Pergamon

Tetrahedron Letters 41 (2000) 8255–8258

TETRAHEDRON
LETTERS

Synthesis and reactions of pentafulvenyl-tropones and tropothiones

Winfried Schmack, Tomoo Nakazawa[†] and Klaus Hafner*

Institut für Organische Chemie, Technische Universität Darmstadt, Petersenstraße 22, D-64287 Darmstadt, Germany

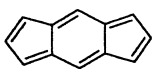
Received 22 August 2000; accepted 4 September 2000

Abstract

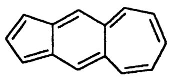
2-(1′,3′-Di-*tert*-butyl-pentafulven-6′-yl)-tropone (**7**) was synthesized by reaction of 6-lithio-1,3-di-*tert*-butyl-pentafulvene (**5**) with 2-chlorotropone (**6**). At elevated temperatures **7** cyclizes to a mixture of the tautomeric azulene derivatives **8** and **9**. With P_2S_5 **7** is transformed into the spiroadduct **12**, presumably via the pentafulvenyl-tropothione **11**, which could not be isolated. Compound **12** reacts by a thermally induced rearrangement to the stable cyclohepta-thialene derivative **14**. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: pentafulvenes; tropones; tropothiones; thialenes; electrocyclization.

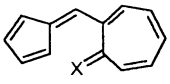
Recently, extended experimental and theoretical studies on *s*-indacene (**1**) revealed a rather unexpected bonding system of the tricyclic hydrocarbon, proving its exceptional position among the 4n π-electron systems known so far.[1] The equilibrium structure of **1** has D_{2h} symmetry and a delocalized 12π-electron system, although it formally represents an antiaromatic 4n-perimeter disturbed by two central single bonds.[2]



1



2



3: X = O
4: X = S

These findings prompted us[3] to synthesize the next higher homologue of **1**, the still unknown cyclohept[*f*]indene (**2**),[4] in order to study the molecular properties of this 14π-electron system. As potential building blocks for a synthesis of **2**, the likewise unknown pentafulvenyl-tropone **3** or the corresponding thione **4** seem to be suitable.

---

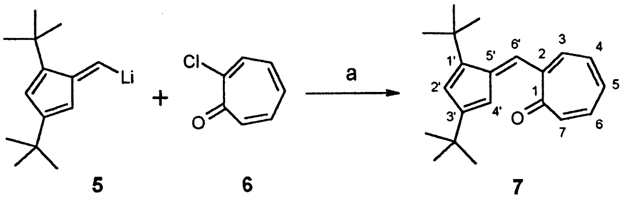
* Corresponding author. Fax: +49-6151-163574; e-mail: khafner@hrz.tu-darmstadt.de

[†] Permanent address: Yamanashi Medical University, 1110 Shimokato, Tamaho, Nakakoma, Yamanashi 409-3898, Japan.

0040-4039/00/$ - see front matter
PII: S0040-4039(00)01473-8

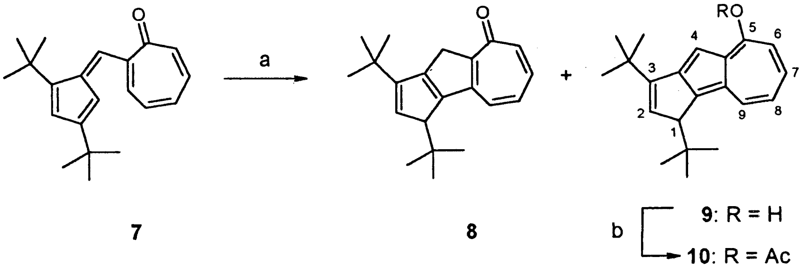
Herein, we report on an efficient synthesis of the 2-(1′,3′-di-*tert*-butyl-pentafulven-6′-yl)-tropone (**7**) and its conversion into the tautomeric cyclopent[*a*]azulene derivatives **8** and **9** as well as into the cyclohepta-thiaspirononatriene system **12** which can be transformed into the novel cyclohepta[*b*]thialene **14** by a thermally induced rearrangement.

