 91, 79, 77, 66; ^{1}H-NMR: 0.59–2.73 (stack, ~15.5H), 2.73–3.56 (stack, 2H), 4.78 (dd, J = 6.6, 5.4 Hz, 1H), 5.38–5.90 (stack, 1.5H); ^{13}C-NMR (without ^{13}C=O): 25.9, 28.8, 35.0 (36.5), 36.7 (44.0), 44.1, 44.2, 44.4, 45.4, 51.9, 54.9, 83.8, 130.6. The MS spectra of the minor component and the other two by-products (3% respectively 4%) also have m/z 218 (M^+).

(*all*-cis)-[5.5.5.5]*Fenestrane* **6**

(a) A sample of 3 mg (0.013 mmol) isomerically pure **14**, 20 mg Pd/C and 4 ml H_2 was sealed in an ampoule and heated to 320° for 4.5 h. Extraction with CH_2Cl_2 gave 1–2 mg oily product, which according to capillary GC consisted of three products in a ratio of 85 : 3 : 4. As revealed by coinjection with an authentic sample onto three columns the major component is **6** [conditions: (a) SE-54 (20 m), 90°, isothermic, 16.2 min; (b) CW 20M (20 m), 65–220°/3° min^{-1}, 17.6 min; (c) OV 1701 (20 m), 40–200°/3° min^{-1}, 27.14 min]. The minor component is starting material **14**, whereas the third product has not been identified.

(b) A sample of 50 mg (0.18 mmol) **13** and 0.3 g Pd/C on charcoal (10%) was sealed under H_2 in an ampoule and heated to 310–315° for 6 h. The products were extracted with trifluorochloromethane to give 10 mg of an oil. Capillary GC (100°) and GC-MS revealed four major components in a ratio of a : b : c : d = 9 : 19 : 27 : 16.

Compound b (≡**6**): (rel. time 6.6 min); MS 176 (M^+), 149, 148, 147, 134, 133, 120, 119, 107, 106, 105, 95, 94, 93, 91.

Compound c: (rel. time 7.5 min); MS 190 (M^+), 175, 148, 147, 133, 120, 119, 107, 106, 105, 94, 93, 91, 80, 79, 77, 67, 55, 41.

Compound d: (rel. time 8.1 min); MS 190 (M^+), 148, 120, 119, 107, 106, 95, 91, 81, 79, 67, 55, 41.

From crude reaction products, obtained from 0.234 g (0.85 mmol) in three analogous runs compounds b, c and d could be isolated by preparative GC separation.

Compounds b: 3 mg (0.017 mmol, 2%, 57% purity); ^{13}C-NMR (400 MHz without quaternary C): δ 31.09 t, 53.66 d, apart from $CDCl_3$ no other signals are to be seen. Shift and multiplicity of these signals are identical with those of authentic **6**.[16c]

Compound c (**21** or **22**): 8 mg (0.042 mmol, 5%, purity 85%); ^{1}H-NMR (400 MHz): 0.80–2.0 (stack with d at 0.91, J = 6.0 Hz). ^{13}C-NMR: 18.6 q, 27.5 t, 29.0 (t, 2C), 29.5 t, 33.1 t, 33.3 t, 40.1 d, 42.1 t, 52.4 d, 53.8 d, 53.9 d, 61.6 d, 73.9 s.

Compound d (**22** or **21**): 4.0 mg (0.02 mmol, 2.5%, purity 63%); ^{1}H-NMR (400 MHz): 0.83–2.23 (stack, with d at 0.83, J = 6.6 Hz); ^{13}C-NMR: 15.89, 27.9, 28.97, 28.98, 32.7, 33.3, 34.1, 34.2, 37.3, 53.1 (2C), 53.7, 54.0, 58.1, 77.2 s.

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REFERENCES

[1a] J. H. van't Hoff, Voorstel tot uitbreiding der tegenwoordig in de scheikunde gebruikte strukturformules in de ruimte, Utrecht (1874); cf. O. Krätz, *Chem. Z.* **8**, 135 (1974); [b] J. A. Le Bel, *Bull. Soc. Chim. Fr.* **22**, 337 (1874); cf. J. Weyer, *Chem. Z.* **8**, 143 (1974); see also, F. G. Ridell and M. J. T. Robinson, *Tetrahedron* **30**, 2001 (1974).

[2] A. v. Baeyer, *Ber. Dtsch. Chem. Ges.* **18**, 2277 (1885).

[3] J. F. Liebman and A. Greenberg, *Strained Organic Molecules*. Academic Press, New York (1978).

[4] P. E. Eaton and T. E. Cole, *J. Am. Chem. Soc.* **86**, 3157 (1964).

