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SYNTHESIS AND PROPERTIES OF 4,6-Di-t-BUTYL-CYCLOPENTA-1,2-DITHIOLE AND ITS 3-AZA-DERIVATIVE

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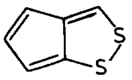
Summary: 2,4-Di-t-butyl-cyclopentadiene-1-carbaldehyde (3) and 2,4-di-t-butyl-cyclopentadienone oxime (7) are easily converted into the title compounds 6 and 10, respectively. The spectroscopic and chemical properties of the new heterocyclic 10π-electron systems are described.

Pentafulvenes have proven to be valuable building blocks in the synthesis of numerous carbo- and heterocyclic conjugated π-electron systems containing at least one 5-membered ring, e.g., pentalenes[1], s-indacenes[2], azulenes[3], azaazulenes[4], or cyclopenta[c]pyridazines[3].

We would like to report simple syntheses of the di-t-butyl derivatives of the bicyclic 10π-electron systems 1 and 2, which are isoelectronic with azulene and are representatives of a new type of pseudoazulenes[5]. Quantummechanical studies[6] of cyclopenta-1,2-dithiole (1) predict this so far unknown heterocyclic system to be stable. The already synthesized indeno[2,1-c]-1,2-dithiole[7] does not allow one to draw conclusions of the physical and chemical properties of the bicyclic system due to the annellation of a benzenoid ring.



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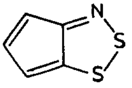

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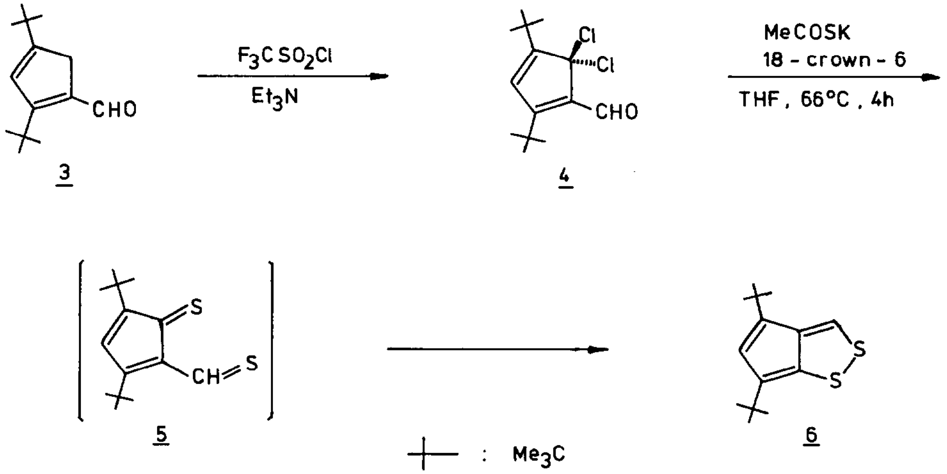
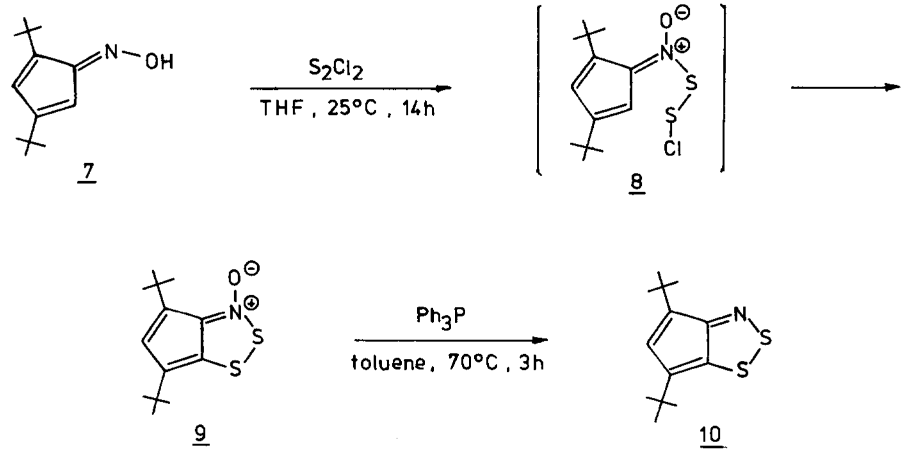
Reaction of 2,4-di-t-butyl-cyclopentadiene-1-carbaldehyde (3)[8], easily accessible from 1,3-di-t-butyl-6-dimethylaminopentafulvene[1], with trifluoromethanesulfonyl chloride[9] in the presence of triethylamine, yields 73% of 2,4-di-t-butyl-5,5-dichlorocyclopentadiene-1-carbaldehyde (4) (yellow rhombic crystals, m.p. 41°C). With potassium thioacetate, 4 forms 72% of the 4,6-di-t-butyl-cyclopenta-1,2-dithiole (6) as thermally stable, air sensitive fine light brown crystals (m.p. 42°C). Presumably 4 reacts with the thioacetate to form 3,5-di-t-butyl-2-thioformyl-cyclopentadienethione (5)[10], which then undergoes an 8π-electrocyclic process to 6.



