SIGMATROPIC ISOMERIZATION OF TETRAPHENYLCYCLOPENTADIENES: REACTION MECHANISM AND QUANTUM CHEMICAL TREATMENT

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Thermal isomerizations of 2,3,5,5-tetraphenylcyclopenta-1,3-diene (*Ia*) or 1,2,4,5-tetraphenylcyclopenta-1,3-diene (*IIa*) in melts lead to identical equilibrium mixtures of hydrocarbon *IIa* with prevailing 1,2,3,4-tetraphenylcyclopenta-1,3-diene (*IIIa*). The isomerization of bis-tert-butyl cyclopentadienes *Ib* or *Ic* produces an equilibrium mixture with preponderant 1,2,3,4-tetrasubstituted cyclopentadienes *IIIb, IIIc* besides minority isomers *IIb, IIc*. On the contrary, the 1,2,4,5-tetrasubstituted phenanthrene hydrocarbon *IXa* having forced coplanarity of both benzene rings only partially isomerizes to *IXb*. Equilibrium constants of the isomerization *IIa* $\rightleftharpoons$ *IIIa* in diphenyl ether at 323 to 433 K were measured (K = 5.8 – 2.3). Relative stability of hydrocarbons *Ia, IIa, IIIa,* and *VIIa* is interpreted on the basis of quantum chemical AM1 calculations. The time course of isomerization of the hydrocarbon *IIc* allowed us to propose two reaction mechanisms based on the [1,3]- and [1,5]-sigmatropic steps. The preparation of 2,3,5,5-tetrasubstituted cyclopentadienes *Ia* – *Ic* by dehydration of *cis*-1,2-diols *IVa* – *IVc* is described.

Intramolecular sigmatropic rearrangements of cyclopentadiene skeletons are among frequently observed isomerizations[1 – 4]. Thermal [1,5]-sigmatropic rearrangement of an aryl group was in the cyclopentadiene series described with (hydroxy)-arylcyclopentadienes[5,6] and their salts[5,7,8]. According to our knowledge, the analogous thermal changes of hydrocarbons of type *I* and *II* are restricted to alkyl derivatives only[1,2]. The isomerizations of type *I* phenyl derivatives were achieved only photochemically[9,10]. Di-π-methane rearrangement accompanied by the migration of one phenyl group was observed in those cases. This communication describes the results of thermal isomerization of 2,3,5,5- and 1,2,4,5-tetraarylcyclopentadienes *Ia* – *Ic, IIa, IIb,* and *IXa* in the liquid phase at 160, 210, and 225 °C (with *IIa* also in diphenyl ether solutions). Expe-

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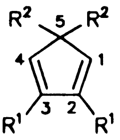
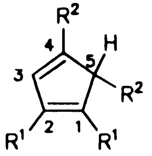
rimental observations are confronted with the results of semiempirical AM1 calculations for the simplest isomers *Ia*, *IIa*, *IIIa*, and *VIIa*.

The starting 2,3,5,5-tetraarylcyclopenta-1,3-dienes *Ia* – *Ic* were prepared by dehydration of *cis*-1,2,4,4-tetraarylcyclopentane-1,2-diols *IVa* – *IVc* obtained by a pinacol reaction of the corresponding 1,3,3,5-tetraarylpentane-1,5-diones *Va* – *Vc*. Tetraarylcyclopentadienes *IIa* – *IIc* have been so far prepared[10] by photochemical isomer-



I



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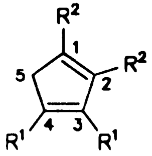

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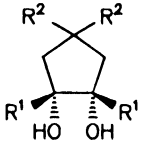

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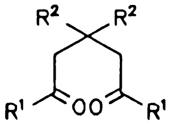

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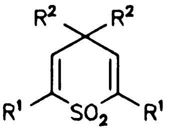
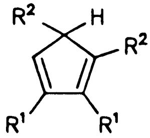
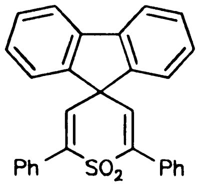


VI

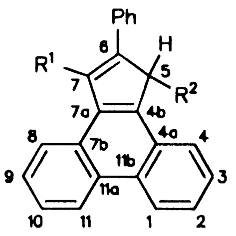


VII

In formulae *I*–*VII*: **a**, $R^1 = R^2 = Ph$
b, $R^1 = 4\text{-}(t\text{-}Bu)C_6H_4$; $R^2 = Ph$
c, $R^1 = Ph$; $R^2 = 4\text{-}(t\text{-}Bu)C_6H_4$



VIII



IXa, $R^1 = H$; $R^2 = Ph$
IXb, $R^1 = Ph$; $R^2 = H$

ization of cyclopentadienes *Ia* – *Ic* only, or by photochemical degradation of the corresponding 2,4,4,6-tetraaryl-4*H*-thiopyran-1,1-dioxides *VIa*, *VIb*. Analogously was obtained[10] the phenanthrene derivative *IXa* from the sulfone *VIII*.

