

SYNTHESIS AND NUCLEOPHILIC SUBSTITUTION OF STABLE 6-HALO-PENTAFLUVENES

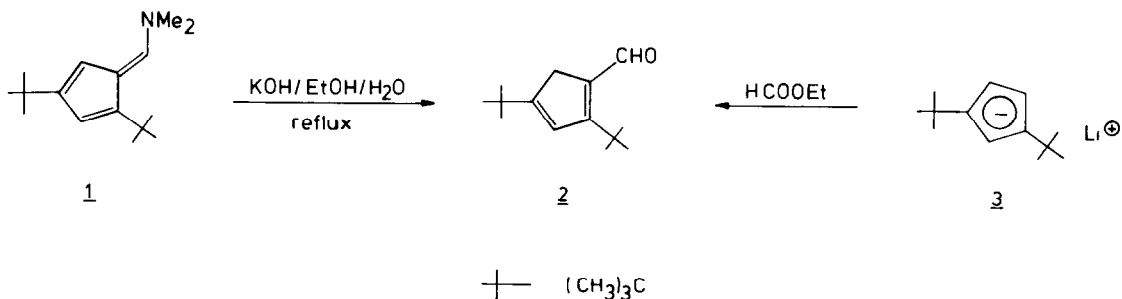
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Summary The reaction of 2,4-di-t-butyl-cyclopentadiene-1-carbaldehyde with oxalyl chloride or oxalyl bromide provides stable 6-chloro- and 6-bromo-pentafulvenes, respectively. Several nucleophilic displacement reactions of the new compounds are described.

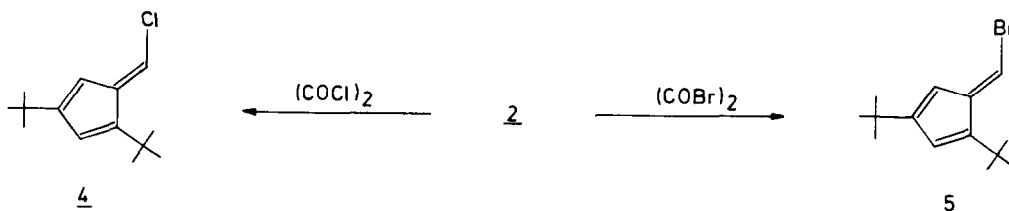
Pentafulvenes carrying electron donating or withdrawing substituents in position 6 are of theoretical and preparative importance. They proved to be valuable synthons, e.g. for the synthesis of pentalenes¹ and azulenes², via nucleophilic displacements³ and cycloaddition reactions⁴. In this respect 6-halo-pentafulvenes demand a special interest, although information on the syntheses and reactions of these compounds are rather limited so far. D'Amore and Bergman⁵ for the first time prepared 6-chloro-pentafulvene by addition of dichlorocarbene to cyclopentadiene. Some other authors⁶ reported on the formation of 6,6-dihalo-pentafulvenes from metallocenes, and recently Neuschwander et al.⁷ on a synthesis of 6-halo-pentafulvenes from cyclopenten-3-one. All these methods provide 6-halo-pentafulvenes only in rather low yields (<10%). Contrary to this, Buchi and Carlson⁸ obtained a bicyclic 6-chloro-pentafulvene lactone in high yield by treatment of the corresponding 6-hydroxy derivative with oxalyl chloride. All 6-halo-pentafulvenes known so far are thermally rather unstable, which prevented an extensive investigation of their reactivity.⁶

We would like to report a simple synthesis of stable 6-chloro- and 6-bromo-pentafulvenes as well as their reactions with nucleophilic reagents. Hydrolysis of 1,3-di-t-butyl-6-dimethylamino-pentafulvene (**1**)¹ with KOH in ethanol/H₂O yields 65% of 2,4-di-t-butyl-cyclopentadiene-1-carbaldehyde (**2**) as colorless oil (m.p. 18°C). **2** is also obtained in 35% yield by reaction of lithium 1,3-di-t-butyl-cyclopentadienide (**3**)⁹ with ethyl formate. It exists entirely in the keto

