

Table 1. 400 MHz  $^1\text{H-NMR}$  data ( $\delta$ -values) of **4** and **5** as  $\text{PF}_6$  salts in  $[\text{D}_6]$  dimethyl sulfoxide at 25 °C. The pyridinium protons appear as doublets ( $J=6.5$  Hz); geminal coupling of the benzyl protons:  $J=15$  Hz.

| Compound          | $\text{H}^\alpha$                  | $\text{H}^{\alpha'}$ | $\text{H}^\beta$                   | $\text{H}^{\beta'}$ | $\text{H}^\gamma$  | $\text{H}^\delta$ | Phenylene   |
|-------------------|------------------------------------|----------------------|------------------------------------|---------------------|--|-------------------|---|
| <i>syn-o,o-4</i>  | 9.43                               | 8.27                 | 8.52                               | 7.97                | 6.49 (d)   | 6.09 (d)          | 8.07 (mc), 7.91 (mc)  |
| <i>anti-o,o-4</i> | 9.33                               | 8.33                 | 8.40                               | 8.21                | 6.47 (d)   | 6.09 (d)          | 8.07 (mc), 7.91 (mc)  |
| <i>o,m-4</i>      | <i>o</i> : 8.90<br><i>m</i> : 9.26 |                      | <i>o</i> : 8.36<br><i>m</i> : 8.57 |                     | <i>o</i> : 6.52 (d; $\text{H}^\gamma$ ), 6.09 (d; $\text{H}^\delta$ ), <i>m</i> : 6.06 (s) |                   | <i>o</i> : 8.09 (mc), 7.95 (mc), <i>m</i> : 7.71 (mc), 6.26 (s) |
| <i>m,m-4</i>      | 9.37                               |                      | 8.51                               |                     |  | 6.05 (s)          | 7.86 (d), 7.62 (t), 7.31 (s) (2:1:1)                            |
| <b>5</b>          | 9.50                               |                      | 8.76                               |                     |  | 6.01 (s)          | 7.62 (s)  |

(30%), respectively, were isolated (after precipitation as the  $\text{PF}_6$  salts and anion-exchange with  $\text{Et}_4\text{NCl}$  in nitromethane)<sup>[1]</sup>. Using this method *o,o-4b* (25%) is formed even from **2** and *o-1b*.

The precursors *o-3* and *m-3*<sup>[1]</sup>, as well as the salt of the ion **5**<sup>[1]</sup> are readily accessible. The purity of all products was monitored by thin-layer chromatography ( $\text{SiO}_2$ ,  $\text{MeOH}/\text{H}_2\text{O}/50\%$  aqueous  $\text{EtNH}_3\text{Cl}$  (6:2:2)). The composition and structure of the three isomers of **4a** were determined by mass spectrometry (FAB-MS<sup>[2]</sup>;  $m/z$  520 (**4**); 555 (**4** + Cl); 590 (**4** + 2Cl) and NMR spectroscopy (also by comparison with the bisbenzylpyridinium ion **5**). In thephanes **4** rotation (R) of the pyridine rings and flipping (F) of the phenyl rings (*syn*- and *anti-4*) have to be borne in mind, as indicated by inspection of the upper half of the molecule (Table 1).

$^1\text{H-NMR}$  spectroscopic studies indeed reveal that the internal mobility of the macrocycles changes dramatically from *o,o-4* via *o,m-4* to *m,m-4* with increasing size of the bridges. This is associated with an increase of the separation of the bipyridinium groups from 290 pm via 290 pm/510 pm to 510 pm<sup>[3]</sup>.

