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SYNTHESIS OF DI-, TETRA- AND PENTA-METHYL-HEPTALENES

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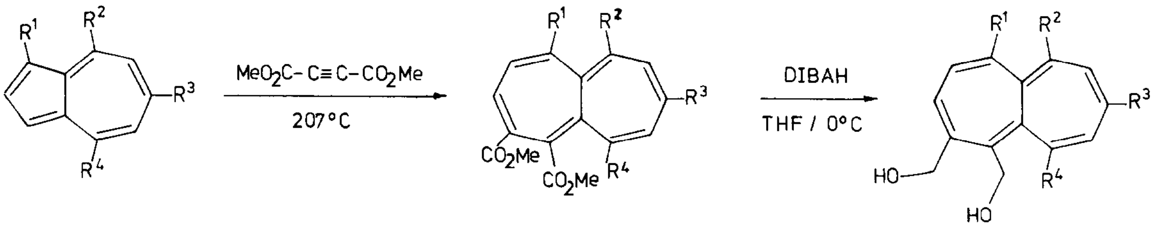
Summary: Some methylheptalenes were synthesized by two different pathways. The new hydrocarbons 7a-d and 10 proved to be, in contrast to the parent compound, thermally and air stable.

Apart from the thermally unstable and air sensitive unsubstituted heptalene[1,2], only derivatives with electron withdrawing substituents in 1-(≡5,6,10) or 3-(≡8) positions[1,2d,3,4], which cause an electronical stabilization of the bicyclic 12π-electron system, were known so far. The unexpected stability of the recently prepared 1,2,5,6,8,10-hexamethylheptalene[5] stimulated efforts to synthesize lower methylated heptalenes in order to prove the stabilizing effect of these substituents depending on their number and position.

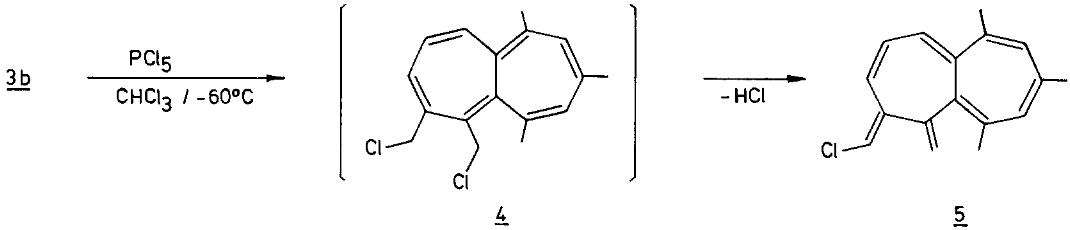
As it seemed promising to prepare these heptalenes in a similar way as the hexamethyl derivative[5], the dimethyl 1,2-heptalenedicarboxylates 2b-d - obtained by cycloaddition reaction of the azulenes 1b-d with dimethyl acetylenedicarboxylate[4] - were reduced with diisobutylaluminum hydride to the 1,2-bis(hydroxymethyl)-heptalenes 3b-d, which could be isolated as stable yellow crystals (Tab. 1).



1 2 3

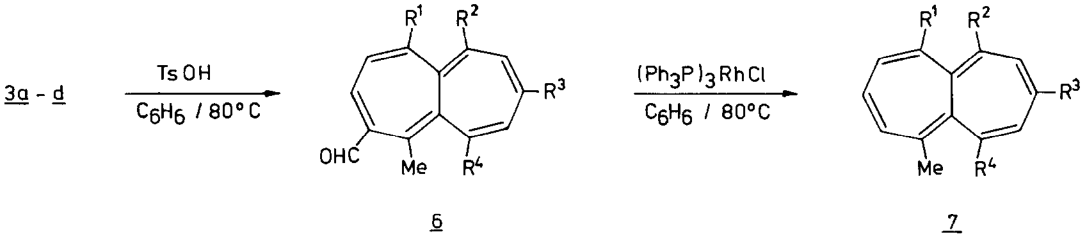
1-3,6,7	a	b	c	d
R^1	Me	H	Me	H
R^2	Me	Me	Me	H
R^3	Me	Me	H	H
R^4	Me	Me	Me	Me