CALCULATIONS

Quantum chemical calculations were performed by a standard program[11] for the AM1 method. Corresponding MO models were first optimized with respect to all geometrical degrees of freedom. For molecular geometries of *Ia, IIa, IIIa,* and *VIIa* obtained in this way, the heats of formation ΔH_{298} 653.4, 606.8, 591.7, and 615.5 kJ mol^{-1}, respectively, were then calculated.

EXPERIMENTAL

Melting points were determined on a Boetius apparatus and are uncorrected. NMR spectra of hydrocarbons *Ia, IIIa, IIIc,* and *IXb* were measured on a Varian VXR-400 instrument (399.95 MHz for ^{1}H, 100.577 MHz for ^{13}C) with digital resolution of 0.02 Hz. All other compounds were measured on a Bruker AM 400 spectrometer (400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C, digital resolution 0.184 Hz). All measurements were performed at 298 K in $CDCl_3$ solutions containing TMS as an internal standard. Chemical shifts are given in the δ-scale. Infrared spectra were registered on a Perkin–Elmer 325 spectrometer. Reaction mixtures were analyzed by HPLC on a Separon^{TM} SGX C18 column (3 x 150 mm, particle size 5 μm, Tessek, Czech Republic) in the system methanol–water 9 : 1 (v/v). Preparation of hydrocarbons *IIa* – *IIc* and *IXa* was described elsewhere[10].

2,3,5,5-Tetraphenylcyclopenta-1,3-diene (*Ia*)

Phosphorus oxychloride (2.7 ml) was added dropwise under nitrogen atmosphere to the cooled solution of the diol[12] *IVa* (3.9 mmol) in dry pyridine (12 ml). The reaction mixture was heated to 130 °C for 1 h and on cooling it was poured onto ice (100 g) in saturated aqueous NH_4Cl (200 ml). The resulting emulsion was extracted with $CHCl_3$, combined organic layers were washed with $NaHCO_3$ solution, water, and dried over $MgSO_4$. Solvents were removed under reduced pressure and the residue was subjected to column chromatography on silica gel (benzene–heptane 1 : 1). Compound *Ia* (0.69 g, 48%), m.p. 135 – 137 °C (benzene–EtOH) was obtained. For $C_{29}H_{22}$ (370.5) calculated: 94.02% C, 5.98% H; found: 93.93% C, 5.97% H. IR spectrum: 1 597, 1 572 cm^{-1} (C=C–C=C). ^{1}H NMR spectrum: 7.050 s, 2 H (H-1, H-4); 7.306 – 7.349 m, 12 H; 7.380 m, 4 H; 7.477 m, 4 H (Ph). ^{13}C NMR spectrum: 66.30 s (C-5); 126.68 d (*p*: Ph5); 127.24 d (*p*: Ph2,3); 127.87 d and 127.91 d (*o*: Ph5 or *o*: Ph2,3); 128.27 d and 128.37 d (*m*: Ph5 or *m*: Ph2,3); 135.82 s (*i*: Ph2,3); 142.41 s (C-2, C-3); 142.65 d (C-1, C-4); 144.22 s (*i*: Ph5).

5,5-Diphenyl-2,3-bis(4-tert-butylphenyl)cyclopenta-1,3-diene (*Ib*)

The procedure described above was applied to diol *IVb* and gave *Ib* (1.10 g, 59%), m.p. 205 – 206 °C (benzene–EtOH). For $C_{37}H_{38}$ (482.7) calculated: 92.06% C, 7.94% H; found: 92.33% C, 8.04% H. IR spectrum: 1 600 cm^{-1} (C=C–C=C). ^{1}H NMR spectrum: 1.31 s, 18 H (t-Bu); 6.89 s, 2 H (H-1, H-4); 7.17 m, 4 H (*m:* Ph2,3); 7.20 – 7.25 m, 6 H (*m,p:* Ph5,5); 7.27 m, 4 H (*o:* Ph2,3); 7.34 m, 4 H (*o:* Ph5,5). ^{13}C NMR spectrum: 31.36 (Me); 34.54 (CMe_3); 66.05 (C-5); 124.76 (*m:* Ph2,3); 126.54 (*p*: Ph5,5); 127.88 (*o:* Ph2,3 and *o:* Ph5,5); 128.28 (*m:* Ph5,5); 133.00 (*i:* Ph2,3); 142.31 (C-1, C-4); 142.62 (C-2, C-4); 143.99 (*i:* Ph5,5); 150.13 (*p:* Ph2,3).