*o,o-4*: Rotation (R) and flipping (F) are frozen-in. The  $^1\text{H-NMR}$  spectrum exhibits two sets of signals for *syn-o,o-4* and *anti-o,o-4* (2.5:1). The assignment reflects the expectation that the para- and diatropic effects of both phenylene bridges increase in *syn-4*, but not in *anti-4*. Compared to **5** ( $\text{H}^\alpha$ ,  $\delta=9.50$ ) the large high-field shift of the signal of  $\text{H}^{\alpha'}$ , which lies above the plane of the *o*-phenyl ring, is particularly noticeable [ $\delta=8.27$  (*syn-o,o-4*), 8.33 (*anti-o,o-4*)], so that the difference between the chemical shifts of  $\text{H}^\alpha$  and  $\text{H}^{\alpha'}$  in *syn-o,o-4* increases to 1.16 ppm. In contrast, the ring current of the rotationally hindered pyridinium groups shifts the benzylic  $\text{H}^\gamma$  signal ca. 0.5 ppm to low field relative to that of the model compound **5**, whereas the proton  $\text{H}^\delta$ , which lies over the long axis of the molecule and is orientated outwards, behaves "normally". This assignment is consistent with the fact that in *syn*- and *anti-o,o-4*  $\text{H}^\delta$  has the same chemical shift, whereas the  $\text{H}^\gamma$ -signals differ by approximately 0.02 ppm.

*o,m-4*: Even the ring expansion of ca. 220 pm on one side is sufficient to reduce the barrier to rotation of all four pyridinium rings. The  $2 \times 2$  doublets ( $\text{H}^\alpha$ ,  $\text{H}^\beta$ ) arise from the different bridge members. In contrast, the phenylene bridges can only undergo flipping on the *m*-side.

*m,m-4*: Introduction of the second *m*-phenylene bridge results in complete (R) and (F) mobility, and hence the sig-

nals largely correspond to those of the open-chain model compound. A discrepancy, which confirms the ring structure, arises from the high-field shift of both isolated *m*-phenylene protons: their signal is shifted in *m,m-4* to  $\delta=7.31$  [*m-3*:  $\delta=7.55$ ]; in the somewhat more narrower *o,m-4* the signal of the corresponding proton appears at  $\delta=6.26$ .

*Temperature effects*: In the 90 MHz  $^1\text{H-NMR}$  spectrum the pyridinium signals of *o,o-4* coalesce at 50 °C ( $\text{CF}_3\text{CO}_2\text{D}$ ) ( $\Delta G^\ddagger \approx 65$  kJ/mol). In *o,m-4* rotation of the pyridinium rings adjacent to the *o*-bridge slows down at -40 °C ( $\text{CD}_3\text{CN}$ ) (broad  $\text{H}^\alpha$  and  $\text{H}^\beta$  signals). At +70 °C the rate of flipping of the *o*-bridge increases (very broad  $\text{H}^\gamma$  and  $\text{H}^\delta$  signals). Inspection of Stuart-Briegleb and Dreiding molecular models suggests that *o,o-4* should have considerably higher barriers to rotation.

Furthermore, the ring systems are interesting as multi-step redox systems (possible  $\pi$ -merization of the double radical cations<sup>[4]</sup>) and as host molecules for inclusion compounds. Using the same synthetic principle the preparation of relatedphanes having other ring members is being undertaken.

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- [1] All compounds gave correct elemental analyses.
- [2] Fast-Atom-Bombardment-MS. We wish to thank Finnigan-MAT for performing the measurements.
- [3] Distances between the benzylic C atoms, measured on a Dreiding model.
- [4] For the term " $\pi$ -merization" cf. E. M. Kosower in W. A. Pryor: *Free Radicals in Biology*, Vol. II, Academic Press, New York 1976, p. 1.

## 1,2-Benzynes from 6-Halopentafulvenes\*\*

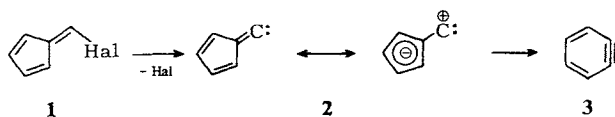
By Klaus Hafner\*, Hans-Peter Krimmer, and Bernd Stowasser

6-Halopentafulvenes **1** are readily accessible by reaction of acylcyclopentadienes with phosgene or oxalyl halides and have proven very useful as educts for the synthesis of a variety of pentafulvenes functionally substituted at the