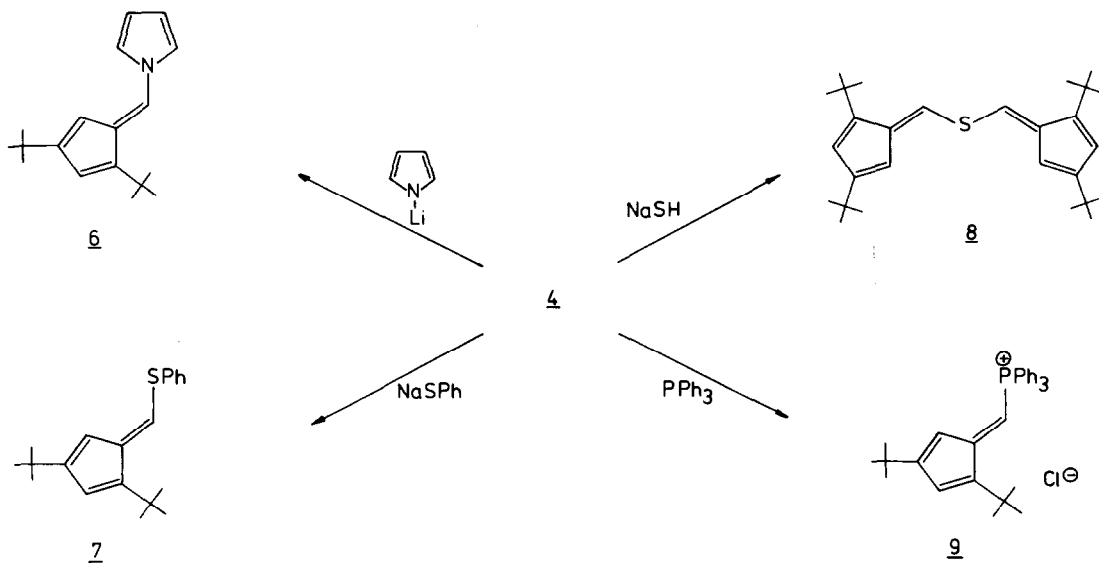


structure while the tautomeric 6-hydroxy-pentafulvene form could not be detected even in traces. Contrary to cyclopentadiene-carbaldehyde^{3,10}, the di-*t*-butyl derivative is stable at room temperature.

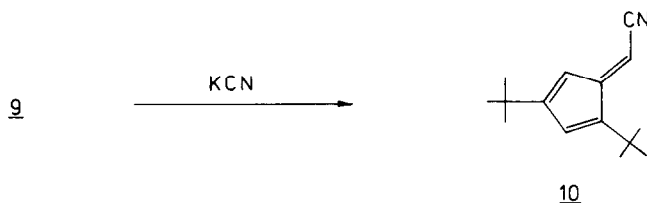
Reaction of 2 with oxalyl chloride or oxalyl bromide provides the thermally and towards moisture completely stable 1,3-di-*t*-butyl-6-chloro-pentafulvene (4) (m.p. 59°C), and 1,3-di-*t*-butyl-6-bromo-pentafulvene (5) (m.p. 57°C), in 70 % or 61 % yield as pale yellow crystals, which are easily purified by simple column chromatography (Al_2O_3 (B-IV), *n*-hexane).



