Pergamon

Tetrahedron Letters, Vol. 38, No. 23, pp. 3999-4002, 1997
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0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00818-6

Synthesis and Properties of an Arylspiralene. A Cisoid Z,Z-1,4-Diphenyl-1,3-butadiene.

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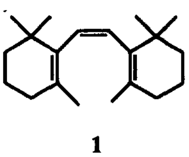
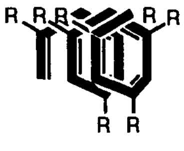
Abstract. A synthetic route to the hindered *Z,Z* isomer of a cisoid 1,4-diphenyl-1,3-butadiene is described. Its crystal structure and properties are reported. © 1997 Elsevier Science Ltd.

A recent study of the crowded cis isomer of Mini-3, **1**, the lowest chain-shortened homolog of β-carotene,[1] led to the suggestion of the possible existence of a new class of compounds marked by the spiral shape of its conjugated polyene chromophore. The name "spiralenes-[n]"[2] (n being the number of conjugated double bonds) was proposed. Their requisite structural features are the presence of all-cis and all cisoid linkages in the polyene chromophore. In this paper we report our effort to prepare the related aryl spiralenes.

Stable cisoid conformation in a conjugated system can be introduced in two different ways. For open chain compounds, such a conformation can be enforced by the presence of bulky substituents at appropriate positions of the polyene backbone ("the t-butyl effect" on diene conformation).[3] Thus, the bis-s-cis conformation in cis-Mini-3 is due to the 1,1'-quaternary carbons. A different approach is to append fused rings onto single bonds of the conjugated chromophore, immobilizing the normally unfavorable cisoid conformation. Some of the target molecules using the latter approach are shown (**2-4**). In this paper our effort to prepare diaryl derivatives of **4** is described.



1



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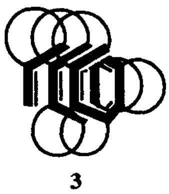

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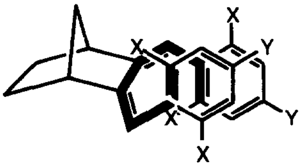
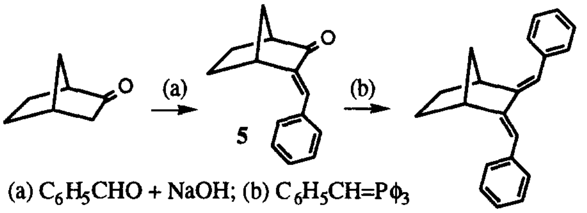
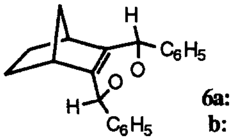


4a: X = Y = H
4b: X = H; Y = Cl
4c: X = Cl; Y = H

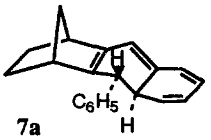
Aldol condensation of norcamphor with benzaldehyde (or a substituted benzaldehyde) gave an isomeric mixture (*E* : *Z* ~ 4 : 1) of enone **5** (>80%). Reaction of the enone with the benzyl Wittig salt yielded a mixture of the *E,E* and *E,Z* isomers of the fused diphenylbutadiene **4a**. Their structures were readily deduced from their spectroscopic data (H & C NMR, UV-Vis and MS, selected data listed in Table 1). Triplet photosensitized (9-fluorenone) irradiation of either the *E,E* isomer or the isomeric mixture led to slow but complete conversion to a set of new isomeric products (MS: $M^+ = 272.1562$, $C_{21}H_{20}$), of an obvious rearranged carbon skeleton. Its H-NMR spectrum shows the presence of two (60:40) stereoisomers and is not consistent with the intended symmetrical Z,Z isomer. A similar product mixture was obtained from irradiation of the 4,4'-dichloro derivative, **4b**. Since cisoid dienes are highly reactive toward singlet oxygen,[4] we carried out independent photooxygenation reactions and obtained the corresponding endoperoxides (**6a** & **b**), which were shown to exhibit different spectral characteristics.