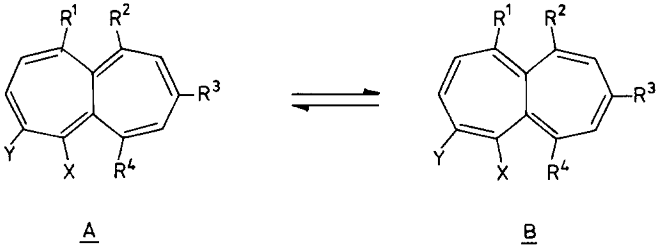
Attempts to synthesize 1,3,5,6,7-pentamethylheptalene via the 1,2-bis(chloromethyl)-heptalene 4 - generated from the diol 3b with phosphorus pentachloride - failed as 4 eliminates spontaneously HCl to give the 1,2-bis(methylidene)-heptalene 5. This result prompted us to study the



dehydration of 1,2-bis(hydroxymethyl)-heptalenes 3, which should lead via an enolic structure (similar to 5, OH instead of Cl) to the 2-heptalene carbaldehydes 6.

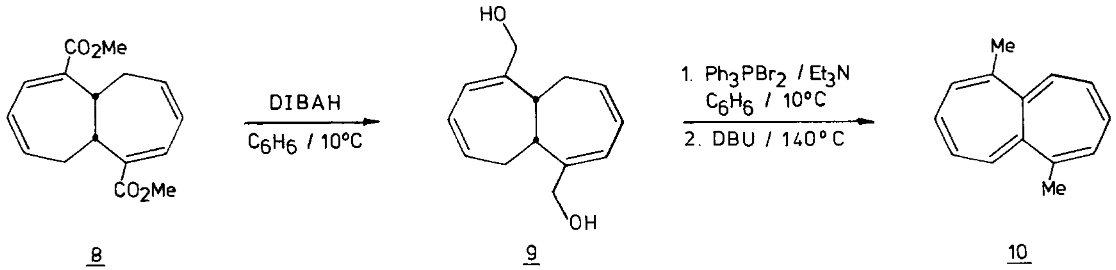
As expected, the heptalene diols 3 can easily be converted into 6 by reaction with catalytic amounts of p-toluenesulfonic acid (Tab. 1). Decarbonylation of the aldehydes 6 with tris(triphenylphosphine)rhodium(I)choride yields the desired methylheptalenes 7 as thermally and air stable compounds (Tab. 1 and 2). Similar to the heptalene derivatives 2, 3, and 6, even the unsymmetrically substituted hydrocarbon 7b exists at 25°C as a mixture of the bond shift isomers A and B[4b] (Tab. 1).





	2	3	6	7
X	CO_2Me	CH_2OH	Me	Me
Y	CO_2Me	CH_2OH	CHO	H

In addition to 7a-d we also could synthesize 1,6-dimethylheptalene 10 by an entirely different pathway after the cis-1,5a,6,10a-tetrahydroheptalene derivative 8 became easily accessible



by a new rearrangement reaction.[6] 10 is obtained by reduction of the diester 8 with diisobutylaluminum hydride and subsequent two-fold dehydration of 9 (Tab. 1 and 2).

The surprising stability of the described methylheptalenes - even of the dimethylheptalenes 7d and 10 - in comparison with the parent compound[1,2] can not only be the result of a kinetic stabilization due to a steric shielding of the heptalene system, but rather to an enhancement of twisting of the nonplanar 12π-perimeter caused mainly by a steric interaction of an increasing number of methyl groups in the peri-positions. This reduces the cyclic conjugation and increases the HOMO-LUMO gap of the [4n]-π-system.

Tab. 1: Yields and Physical Data of the Compounds 2, 3, 5, 6, 7, 9, and 10.[7]

