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SYNTHESIS AND DYNAMIC PROPERTIES OF 1,2,5,6,8,10-HEXAMETHYL-HEPTALENE

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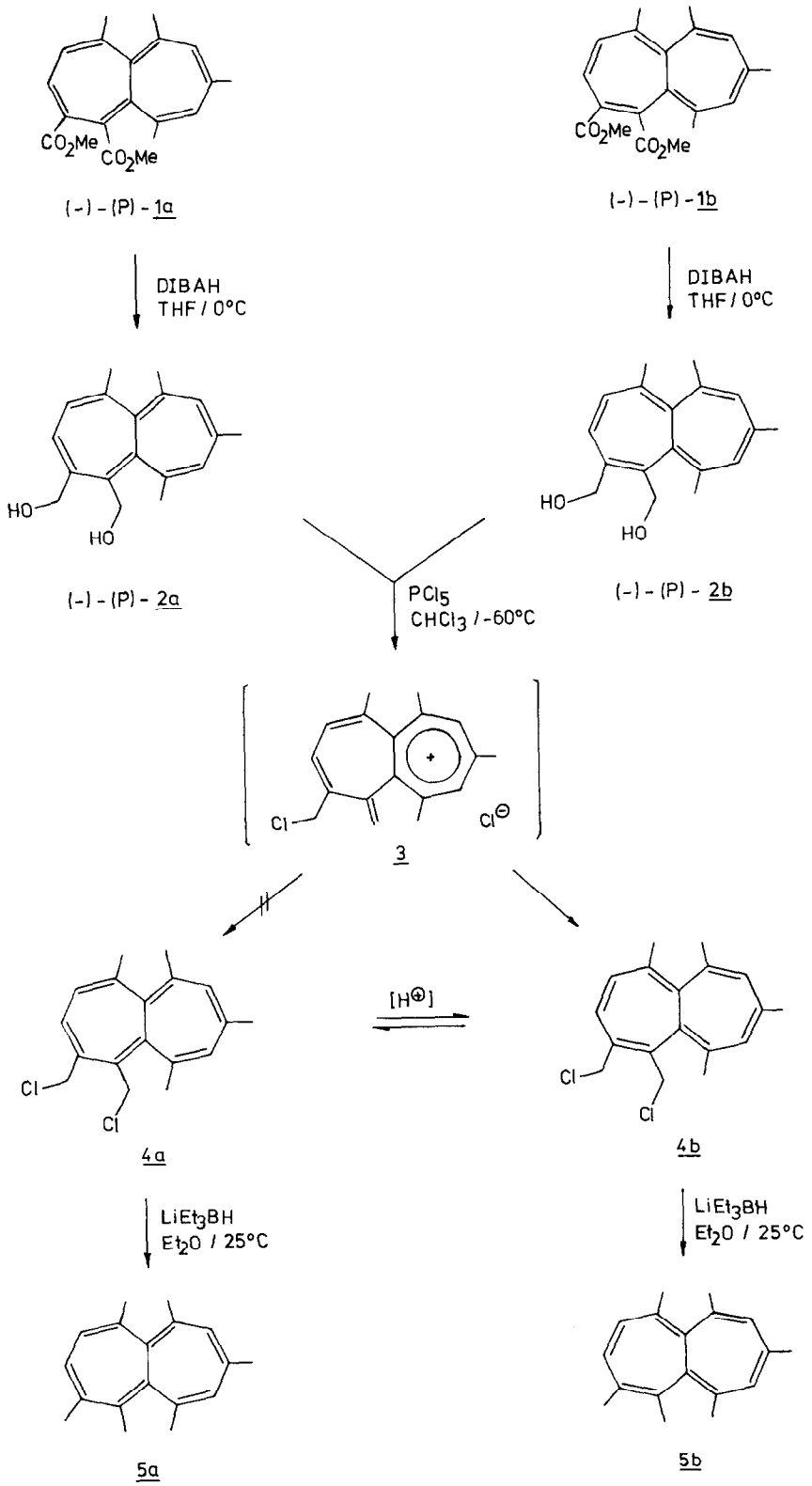
Summary: The optically active bond shift isomers 5a and 5b of the title compound were synthesized and the kinetic parameters of bond shifting and ring inversion determined.