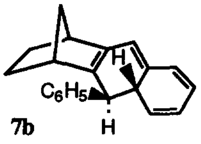
(a) $C_6H_5CHO + NaOH$; (b) $C_6H_5CH=P\phi_3$



6a: diphenyl
b: *p*-chloro-



7a



7b

Table 1. Partial NMR (H & C) and UV data of isomers of **4a-c**.

Cpd.	H. chemical shift, ppm			# ^{13}C	UV, λ_{max}, (ε)
isomer	brg-hd	vinyl	aromatic	Sgns.	in hexane
4a, *E,E*	3.48	6.79	7.23, 7.38, 7.41	9	322 nm
4a, *E,Z*	3.40	6.62,	7.14, 7.23, 7.27,	17	306 nm
	2.89	6.46	7.23, 7.41, 7.52		
4b, *E,E*	3.40	6.69	7.30(s)	9	327 nm
4b, *E,Z*	3.33	6.53,	7.06, 7.23, 7.30,	17	314 nm
	2.88	6.38	7.33		
4c, *E,E*	2.77	6.55	7.14, 7.35	9	282 (1.87 x 10^3)
4c, *E,Z*	3.05	6.24	7.05, 7.11, 7.23,	19	275 (8.52 x 10^2)
	2.65	5.44	7.30, 7.33		
4c, *Z,Z*	3.11	6.17	6.71, 6.86	9	284 (5.17 x 10^2)

The structure of one of the photoproducts was eventually ascertained by a low resolution X-ray crystal structure, which happened to crystallize from a hexane solution of the product mixture. It revealed a 6e-electrocyclization structure, consistent with that of **7a**, a product not expected directly from the triplet state but accountable by way of sensitized isomerization to the Z,Z isomer then cyclization in the dark. The loss of one aromatic ring was probably facilitated by steric relief and the close proximity of the reacting centers in the crowded Z,Z isomer. The other stereoisomeric product is, therefore, likely to be **7b**.

Thus, it became clear that successful preparation of the novel Z,Z isomer required redesigning the starting diaryldiene so that the electrocyclization process of the eventual Z,Z isomer could be suppressed. Accordingly, an analog, **4c**, containing chlorine atoms at all four *ortho*-positions was synthesized. Triplet photosensitized irradiation led to one new product, with a maximum conversion of ~20%, an amount insensitive to the triplet energy of the sensitizer (benzophenone, 9-fluorenone or benzanthrone). A lower energy sensitizer (Rose Bengal) did not lead to increased amount of the Z,Z isomer (by NMR), instead to unidentified side products.[5] The new product was subsequently isolated by preparative hplc. Its simple H & C NMR spectra (data in Table 1) indicate that the compound is highly symmetrical, which is consistent with the intended Z,Z isomer. Colorless crystals of this compound in unusual tubular shape were obtained from methanol. A low temperature (140 K) X-ray diffraction study confirmed the suspected dicis structure (Figure 1).[6]

