

Parallel Preorganized Polyenes: a New Skeletal Rearrangement

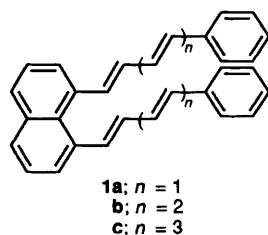
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The synthesis of a homologous series of polyenes by the bis-Wittig-reaction of 1,8-bis(triphenylphosphoniomethyl)naphthalene dibromide **3** with unsaturated aldehydes **2b** and **2c** leads, according to X-ray analyses, to the unexpected chiral hydrocarbons **4b** and **4c** owing to spontaneous intramolecular rearrangement; in contrast the shorter chain bis-diene **1a** can be isolated by reaction of aldehyde **2a** with phosphonium salt **3**.

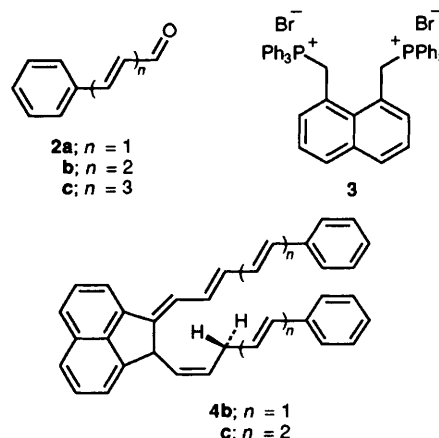
What happens if two polyene chains¹ become squeezed together? Hydrocarbons containing two adjacent olefinic chains which are preorganized essentially parallel to one another might exhibit significant electronic and steric interactions and even chemical reactions (Diels–Alder-, ene-reaction)² owing to their close proximity. Thus, using 1,8-perisubstituted naphthalene³ [distance C(1)–C(8) 2.44 Å]⁴ as a narrow spacer, we intended to synthesize the hitherto unknown homologous series of hydrocarbons **1** with two extended unsaturated chains *via* bis-Wittig reaction of aldehydes **2**⁵ with phosphonium salt **3**.⁶

All Wittig reactions were carried out under identical conditions. A suspension containing phosphonium salt **3** in tetrahydrofuran (THF) was treated with 2.2 equiv. of *n*-butyllithium and subsequently with 2.2 equiv. of aldehyde **2a–c** at room temp. Reaction of cinnamaldehyde (**2a**) with **3** indeed yields the desired product 1,8-bis[4-phenylbuta-1(*E*),3(*E*)-

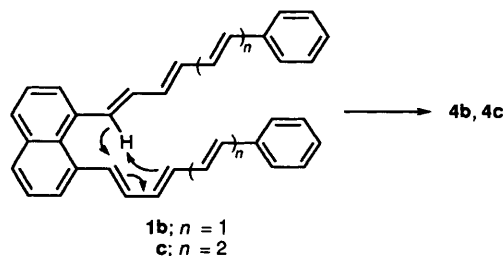


dienyl]naphthalene⁷ (**1a**, yield 25%), which shows the expected signals in the NMR spectra.[†]

However, the analogous reactions of phosphonium salt **3**



[†] 1,8-Bis[4-phenylbuta-1(*E*),3(*E*)-dienyl]naphthalene **1a**; analogous preparation in ref. 7; yield 25% m.p. = 165 °C; ¹³C NMR (125 MHz, CD₂Cl₂): δ = 137.57 (C_q), 163.88 (C_q), 163.51 (CH), 134.92 (C_q), 132.58 (CH), 130.22 (C_q), 129.59 (CH), 129.55 (CH), 128.75 (CH), 128.63 (CH), 127.60 (CH), 126.64 (CH), 126.44 (CH), 125.72 (CH); HRMS calcd. for C₃₀H₂₄ 384.1878; found 384.1872.



with diene **2b** and triene **2c** do not give the anticipated products **1b** and **1c**, instead the unexpected chiral hydrocarbons **4b** (yield 14%) and **4c** (yield 12%) are isolated. The structure of the reaction product **4b** was confirmed by an X-ray diffraction study[‡] which shows two independent molecules with only slightly differing conformations. The molecules contain a five-membered ring and two sp^3 -hybridized C-atoms [C(9) and C(12)] in one chain. This chain is no longer conjugated and is situated above or below the plane of the residual molecular skeleton owing to an asymmetrically substituted C-atom [C(12)].

