1,2-Di(arylmethylidene)cycloalkanes; the Conformation of Non-transoid Conjugated Dienes

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Compounds with 1,4-diarylbuta-1,3-diene chromophores fused exocyclically to five-, six-, and seven-membered saturated rings have been synthesized by the Wittig reaction. *cis,trans*-Equilibria and UV spectra indicate that the diene system is planar (*syn*) when the saturated ring is five-membered, but non-planar (*gauche*) when it is larger.

The *cis,trans*-isomers undergo a thermal cyclization to *cis*-1,2-dihydronaphthalene derivatives.

The strong preference for the *anti* (or transoid) conformation of open-chain conjugated dienes may be understood on the basis that this planar geometry fits both main mesomeric structures, while the non-transoid conformation cannot satisfy at the same time the conflicting requirements of the nonpolar and dipolar mesomeric structures. Thus, the nonpolar structure demands a *gauche* geometry to avoid eclipsing in the central bond, while the dipolar structure fits best a planar *syn* geometry.
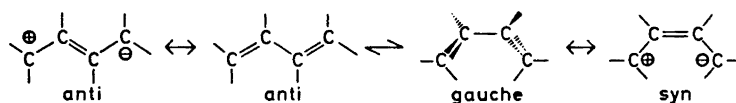
Scheme 1

Unfortunately, it is very difficult to conclude from observed dihedral angles which factor is the most important. Whenever a non-transoid diene (or polyene) chromophore is observed, the same constraints which are necessary to preclude the *anti* conformation (ring structure or steric hindrance) may also prevent the obtention of the intrinsically best non-transoid conformation. The available structural data [1] so often reveal a dihedral angle close to the 60° of a normal *gauche* angle that this can hardly be accidental. Especially Trætteberg's recent data for the three 3,4-dimethylhexa-2,4-diene isomers [2] argue strongly for a *gauche*-preference.

The present approach has been to study diene systems exocyclic to ring systems so as to allow the chromophore more freedom than in endocyclic dienes. Furthermore, when two aryl substituents are present in 1,4-position, *cis-trans* equilibration should be a sensitive probe for planarity, since only the *trans,trans*-isomer (I) can become planar. The *cis,trans*-isomer (II) would require a dihedral angle in the neighbourhood of 60°, and the *cis,cis*-isomer (III) even more.
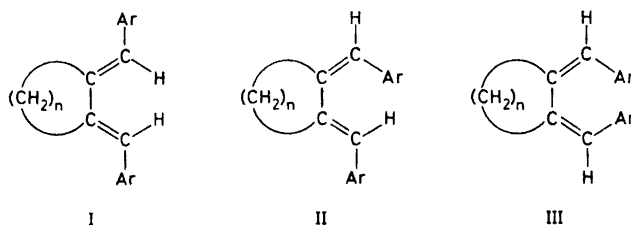
Scheme 2

The compounds which have been synthesized comprise ring sizes from five to seven ($n = 3$, 4, and 5), and the aryl groups are phenyl, 4-bromophenyl, and β-naphthyl.

SYNTHESES

For the syntheses a double Wittig reaction [3] was the obvious choice. Potassium *t*-butoxide in *t*-butyl alcohol proved to be the most suitable base system and was in most cases added to the mixture of the ylide and the cyclic 1,2-diketone. The yields are given in Table 1 together with the properties of the individual isomers. Attempts to prepare compounds with 4-nitrophenyl and 4-biphenylyl substituents failed. Not only the 4-nitrobenzylidenephosphorane,[4] but also the 4-biphenylylmethylidenephosphorane was isolable, and none of them reacted with the diketones. Oxidative coupling [5] of the latter phosphorane to 4,4'-diphenylstilbene occurred on prolonged refluxing in toluene in the presence of cyclohexane-1,2-dione.

As concerns isomer composition, the synthesis gave only one isomer when the ring was five-membered, and two when it was six- and seven-membered. In no case was any additional stereo-isomer formed during subsequent thermal, catalytic, or photochemical equilibration. It was quite straightforward to assign *trans,trans*-configuration (I) to the exclusive isomer of the five-ring compounds and to the higher-melting isomer of the others, based on the intense long-wave absorption band in the UV-spectrum (Table 1 and Figs. 1 and 2) and the simplicity of the NMR-spectrum, notably a single line for the olefinic protons. In the case of 1,2-di(4-bromobenzylidene)cyclohexane, the lower dipole moment of the higher melting isomer (2.1 D against 3.5 D) supported the assignment. The second isomer was first [6] assumed to have the *cis,cis*-configuration (III) because of the accidental coincidence of the NMR-lines for the olefinic protons in both CCl$_4$- and CDCl$_3$-solution. However, the X-ray

Table 1. Data for 1,2-di(arylmethylidene)cycloalkanes (I and II).

