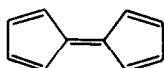


t-BUTYL-SUBSTITUTED PENTAFULVALENES AND PENTAFULVADIENES

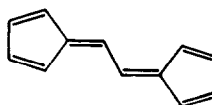
Reinhold Brand, Hans-Peter Krimmer, Hans-Jörg Lindner, Volker Sturm, and Klaus Hafner*
Institut für Organische Chemie der Technischen Hochschule, Petersenstr. 22, D-6100 Darmstadt

Summary. 2,2'-Di- and 1,1',3,3'-tetra-t-butyl-pentafulvalene as well as 2,2'-di- and 1,1',3,3'-tetra-t-butyl-pentafulvadiene could be prepared as thermally stable crystalline compounds for the first time.

Among fulvalenes, pentafulvalene (1) as well as its vinylogous, pentafulvadiene (2), attracted particular theoretical and synthetic interest 1, first prepared by Doering and Matzner¹ in 1958,



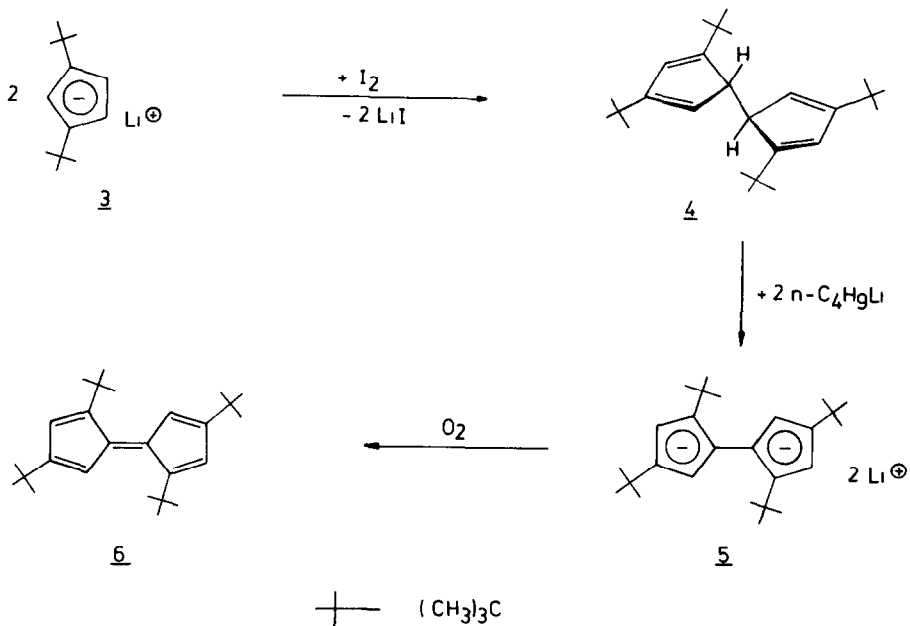
1



2

is an extremely unstable compound which can be handled only in highly diluted solution (<0.01 M) under inert gas at -60°C. Derivatives of 1, like perhalogenated², benzoannellated³, or manifold phenylated⁴ pentafulvalenes proved to be stable at room temperature. These, however, do not allow to draw conclusions on bond structure and reactivity of the parent compound, because portions of the 10 π -electron system are part of the benzenoid sextett systems or influenced by electronic substituent effects. Similar to 1 also pentafulvadiene (2), prepared by Prinzbach et al.⁵ in 3-6 % yield, is thermally rather unstable and reacts above -15°C to trans-8a,8b-dihydro-as-indacene in a conrotatoric 12 π -electron process.

