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SYNTHESES OF 4.6-DI-TERT.-BUTYL-PENTALENE DERIVATIVES AND THEIR REVERSIBLE DIMERIZATION

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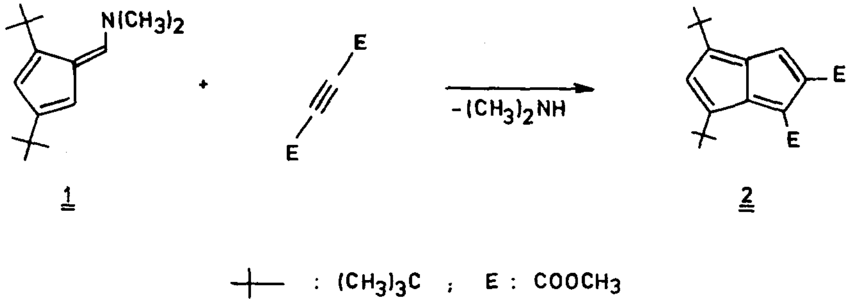
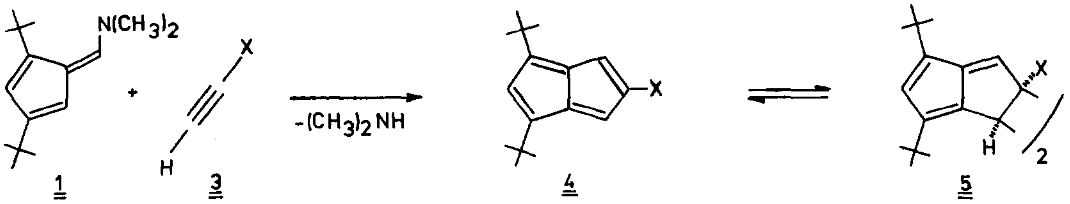
Recently we reported a facile synthesis of the thermally stable pentalene derivative **2** from easily available 1.3-di-tert.-butyl-6-dimethylaminofulvene **1** and dimethyl acetylenedicarboxylate[1]. In the course of further investigations about the scope and limitations of this new synthetic scheme we have found, that **1** reacts in a similar way with acetylenes **3**, possessing only one electron-withdrawing group, by formation of the pentalenes **4a** - **4c**. Contrary to **2**, however, the pentalenes **4a** - **4c** are at room temperature in equilibrium with their dimers **5a** - **5c**[2]. When **1** is treated with methyl propiolate **3a** (45°C, 18 h), propiolaldehyde **3b** (0°C, 1o min) or cyanoacetylene **3c** (-20°C, 3o min) one obtains after chromatography on silica gel





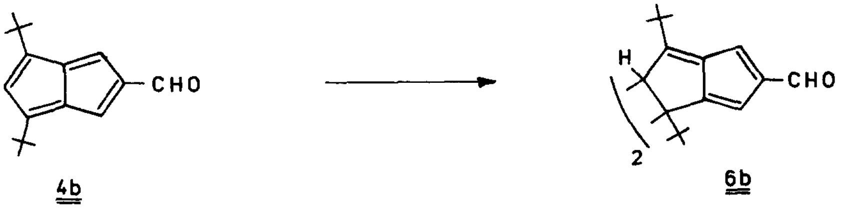
	a	b	c
X	COOCH3	CHO	CN

yellow crystals of **5a** (58 %; m.p. 135 - 136°C), **5b** (48 %; m.p. 84 - 85°C), and **5c** (45 %; m.p. 153 - 154 °C)[3]. Upon dissolving these pentalene dimers in organic solvents one observes a color change of the solution from yellow to green. This change could be monitored quantitatively by nmr and uv-visible spectroscopy and is due to a reversible dissociation of **5** to the corresponding monomeric pentalenes **4**. Removal of the solvent regenerates pure yellow crystals of **5**.

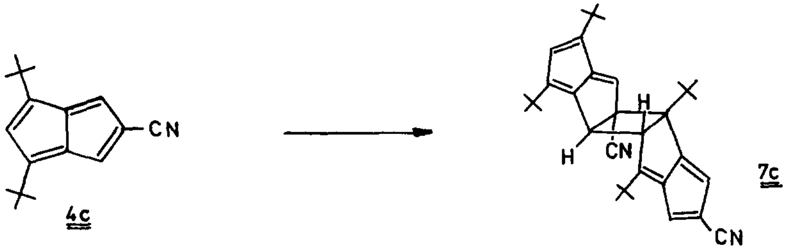
Respective nmr spectra of a mixture of **4** and **5** as well as uv-visible spectra of almost pure monomer in a diluted solution ($1o^{-3}$ - $1o^{-5}$M) and of pure dimer by low temperature measurements could be obtained (except **5b**) (Table 1).