Ar	n	Configuration	Yield %	M.p. °C	Cryst. from	Analysis Found C	Analysis Found H	Analysis Calc. C	Analysis Calc. H	UV-absorption (in heptane) λ₁ (nm)	ε	λ₂ (nm)	ε	NMR for olefinic H (δ in CCl₄)	Thermodynamic equilibrium %	Photostationary state %
Phenyl	3	t,t	6	168	CHCl₃	92.30	7.61	92.63	7.37	330	25400	238	11300	6.9	100	100
"	4	t,t	}22	141	Acetone	91.96	7.91	92.26	7.74	286	19000	245	10800	6.6	76	21
"	5	c,t		82	Acetone	91.96	7.84	92.26	7.74	275	10800	240	19300	6.2[b]	24	79
"	5	t,t	}70	48	Hexane	92.08	8.01	91.92	8.08	280	18800	245	13700	6.6	50	16
"	5	c,t		Liq.				91.92	8.08					6.2	50	84
β-Naphthyl	3	t,t	8	216	CHCl₃	92.46	6.27	93.60	6.40	330	40000	273	36000	Insol.	100	d
"	4	t,t	a	188		92.51	6.51	93.29	6.71	312	22000	270	31500	6.9	73	d
"	4	c,t	a	119		92.19	6.28	93.29	6.71	310		273		6.4	27	d
"	5	t,t	18	166	CHCl₃/ethanol 3:1	91.74	7.03	93.00	7.00	310	21500	260	32000	6.9	51	d
"	5	c,t		Liq.				93.00	7.00					6.5	49	d
4-Bromophenyl	4	t,t	}41	128	Ethanol	57.66	4.21	57.44	4.34	297	27000	263	16000	6.6	75	25
"	4	c,t		114	Ethanol	57.60	4.19	57.44	4.34	286	10000	255	27500	6.1[c]	25	75

[a] Prepared by cand. pharm. N. A. Klitgaard.
[b] 6.10 and 6.30 in dimethyl sulfoxide.
[c] 6.15 and 6.20 in CDCl₃.
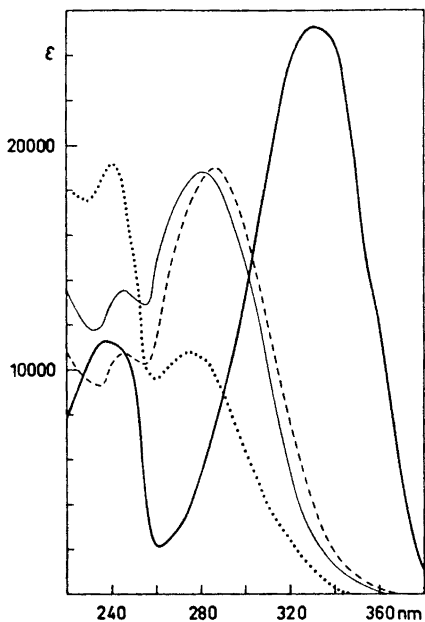[d] Destruction on prolonged UV-irradiation.

Fig. 1. UV absorption spectra in heptane of 1,2-dibenzylidenecycloalkanes (Ar = phenyl). Heavy full curve: I, $n = 3$. Dashed curve: I, $n = 4$. Thin full curve: I, $n = 5$. Dotted curve: II, $n = 4$.
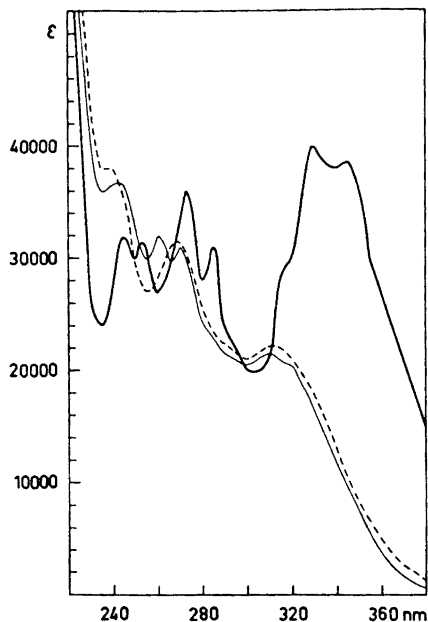
Fig. 2. UV absorption spectra in heptane of 1,2-di(β-naphthylmethylidene)cyclo-alkanes (Ar = β-naphthyl). Heavy full curve: I, $n = 3$. Dashed curve: I, $n = 4$. Thin full curve: I, $n = 5$.

structure of the 1,2-di(4-bromobenzylidene)cyclohexane isomer believed to be *cis,cis* was later determined by Groth,[7] and it revealed the *cis,trans*-configuration. A reexamination of the NMR-spectra in other solvents (dimethyl sulfoxide, benzene) showed in fact a splitting into two olefinic lines.