In order to gain a deeper understanding about these systems, the synthesis of thermally stable derivatives of 1 and 2, exclusively stabilized by steric effects of alkyl substituents, was desirable. As expected, t-butyl groups fulfill this requirement. In analogy to 1, E-1,1'-3,3'-tetra-t-butyl-pentafulvalene (6) is easily synthesized starting from lithium 1,3-di-t-butyl-cyclopentadienide (3). Oxidative coupling of 3 with iodine in tetrahydrofuran at -78°C leads in quantitative yield to a mixture of tautomeric 1,1',3,3'-tetra-t-butyl-dihydropentafulvalenes, from which the meso-5,5-dihydro derivative 4 crystallizes in 20 % yield (pale yellow prisms, m.p. 122°C). A twofold deprotonation of the tautomeric mixture with n-butyllithium in boiling n-hexane in the presence of tetramethyldiaminoethane yields the dianion 5, which is oxidized by air at 25°C to 65% of the hydrocarbon 6. The deep red needles of 6 (m.p. 145°C) are stable towards light and air as well as in boiling xylene. With trifluoroacetic acid 6 can be reversibly protonated at C-2 or C-4



Some features of the molecular structure of 6 determined by X-ray analysis⁷ are shown in Fig. 1. The strain in the molecule of C₁-symmetry with alternating bond lengths introduced by the t-butyl groups in position 1 and 1' does not lead to a torsion of the central bond, but besides a slight pyramidal deformation on C-5 (deviation of C-5 from the plane C-5', C-1, C-4 = 0.05 Å) to an elongation of the central bond and angle deformation at C-5 and C-4.

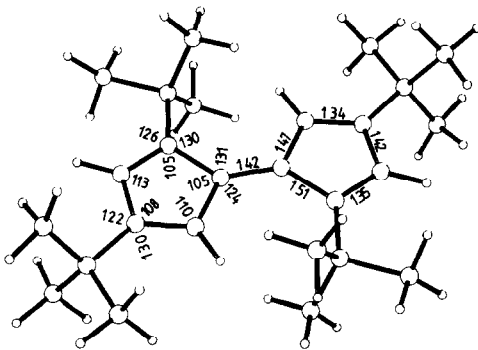
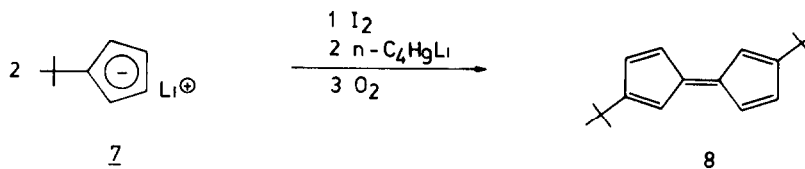


Fig. 1. Molecular structure of 6 with some bond lengths and bond angles ($\sigma_r = 0.02$ Å, $\sigma_\alpha = 1^\circ$)

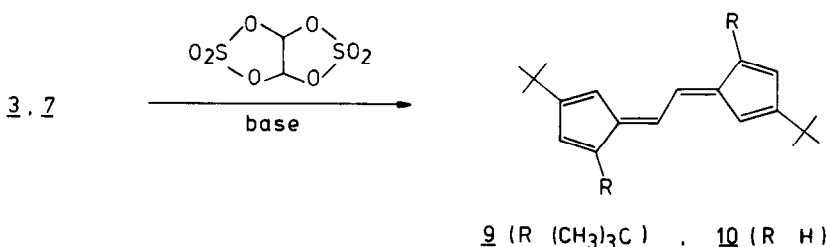
Similar to 6 a mixture of Z/E-isomers of 2,2'-di-t-butyl-pentafulvalene is obtained from lithium t-butyl-cyclopentadienide (7) in 32% yield. From this 22% of the E-isomer 8 can be isolated by fractional crystallization from n-pentane as deep red crystals (m.p. 105°C), which are stable.

thermally and towards air for several days. In n-pentane solution it slowly forms yellow polymeric products.



The t-butyl groups in 6 and 8 cause a bathochromic shift of the uv-absorption compared with that of 1, whereas the ring proton resonance frequencies of 6 and 8 are comparable with those of the parent compound 1 ($\delta = 6.47$ in D_8 -THF at -60°C).