¹H/¹H 2D-COSY NMR and ¹³C NMR spectra show the expected resonance signals. Comparison of the spectroscopic data supports the analogous structures of hydrocarbons **4c**[§] and **4b**.[¶] In the ¹H NMR spectra the nonequivalent CH₂-protons at C(9) in **4b** absorb at δ 3.40 and 3.57 (AB-system),

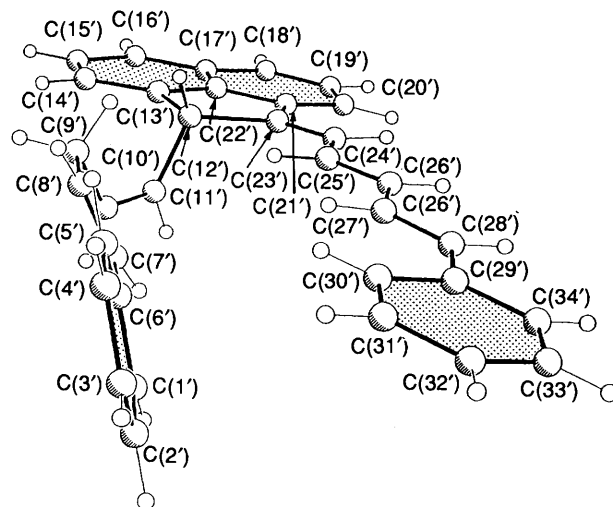


Fig. 1 X-Ray structure of **4b**

in **4c** at δ 3.31 and 3.55, H-C(12) of **4b** at δ 5.32 and the analogous proton of **4c** at δ 5.28; ¹³C NMR signals of the CH₂-group [C(9)] appear for **4b** at δ 31.28, for **4c** at δ 31.07, C(12) of **4b** at δ 46.08 and for the analogous carbon of **4c** at δ 46.05. It is reasonable to assume that the hydrocarbons **1b** and **1c** are intermediates that spontaneously thermally rearrange at room temperature yielding **4b** and **4c** respectively; apparently **1b** and **1c** rapidly rearrange because of the proximity of the two conjugated π -systems. This new carbon skeleton rearrangement resembles transannular reactions, in which nonbonded interactions and migrations take place between non-neighbouring atoms that come sufficiently close together. Such favourable steric factors may facilitate the skeletal rearrangement and hydrogen migration from one chain of **1b** and **1c** to the other.^{||} Both steric and electronic factors may have to be taken into account in order to explain why the shortest chain diolefin **1a** does not rearrange under similar conditions.

The possible rearrangement of isolated hydrocarbon **1a** under more drastic conditions and the separation into enantiomers of the products **4b** and **4c** will be further investigated. Studies of hydrocarbons with two or more adjacent polyene π -systems preorganized parallel or crossed,** which are spaced by 1,8-disubstituted biphenyl-

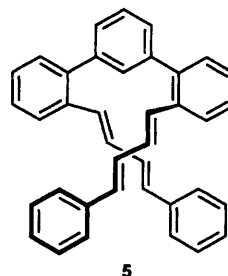
[‡] Crystal data of **4b**: C₃₄H₂₈; $M_r = 436.6$, yellow crystals, $0.20 \times 0.20 \times 0.35$ mm, monoclinic, space group $P2_1/c$ with $a = 33.217(6)$ Å, $b = 5.513(1)$ Å, $c = 27.033(4)$ Å, $\beta = 96.73(2)^\circ$, $U = 4916(1)$ Å³, $Z = 8$, $D_c = 1.180$ mg m⁻³, $\mu(\text{Cu-K}\alpha) = 0.47$ mm⁻¹, $F(000) = 1856$. 7265 symmetry independent reflexions ($4^\circ < 2\theta < 120^\circ$) were measured on an Enraf-Nonius CAD 4 diffractometer ($T = 293$ K); 4315 with $F > 3\sigma(F)$ were used for structure solution (direct methods) and refinements (615 parameters). Non-hydrogen atoms were refined anisotropically, H-atoms localized by difference electron density determination were refined using a rigid model. An empirical absorption correction was applied.⁹ The final value of R was 0.069. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[§] 1-[5-Phenylpenta-2(*E*),4(*E*)-dienylidene]-2-[5-phenylpenta-1(*Z*),-4(*E*)-dienyl]acenaphthene **4b**, yield 14%; m.p. = 153–155 °C; ¹H NMR (500 MHz, CD₂Cl₂): δ = 3.40 (dtt, ² J_{gem} 16.0, ³ J 6.5, ⁴ J 1.5 Hz, 1 H, -CH₂-), 3.57 (dtdd, ² J_{gem} 16.0, ³ J 8.0, ³ J 6.5, ⁴ J 1.5 Hz, 1 H, -CH₂-), 5.32 (d, ³ J 10.0 Hz, 1 H, -CH), 5.51 (tt, ³ J_{cis} 10.0, ⁴ J 1.5 Hz, 1 H, -CH), 5.78 (m, 1 H, -CH), 6.51 (dt, ³ J_{trans} 16.0, ³ J 6.0 Hz, 1 H, -CH), 6.55 (dd, ³ J_{trans} 15.5, ³ J 11.0 Hz, 1 H, -CH), 6.59 (d, ³ J_{trans} 15.5 Hz, 1 H, -CH), 6.67 (d, ³ J_{trans} 16.0 Hz, 1 H, -CH), 6.77 (dd, ³ J_{trans} 15.5, ³ J 11.0 Hz, 1 H, -CH), 6.82 (dd, ³ J_{trans} 15.5, ³ J 11.0 Hz, 1 H, -CH), 7.01 (dd, ³ J 12.0, ⁴ J 2.0 Hz, 1 H, -CH), 7.18–7.27 (m, 7 H, Ar-H), 7.34 (t, ³ J 7.5 Hz, 2 H, Ar-H), 7.47–7.52 (m, 3 H, Ar-H), 7.54 (d, ³ J 7.5 Hz, 1 H, Ar-H), 7.59 (d, ³ J 7.0 Hz, 1 H, Ar-H), 7.65 (t, ³ J 7.5 Hz, 2 H, Ar-H); ¹³C NMR (125 MHz, CD₂Cl₂): δ = 31.28 (-CH₂-), 46.08 (-CRH-), 115.64 (CH), 119.24 (CH), 123.00 (CH), 123.25 (CH), 124.13 (CH), 126.14 (CH), 126.44 (CH), 127.29 (CH), 127.55 (CH), 128.29 (CH), 128.45 (CH), 128.56 (CH), 128.68 (CH), 128.77 (CH), 129.16 (CH), 130.14 (CH), 130.57 (CH), 131.56 (C_q), 131.79 (CH), 133.19 (CH), 134.78 (CH), 137.25 (C_q), 138.63 (C_q), 139.41 (C_q), 141.56 (C_q); HRMS calcd. for C₃₄H₂₈ 436.2191; found 436.2195.