2,3-Diphenyl-5,5-bis(4-tert-butylphenyl)cyclopenta-1,3-diene (*Ic*)

Analogous procedure to that used for *Ia*, starting from diol *IVc* gave *Ic* (1.20 g, 64%), m.p. 200 – 201 °C (benzene–EtOH). For $C_{37}H_{38}$ (482.7) calculated: 92.06% C, 7.94% H; found: 91.95% C, 8.14% H. IR spectrum: 1 600 and 1 576 cm^{-1}. ^{1}H NMR spectrum: 1.30 s, 18 H (t-Bu); 6.94 s, 2 H (H-1, H-4); 7.18 – 7.24 m, 10 H (Ph2,3); 7.26 – 7.32 m, 8 H (Ph5,5). ^{13}C NMR spectrum: 31.38 (Me); 34.41 (CMe_3); 65.52 (C-5); 125.20 (*m:* Ph5,5); 127.10 (*p:* Ph2,3); 127.52 (*o:* Ph5,5); 127.86 (*o:* Ph2,3); 128.29 (*m:* Ph2,3); 136.03 (*i:* Ph2,3); 139.8 (*i:* Ph5,5); 143.06 (C-1, C-4); 143.81 (C-2, C-3); 149.35 (*p:* Ph5,5).

cis-4,4-Diphenyl-1,2-bis(4-tert-butylphenyl)cyclopentane-1,2-diol (*IVb*)

Reaction of dione *Vb* (4.2 g) with Mg (1.2 g) activated by iodine (4.1 g) was performed as described[12] for the preparation of the diol *IVa*. Chromatography of the crude reaction product on a silica gel column (40/100 mm, benzene–heptane) yielded *IVb* (3.10 g, 73%), m.p. 105 – 106 °C (aqueous MeOH). For $C_{37}H_{42}O_2$ (518.7) calculated: 85.67% C, 8.17% H; found: 85.44% C, 8.38% H. IR spectrum: 3 594 and 3 525 cm^{-1} (OH). ^{1}H NMR spectrum: 1.17 s, 18 H (t-Bu); 3.15 s, 2 H (OH); 3.34 and 3.55 AB system, 4 H (H-3 and H-5, ^2J = 14.7 Hz); 6.86 m, 4 H (*o:* Ph1,2); 6.94 m, 4 H (*m:* Ph1,2); 7.12 m, 1 H and 7.18 m, 1 H (*p:* Ph4,4); 7.29 m, 2 H and 7.32 m, 2 H (*m:* Ph4,4); 7.44 m, 2 H and 7.60 m, 2 H (*o:* Ph4,4). ^{13}C NMR spectrum: 31.22 (Me); 34.15 (CMe_3); 49.82 (C-3, C-5); 51.45 (C-4); 85.72 (C-1, C-2); 123.82 (*m:* PH1,2); 125.76 (*p:* Ph4,4); 125.86 (*o:* Ph1,2); 126.36 and 126.41 (*o:* Ph4,4); 128.61 and 128.64 (*m:* Ph4,4); 139.37 (*i:* Ph1,2); 149.60 (*p:* Ph1,2); 150.05 and 150.87 (*i:* Ph4,4).

cis-1,2-Diphenyl-4,4-bis(4-tert-butylphenyl)cyclopentane-1,2-diol (*IVc*)

Reaction of dione *Vc* (3.08 g) with Mg (0.87 g) and I_2 (3.0 g) carried out as already described provided the crude product. Its recrystallization from the mixture MeOH–benzene gave *IVc* (2.15 g, 70%), m.p. 110 – 112 °C. For $C_{37}H_{42}O_2$ (518.7) calculated: 85.67% C, 8.17% H; found: 85.31% C, 8.19% H. IR spectrum: 3 595 and 3 525 cm^{-1} (OH). ^{1}H NMR spectrum: 1.27 s, 9 H (t-Bu); 1.31 s, 9 H (t-Bu); 3.26 s, 2 H (OH); 3.42 and 3.49 AB system, 4 H (H-3, H-5, ^2J = 14.7 Hz); 6.92 – 7.06 m, 10 H (Ph1,2); 7.30 – 7.39 m, 6 H (*o,m:* Ph4,4); 7.56 m, 2 H (*o:* Ph4,4). ^{13}C NMR spectrum: 31.30 and 31.36 (Me); 34.28 and 34.32 (CMe_3); 50.41 (C-3, C-5); 50.58 (C-4); 85.88 (C-1, C-2); 125.49, 125.83, 125.96, and 126.07 (*o,m:* Ph4,4); 126.36 (*o:* Ph1,2); 126.70 (*p:* Ph1,2); 127.13 (*m:* Ph1,2); 142.41 (*i:* Ph1,2); 146.28 and 147.50 (*i:* Ph4,4); 148.41 and 148.78 (*p:* Ph4,4).

3,3-Diphenyl-1,5-bis(4-tert-butylphenyl)pentane-1,5-dione (*Vb*)

Reaction of 4-tert-butylacetophenone (0.1 mol), benzophenone (0.05 mol), and $NaNH_2$ (0.1 mol) in ether carried out as described[13] for dione *Va* gave dione *Vb*, m.p. 192 – 193 °C (heptane–benzene) in 31% yield. For $C_{37}H_{40}O_2$ (516.7) calculated: 86.05% C, 7.81% H; found: 86.37% C, 8.06% H. IR spectrum: 1 683 cm^{-1} (C=O). ^{1}H NMR spectrum: 1.29 s, 18 H (t-Bu); 4.38 s, 4 H (CH_2); 7.13 m, 2 H (*p:* Ph3,3); 7.20 – 7.30 m, 8 H (*o,m:* Ph3,3); 7.36 m, 4 H (*m:* Ph1,5); 7.78 m, 4 H (*o:* Ph1,5). ^{13}C NMR spectrum: 31.06 (Me); 35.00 (CMe_3); 44.95 (C-2, C-4); 47.23 (C-3); 125.25 (*m:* Ph1,5); 125.97 (*p:* Ph3,3); 127.52 (*o:* Ph3,3); 127.90 (*o:* Ph1,5); 128.01 (*m:* Ph3,3); 135.54 (*i:* Ph1,5); 148.14 (*i:* Ph3,3); 156.27 (*p:* Ph1,5); 198.61 (C-1, C-5).