The determination of the kinetic parameters for both dynamic processes - bond shifting (BS) and ring inversion (RI) - of dimethyl 5,6,8,10-tetramethyl-1,2-heptalenedicarboxylate (1) revealed a higher activation enthalpy for RI ($\Delta H^{\neq}_{25°C}$= 28.3 kcal·mol^{-1}) than für BS ($\Delta H^{\neq}_{25°C}$= 22.8/25.7 kcal·mol^{-1}).[1] These results are not in accord with planar transition states for both processes as assumed for the corresponding processes of substituted cyclooctatetraenes.[2] On the contrary, for the bond shift with retention of configuration a helical chiral delocalized transiton state must be assumed. In order to obtain information about the electronic effect of the carboxylate groups on the dynamic behavior of the heptalene system, we synthesized the two optically active bond shift isomers 5a and 5b of the so far unknown 1,2,5,6,8,10-hexamethylheptalene and determined the kinetic data for the BS and RI of this 12π-electron system.[3]

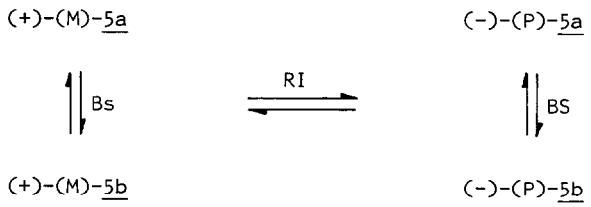
Reduction of the enantiomerically pure dimethyl 5,6,8,10-tetramethyl-1,2-heptalenedicarboxylates ((-)-(P)-1a) and ((-)-(P)-1b)[1,4] with diisobutylaluminium hydride affords 85% of the 1,2-bis(hydroxymethyl)-5,6,8,10-tetramethylheptalenes ((-)-(P)-2a) (m.p. 150-151°C)[4a] and ((-)-(P)-2b) (m.p. 135-136°C) as stable yellow crystals with an enantiomeric purity greater than 98%.[5]

Reaction of both pure bond shift isomers 2a and 2b with phosphorus pentachloride at -60°C yields selectively 78% of the bond shift isomer 4b of the


CO2Me
CO2Me
(-) - (P) - 1a
(-) - (P) - 1b
DIBAH
THF / 0°C
DIBAH
THF / 0°C
HO
HO
(-) - (P) - 2a
(-) - (P) - 2b
PCl5
CHCl3 / -60°C
Cl
Cl⊖
3
[H⊕]
Cl
Cl
4a
4b
LiEt3BH
Et2O / 25°C
LiEt3BH
Et2O / 25°C
5a
5b

1,2-bis(chloromethyl)-5,6,8,10-tetramethylheptalene, which attains acid-catalyzed equilibrium with the bond shift isomer 4a. The formation of 4 is accompanied by nearly complete racemization. This can be explained with the formation of an almost planar tropylium cation moiety in the intermediate 3. The reduction of 4a (yellow plates, m.p. 135-136°C) and 4b (yellow needles, m.p. 128-129°C), separated by crystallization, with lithium triethylborohydride yields 86 and 47% of the bond shift isomers 5a (yellow crystals, m.p. 93-95°C) and 5b (yellow crystals, m.p. 86-87°C) of the title compound as thermally stable yellow crystals.

The activation enthalpy for the bond shift, starting from 5a, was determined by ^{1}H-NMR-spectroscopy in [D_{14}]-diglyme between 70 and 95°C to $\Delta H^{\neq}_{25°C}$= 26.7±1.2 kcal·mol^{-1} ($\Delta S^{\neq}_{25°C}$= -4.4±3.3 eu). As the equilibrium ratio of the bond shift isomers 5a and 5b at these temperatures is about 2:3, the activation parameters for the reverse isomerization should differ only slightly from these values.



The rates of racemization were established on the basis of the decrease in optical rotation of solutions of mixtures of optically active (ee ~ 5%) heptalenes 5a and 5b in diglyme at 170 to 190°C. This affords an activation enthalpy for the ring inversion of $\Delta H^{\neq}_{25°C}$= 36.7±2.1 kcal·mol^{-1} ($\Delta S^{\neq}_{25°C}$= 1.9± 4.6 eu).

These findings let assume that the ester groups in 1 do not cause a pronounced electronic effect on the dynamic process of heptalenes. The differences of the activation barriers for BS and RI between 2 and 5 can rather be explained by a stronger steric interaction of the spherical methyl groups compared with that of an ester with a methyl group in the peri-position.

Tab. 1: Spectroscopic data of compounds 2, 4, and 5[6]

2a: ^{1}H NMR: δ= 1.72(s; 3H, 6-Me), 1.99(2s; 3H each, 5/8-Me), 2.10(d, J=1.3Hz; 3H, 10-Me), 2.85 (br.s; 2H, 2OH), 4.28, 4.39(2d, J= 12.6Hz; 1H each, -CH_2O-), 4.31(s; 2H, -CH_2O-), 6.00(q,

J= 1.0Hz; 1H, 9-H), 6.08(br.s; 1H, 7-H), 6.14(dq, J= 5.9, 1.4Hz; 1H, 4-H), 6.51(d, J=5.9Hz; 1H, 3-H); UV(dioxane): λ_{max}(lgε)= 248sh (4.33), 254(4.37), 3.00sh(3.53)nm; (-)-(P)-2a: $[\alpha]_{546}^{20}$= -1270 (c=0.993, $CHCl_3$).