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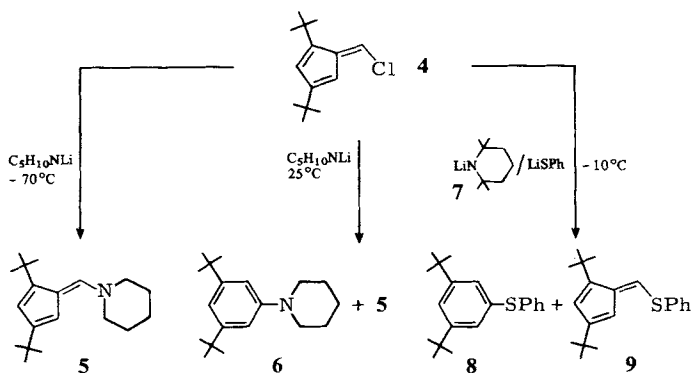
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exocyclic C-atom<sup>[1]</sup>.  $\alpha$ -Elimination of hydrogen halide from **1** should furnish the hitherto unknown pentafulvenylidencarbene **2**.

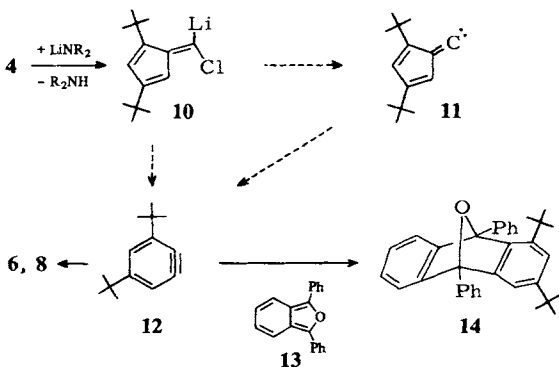


According to quantum chemical calculations by *Apeloig et al.*<sup>[2]</sup>, **2** is expected to be highly electrophilic and undergo rearrangement into the 1,2-benzynes **3**, which should be 14 kcal·mol<sup>-1</sup> more stable than **2**.

To check this prognosis we have investigated the reaction of the stable 1,3-di-*tert*-butyl-6-chloropentafulvene **4** with bases. Reaction of **4** with lithium piperidide in tetrahydrofuran (THF) at -70 °C affords 1,3-di-*tert*-butyl-6-piperidinopentafulvene **5** in 76% yield<sup>[3,4a]</sup> with retention of configuration. On the other hand, the same reaction at 25 °C leads to 1,3-di-*tert*-butyl-5-piperidinobenzene **6** in 61% yield<sup>[4b]</sup> and only 6% of **5**, while reaction with lithium 2,2,6,6-tetramethylpiperidide **7** in presence of an excess of lithium thiophenolate in THF at -10 °C leads to 54% of 3,5-di-*tert*-butyldiphenyl sulfide **8**<sup>[4c]</sup> and 6% of 1,3-di-*tert*-butyl-6-phenylthiopentafulvene **9**<sup>[1]</sup>.



These findings confirm the quantum chemical predictions. From **4** the carbenoid **10** can be generated, and from this the carbene **11**, which obviously rapidly rearranges into 3,5-di-*tert*-butyl-1,2-benzynes **12**. This subsequently reacts with nucleophiles<sup>[5a]</sup>, whereupon **6** and **8** are formed regioselectively under the influence of the bulky *tert*-butyl groups. So far, however, it cannot be ruled out that **12** is generated directly from **10** by a rearrangement analogous to the Fritsch-Buttenberg-Wiechell reac-



tion<sup>[5b]</sup>. Attempts to trap the carbene **11** by [2 + 1]-cycloaddition have so far remained unsuccessful. On the other hand, by means of 1,3-diphenylisobenzofuran **13** it was possible to trap the 1,2-benzynes **12** formed on reaction of **4** with **7** as the Diels-Alder adduct **14** (50%)<sup>[4d]</sup>.