Surprisingly, in cases where the thermodynamic equilibrium was later shown to contain the *cis,trans*-isomer as a minor constituent, this isomer was nevertheless formed predominantly when the reaction was run quickly. This must be due to some stereospecificity of the last step, since the reaction between cyclohexane-1,2-dione and one mol of the Wittig reagent gave exclusively *trans*-2-benzylidenecyclohexanone, and since the same *cis,trans*-rich
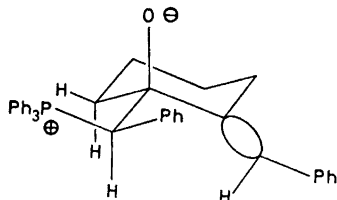

Fig. 3. Proposed favoured conformation of the intermediate betaine in the reaction between benzylidenetriphenylphosphorane and *trans*-2-benzylidenecyclohexanone. Elimination leads to *cis,trans*-1,2-dibenzylidenecyclohexane.

mixture of 1,2-dibenzylidenecyclohexanes was obtained in a one-step reaction from pure *trans*-2-benzylidenecyclohexanone. By considering the conformational situation of the intermediate betaine [3] it is possible to explain simply this stereospecificity (Fig. 3).

ISOMERIZATIONS

The *thermodynamic equilibrium* between the two isomers of the six- and seven-ring compounds could be reached rapidly and cleanly from both sides by irradiation in the presence of iodine. The results (Table 1) show that the six-ring compounds contain about 25 % and the seven-ring compounds as much as 50 % of the *cis,trans*-isomer. On the other hand, the *trans,trans*-isomer of the five-ring compounds undergoes absolutely no change under these conditions, and it seems safe to conclude that there is no other isomer present in the equilibrium.

Ultraviolet irradiation alone produces a *photostationary state* which is by far richest in the *cis,trans*-isomer when the ring is six- and seven-membered and the aryl substituent is phenyl or 4-bromophenyl (Table 1). Again, when the ring is five-membered, the *trans,trans*-isomer remains unaltered. Total destruction takes place with all β-naphthyl compounds under the same conditions.

Heating to 300° converts 1,2-dibenzylidenecyclohexane, the *trans,trans*-isomer *via* the *cis,trans*-isomer of the equilibrium mixture, cleanly to a structurally isomeric compound, shown to be *cis*-1,2-dihydro-1-phenyl-2,3-tetra-methylenenaphthalene (V, $n = 4$). The *cis*-relationship between the hydrogen
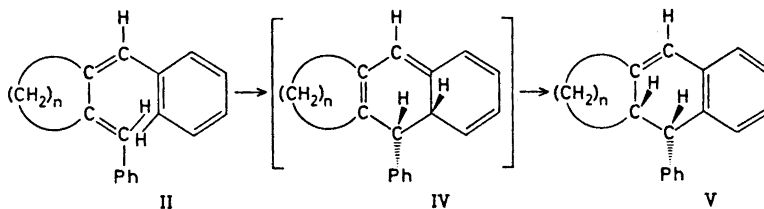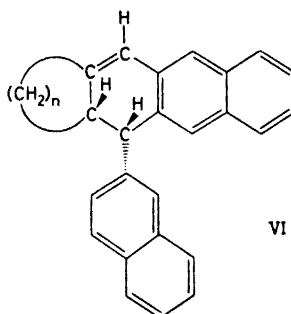

Scheme 3

atoms in 1,2-position was deduced from the value of 8 cps observed for the NMR-coupling constant. The same argument has been used in similar cases.[8] This stereochemistry is to be expected from a disrotatory thermal ring closure [9] to the intermediate (IV) followed by a suprafacial 1,5-hydrogen shift.[9]

1,2-Di(β-naphthylmethylidene)cycloheptane undergoes this kind of cyclization already at 170° to give *cis*-1,2-dihydro-1-β-naphthyl-2,3-pentamethylene-anthracene (VI, $n = 5$).

Analogous reactions occur with the other compounds except of course the cyclopentane derivatives which have no *cis,trans*-isomer in the equilibrium. Only general destruction of these compounds takes place at high temperatures.