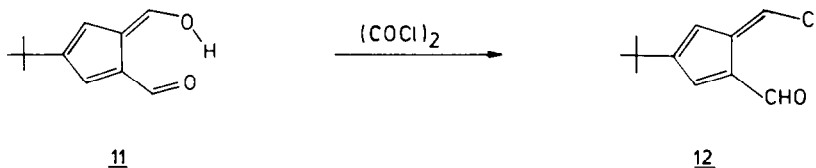
4 and 5 display a pronounced tendency for substitution reactions even with weak nucleophiles, which open an easy access to new pentafulvenes substituted in 6-position. With pyrrolyllithium or sodium thiophenolate 4 reacts to the so far unknown pentafulvenes 6 (yellow plates, m.p. 86°C) and 7 (orange needles, m.p. 91°C) in 30 % or 82 % yield respectively. With sodium hydrosulfide 4 does not form the corresponding 6-mercapto-pentafulvene, but instead in 40 % yield the bis-pentafulvenyl-thioether 8 (yellow crystals, m.p. 129°C). By reaction of 4 with triphenylphosphine the reactive (1,3-di-*t*-butyl-pentafulvene-6-yl)-triphenylphosphonium chloride (9) (orange-yellow crystals, m.p. 215°C) is obtained in 90 % yield.



Like 4 and 5 also 9 undergoes displacement reactions with nucleophiles, but already in aqueous solution. Contrary to 4 it reacts with potassium cyanide to the pentafulvene-6-carbonitrile 10 (red needles, m.p. 76°C) in 55 % yield. Although the strong electron withdrawing group in 6-position of 10 should destabilize the pentafulvene system, the new compound could be isolated as thermally stable crystals.



In analogy to 4 3-*t*-butyl-6-chloro-pentafulvene-1-carbaldehyde (12) (yellow needles, m p -19°C)



can be prepared by reaction of 3-*t*-butyl-6-hydroxy-pentafulvene-1-carbaldehyde (11)¹¹ with oxalyl chloride. Like the previously synthesized 2,4-di-*t*-butyl-6-chloro-pentafulvene-1-carbaldehyde¹², also the bifunctional 6-chloro-pentafulvene 11 reacts as vinylogous acid chloride readily with a variety of nucleophiles by displacement and ring closure reactions.

Physical data of the compounds 2, 4 - 12¹³

2 $^1\text{H-NMR}$ δ = 1.19 (s, 9H, *t*Bu), 1.40 (s, 9H, *t*Bu), 3.36 (d, J = 0.9 Hz, 2H, 5- CH_2), 6.34 (t, J = 0.9 Hz, 1H, 3-H), 10.14 (s, 1H, formyl-H)
UV (λ_{max} (nm)(lg ϵ)) 207(3.91), 302(4.01)

4 $^1\text{H-NMR}$ δ = 1.15 (s, 9H, *t*Bu), 1.25 (s, 9H, *t*Bu), 6.07 (dd, J_1 = 2.1 Hz, J_2 = 0.8 Hz, 1H, 2-H), 6.13 (d, J = 2.1 Hz, 1H, 4-H), 6.95 (d, J = 0.8 Hz, 1H, 6-H)
UV (λ_{max} (nm)(lg ϵ)) 261(4.25)sh, 266(4.27), 274(4.11)sh, 315(2.31)sh, 380(2.59)

5 $^1\text{H-NMR}$ δ = 1.15 (s, 9H, *t*Bu), 1.25 (s, 9H, *t*Bu), 6.01 (dd, J_1 = 2.1 Hz, J_2 = 0.9 Hz, 1H, 2-H), 6.17 (d, J = 2.1 Hz, 1H, 4-H), 7.17 (d, J = 0.9 Hz, 1H, 6-H)
UV (λ_{max} (nm)(lg ϵ)) 266(4.24)sh, 272(4.31), 280(4.18)sh, 382(2.58)

6 $^1\text{H-NMR}$ δ = 1.17 (s, 9H, *t*Bu), 1.35 (s, 9H, *t*Bu), 6.18 (s, 2H, 2,4-H), 6.34 (m, 2H, pyrrol-3',4'-H), 7.02 (m, 2H, pyrrol-2',5'-H), 7.58 (s, 1H, 6-H)
UV (λ_{max} (nm)(lg ϵ)) 319(4.41), 329(4.32), 369(2.86)