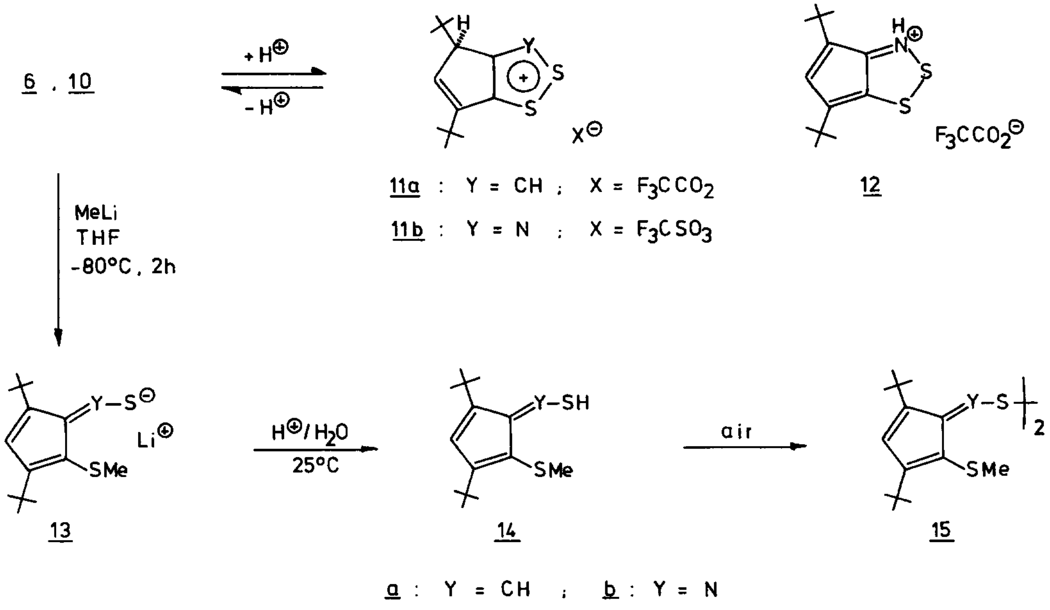
The corresponding 3-aza derivative 10 can be synthesized from 2,4-di-t-butyl-cyclopentadienone oxime (7) (orange-yellow crystals, m.p. 146-147°C) which is obtained in 75% yield from lithium 1,3-di-t-butyl-cyclopentadienide and i-amyl-nitrite.[11] Reaction of 7 with sulfur monochloride in THF produces the N-oxide 9 (dark blue fine crystals, m.p. 71°C) in 70% yield. N-Oxide 9 is quantitatively converted into 10 (violet oil) by treatment with triphenylphosphane. Both bicyclic compounds 9 and 10 are stable towards heat and air. The formation of 9 should proceed



by an electrophilic attack of S_2Cl_2 on the nitrogen of 7 to give intermediate 8, followed by cyclization to 9. Primary substitution of the 5-membered ring of 7 by S_2Cl_2 can be ruled out, as 7 resists C-substitution by various electrophilic reagents.

The UV spectra of 6 and 10 resemble those of azulenes and pseudoazulenes. The light absorption of 6 is in good agreement with PPP-calculations[6b] for 1. The electron spectrum of the aza derivative 10 shows pronounced influence of the nitrogen atom in a position of low electron density, on the bicyclic 1,2-dithiole system, which effects a bathochromic shift of the longest wave length absorption by 56 nm (Tab. 1). In the ^{1}H-NMR-spectra of 6 and 10 the signals of the ring protons are significantly shifted downfield compared to those of pentafulvenes, due to a delocalized 10π-electron system.