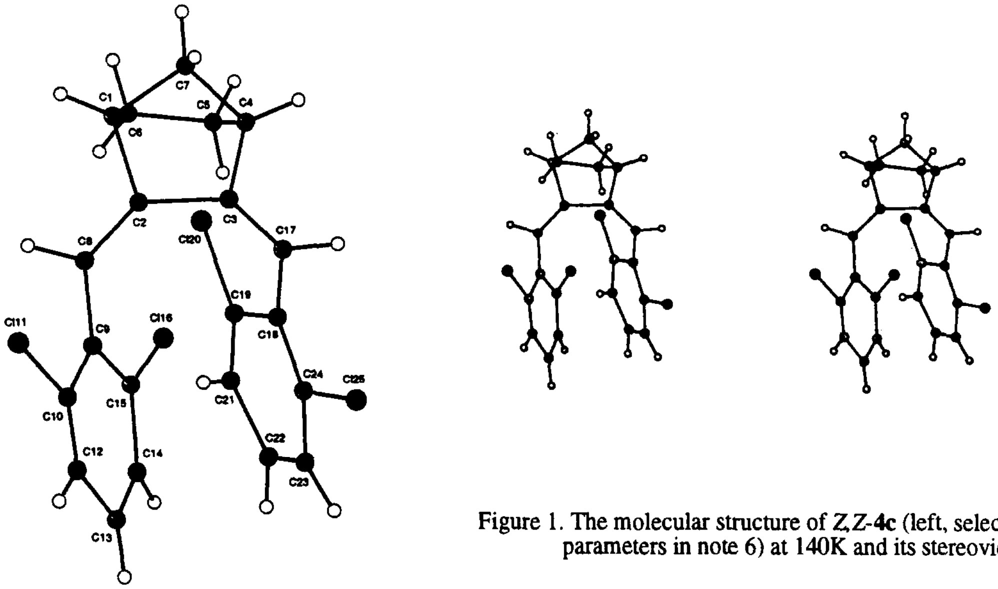


Figure 1. The molecular structure of Z,Z-**4c** (left, selected parameters in note 6) at 140K and its stereoview.

The crystal structure revealed the highly crowded nature of the Z,Z isomer: the two phenyl rings are forced into an orientation nearly parallel to each other by twisting at both the phenyl diene single bonds (~50°) and the diene double bonds (~28°).[7] Its UV-Vis absorption spectrum shows an absorption band centered at 284 nm, more red-shifted than that of the *E,E* and *E,Z* isomers (Table 1).[8] Secondary orbital interactions, postulated to contribute to the red-shift observed in cis-Mini-3, are also likely to be operative in Z,Z-**4c**. In fact, its UV characteristics suggest a logical explanation for the small amount of the Z,Z isomer in the photostationary state: the one-way photosensitized isomerization, useful for preparation of hindered isomers of compounds in the vitamin A series,[9] does not occur in this system because of the likelihood of a lower triplet energy for the Z,Z isomer.

A closer examination of the NMR spectra of the three isomers of **4c** reveals several unexpected features. In the H NMR spectra of both the *E,E* and *Z,Z* isomers, the aromatic H's appear as a doublet (*p*-H) and a triplet (*m,m'*-H), indicating rapid rotation of the two phenyl rings at room temperature. The corresponding signals in the *E,Z* isomers appear instead as a set of a doublet and a triplet and a set of two doublets and a triplet of equal intensity, reflecting inhibited rotation of one (Z) of the two rings. Indeed, its ^{13}C NMR exhibits 19 signals, two more than the less crowded, *E,Z* isomers of **4a** & **4b** (Table 1). Furthermore, upon lowering the sample temperature to less than -50°C, the aromatic H-signals change to two sets of two doublets and a triplet, reflecting restricted rotation of both aromatic rings. Surprisingly, the seemingly more crowded Z,Z isomer shows no signs of inhibited rotation (to -70°C). A ready explanation for this anomaly is provided by its structure shown in Figure 1. The *m,m'* and *o,o'* signals of the two parallel rings could be averaged through a concerted conrotatory motion of the rings.

In compound **4c**, we have prepared a complete set of isomers of a diphenylbutadiene with a central cisoid conformation.[10] The structure of the crowded Z,Z isomer resembles some of those found among the fulgides where the diene units are fused with a succinic anhydride unit.[8,11] In the present case, the fused hydrocarbon ring allows more possibilities to examine effects of polar substituents on properties of such crowded molecules. Thus, the method described here will allow preparation of other compounds containing donor-acceptor substituents for evaluating the relative importance of through-bond and through-space interactions of polar groups on, e.g., the non-linear optical properties of polyenes.[12] Attempts to prepare such compounds are underway.[13]

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[1] J-R Thiel, C. J. Simmons, R. S. H. Liu, *Tetrahedron Lett.* **1997**, *38*, 19-20.