7 $^1\text{H-NMR}$ δ = 1.18 (s, 9H, *t*Bu), 1.30 (s, 9H, *t*Bu), 6.12 (dd, J_1 = 2.0 Hz, J_2 = 1.0 Hz, 1H, 2-H), 6.18 (d, J = 2.0 Hz, 1H, 4-H), 7.40 (d, J = 1.0 Hz, 1H, 6-H), 7.30 - 7.50 (m, 5H, phenyl-H)
UV (λ_{max} (nm)(lg ϵ)) 229(3.79), 261(3.74), 331(4.41), 392(2.76)

8 $^1\text{H-NMR}$ δ = 1.18 (s, 9H, *t*Bu), 1.32 (s, 9H, *t*Bu), 6.03 (dd, J_1 = 2.0 Hz, J_2 = 0.7 Hz, 1H, 2-H), 6.17 (d, J = 2.0 Hz, 1H, 4-H), 7.24 (d, J = 0.7 Hz, 1H, 6-H)
UV (λ_{max} (nm)(lg ϵ)) 229(3.93), 239(3.88), 260(3.49), 362(4.58)

9 $^1\text{H-NMR}$ δ = 0.86 (s, 9H, *t*Bu), 1.36 (s, 9H, *t*Bu), 4.65 (m, 1H, 4-H), 6.12 (m, 1H, 2-H), 6.73 (d, J = 18 Hz, 1H, 6-H), 7.20 - 7.90 (m, 15H, phenyl-H)
UV (λ_{max} (nm)(lg ϵ)) 231(3.40), 271(4.37), 275(4.36), 452(2.61)

10 $^1\text{H-NMR}$ δ = 1.14 (s, 9H, *t*Bu), 1.24 (s, 9H, *t*Bu), 5.87 (s, 1H, 6-H), 5.94 (d, J = 2.0 Hz, 1H, 2-H), 6.22 (d, J = 2.0 Hz, 1H, 4-H)
UV (λ_{max} (nm)(lg ϵ)) 267(4.33), 274(4.26), 424(2.42)

- 11 $^1\text{H-NMR}$ δ = 1.23(s, 9H, tBu), 7.10(s, 2H, 2,4-H), 8.55(d, J =7Hz, 2H, 6-H, formyl-H), 15.30(t, J =7Hz, 1H, OH)
UV (λ_{max} (nm)(lg ϵ)) 252(4.0), 317(3.95), 396(3.71), 403(3.71), 419(3.60)
- 12 $^1\text{H-NMR}$ δ = 1.24(s, 9H, tBu), 6.62(ddd, J_1 =1.9Hz, J_2 =1Hz, J_3 =0.8Hz, 1H, 4-H), 7.34(dd, J_1 =1.9Hz, J_2 =0.45Hz, 1H, 2-H), 7.89(dd, J_1 =0.8Hz, J_2 =0.45Hz, 1H, 6-H), 9.76(d, J =1Hz, 1H, formyl-H)
UV (λ_{max} (nm)(lg ϵ)) 235(4.23), 276(3.88), 287(4.06), 293(4.13), 302(3.98), 376(2.16)

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- 9 **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, see also L Knothe, H Prinzbach, and E Hadicke, Chem Ber **114**, 1656 (1981)
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- 11 **11** can be obtained from lithium *t*-butyl-cyclopentadienide and ethyl formate in boiling *n*-hexane. Yellow needles, mp 34°C
- 12 K Hafner, Pure Appl Chem **54**, 939 (1982)
- 13 NMR spectra were recorded with a Varian XL-100 spectrometer in CDCl_3 with tetramethylsilane as internal standard. UV spectra were recorded with a Beckman spectrophotometer UV 5240 in *n*-hexane, except **9**, which was recorded in dichloromethane. All compounds gave correct elemental analyses

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