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- [1] K. Hafner, *Pure Appl. Chem.* 54 (1982) 939; H.-P. Krimmer, B. Stowasser, K. Hafner, *Tetrahedron Lett.* 23 (1982) 5135.  
[2] Y. Apeloig, R. Schrieber, P. J. Stang, *Tetrahedron Lett.* 21 (1980) 411; P. J. Stang, *Acc. Chem. Res.* 15 (1982) 348.  
[3] All compounds isolated gave correct elemental analyses.  
[4] <sup>1</sup>H-NMR (in CDCl<sub>3</sub>); UV (in *n*-hexane). a) **5**: yellow needles, m.p. 110 °C; <sup>1</sup>H-NMR (300 MHz):  $\delta$  = 1.23 (s; 9H, *t*Bu); 1.36 (s; 9H, *t*Bu); 1.70 (m; 6H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>); 3.56 (m; 4H, CH<sub>2</sub>-N-CH<sub>2</sub>); 6.07 (d, *J* = 2.3 Hz; 1H, H-2); 6.16 (d, *J* = 2.3 Hz; 1H, H-4); 7.37 (s; 1H, H-6). UV:  $\lambda_{\text{max}}$ (lg $\epsilon$ ) = 220 (3.82) sh; 327 (4.47) nm.—b) **6**: colorless platelets m.p. 50 °C; <sup>1</sup>H-NMR (300 MHz):  $\delta$  = 1.31 (s; 18H, *t*Bu); 1.56 (m; 2H, CH<sub>2</sub>); 1.73 (m; 4H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>); 3.13 (m; 4H, CH<sub>2</sub>-N-CH<sub>2</sub>); 6.83 (d, *J* = 2 Hz; 2H, H-2, H-6); 6.95 (t, *J* = 2 Hz; 1H, H-4). UV:  $\lambda_{\text{max}}$ (lg $\epsilon$ ) = 217 (4.36); 254 (4.03); 285 (3.20) sh nm.—c) **8**: colorless oil b.p. 85 °C/10<sup>-4</sup> torr; <sup>1</sup>H-NMR (60 MHz):  $\delta$  = 1.32 (s; 18H, *t*Bu); 7.15–7.45 (m; 8H, arom. H). UV:  $\lambda_{\text{max}}$ (lg $\epsilon$ ) = 235 (3.96); 252 (4.08); 276 (3.76) nm.—d) **14**: colorless needles m.p. 245 °C; <sup>1</sup>H-NMR (300 MHz):  $\delta$  = 1.12 (s; 9H, *t*Bu); 1.24 (s; 9H, *t*Bu); 6.98–8.02 (m; 16H, arom. H).  
[5] a) R. Huisgen, J. Sauer, *Angew. Chem.* 72 (1960) 91; b) G. Köbrich, *Angew. Chem.* 79 (1967) 22; *Angew. Chem. Int. Ed. Engl.* 6 (1967) 41; *ibid.* 84 (1972) 557 and 11 (1972) 473; H. Siegel, *Top. Curr. Chem.* 106 (1982) 55.

### The Cation Di- $\mu$ -oxo-*trans*-dioxobis(1,4,7-triazacyclononane)molybdenum(v)(Mo—Mo) and its Acid-Catalyzed *cis*-Isomerization\*\*

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Dinuclear molybdenum(v) complexes with the central structural element di- $\mu$ -oxodioxobis(molybdenum(v)), Mo<sub>2</sub>O<sub>4</sub><sup>2+</sup>, are diamagnetic; their short Mo—Mo distance (254–258 pm) is interpreted as originating from a metal-metal single bond<sup>[1a–d, f]</sup>. The Mo<sub>2</sub>O<sub>2</sub> four-membered ring is puckered and both terminal oxo groups are always located in a *cis*-arrangement<sup>[1a, d, f]</sup>. This configuration is apparently the most thermodynamically stable; a structure with *trans*-oxo groups has not previously been reported.

We now report the preparation and structure of the first Mo<sub>2</sub>O<sub>4</sub><sup>2+</sup> complex with *trans*-oxo groups, as well as its irreversible acid-catalyzed conversion into the stable *cis*-form. Hydrolysis of the monomeric, paramagnetic complex **1** in aqueous solution containing NaHCO<sub>3</sub> leads to formation of the diamagnetic, green, dinuclear cation **2**. After addition of NaI, the crystalline iodide **2**·2I is obtained. The reaction of aqueous solutions of **2** with dilute perchloric acid under argon affords cherry-red solutions from which red, diamagnetic **3**·2I can be precipitated upon addition of NaI. In solution, **3** undergoes acid-catalyzed reaction to yield **4**, a diamagnetic, yellow, dinuclear  $\mu$ -oxo complex of molybdenum(v) (for spectroscopic data, see Table 1).

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