Compound	Yield[%]	mp[°C]	ratio A:B	UV λ_{max}(lgε)[nm]
2b[d]	56	99-100	4:1	268(4.19), 323sh(3.57), 393sh(2.79)[b]
2c	32	113-114		262(4.19), 273sh(4.17), 326sh(3.38)[b]
2d[e]	35	113	>98:<2	205(4.40), 264(4.21), 323sh(3.52), 405sh(2.66)[a]
3b	86	124-129	1:2	246sh(4.22), 258(4.33), 316(3.58)[b]
3c	86	130-131	9:1	253(4.32), 300sh(3.49)[b]
3d	33	128-130	7:5	255(4.34), 317(3.53)[b]
5	18	133-136		223(4.37), 286(3.82), 389(4.01)[b]
6a	94	132-134	1:2	218(4.26), 247sh(4.19), 256sh(4.23), 271(4.28), 372sh(2.92)[b]
6b	67	112-114	1:20	253(4.25), 271(4.29), 328(3.63), 396sh(2.85)[b]
6c	56	90-91	1:6	253(4.27), 271(4.30), 330(3.65), 394sh(2.84)[b]
6d[f]	28	oil		
7a	86	78-83		252(4.36), 299sh(3.49)[a]
7b	63	59-61	1:3	252(4.36), 317sh(3.57)[a]
7c	46	73-74		251(4.34), 295sh(3.47)[a]
7d	44	oil		250(4.33), 333(3.59)[a]
9	76	140-142		236(4.11), 243(4.12), 248(4.11), 254(4.11)[c]
10	32	oil		251(4.34), 332(3.59)[a]

a) in hexane b) in dioxane c) in methanol d) in contrast to an earlier publication[4a] the reaction affords no dimethyl 5,6,8-trimethyl-2,3-heptalenedicarboxylate e) additionally 13% dimethyl 6-methyl-1,2-heptalenedicarboxylate (orange plates, m.p.: 139-140°C) can be isolated f) could not be obtained as pure compound so far

Tab. 2: 300 MHz-^{1}H-NMR spectra of the methylheptalenes 7 and 10 (in $CDCl_3$);TMS as int.stand.):

7a: δ= 1.72, 1.74(2s; 3H each, 1/6-Me), 1.97(d, J= 1.4Hz; 3H, 10-Me), 1.98(d, J= 1.6Hz; 3H, 5-Me), 1.98(d, J= 0.6Hz; 3H, 8-Me), 6.00, 6.10(2br.s; 1H each, 7/9-H), 6.10(m; 1H, 2-H), 6.28(m; 2H, 3/4-H).

7bA: δ= 1.71, 1.74(2s; 3H each, 1/6-Me), 1.95(covered; 3H, 5-Me), 1.98(d, J=1.3Hz; 3H, 3-Me), 5.78(d, J= 10.4Hz; 1H, 10-H), 5.93(br.s; 1H, 2-H), 6.07(br.s; 1H, 4-H), 6.10(covered; 1H, 7-H), 6.20-6.40(m; 2H, 8/9-H).

7bB: δ= 1.71(s; 3H, 5-Me), 1.95(d, J= 1.3Hz; 3H, 1-Me), 2.01(br.s; 3H, 6-Me); 2.05(d, J= 1.2Hz; 3H, 3-Me), 5.71(d, J= 6.0Hz; 1H, 10-H), 5.90(q, J= 1.2Hz; 1H, 2-H), 6.11(br.s; 1H, 4-H), 6.14(d, J= 5.8Hz; 1H, 7-H), 6.27(ddd, J= 11.1, 6.0, 0.6Hz; 1H, 8-H), 6.38(dd, J= 11.1, 6.0Hz; 1H, 9-H).

7c: δ= 1.74(s; 6H, 5/10-Me), 1.99(d, J= 1.4Hz; 6H, 1/6-Me), 6.13(m; 2H, 2/7-H), 6.30(m; 4H, 3/4/8/9-H).

7d: δ= 1.73(s; 3H, 1-Me), 1.99(d, J= 0.9Hz; 3H, 10-Me), 5.44(br.d, J= 5.9Hz; 1H, 2-H), 5.66 (d, J= 6.0Hz; 1H, 5-H), 5.86(d, J= 10.9Hz; 1H, 6-H), 5.94-6.40(m; 5H, 3/4/7/8/9-H).

10: δ= 2.10(d, J= 0.5Hz; 6H, 1/6-Me), 5.64(d, J= 6.3Hz; 2H, 5/10-H), 5.99(br.d, J= 6.3Hz; 2H, 2/7-H), 6.12(dd, J= 11.1, 6.3Hz; 2H, 3/8-H), 6.32(dd, J= 11.1, 6.3Hz; 2H, 4/9-H).

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