For the synthesis of pentafulvenyl-tropone **7**, the easily available 6-bromo-1,3-di-*tert*-butyl-pentafulvene[5] proved to be an appropriate starting material. Halogen–metal exchange with *tert*-butyllithium at −110°C affords 6-lithiopentafulvene **5**[5] which reacts with 2-chlorotropone (**6**) to give **7** in 71% yield as thermally fairly stable, reddish brown crystals[6] (Scheme 1).



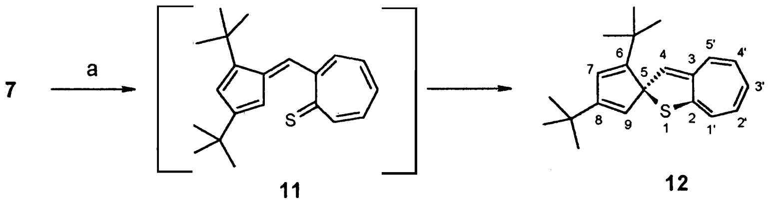
Scheme 1. (a) THF/Et$_2$O/*n*-pentane (4:1:1), −110°C

At elevated temperature, **7** reacts in analogy to 6-(2′-dialkylaminovinyl)-pentafulvenes,[7] presumably by an 8π-electrocyclization followed by subsequent 1,5-H shifts, to give a mixture of the cyclopent[*a*]azulene derivatives **8** and **9** (1:1.7 in CDCl$_3$). *O*-Acetylation of the inseparable mixture with acetyl chloride furnishes the acetoxyazulene **10** as deep blue crystals in 41% yield[6] (Scheme 2).



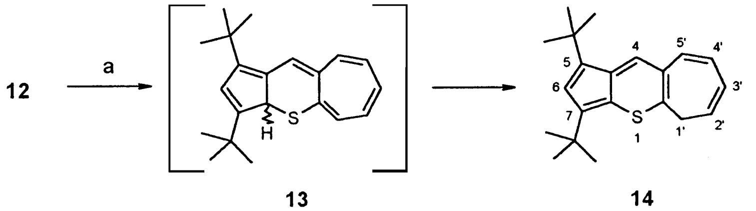
Scheme 2. (a) Toluene, 110°C, 25 min; (b) *n*-pentane, pyridine, acetyl chloride, 0°C

Unexpectedly, the treatment of the pentafulvenyl-tropone **7** with phosphorus pentasulfide in analogy to the synthesis of tropothione[8] does not yield the desired pentafulvenyl-tropothione **11**, but instead 49% of the racemic cyclohepta-1-thiaspiro[4.4]nonatriene **12**[9] as red needles[6] (Scheme 3). The structure of **12** could be unequivocally deduced by its ^{1}H and ^{13}C NMR as well as MS spectra. The formation of **12** can be rationalized by an initial conversion of **7** into the tropothione **11** which should be thermally rather unstable, like the parent tropothione.[8] While the latter dimerizes by a ground state nontopochemically controlled reaction in the solid state[10]



Scheme 3. (a) 2 equiv. P$_2$S$_5$, 2 equiv. Et$_3$N, 0°C, 30 min

and reacts with cyclopentadiene, pentafulvenes, diphenylketene or maleic anhydride, respectively, in [8+2]-cycloadditions to the corresponding adducts,[11] **11** presumably rearranges by a 10π-electrocyclization of its 2-vinyltropothione moiety to give the more stable isomeric spiro adduct **12**. In boiling toluene **12** is converted into the tricyclic thialene derivative **14** which is obtained as deep blue leaflets in 44% yield.[6] Conceivably **12** reacts either by a cycloreversion and a subsequent 14π-electrocyclization of **11** or by a 1,5-vinyl shift[12] to **13** which, by two 1,5-H shifts, furnishes **14**. The driving force for the formation of **14**, a thia-dihydro derivative of the target molecule **2**, is obviously the generation of the aromatic thialene (cyclopenta[*b*]thiapyran) substructure with 10π-electrons[13] (Scheme 4).