Like pentafulvalene (1) also pentafulvadiene (2) can be stabilized by t-butyl groups. In analogy to the synthesis of 2 described by Prinzbach et al.⁵ also the E,E-1,1',3,3'-tetra-t-butyl-pentafulvadiene (9) (red prisms, m.p. 203°C) as well as the 2,2'-di-t-butyl-pentafulvadiene (10) (red crystals, m.p. 151°C) are easily obtained in 79% or 15% yield by reacting 3 or 7 with glyoxal sulfate in the presence of triethylamine in tetrahydrofuran at 0°C as thermally and towards air



and light stable crystals. Contrary to 2, however, 9 reacts in an electrocyclic 12π -electron process to the corresponding dihydro-as-indacene derivative only in boiling tetralin (b.p. 207°C), while 10 cyclizes already in boiling xylene (b.p. 140°C).

Physical data of the compounds 4, 6, 8, 9, and 10⁹

- 4 $^1\text{H-NMR}$ $\delta = 1.02$ (s, 18H, tBu), 1.32 (s, 18H, tBu), 3.70 (s, 2H, 5,5'-H), 5.27 (d, $J = 1.7\text{Hz}$, 2H), 6.18 (d, $J = 1.7\text{Hz}$, 2H)
- $^{13}\text{C-NMR}$ $\delta = 29.5$ (q, $\text{C}(\text{CH}_3)_3$), 32.0 (s, $\text{C}(\text{CH}_3)_3$), 31.4 (q, $\text{C}(\text{CH}_3)_3$), 33.8 (s, $\text{C}(\text{CH}_3)_3$), 51.9 (d, C-5), 123.3 (d), 125.7 (d), 154.4 (s), 159.7 (s)
- UV (λ_{max} (nm) (lg ϵ)) 321(2.09)sh, 307(2.19)sh, 255(3.74)
- 6 $^1\text{H-NMR}$ $\delta = 1.18$ (s, 18H, 3,3'-tBu), 1.50 (s, 18H, 1,1'-tBu), 6.60 (d, $J = 1.9\text{Hz}$, 2H), 6.72 (d, $J = 1.9\text{Hz}$, 2H)
- $^{13}\text{C-NMR}$ $\delta = 29.1$ (q, 3- $\text{C}(\text{CH}_3)_3$), 32.3 (s, $\text{C}(\text{CH}_3)_3$), 33.3 (q, 1- $\text{C}(\text{CH}_3)_3$), 33.3 (s, $\text{C}(\text{CH}_3)_3$), 118.7 (d, C-4), 132.2 (d, C-2), 148.2 (s, C-5), 149.5 (s, C-1), 155.1 (s, C-3)
- UV (λ_{max} (nm) (lg ϵ)) 478(2.90), 327(4.45), 317(4.40)sh, 303(4.18)sh, 289(3.81)sh, 249(3.64)
- 8 $^1\text{H-NMR}$ $\delta = 1.20$ (s, 18H, 2,2'-tBu), 6.16 (t, $J = 1.9\text{Hz}$, 2H, 1,1'-H), 6.58 (dd, $J_1 = 5.4\text{Hz}$, $J_2 = 2.0\text{Hz}$, 2H, 4,4'-H), 6.70 (dd, $J_1 = 5.4\text{Hz}$, $J_2 = 1.7\text{Hz}$, 2H, 3,3'-H)

$^{13}\text{C-NMR}$ δ = 29 2(q, C(CH₃)₃), 32 7(s, C(CH₃)₃), 112 9(d, C-1), 123 2(d, C-4), 135 3(d, C-3), 147 5(s, C-5), 161 4(s, C-2)

UV (λ_{max} (nm) (lg ϵ)) 435(2 77), 326(4 77), 311(4 72), 298(4 43), 287(4.05)sh, 276(3 64)sh, 234(3 29)sh

9 $^1\text{H-NMR}$ δ = 1 19(s, 18H, 3,3'-tBu), 1.34(s, 18H, 1,1'-tBu), 6 o4(d, J= 1.8Hz, 2H), 6 19(d, J= 1 8Hz, 2H), 7 44(s, 2H, 6,6'-H)