2b: ^{1}H NMR: δ= 1.65(s; 3H, 10-Me), 1.76(s; 3H, 5-Me), 1.99(d, J=1.2Hz; 3H, 8-Me), 2.01(d, J= 1.3Hz; 3H, 6-Me), 1.90-2.30(br.s; 2H, 20H); 4.09, 4.59(2d, J=12.9Hz; 1H each, $-CH_2O-$), 4.28, 4.50(2d, J=12.1Hz; 1H each, $-CH_2O-$), 6.01(q, J=1.2Hz; 1H, 7-H), 6.10(br.s; 1H, 9-H), 6.40(s; 2H, 3/4-H); UV(dioxane): λ_{max}(lgε)= 257(4.31), 300sh(3.53)nm;(-)-(P)-2b: $[\alpha]_{546}^{20}$= -1420 (c= 0.976, $CHCl_3$).

4a: ^{1}H NMR: δ= 1.73(s; 3H, 6-Me); 1.97(d, J= 1.0Hz; 3H, 5-Me), 2.00(d, J= 1.2Hz; 3H, 8-Me), 2.12 (d, J= 1.3Hz; 3H, 10-Me), 4.13, 4.70(2d, J= 11.8Hz; 1H each, $-CH_2Cl$), 4.30, 4.37(2d, J= 12.1Hz; 1H each, $-CH_2Cl$), 6.03(q, J= 1.0Hz; 1H, 9-H), 6.10(dq, J=6.0, 1.0Hz; 1H, 4-H), 6.11 (q, J= 1.1Hz; 1H, 7-H), 6.52(d, J= 6.0Hz; 1H, 3-H); UV(dioxane): λ_{max}(lgε)= 246sh (4.26), 257(4.32), 300sh(3.55)nm.

4b: ^{1}H NMR: δ= 1.67(s; 3H, 10-Me), 1.74(s; 3H, 5-Me), 2.00(d, J= 1.2Hz; 3H, 6-Me), 2.07(d, J= 1.3Hz; 3H, 8-Me), 3.98, 4.57(2d, J= 11.2Hz; 1H each, $-CH_2Cl$), 4.19, 4.44(2d, J= 11.6Hz; 1H each, $-CH_2Cl$), 6.02(q, J= 1.2Hz; 1H, 7-H), 6.10(br.s; 1H, 9-H), 6.39(s; 2H, 3/4-H); UV (n-hexane): λ_{max}(lgε)= 211(4.34), 247sh(4.21), 263(4.33), 305sh(3.53), 364sh(2.78)nm.

5a: ^{1}H NMR: δ= 1.71, 1.73(2s; 3H each, 1/6-Me), 1.95(d, J= 0.4Hz; 3H, 2-Me), 1.97(2s; 3H each, 5/10-Me), 1.99(d, J= 1.2Hz; 3H, 8-Me), 5.97(br.s; 1H, 9-H), 6.01(d, J= 6.1Hz; 1H, 4-H), 6.07 (br.s; 1H, 7-H); 6.17(d, J= 6.1Hz; 1H, 3-H); UV(n-hexane): λ_{max}(lgε)= 252(4.37, 297sh(3.49)nm.

5b: ^{1}H NMR: δ= 1.67, 1.73(2s; 3H each, 5/10-Me), 1.88(d, J= 0.5Hz; 3H, 1-Me), 1.90(d, J= 0.8Hz; 3H, 2-Me), 1.97(d, J= 1.3Hz; 3H, 8-Me), 1.98(d, J=1.3Hz; 3H, 6-Me), 5.98(br.s; 1H, 7-H), 6.10(br.s; 1H, 9-H); 6.16(d, J=11.6Hz; 1H, 3-H), 6.27(d, J= 11.6Hz; 1H, 5-H); UV(n-hexane): λ_{max}(lgε)= 253(4.37), 300 sh(3.54)nm.

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5. Determined by ^{1}H NMR spectroscopic measurement with the chiral shift reagent tris[3-(hepta-fluoropropylhydroxymethylene)-d-camphorato]-europium(III) ($Eu(hfc)_3$).
6. NMR spectra were recorded with a Bruker NMR spectrometer WM 300 in $CDCl_3$ with tetramethylsilane as internal standard. UV spectra were recorded with a Beckman spectrophotometer UV 5240. All compounds gave correct elemental analyses.

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