1,5-Diphenyl-3,3-bis(4-tert-butylphenyl)pentane-1,5-dione (*Vc*)

Reaction of acetophenone, 4,4'-di-tert-butylbenzophenone, and $NaNH_2$ performed as in the preceding case gave *Vc* in 18% yield, m.p. 203 – 204 °C (EtOH–benzene). For $C_{37}H_{40}O_2$ (516.7) calculated: 86.05% C, 7.81% H; found: 86.03% C, 7.77% H. IR spectrum: 1 687 cm^{-1} (C=O). ^{1}H NMR spectrum: 1.24 s, 18 H

(Me); 4.32 s, 4 H (CH$_2$); 7.15 m, 4 H (*m:* Ph3,3); 7.19 m, 4 H (*o*: Ph3,3); 7.32 m, 4 H (*m:* Ph1,5); 7.43 m, 2 H (*p:* Ph1,5); 7.77 m, 4 H (*o:* Ph1,5). ^{13}C NMR spectrum: 31.29 (Me); 34.22 (CMe$_3$); 45.17 (C-2); 47.13 (C-2, C-4); 124.83 (*m:* Ph3,3); 127.19 (*o:* Ph3, 3); 127.91 (*o:* Ph1); 128.19 (*m:* Ph1,5); 132.43 (*p:* Ph1,5); 138.16 (*i:* Ph1,5); 144.59 (*i:* Ph3,3); 148.67 (*p:* Ph3,3); 198.61 (C-1, C-5).

Isomerization of Hydrocarbons *Ia – Ic, IIa, IIb,* and *IXa* in the Melt

General procedure. Starting hydrocarbon was heated above its melting point in the argon atmosphere for 30 min. The reaction mixture was then cooled with crushed ice and the main product was isolated by flash chromatography on a silica gel column (40/100 mm, weight ratio SiO$_2$/mixture 100 : 1). The composition of the equilibrium mixtures is given in Table I.

1,2,3,4-Tetraphenylcyclopenta-1,3-diene (*IIIa*)

Hydrocarbon *IIIa* (180 mg, 60%), m.p. 182 – 183 °C (EtOH, ref.[14] gives m.p. 178.5 – 179.5 °C) was obtained (besides the mixture of *IIa* and *IIIa*) upon chromatography of the isomerized *Ia* (300 mg) in the system benzene–heptane (1 : 9). For C$_{29}$H$_{22}$ (370.5) calculated: 94.01% C, 5.99% H; found: 94.02% C, 6.43% H. ^{1}H NMR spectrum: 4.052 s, 2 H (CH$_2$); 6.998 m, 4 H (*o*: Ph1,4); 7.119 – 7.234 m, 16 H (Ph). ^{13}C NMR spectrum: 45.82 t (C-5); 126.40 d (*p:* Ph2,3); 126.69 d (*p:* Ph1,4); 127.85 d (*o:* Ph2,3); 128.05 d (*m:* Ph2,3); 128.15 d (*m:* Ph1,4); 129.86 d (*o:* Ph1,4); 136.49 s (*i:* Ph2,3); 136.62 s (*i:* Ph1,4); 139.76 s (C-2, C-3); 144.56 s (C-1, C-4). Further, a mixture (10 mg) containing 16% of *IIa* and 74% of *IIIa* was isolated.

1,2-Diphenyl-3,4-bis(4-tert-butylphenyl)cyclopenta-1,3-diene (*IIIc*)

The above described procedure applied to hydrocarbon *Ic* (300 mg) yielded upon chromatography in the system benzene–heptane (15 : 85) pure *IIIc* (162 mg, 54%, m.p. 203 – 204 °C), besides the mixture of isomers *IIb, IIc,* and *IIIc*. For C$_{37}$H$_{38}$ (482.7) calculated: 92.06% C, 7.94% H; found: 91.86% C, 7.89% H. IR spectrum: 1 598 and 1 575 cm^{-1} (C=C–C=C). ^{1}H NMR spectrum: 1.274 s, 9 H (t-Bu); 1.208 s, 9 H (t-Bu); 4.008 s, 2 H (CH$_2$); 6.895 – 6.976 m, 4 H and 7.075 – 7.211 m, 14 H (Ph and C$_6$H$_4$). ^{13}C NMR spectrum: 31.26 (Me); 31.35 (Me); 34.43 (CMe$_3$); 45.64 (C-5); 124.83 (*m*: Ph3); 124.98 (*m*: Ph4); 126.19 (*p*: Ph2); 126.48 (*p*: Ph1); 127.20 (*o*: Ph3); 127.80 (*o*: Ph2); 127.85 (*m*: Ph2); 128.07 (*m*: Ph1); 129.37 (*o:*