[¶] 1-[7-Phenylhepta-2(*E*),4(*E*),6(*E*)-trienylidene]-2-[7-phenylhepta-1(*Z*),4(*E*),6(*E*)-trienyl]acenaphthene **4c**, yield 12%, m.p. = 198 °C; ¹H NMR (500 MHz, CD₂Cl₂): δ = 3.31 (dtt, ³ J_{gem} 16.5, ³ J 5.5, ⁴ J 1.0 Hz, 1 H, -CH₂-), 3.55 (dm, ³ J_{gem} 16.5 Hz, 1 H, -CH₂-), 5.28 (d, ³ J 10.5 Hz, 1 H, -CRH-), 5.45 (tt, ³ J_{cis} 10.5, ⁴ J 1.5 Hz, 1 H, -CH), 6.12 (dt, ³ J_{trans} 15.5, ³ J 6.0 Hz, 1 H, -CH), 6.44–6.77 (m, 8 H, -CH), 6.95–7.00 (m, 2 H, -CH), 7.11–7.24 (m, 7 H, Ar-H), 7.30 (t, ³ J 7.5 Hz, 2 H, Ar-H), 7.45–7.54 (m, 4 H, Ar-H), 7.58 (d, ³ J 6.5 Hz, 1 H, Ar-H), 7.64 (t, ³ J 7.5 Hz, 2 H, Ar-H); ¹³C NMR (125 MHz, CD₂Cl₂): δ = 31.07 (-CH₂-), 46.05 (-CRH-), 115.64 (CH), 119.25 (CH), 123.00 (CH), 123.34 (CH), 124.11 (CH), 126.14 (CH), 126.30 (CH), 126.39 (CH), 127.49 (CH), 128.29 (CH), 128.47 (CH), 128.65 (CH), 128.81 (CH), 129.02 (CH), 129.25 (CH), 130.18 (CH), 131.03 (CH), 131.20 (CH), 131.65 (CH), 133.04 (CH), 133.16 (CH), 133.79 (CH), 134.24 (CH), 134.72 (CH); HRMS calcd. for C₃₈H₃₂ 488.2504; found 488.2504.

^{||} Provided that a one-step reaction is valid, the following mechanism could represent a possible pathway in particularly explaining the formation of the (*Z*) double bond. Alternatively, multistep reactions including ene- or retro-ene-reactions² could be involved. Deuterium substitution of aldehydes **1b** and **1c** should help in clarifying the detailed mechanism. In any case the formation of the five-membered ring could act as a driving force. In analogy to transannular reactions this reaction could be called a 'trans-chain-rearrangement' with the following characteristic features: C–C bond formation, hydrogen migration, formation of a (*Z*)-double bond and a chiral centre.

** The hydrocarbon 2,2'-bis[4-phenylbuta-1(*E*),3(*E*)-dienyl]-1,1':3',1''-terphenyl (**5**) derived from 1,1':3',1''-terphenyl as an anchor group is stable and did not show thermal or photochemical rearrangement; an X-ray determination of **5** was carried out: N. Korber, E. Schmolke and F. Vögtle, unpublished results.



lene and 2,2'-biphenyl as anchor groups are in progress. We thank Dr R. Hartmann for the NMR measurements and Dipl.-Chem. H.-B. Mekelburger for his assistance in improving the manuscript.

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