$^{13}\text{C-NMR}$ δ = 19 2(q, 3-C(CH₃)₃), 32 2(q, 1-C(CH₃)₃), 32 4(s, C(CH₃)₃), 33 o(s, C(CH₃)₃), 11o o(d, C-4), 127 7(d, C-2), 129 8(d, C-6), 147 7(s, C-1), 148 8(s, C-5), 157 5(s, C-3)

UV (λ_{max} (nm) (lg ϵ)) 433(2 97), 365(4 8o), 346(4 79), 33o(4 56), 317(4 23)sh, 3o2(3 86)sh, 246(3 48)

1o $^1\text{H-NMR}$ δ = 1 2o(s, 18H, 2,2'-tBu), 6 22-6 3o(m, 4H, 1,1',4,4'-H), 6 52-6 63(m, 2H, 3,3'-H), 7 15(s, 2H, 6,6'-H)

$^{13}\text{C-NMR}$ δ = 29 3(q, 2-C(CH₃)₃), 32 6(s, 2-C(CH₃)₃), 1o9 9(d, C-1), 126 5(d, C-4), 13o 5(d, C-6), 133 3(d, C-3), 15o 9(s, C-5), 16o 9(s, C-2)

UV (λ_{max} (nm) (lg ϵ)) 413(2 95)sh, 364(4 89), 346(4 83), 33o(4 57), 317(4 22)sh, 239(3 51)

REFERENCES AND NOTES

- W v E Doering in "Theoretical Organic Chemistry", Butterworth London 1959, p 35, E Matzner, Ph D. thesis, Yale University 1958, K V Scherer, Jr, J Am Chem Soc **85**, 1550 (1963), W B DeMore, H O Pritchard, and N Davidson, J Am Chem Soc **81**, 5874 (1959)
- P T Kwitowski and R West, J. Am Chem Soc **88**, 4541 (1966), V Mark, Tetrahedron Lett **1961**, 333, A E Ginsberg, R Paatz, and F Korte, Tetrahedron Lett **1962**, 779, R West, Pure Appl Chem **28**, 379 (1971), R E Banks, M Bridge, R N Haszeldine, D W Roberts, and N I Tucker, J Chem Soc ,C **197o**, 2531
- E D Bergmann in "Progress in Organic Chemistry" **3**, 81 (Edit J W Cook), Butterworth, London 1955, E D Bergmann, Chem Rev **68**, 41 (1968)
- P L Pauson and B J Williams, J Chem Soc **1961**, 4153, H Prinzbach and H Sauter, Angew Chem **84**, 115 (1972), Angew Chem Int Ed Engl **11**, 133 (1972), H Prinzbach, Pure Appl. Chem. **28**, 182 (1971), H Prinzbach, H Sauter, H -G Horster, H -H Limbach, and L Knothe, Liebigs Ann Chem. **1977**, 869
- H Sauter and H Prinzbach, Angew Chem **84**, 297 (1972), Angew Chem Int Ed. Engl **11**, 296 (1972), H Sauter, B Gallenkamp, and H Prinzbach, Chem Ber **11o**, 1382 (1977)
- 3 was prepared from a mixture of 1,3- and 1,4-di-t-butyl-cyclopentadiene and n-butyllithium in n-hexane in the presence of tetramethyldiaminoethane
- X-ray analysis C₂₆H_{4o}, P₂₁n, a= 5 91, b= 18 3o, c= 1o 89, β = 89 78°, Z = 2 Refined to R= o 15 using 621 reflections with $|F| \geq 3\sigma_F$
- It could not be distinguished so far between the possible E,E-, E,Z- and Z,Z-stereoisomers
- NMR spectra were recorded with Varian XL-100 or Bruker WM 300 spectrometers in CDCl₃, except the $^1\text{H-NMR}$ spectrum of 6 in C₆D₆ with tetramethylsilane as internal standard UV spectra were recorded with a Beckman spectrometer UV 5240 in n-hexane. All compounds gave correct elemental analyses

ACKNOWLEDGMENT

Support of this work by the Fonds der Chemischen Industrie, Degussa A G, Frankfurt/Main, and BASF A G, Ludwigshafen, is gratefully acknowledged

(Received in Germany 25 August 1982)