TABLE I
Isomerization of tetraarylcyclopenta-1,3-dienes in the melt

Starting compound	Temperature, °C	Equilibrium composition[a], %		
Ia	160	*IIa* (19)	–	*IIIa* (81)[b]
	210	*IIa* (28)	–	*IIIa* (72)
Ib	210	*IIb* (15)	*IIc* (12)	*IIIb* (73)
Ic	210	*IIb* (16)	*IIc* (14)	*IIIc* (70)[b]
IIa	160	*IIa* (16)	–	*IIIa* (84)
	210	*IIa* (29)	–	*IIIa* (71)
IIb	210	*IIb* (14)	*IIc* (11)	*IIIb* (75)
IXa	210	*IXa* (47)	–	*IXb* (53)[b]

[a] Estimated from ^{1}H NMR; [b] isolated isomer, see Experimental.

Ph4); 129.89 (*o*: Ph1); 133.64 (*i*: Ph3); 133.79 (*i*: Ph4); 136.67 (*i*: Ph2); 136.77 (*i*: Ph1); 139.06 (C-3); 139.12 (C-2); 144.02 (C-4); 144.95 (C-1); 149.11 (*p*: Ph3); 149.41 (*p*: Ph4).

6,7-Diphenyl-5*H*-cyclopenta[*l*]phenanthrene (*IXb*)

Hydrocarbon *IXa* (ref.[10]) (300 mg) was treated as described above. Chromatography of the reaction mixture in the system benzene–heptane (20 : 80) gave the isomer *IXb* (57 mg, 19%), m.p. 232 – 233 °C (benzene–EtOH; ref.[15] reports m.p. 183.0 – 183.8 °C). For $C_{29}H_{20}$ (368.5) calculated: 94.53% C, 5.47% H; found: 94.98% C, 5.49% H. IR spectrum: 1 618 and 1 592 cm^{-1} (C=C–C=C). ^1H NMR spectrum: 4.344 s, 2 H (CH_2); 7.164 m, 1 H (*p*: Ph6); 7.204 m, 2 H (*m*: Ph6); 7.216 ddd, 1 H (H-8, *J* = 7.6, 1.3, and 0.9 Hz); 7.277 m, 2 H (*o*: Ph6); 7.456 m, 2 H (*o*: Ph7); 7.471 m, 2 H (*m*: Ph7); 7.483 ddd, 1 H (H-9, *J* = 7.6, 7.0, and 1.4 Hz); 7.509 m, 1 H (*p*: Ph7); 7.526 ddd, 1 H (H-10, *J* = 8.0, 7.0, and 1.3 Hz); 7.601 ddd, 1 H (H-2, *J* = 8.0, 7.0, and 1.5 Hz); 7.645 ddd, 1 H (H-3, *J* = 7.9, 7.0, and 1.4 Hz); 8.124 ddd, 1 H (H-4, *J* = 7.9, 1.5, and 0.9 Hz); 8.713 ddd, 1 H (H-1, *J* = 8.0, 1.4, and 0.9 Hz); 8.740 ddd, 1 H (H-11, *J* = 8.0, 1.4, and 0.9 Hz). ^{13}C NMR spectrum: 40.76 t (C-5); 123.30 d (C-11); 123.36 d (C-1); 123.94 d (C-4); 124.64 d (C-9); 125.33 d (C-10); 125.59 d (C-2); 125.84 d (C-8); 126.62 d (*p*: Ph6); 126.90 d (C-3); 127.64 d (*p*: Ph7); 128.06 d (*o*: Ph6); 128.13 d (*m*: Ph6); 128.45 s, 129.03 s, and 129.11 s (C-4a, C-11a, and C-11b); 129.16 d (*m*: Ph7); 129.83 d (*o*: Ph7); 130.92 s (C-7b?); 136.63 s (C-7); 138.21 s (*i*: Ph7); 139.14 s (*i*: Ph6); 139.35 s (C-7a); 141.78 s (C-6); 142.21 s (C-4b). From the other chromatographic fractions another 56 mg (18%) of the mixture *IXa* and *IXb* (ratio 9 : 1) was isolated.

Isomerization of Hydrocarbon *IIc* in Solution

The solution of hydrocarbon *IIc* (10 mg) in toluene (2 ml) was heated under argon in the dark to 80 °C. Samples (40 μl) were periodically taken out and added to $CHCl_3$ (40 μl) cooled to −60 °C. These solutions were stored at −20 °C and analyzed by HPLC. The measured data were used for plotting the time course of the isomerization (Fig. 1).

Determination of the Equilibrium Constants of the Isomerization *IIa* $\rightleftharpoons$ *IIIa* in Solution

Solutions of hydrocarbon *IIa* (10 mg) in diphenyl ether (1 ml) were kept at temperatures 323, 353, 373, 393, and 433 K within ±0.5 K. Further processing was the same as that already described. Calculated values of the equilibrium constants K were 5.8, 3.9, 3.4, 3.1, and 2.3 (±6 rel.%), respectively.