[5] H. Irngartinger, A. Goldmann, R. Jahn, M. Nixdorf, H. Rodewald, G. Maier, K.-D. Malsch and R. Emrich, *Angew. Chem.* **96**, 967 (1984); *Int. Ed. Engl.* **23**, 993 (1984).

[6] L. A. Paquette, R. J. Ternamsky, D. W. Balogh and G. Kentgen, *J. Am. Chem. Soc.* **105**, 5446 (1983).

[7] K. B. Wiberg, *Accts Chem. Res.* **17**, 379 (1984).

[8a] W. Hückel, *Theoretische Grundlagen der organischen Chemie*, Vol. I, p. 252. Akad. Verlagsges., Leipzig (1931); [b] T. Wagner-Jauregg, *Stereochemistry* (Edited by K. Freudenberg and F. Deuticke), p. 852. Leipzig (1933).

[9a] H. J. Monkhorst, *Chem. Commun.* 1111 (1968); [b] R. Hoffmann, R. W. Alder and C. F. Wilcott, Jr., *J. Am. Chem. Soc.* **92**, 4992 (1970); [c] K. B. Wiberg, G. B. Ellison and J. J. Wendoloski, *Ibid.* **98**, 1212 (1976); [d] J. B. Collins, J. D. Hill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger and J. A. Pople, *Ibid.* **98**, 5419 (1976).

[10a] R. Keese, A. Pfenninger and A. Roesle, *Helv. Chim. Acta* **62**, 326 (1979); [b] A. Pfenninger, A. Roesle and R. Keese, *Ibid.* **68**, 493 (1985); [c] R. Keese, *Nachr. Chem. Techn. Lab.* **30**, 844 (1982).

[11] W. Luef and R. Keese, *Helv. Chim. Acta*, to be submitted.

[12] P. Murray-Rust, H. B. Bürgi and J. D. Dunitz, *Acta Cryst.* **B34**, 1793 (1978).

[13] **2**: W. C. Han, K. Takahashi, J. M. Cook, U. Weiss and J. V. Silverton, *J. Am. Chem. Soc.* **104**, 318 (1982). **3**: W. G. Dauben, unpublished results. We thank Prof. W. G. Dauben for communication of these results prior to publication. **4**: V. B. Rao, C. F. George, S. Wolff, W. C. Agosta, *J. Am. Chem. Soc.* **107**, 5732 (1985). We thank Prof. W. C. Agosta for communicating these results prior to publication.

[14a] R. Mitschka, J. M. Cook and U. Weiss, *J. Am. Chem. Soc.* **100**, 3973 (1978); [b] R. Mitschka, J. Oehldrich, K. Takahashi, U. M. Cook, U. Weiss and J. V. Silverton, *Tetrahedron* **37**, 4521 (1981); [c] M. Luyten and R. Keese, *Angew. Chem.* **96**, 358 (1984); *Ibid. Int. Ed. Engl.* **23**, 390 (1984); [d] M. Luyten and R. Keese, *Helv. Chim. Acta* **67**, 2242 (1984); [e] J. Mani and R. Keese, *Tetrahedron* 5697 (1985); [f] W. G. Dauben and D. M. Walker, *Tetrahedron Lett.* **23**, 711 (1982); [g] M. T. Crimmins, S. W. Mascarella and L. D. Bredon, *Ibid.* **26**, 997 (1985); [h] V. B. Rao, S. Wolff and W. C. Agosta, *J. Chem. Soc. Chem. Commun.* 293 (1984).

[15] R. E. Corbett, C. M. Couldwell, D. R. Lauren and R. T. Weavers, *J. Chem. Soc. Perkin Trans. I* 1791 (1978).

[16] H. Schori, B. B. Patil and R. Keese, *Tetrahedron* **37**, 4457 (1981).

[17] J. P. Schaefer and J. J. Bloomfield, *Organic Reactions*, Vol. 15, p. 1. Wiley, New York (1967).

[18] W. F. Maier, W. Roth, I. Thies and P. v. R. Schleyer, *Chem. Ber.* **115**, 808 (1982).

[19] K. B. Wiberg and G. B. Ellison, *Tetrahedron* **30**, 1573 (1974).

[20] U. Aeberhard, R. Keese, E. Stamm, U.-C. Vögeli, W. Lau and J. K. Kochi, *Helv. Chim. Acta* **66**, 2753 (1983).

[21] T. Saraie, T. Jshiguro, K. Kawashima and K. Morita, *Tetrahedron Lett.* 2121 (1973).

[22] H. Lobner and U. G. Seidl, *Chromatographia* **12**, 600 (1979).

[23] A. R. Chamberlin, J. E. Stemke and F. T. Boud, *J. Org. Chem.* **43**, 147 and 154 (1978).