Both new heterocyclic systems can be reversibly protonated to the conjugated acids. While 6 reacts with trifluoroacetic acid quantitatively to give the stable 4,6-di-t-butyl-4H-cyclopenta-1,2-dithiolium trifluoroacetate (11a) (yellow oil), 10 yields, under the same conditions, the N-protonation product 12 (violet solution in $CDCl_3$) and with trifluoromethanesulfonic acid the tautomeric 3-aza-1,2-dithiolium salt 11b (yellow solution in $CDCl_3$). With nucleophiles no addition at the pentafulvene moiety of 6 or 10 takes place. However, like other disulfides[12], they react by cleavage of the S-S bond. With methyl lithium the deep blue 6-pentafulvenylthiolates



13a and b are obtained, which after hydrolysis to 14a and b and oxidation by air give 40% of the bis(6-pentafulvenyl)-disulfide 15a (red needles, m.p. 172°C) and 21% of 15b (brown needles, m.p. 171°C).

Tab. 1: Physical data of the compounds 4, 6, 7, 9, 10, 11, 12, 15:[13]

4: ^{1}H-NMR: δ= 1.10(s, 9H, tBu), 1.36(s, 9H, tBu), 6.44(d, J= 0.7Hz, 1H, 3-H), 9.96(d, J= 0.7Hz, 1H, CHO). UV(λ_{max}(nm, lgε)): 221(3.99), 318(3.55).

6: ^{1}H-NMR: δ= 1.32(s, 9H, tBu); 1.34(s, 9H, tBu); 6.75(s, 1H, 5-H); 7.70(s, 1H, 3-H). UV(λ_{max}(nm, lgε)): 229(3.72)sh, 321(3.92), 339(3.70)sh, 469(3.25).

7: ^{1}H-NMR: δ= 1.12(s, 9H, tBu), 1.24(s, 9H, tBu), 5.95(d, J= 2Hz, 1H, 5-H), 6.12(d, J= 2Hz, 1H, 3-H), 6.3-8.5(br.s, 1H, OH). UV(λ_{max}(nm, lgε)): 255(4.12), 378(2.56).

9: ^{1}H-NMR: δ= 1.17(s, 9H, tBu), 1.28(s, 9H, tBu), 6.66(s, 1H, 5-H). UV(λ_{max}(nm, lgε)): 247 (3.79), 373(2.81), 560(2.73).

10: ^{1}H-NMR: δ= 1.31(s, 9H, tBu), 1.37(s, 9H, tBu), 7.11(s, 1H, 5-H). UV(λ_{max}(nm, lgε)): 246 (3.08)sh, 332(3.83)sh, 339(3.88)sh, 343(3.89), 352(3.82)sh, 358(3.71)sh, 525(3.16).

11a: ^{1}H-NMR: δ= 1.11(s, 9H, 4-tBu), 1.42(s, 9H, 6-tBu), 3.67(d, J= 2Hz, 1H, 4-H), 7.77(d, J= 2Hz, 1H, 5-H), 9.58(s, 1H, 3-H)[14]. UV(λ_{max}(nm, lgε)): 246(3.27), 291(3.75), 351(4.19).

11b: ^{1}H-NMR: δ= 1.17(s, 9H, 4-tBu), 1.44(s, 9H, 6-tBu), 3.88(d, J= 2Hz, 1H, 4-H), 8.08(d, J= 2Hz, 1H, 5-H). UV(λ_{max}(nm, qualit.)): 388.

12: ^{1}H-NMR: δ= 1.30(s, 9H, tBu), 1.36(s, 9H, tBu), 7.10(s, 1H, 5-H), 8.68(s, 1H, NH). UV(λ_{max}(nm, qualit.)): 333sh, 340sh, 344, 350sh, 358sh, 524.

15a: ^{1}H-NMR: δ= 1.11(s, 18H, 2tBu), 1.29(s, 18H, 2tBu), 2.49(s, 6H, 1,1'-SCH_3), 6.04(s, 2H, 3-H, 3'-H), 7.52(s, 2H, 6-H, 6'-H). UV(λ_{max}(nm, lgε)): 232(4.11), 308(4.13)sh, 347(4.44), 457(3.55).

15b: ^{1}H-NMR: δ= 1.16(s, 18H, 2tBu), 1.22(s, 18H, 2tBu), 2.77(s, 6H, 1,1'-SCH_3), 6.22(s, 2H, 3-H, 3'-H). UV(λ_{max}(nm, lgε)): 232(4.10), 317(3.95)sh, 362(4.29), 470(3.49)sh.

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13. NMR-spectra were recorded with a Bruker-NMR-spectrometer WM 300 and a Varian-NMR-spectrometer XL-100-15 in $CDCl_3$ with tetramethylsilane as internal standard. UV-spectra were recorded with a Beckman spectrophotometer UV 5240 in n-hexane, except 11b and 12, which were recorded in solutions of trifluoromethanesulfonic acid or trifluoroacetic acid in dichloromethane. All compounds gave correct elemental analyses.
14. The structure of 11a was confirmed by NOE-measurement.

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