[2] These crowded polyenes parallel the well known helicenes where the twisted chromophores are made of fused benzenoid rings. See, e.g., K. P. Meurer, F. Vogtle, *Topic Curr. Chem.* **1985**, *127*, 1-76.

[3] D. Craig, J. J. Shipman, R. B. Fowler, *J. Am. Chem. Soc.* **1961**, *83*, 2885-2891.

[4] See, e.g., W. Adam, M. Prein, *Acc. Chem. Res.* **1996**, *29*, 275-283 and references cited therein.

[5] One referee noted that the isomer composition of the parent 1,4-diphenylbutadiene under triplet sensitization is concentration dependent (W. A. Yee, S. J. Hug, D. S. Kliger, J. Am Chem. Soc., **1988**, *110*, 2164-2169). In two preparative irradiation runs with three fold differences in concentration, we failed to detect a change in isomer mixtures of **4c**. A quantitative study of product distribution including wavelength dependence will be examined along with substituted (donor-acceptor) compounds being prepared.

[6] For *Z,Z*-**4c**, $C_{21}H_{16}Cl_4$, space group: $P4_2/n$ (tetragonal); cell dimensions: a = b = 21.516(2), c = 7.8619(8) Å. $\alpha = \beta = \gamma = 90°$, V = 3639.78(5) Å^3, Z = 8, d_{calc} = 1.50 g cm^{-3}, F(000) = 1680, μ = 6.50 cm^{-1}. X-ray diffraction data were collected at 140 K using an Enraf-Nonius CAD4 MACH diffractometer; l (Mo Ka) = 0.7107 Å. θ-2θ scan mode to $2\theta_{max}$ = 41.5°; crystal shape and size - rod, 0.35 x 0.50 mm. Of the 2264 unique reflections collected, 415 had $1 > 2.5\sigma(1)$. Diffraction intensities were corrected for Lorentz polarization and absorption (ψ scans; trans-mission range 0.78-1.0). The structure was determined using the direct method programs in Texsan and refined by full-matrix least-squares procedures. H atom positions were calculated assuming C-H = 0.95 Å. Final values for the observed data are: R = 11.0; R_w = 10.4; S = 1.95; over determination ratio = 3.6.

[7] Selected bond lengths: C(2)-C(3) = 1.50(9); C(2)-C(8) = 1.35(7); C(3)-C(17) = 1.28(9); C(8)-C(9) = 1.42(7); C(17)-C(18) = 1.46(7) Å. Selected bond angles: C(3)-C(2)-C(8) = 131(7); C(2)-C(3)-C(17) = 134(8); C(2)-C(8)-C(9) = 132(7); C(3)-C(17)-C(18) = 131(7)°. Selected torsion angles: C(3)-C(2)-C(8)-C(9) = -29(13); C(8)-C(2)-C(3)-C(17) = 3(16); C(2)-C(3)-C(17)-C(18) = -28(16)°.

[8] It is interesting that isomers of the similar bis-benzylidenesuccinic anhydride do not exhibit a similar trend in their UV absorption: H. G. Heller, M. Davis, *J. Chem. Soc.* **1974**, 1487-1492.

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[10] (a) See, e.g., "Cis-trans Isomeric Carotenoids, Vitamin A and Arylpolyenes" by L. Zechmeister, Academic Press, N.Y., 1962; (b) S. E. Wallace-Williams, S. Moller, R. A. Goldbeck, K. M. Hanson, J. W. Lewis, W. A. Yee, D. S. Kliger, *J. Phys. Chem.* **1993**, *97*, 9587-9592.

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[13] The work was partially supported by a grant from the Army Research Office (DAAH04-96-1-0031).

(*Received in USA* 25 *February* 1997; *revised* 18 *April* 1997; *accepted* 21 *April* 1997)