Scheme 4. (a) Toluene, 110°C, 1 h

Physical data of compounds **7**, **10**, **12**, **14**.[14,15] Compound **7**: reddish brown crystals, mp 116–117°C (dec.), MS (EI): *m*/*z* (%) 294 [M^+, 28%]; ^{1}H NMR: δ 1.13 (s, 9H, 3′-$C(CH_3)_3$), 1.35 (s, 9H, 1′-$C(CH_3)_3$), 5.81 (d, 1H, J = 1.9 Hz, 4′-H), 6.22 (d, 1H, J = 1.9 Hz, 2′-H), 7.00–7.18 (m, 4H, 4-H–7-H), 7.50 (d, 1H, J = 8.7 Hz, 3-H), 7.65 (s, 1H, 6′-H); ^{13}C NMR: δ 29.17, 32.18, 32.36, 33.11, 111.38, 127.52, 133.10, 133.36, 133.63, 135.63, 138.59, 141.03, 146.71, 148.18, 149.71, 158.51, 186.68; UV–vis (*n*-hexane): λ_{max} (lg ε) = 221 nm (4.22), 272 (4.02) (sh), 277 (4.03), 369 (4.09). Compound **10**: deep blue crystals, mp 154–156°C (dec.), MS (EI): *m*/*z* (%) 336 [M^+, 37%]; ^{1}H NMR: δ 1.02 (s, 9H, 1-$C(CH_3)_3$), 1.39 (s, 9H, 3-$C(CH_3)_3$), 2.47 (s, 3H, CH_3CO), 3.41 (d, 1H, J = 1.9 Hz, 1-H), 6.53 (d, 1H, J = 1.9 Hz, 2-H), 6.93 (d, 1H, J = 10.9 Hz, 6-H), 7.03 (t, 1H, J = 9.9 Hz, 7-H), 7.16 (s, 1H, 4-H), 7.35 (t, 1H, J = 10.2 Hz, 8-H), 8.24 (d, 1H, J = 10.2 Hz, 9-H); ^{13}C NMR: δ 21.21, 28.27, 29.71, 33.04, 34.58, 55.58, 103.67, 119.34, 120.73, 130.12, 131.73, 133.44, 136.71, 138.94, 139.83, 151.35, 160.22, 169.64; UV–vis (dioxane): λ_{max} (lg ε) = 258 nm (4.12), 283 (4.29) (sh), 292 (4.46) (sh), 302 (4.68), 313 (4.73), 331 (3.92), 349 (3.43), 367 (3.60), 386 (3.77), 406 (3.76), 542 (2.42) (sh), 571 (2.54), 613 (2.51), 663 (2.14). Compound **12**: red needles, mp 114–115°C (dec.), MS (EI): *m*/*z* (%) 310 [M^+, 25%]; ^{1}H NMR: δ 1.09 (s, 9H, 8-$C(CH_3)_3$), 1.29 (s, 9H, 6-$C(CH_3)_3$), 4.77 (d, 1H, J = 1.5 Hz, 4-H), 5.39–5.53 (m, 3H, 2′-H–4′-H), 5.68 (ddd, 1H, $J_1 = J_2$ = 1.3 Hz, J_3 = 8.0 Hz, 1′-H), 5.78 (d, 1H, J = 1.9 Hz, 9-H), 5.85–6.00 (m, 1H, 5′-H), 5.99 (d, 1H, J = 1.9 Hz, 7-H); ^{13}C NMR: δ 29.03, 31.36, 31.71, 35.01, 74.18, 114.42, 124.99, 126.01, 126.31, 126.61, 126.86, 126.89, 128.35, 133.25, 144.16, 149.32, 156.66, 163.75; UV–vis (*n*-hexane): λ_{max} (lg ε) = 257 nm (4.18) (sh), 262 (4.24), 268 (4.21) (sh), 310 (4.23), 372 (3.03) (sh), 434 (3.00) (sh), 451 (3.06), 481 (3.06), 518 (2.93), 560 (2.61). Compound **14**: deep blue leaflets, mp 96–97°C, MS (EI): *m*/*z* (%) 310 [M^+, 28%]; ^{1}H NMR: δ 1.42 (s, 9H, 7-$C(CH_3)_3$), 1.45 (s, 9H, 5-$C(CH_3)_3$), 3.12 (d, 2H, J = 6.8 Hz, 1′-H), 5.58 (dt, 1H, J_1 = 7.0 Hz, J_2 = 9.4 Hz, 2′-H), 6.14 (dd, 1H, J_1 = 5.4 Hz, J_2 = 9.4 Hz, 3′-H), 6.49 (dt, 1H, J_1 = 5.4 Hz, J_2 = 11.3 Hz, 4′-H), 6.93 (s, 1H, 6-H), 6.96 (d, 1H, J = 11.3 Hz, 5′-H), 7.87 (s, 1H, 4-H); ^{13}C NMR: δ 29.90, 32.42, 32.85, 33.28, 112.40, 122.58, 123.64, 127.44, 127.51, 127.96, 131.26, 131.38, 132.02, 133.20, 134.29, 135.27; UV–vis (cyclohexane): λ_{max} (lg ε) = 240 nm (4.13), 278 (4.17), 335 (4.07), 370 (3.69) (sh), 390 (3.38) (sh), 557 (2.90).