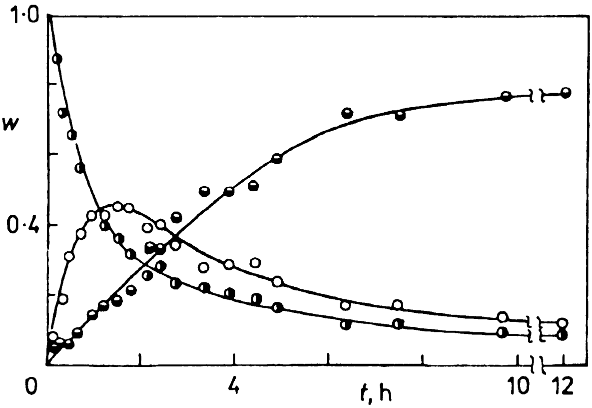


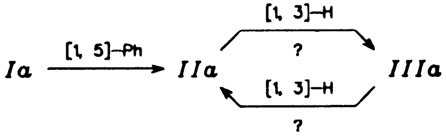
FIG. 1.
Time course of the isomerization of 1,2-diphenyl-4,5-bis(4-tert-butylphenyl)cyclopenta-1,3-diene (*IIc*) in toluene at 80 °C; *w* are the mass fractions of *IIb* (○), *IIc* (◑), and *IIIc* (◒)

RESULTS AND DISCUSSION

Thermal isomerizations of hydrocarbons *Ia* – *Ic*, *IIa*, *IIb*, and *IXa* were always conducted to the establishment of equilibrium at the given temperature (Table I). The course of the isomerization was monitored by HPLC; individual isomers were determined by ^{1}H NMR spectroscopy. Structure verification of components present in the equilibrium mixtures was based on the comparison of the ^{13}C NMR spectra of the mixture with those of pure compounds described earlier[10] or isolated by chromatography (*IIIa*, *IIIc*, and *IXb*). Similarity index[16] was greater than 0.99 in all cases. Standard 2D NMR techniques were used to assign the ^{1}H and ^{13}C NMR signals of the hydrocarbons *IIIa* and *IXb*. Although the assignment of carbons 4a, 7b, 11a, and 11b in the phenanthrene derivative *IXb* was not achieved, the unambiguous assignment of the remaining carbon signals was sufficient to confirm its structure. NMR spectra of cyclopentadienes *Ia* – *Ic* were interpreted by mutual comparison. ^{1}H and ^{13}C NMR spectra of 1,5-diols *IVb*, *IVc*, and 1,5-diones *Vb* and *Vc* were interpreted using the analogy with the spectra[12,17] of compounds *IVa* and *Va*.

Isomerization of Hydrocarbons Ia – Ic

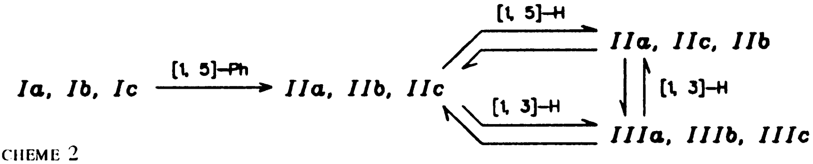
Equilibrium between approximately 20% of *IIa* and 80% of *IIIa* is established upon heating *Ia* at 160 °C for 15 min. Practically the same mixture of both isomers *IIa* and *IIIa* results when hydrocarbon *IIa* is heated (Table I). These findings might be interpreted by primary [1,5]-sigmatropic migration of the 5-phenyl group to the position 1 or 4, followed by a shift of both double bonds between carbons 2,3 and 4,5 in *I* and subsequent [1,3]-sigmatropic equilibrium according to Scheme 1.



SCHEME 1

The equilibrium *IIa* $\rightleftharpoons$ *IIIa* might be also investigated at 50 – 160 °C in diphenyl ether solution. The dependence of the logarithm of the equilibrium constant on the reciprocal temperature is linear in this temperature range (Fig. 2). At the same time, it is evident that *IIIa* is thermodynamically more stable (ΔG_{298} = –5.0 kJ mol^{-1}) in the studied temperature range. Calculated enthalpy term (ΔH = –9.5 kJ mol^{-1}) is markedly greater than the entropy contribution (ΔS = –15 J mol^{-1} K^{-1}). Therefore, it might be expected that the energy preference of hydrocarbon *IIIa* is related to the more effective π-electron delocalization in the molecule.