The equilibrium constant $K=[4a]^2/[5a]$ (mol/l) at about 40°C, obtained by the peak area measurement method utilizing nmr spectroscopy, shows no correlation with solvent polarity [K = o.o4 (benzene-d_6), o.o5 (CS_2), o.o2 (CCl_4), o.1o ($CDCl_3$) and o.o6 (CH_2Cl_2)]. A first order rate constant for this dissociation reaction was established by uv-visible spectroscopy (in CH_2Cl_2 and n-hexane). The activation energy was determined to E_a= 22.8 ± 1 kcal/mol in CH_2Cl_2 and 2o.3 ± 1 kcal/mol in n-hexane. According to this **5a** dissociates faster in n-hexane than in methylene chloride.

In case of the pentalene aldehyde 4b the equilibrium is displaced so far to the side of the monomer that no spectroscopic data could be obtained for the dimer 5b. On the other hand, when a concentrated solution of 4b was kept at 25°C for one week, a second yellow crystalline dimer 6b (m.p. 170 - 173°C) was isolated in 37 % yield, whose structure was established by spectroscopic and analytical means. Like the previously described dimers of alkylated pentalenes[4,5], this dimer does not dissociate thermally to 4b.



The dissociation of 5c to 4c is faster than that of 5a, but slower than that of 5b. The equilibrium constant K at 40°C in $CDCl_3$ was determined to 0.16 mol/l. After one month at 25°C 4c forms yet another non-equilibriated



dimer 7c, the first example for the formation of a "head-to-tail" dimer in this series of pentalene dimers. The stereochemistry of 7c was deduced from its nmr and uv spectra.

These results show, that both the equilibrium constants and the rate constants of the dissociation reaction of $5 \rightleftharpoons 4$ depend on the electron withdrawing group and decrease in the following order $-CO_2CH_3 \gg -CN > CHO$.

Spectroscopic Data

compound	^{1}H-nmr spectra (60 MHz, TMS-internal standard)	uv-visible spectra (λ_{max}(nm)(log ε))
4a	1.01(18H,s), 3.67(3H,s), 4.85(1H,s), 5.97(2H,s) a)	736 (2.35) b) 677 (2.35) 358 (3.66) 265 (4.28)
5a	1.24(18H,s), 3.70(3H,s), 3.49(1H,s), 6.40(1H,s), 6.45(1H,s) a)	416 (3.23) c) 260 (4.27)
4b	1.06(18H,s), 5.00(1H,s), 6.10(2H,s), 9.18(1H,s) a)	703 (2.45) d) 666 (2.46) 354 (3.62) 277 (4.31) 231 (4.07)
4c	1.00(18H,s), 4.92(1H,s), 5.75(2H,s) e)	744 (2.43) b) 678 (2.43) 357 (3.70) 252 (4.36)
5c	1.21(9H,s), 1.29(9H,s), 3.61(1H,s), 6.49 (1H,s), 6.56(1H,s) a)	417 (3.19) f) 254 (4.29)
6b	1.10(9H,s), 1.20(9H,s), 4.20(1H,s), 6.30(1H,s), 6.38(1H,s), 9.90(1H,s) a)	395 (3.13) d) 258 (4.30)
7c	0.92(9H,s), 1.20(9H,s), 1.28(9H,s), 1.42(9H,s), 3.30(1H,d, J=5Hz), 3.58(1H,d, J=5Hz), 6.43(1H,s), 6.49(1H,d, J=1Hz), 6.60(1H,s), 7.02(1H,d,J=1Hz) a)	

a) in $CDCl_3$; b) in CH_2Cl_2; c) in CH_2Cl_2 at -16°C; d) in hexane;
e) in CD_2Cl_2, as a mixture; f) in CH_2Cl_2 at -40°C.

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[2] The anti-cis-configuration of 5 is likely by comparison of their uv spectra with those of alkylated pentalene dimers, whose stereochemistry has been established[4].

[3] All new compounds gave correct elementary analyses.

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