Scheme 4

PLANARITY AND ULTRAVIOLET SPECTRA

The fact that the five-ring compounds exist exclusively as the *trans,trans*-isomer, while on the other hand the energy difference between the *cis-trans*- and *trans,trans*-isomer comes out negligibly small for the six- and seven-ring compounds (0.6 kcal/mol and zero, respectively), suggests that the diene chromophore does not seek a compromise between the *syn*- and *gauche*-conformations, but rather makes a choice. This is strongly supported by a comparison of the ultraviolet spectra of the *trans,trans*-isomers (Figs. 1 and 2). A higher wavelength and intensity of the main band characterize the spectra of the five-ring compounds, as compared with the spectra of the six- and seven-ring compounds, which resemble each other strikingly. Furthermore, since the excited state for any conjugated diene most probably has a high degree of double-bond character in the central CC-bond,[10] it will strive towards planarity, and the appearance of better resolved vibrational structure for the five-ring β-naphthyl compound therefore suggests that also the ground state is here planar. Rounded structureless bands, as observed for all six- and seven-ring compounds, are expected for a nonplanar ground state, since the change of shape according to the Franck-Condon principle would lead to co-excitation of many quanta of the low-frequency torsional vibration.

As to the degree of nonplanarity, Groth reports [7] a dihedral angle of 61° for 1,2-di(4-bromobenzylidene)cyclohexane. The similarity of the ultraviolet spectra indicates that this angle is the same also in the seven-membered rings; the equilibrium data suggest perhaps slightly more. Such a dihedral angle between the two exocyclic double bonds might conceivably have been imposed by the rigid cyclohexane chair, but definitely not by the cycloheptane ring which is conformationally flexible [11] and could profitably have concentrated most of its inherent bond eclipsing between the double bonds if planarity had been desirable. We therefore conclude that the 1,4-diarylbuta-1,3-diene chromophore adopts a *gauche*-conformation when allowed sufficient freedom to choose (and when *anti* is impossible), but is forced into planarity by the five-membered ring.

The spectral changes when passing from the *trans,trans-* to the *cis,trans-*isomer in each set (Table 1 and Fig. 1) are close to what one would expect for this kind of geometrical change.[10] For the 1,4-diphenylbuta-1,3-diene molecule itself, dramatic spectral changes occur when the geometry is changed by converting the *trans,trans-*isomer to the *cis,trans-*isomer.[12] The structured intense main band at ~ 330 nm of the planar *trans,trans-*isomer is replaced by a weaker and structureless band at ~ 310 nm for the bent nonplanar *cis,trans-*isomer, and at the same time a "*cis-*peak" absorption grows up at ~ 245 nm, the position for half the chromophore, corresponding to the main band of styrene.[10,13] All our *trans,trans-*1,2-dibenzylidenecycloalkanes, even the planar five-ring compound, have a non-linear chromophore and show therefore a weak *cis-*peak around 240 nm, but the intensity becomes much higher for the more bent chromophore of the *cis,trans-*isomer (Fig. 1). The main band at 280 nm is correspondingly decreased in intensity because the end-to-end distance of the chromophore becomes shorter.[10]

Analogous spectral behaviour is observed (Table 1 and Fig. 2) for the β-naphthyl-substituted compounds, where the *cis-*peak appears at ~ 275 nm, to be compared with the main band of the half-chromophore, β-vinyl-naphthalene, reported at 283 nm.[14]

EXPERIMENTAL

General preparative procedure for 1,2-di(arylmethylidene)cycloalkanes. To a stirred solution of the cycloalkane-1,2-dione (0.1 mol) and the triphenyl(arylmethyl-phosphonium halide (0.2 mol) in *t*-butyl alcohol (200 – 300 ml) was added dropwise over 2 – 3 h a solution of potassium *t*-butoxide (prepared from 0.2 mol of potassium) in *t*-butyl alcohol (200 ml). The mixture was left overnight and then refluxed for 5 h. After cooling, the *t*-butyl alcohol was evaporated at reduced pressure, and the semisolid residue extracted in a Soxhlet with pentane or hexane for several hours. Evaporation of the solution after the extraction gave the desired hydrocarbons contaminated with only little triphenyl-phosphine oxide; this could be removed by washing the solid with some ethanol. Isomer mixtures were fractionated by crystallization. Chemical and physical data for individual compounds are presented in Table 1.