Acknowledgements

We thank the Fonds der Chemischen Industrie and the Dr. Otto Röhm Gedächtnisstiftung, Darmstadt for generous support. Professor Dr. T. Nakazawa thanks the Alexander von Humboldt Foundation for a re-invitation.

References

1. Hafner, K. *Pure Appl. Chem.* **1982**, *54*, 939–956; Hafner, K.; Stowasser, B.; Krimmer, H.-P.; Fischer, S.; Böhm, M. C.; Lindner, H. J. *Angew. Chem.* **1986**, *98*, 646–648; *Angew. Chem.*, *Int. Ed. Engl.* **1986**, *25*, 630–632; Gellini, C.; Cardini, G.; Salvi, P. R.; Marconi, G.; Hafner, K. *J. Phys. Chem.* **1993**, *97*, 1286–1293; Gellini, C.; Salvi, P. R.; Hafner, K. *J. Phys. Chem.* **1993**, *97*, 8152–8157; Bachmann, R.; Gerson, F.; Gescheidt, G.; Hafner, K. *Magn. Reson. Chem.* **1995**, *33*, 60–65; Nendel, M.; Goldfuss, B.; Beno, B.; Houk, K. N.; Hafner, K.; Lindner, H. J. *Pure Appl. Chem.* **1999**, *71*, 221–229.
2. Heilbronner, E.; Yang, Z. *Angew. Chem.* **1987**, *99*, 369–371; *Angew. Chem.*, *Int. Ed. Engl.* **1987**, *26*, 360–362; Dunitz, J. D.; Krüger, C.; Irngartinger, H.; Maverick, E. F.; Wang, Y.; Nixdorf, M. *Angew. Chem.* **1988**, *100*, 415–418; *Angew. Chem.*, *Int. Ed. Engl.* **1988**, *27*, 387–390; Hertwig, R. H.; Holthausen, M. C.; Koch, W.; Maksic, Z. B. *Angew. Chem.* **1994**, *106*, 1252–1254; *Angew. Chem.*, *Int. Ed. Engl.* **1994**, *33*, 1192–1194; Nendel, M.; Goldfuss, B.; Houk, K. N.; Hafner, K. *J. Mol. Struct. (Theochem.)* **1999**, *461–462*, 23–28.
3. Eckerle, A. Diploma Thesis, Technische Hochschule Darmstadt, 1990; Schmack, W. Ph.D. Thesis, Technische Universität Darmstadt, 2000.
4. Griffith, M. G.; Dixon, J. H. *J. Org. Chem.* **1967**, *32*, 4020–4025 and references cited therein; Gerhartz, W. Ph.D. Thesis, Technische Hochschule Darmstadt, 1973 and references cited therein; Böhm, M. C.; Schütt, J. *J. Phys. Chem.* **1992**, *96*, 3674–3683.
5. Krimmer, H.-P.; Stowasser, B.; Hafner, K. *Tetrahedron Lett.* **1982**, *23*, 5135–5138; Hafner, K.; Krimmer, H.-P.; Stowasser, B. *Angew. Chem.* **1983**, *95*, 496–497; *Angew. Chem.*, *Int. Ed. Engl.* **1983**, *22*, 490–491; Hafner, K. *Pure Appl. Chem.* **1990**, *62*, 531–540; Stowasser, B. Ph.D. Thesis, Technische Hochschule Darmstadt, 1987; Hock, S. Ph.D. Thesis, Technische Hochschule Darmstadt, 1992.