To obtain a further proof in favour of the isomerization according to Scheme 1, we investigated the behaviour of bis(tert-butyl) derivatives *Ib* and *Ic* at 210 °C. From Table I it is evident that, besides the expected isomers *IIb* and *IIIb* or *IIc* and *IIIc*, some unexpected isomers also appear in the reaction mixtures: *IIc* formed from *Ib* and *IIb* arising from *Ic*. That points out to two reaction pathways of isomerization which in the case of hydrocarbon *Ia* ($R^1 = R^2$) lead to the same product *IIa* and cannot be distinguished by spectral and chromatographic methods. Furthermore, the time course of the isomerization of bis(tert-butyl) derivative *IIc* (Fig. 1) shows that a sequence of two sigmatropic steps takes place $\mathit{IIc} \xrightarrow{[1,5]} \mathit{IIb} \xrightarrow{[1,3]\ ?} \mathit{IIIc}$. Thus, Scheme 1 might be extended to include further isomers of type *II* (Scheme 2).



SCHEME 2

Two other possible products of the alternative [1,5]-sigmatropic rearrangements of bis(tert-butyl)derivatives *Ib* and *Ic*, i.e. isomers *VIIb* and *VIIc*, were not identified in the reaction mixtures. They are either not involved in the reaction pathway at all or the rate of their subsequent isomerization to products *IIIb* and *IIIc*, respectively, is substantially larger then the rate of their formation from the precursors *IIb* and *IIc*.

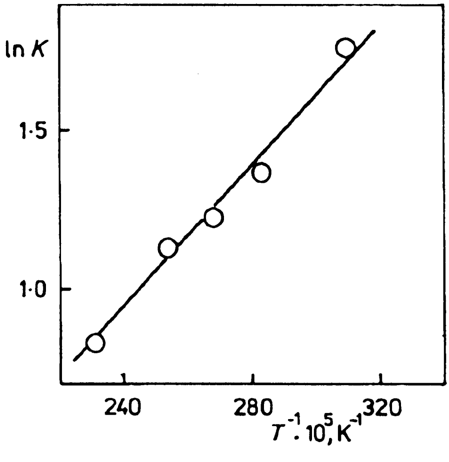


FIG. 2

The dependence of the logarithm of the equilibrium constant K of the isomerization $\mathit{IIa} \rightleftharpoons \mathit{IIIa}$ in diphenyl oxide on the reciprocal temperature T^{-1}

Isomerization of the Hydrocarbon IXa

As a consequence of its phenanthrene skeleton, the molecule of *IXa* has undoubtedly somewhat restricted motion, namely internal rotation. Therefore, it could be expected that the thermal isomerization will be less affected by the effects of the π-electron delocalization in this case since the phenanthrene aromatic system is preserved also in the isomer *IXb*. From Table I it is apparent that hydrocarbon *IXb* indeed does not prevail in the reaction mixture to such an extent as in the case of the analogous products *IIIa* – *IIIc* formed from *Ia* – *Ic* or *IIa*, *IIb*.

Quantum Chemical Interpretation

In order to assess the relative energetic stability of isomeric hydrocarbons *Ia*, *IIa*, *IIIa*, and *VIIa*, their molecular geometry was optimized by semiempirical AM1 method[11]. Comparison of calculated bond lengths and angles for *IIIa* with X-ray results[18] shows that the differences of these characteristics, usually only slightly dependent on the phase state, vary in an acceptable range, –0.026 to +0.016 Å and from –1.7 to +1.3° (Table II). However, the differences in the dihedral angles defining an extent of the deviation of the phenyl groups from the plane of the cyclopentadiene double bonds are larger (–6.1 to +6.8°, Table III) but the experimental data are in this case undoubtedly more affected by the arrangement of the molecules *IIIa* in the crystal lattice. Nevertheless, the AM1 calculations point out to the same asymmetry of molecular geometry of

TABLE II
Calculated and experimental bond lengths (Å) and angles (°) in 1,2,3,4-tetraphenylcyclopenta-1,3-diene molecule (*IIIa*)

Atoms	Bond length, Å		Atoms	Bond angle, °	
	AM1	X-ray[a]		AM1	X-ray[a]
C1–C2	1.370	1.354	C1–C2–C3	109.0	108.9
C2–C3	1.481	1.478	C2–C3–C4	109.1	108.9
C3–C4	1.372	1.372	C3–C4–C5	109.0	108.5
C4–C5	1.510	1.494	C4–C5–C1	103.8	104.3
C5–C1	1.510	1.498	C5–C1–C2	109.1	109.3
C1–Ph	1.445	1.468	C1–C2–Ph	128.0	126.7
C2–Ph	1.454	1.480	C2–C3–Ph	122.6	124.3
C3–Ph	1.465	1.476	C3–C4–Ph	130.2	130.2
C4–Ph	1.457	1.461	C5–C1–Ph	120.9	121.1

[a] See ref.[18].

IIIa associated evidently with internal degenerated conformational equilibria of the cyclopentadiene ring in mobile phases, in accord with the averaged NMR spectra (see Experimental).