1,2-Di(4-bromobenzylidene)cyclohexane. To a stirred suspension of triphenyl(4-bromo-benzyl)phosphonium bromide (103 g = 0.2 mol) in dry benzene (250 ml) was added over 1½ h a solution of potassium *t*-butoxide (22.4 g = 0.2 mol) in *t*-butyl alcohol (170 ml). To this deep-red solution of the phosphorane was added over 2 ½ h a warm solution of cyclohexane-1,2-dione (10 g = 0.09 mol) in benzene (200 ml). The temperature was then raised to 75° and stirring continued overnight. After evaporation of the solvents, the residue was extracted with pentane in a Soxhlet. Evaporation left a red oil whose NMR-spectrum revealed equal amounts of the two isomers. Dilution with ethanol (10 – 20 ml) precipitated white crystals of the *trans,trans-*isomer, m.p. 128° after recrystallization from ethanol. After standing, the *cis,trans-*isomer crystallized, m.p. 114° after recrystallization from ethanol. The total yield of crystals (pure isomers and isomer mixture) was 16 g (41 %). In addition to the data in Table 1 the bromine analyses were satisfactory.

Attempt to prepare 1,2-di(4-biphenylylmethylidene)cyclohexane. The same procedure as for the previous compound was followed, using now triphenyl(4-biphenylylmethyl)phosphonium bromide, but no trace of the desired product was obtained. Instead, a deep red solid was isolated by recrystallization of the reaction residue. It melted with decomposition at 220°, and was slowly decomposed in air. The mass spectrum showed the P(Ph)$_3$ ion. The NMR-spectrum in C_6D_6 was very complex with only aromatic protons, but simplified on addition of a few drops of trifluoroacetic acid to become identical with the spectrum of the initial phosphonium salt. Clearly, the *phosphorane* had been isolated.

A solution of this phosphorane (6 g = 0.014 mol) and cyclohexane-1,2-dione (0.6 g = 0.0054 mol) in toluene was refluxed for 1 h. After cooling, light-yellow crystals (1.2

g), m.p. 299°, precipitated. This substance was identified as *4,4'-diphenylstilbene* [15] by mass spectrometry (mol.wt. 332), infrared spectroscopy, the typical strong blue fluorescence, and the extreme insolubility.

Isomerization procedure. For the determination of thermodynamic equilibria and photostationary states, both NMR-spectroscopy and UV-spectroscopy were used as analytical tools. The irradiation of relatively concentrated solutions (5 %) was carried out directly in the NMR-tube, and the ratio *cis,trans* to *trans,trans* obtained by integration of the signals for the olefinic protons. Dilute solutions (10^{-5} to 10^{-4} M) were irradiated directly in the UV-cells, and the ratio obtained by comparison with the spectra of mixtures prepared from the pure isomers. The results from both methods were identical. That no *cis,cis*-isomer (III) was formed, either by iodine catalysis or by long UV-irradiation alone, was concluded from the absence of any extra olefinic line in the NMR-spectrum and by the complete reproducibility of the UV-spectra of the isomerized samples with mixtures of the two pure isomers (I and II).

When the *cis,trans*-isomer was liquid and not available in pure form, the equilibrium was approached from that side by using a *cis,trans*-rich sample, for example the photostationary state mixture. Only NMR-analysis could then be applied, since standard mixtures for UV-analysis could not be prepared.

Cyclization products. Each of the isomeric 1,2-dibenzylidenecyclohexanes were heated at 300° in a sealed tube. The *cis,trans*-isomer was quickly converted to a new crystalline compound, m.p. 121°, shown by NMR to be cis-*1,2-dihydro-1-phenyl-2,3-tetramethylene-naphthalene* (V, $n = 4$) (80 %). (Found: C 92.24; H 7.60. Calc. for $C_{20}H_{20}$: C 92.26; H 7.74.) The *trans,trans*-isomer was converted more slowly to the same product and accumulated no *cis,trans*-isomer.

Table 2. NMR-data (in CCl_4) for the cyclization products (V and VI).

Compound	δ for olefinic H at C_4	δ for tertiary H at C_1	Vicinal coupling constant H_1H_2 (cps)
V, $n = 4$	6.17	4.10	8
V, $n = 5$	6.35	3.96	7
VI, $n = 4$	6.65	4.90	7
VI, $n = 5$	6.50	4.70	7

Similarly, both 1,2-di(β-naphthylmethylidene)cycloheptane isomers on heating to 170° gave a new crystalline compound, m.p. 186 − 188°, shown by NMR to be cis-*1,2-dihydro-1-β-naphthyl-2,3-pentamethyleneanthracene* (VI, $n = 5$). (Found: C 92.74; H 8.13. Calc. for $C_{29}H_{26}$: C 93.00; H 7.00.)

The important NMR-data for these compounds are given in Table 2 together with data for other compounds that were not isolated, but examined spectroscopically as crude products after the heating process.

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