6. The described new compounds were purified by chromatography on silica gel using *n*-pentane/diethyl ether (2:1 for compound **7**, 3:1 for compound **10**) and *n*-pentane (for compound **12** and **14**).
7. Kaiser, R.; Hafner, K. *Angew. Chem.* **1970**, *82*, 877–878; *Angew. Chem.*, *Int. Ed. Engl.* **1970**, *9*, 892–893; *Angew. Chem.* **1973**, *85*, 361–362; *Angew. Chem.*, *Int. Ed. Engl.* **1973**, *12*, 335–337; Hafner, K.; Süss, U. *Angew. Chem.* **1973**, *85*, 626–628; *Angew. Chem.*, *Int. Ed. Engl.* **1973**, *12*, 575–577; Hafner, K. *Nachr. Chem. Tech. Lab.* **1980**, *28*, 222–226.
8. Machiguchi, T.; Otani, H.; Ishii, Y.; Hasegawa, T. *Tetrahedron Lett.* **1987**, *28*, 203–206; Machiguchi, T.; Kano, Y.; Hasegawa, T. *Chem. Lett.* **1990**, 563–566; Machiguchi, T. *Tetrahedron* **1995**, *51*, 1133–1142.
9. Only one of the two enantiomers is depicted.
10. Machiguchi, T.; Hasegawa, T.; Itoh, S.; Mizuno, H. K. *J. Am. Chem. Soc.* **1989**, *111*, 1920–1921.
11. Machiguchi, T.; Hasegawa, T.; Otani, H.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1375–1376; Machiguchi, T.; Yamabe, S. *Tetrahedron Lett.* **1990**, *31*, 4169–4172; Machiguchi, T.; Hasegawa, T.; Ishii, Y.; Yamabe, S.; Minato, T. *J. Am. Chem. Soc.* **1993**, *115*, 11536–11541; Minato, T.; Yamabe, S.; Ishikawa, A; Hasegawa, T.; Machiguchi, T. *J. Mol. Struct. (Theochem.)* **1999**, *461–462*, 359–377.
12. Semmelhack, M. F.; Weller, H. N.; Foos, J. S. *J. Am. Chem. Soc.* **1977**, *99*, 292–294; Semmelhack, M. F.; Weller, H. N. *J. Org. Chem.* **1978**, *43*, 3791–3792.
13. Klein, R. F. X.; Horak, V. *J. Org. Chem.* **1986**, *51*, 4644–4651.
14. All new compounds described gave satisfactory elemental analyses.
15. NMR spectra were recorded with a Bruker NMR spectrometer WM 300 in $CDCl_3$ with tetramethylsilane as internal standard. UV–vis spectra were recorded with a Beckman UV-5240 spectrometer. Mass spectra (MS) were obtained with a Varian 311A instrument. For the elucidation of the structures **10**, **12** and **14**, NOE experiments were carried out.