The reliability of the mentioned results of molecular geometry of hydrocarbon *IIIa* justifies the assumption of equally physically meaningful results of the AM1 optimization also with other isomeric molecules *Ia*, *IIa*, and *VIIa*. Obtained heats of formation for these molecular geometries (see Calculations) show that the energetical stability of the studied isomers decreases in order *IIIa* > *IIa* > *VIIa* >> *Ia*, i.e. in full agreement with the mentioned information on the equilibrium *IIa* $\rightleftharpoons$ *IIIa* and with thermal [1,5]-sigmatropic rearrangement of the isomer *Ia*. Furthermore, theoretical difference in the above mentioned energies for the pair *IIIa* and *IIa* (-15.1 kJ mol^{-1}) is comparable with the above reported values of experimental enthalpy ($\Delta H = -9.5$ kJ mol^{-1}) for the equilibrium *IIa* $\rightleftharpoons$ *IIIa*. The absence of isomer *VIIa* in the reaction mixture

TABLE III
Calculated and experimental dihedral angles (ϕ, °) between phenyl rings and cyclopenta-1,3-diene double bond planes in *IIIa*

Phenyl position	AM1	X-Ray[a]
1	+32.8	+32.5
2	+75.8	+69.0
3	−75.3	−69.2
4	−28.5	−22.8

[a] See ref.[18].

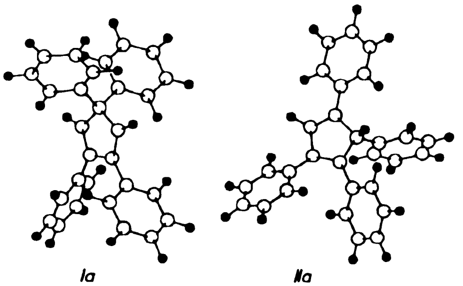

Ia *IIa*

FIG. 3
Molecular models of 2,3,5,5- (*Ia*) and 1,2,4,5-tetraphenylcyclopenta-1,3-diene (*IIa*) obtained by AM1 optimization of their geometry

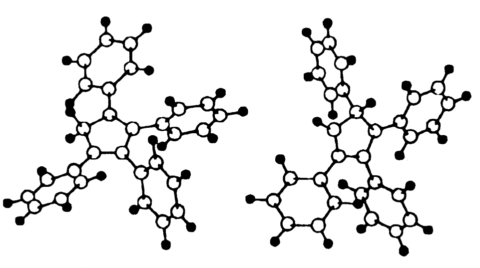

IIIa *VIIa*

FIG. 4
Molecular models of 1,2,3,4- (*IIIa*) and 1,2,3,5-tetraphenylcyclopenta-1,3-diene (*VIIa*) obtained by AM1 optimization of their geometry

(not too much energetically stabilized either) might be explained not only by its thermodynamical but also by its kinetic instability in comparison with observed isomers *IIa* and *IIIa*.

Figures 3 and 4 show the optimized molecular geometries of all four theoretically investigated hydrocarbons. It is conspicuous that particularly with the least stable isomers *Ia* and *VIIa*, the phenyl group conformations unfavourable for π-bond interactions with the multiple bonds of the cyclopentadiene ring are present. Therefore, it might be concluded that an important factor influencing the relative stability of the isomeric molecules *Ia*, *IIa*, *IIIa*, and *VIIa* is indeed the assumed degree of the π-electron delocalization restricted by nonbonding interaction between phenyl groups in the corresponding positions.

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REFERENCES

1. Spangler C. W.: Chem. Rev. *76*, 187 (1976).
2. Mironov V. A., Fedorovich A. D., Akhrem A. A.: Usp. Khim. *50*, 1272 (1981).
3. Childs R. F.: Tetrahedron *38*, 567 (1982).
4. Jutzi P.: Chem. Rev. *86*, 983 (1986).
5. Yousseff A. K., Ogliaruso M. A.: J. Org. Chem. *37*, 2601 (1972).
6. Oldaker G. B., Perfetti T. A., Ogliaruso M. A.: J. Org. Chem. *45*, 3910 (1980).
7. Mason J. G., Yousseff A. K., Ogliaruso M. A.: J. Org. Chem. *40*, 3015 (1975).
8. Battye P. J., Jones D. W.: J. Chem. Soc. Chem. Commun. *1984*, 990.
9. Zimmerman H. E., Kreil D. J.: J. Org. Chem. *47*, 2060 (1982).
10. Šebek P., Sedmera P., Kuthan J.: Collect. Czech. Chem. Commun. *58*, 869 (1993).
11. Dewar M. J. S., Zoerisch E. G., Healy E. F., Stewart J. J. P.: J. Am. Chem. Soc. *107*, 3902 (1985).
12. Šebek P., Novotný J., Kratochvíl B., Schwarz M., Kuthan J.: Collect. Czech. Chem. Commun. *57*, 2383 (1992).
13. Kurfürst A., Zelený J., Schwarz M., Kuthan J.: Chem. Papers *41*, 623 (1987).
14. Schumann H., Janiak C., Zuckerman J. J.: Chem. Ber. *121*, 207 (1988).
15. Toshima N., Moritani I.: Bull. Chem. Soc. Jpn. *40*, 1495 (1967).
16. Bremser W., Klier M., Meyer E.: Org. Magn. Reson. *7*, 97 (1975).
17. Schwarz M., Kuthan J.: Unpublished results.
18. Evrard P. G., Piret P., Germain G., Meerssche M.: Acta Crystallogr., B *27*, 661 (1971).

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