88. Helicenes: Thermally Induced Intramolecular 4 + 2 Cycloadditions Involving the [6]Helicene Skeleton

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Summary. Treatment of *dl*-1-formyl[6]helicene (**1**) with the ylid of $(EtO)_2P(O)CH_2CO_2Et$ in boiling C_6H_6 gave a mixture of two *dl* epimeric cycloaddition products: *trans*-**2a** (80%) and *cis*-**2b** (12%). An X-ray diffraction study (Van Meerssche et al. [2]) fully confirmed the structure and the stereochemistry assigned to the most abundant stereoisomer **2a** by UV., ^{1}H-INDOR, NOE and catalytic hydrogenation of the non-benzenoid double bonds.

Soon after the discovery of the acid catalysed rearrangement of *dl*-1-hydroxymethyl[6]helicene [1], we have observed another reaction involving the [6]helicene skeleton, namely: a thermally induced intramolecular 4 + 2 cycloaddition.

When a solution of *dl*-1-formyl[6]helicene (**1**) (0.356 g) in C_6H_6 (30 ml) is added to a solution of $(EtO)_2P(O)\overset{(-)}{C}HCO_2Et$ [prepared from $(EtO)_2P(O)CH_2CO_2Et$ (1.12 g) + NaH (0.24 g) in C_6H_6 (30 ml)] and the reaction mixture refluxed during 12 h, two *dl*-isomers (M^+ for *m/e* 426) are formed in 80% (**2a**) and 12% (**2b**) yields, respectively. The products are separated by dry-column chromatography (*Woelm* silicagel, C_6H_6): **2a** m.p. 215–216° (CH_3CN); **2b** m.p. 195–197° (CH_3CN).

$C_{31}H_{22}O_2$ (426.5)	Calc.	C 87.3	H 5.2%
2a	Found	C 87.1	H 5.1%
2b	,,	C 87.2	H 5.3%

When the same reaction is carried out at room temperature (14 h), only one isomer (**2a**) is obtained in 90% yield.

The ^{1}H-NMR. and UV. spectra clearly show that **2a** and **2b** are not the expected (*Z*)- and (*E*)-ethyl β-(1-hexahelicyl)acrylates.

Table 1. *NMR.-spectra in $CDCl_3$* (ppm from TMS – *Bruker* HX 90 MHz)

H	**2a**	**2b**	**3a**	H	**2a**	**2b**	**3a**
1	5.83	5.78	5.67	11 or 12	7.57a)	7.61a)	7.65a)
2	6.50	6.56	6.68	12 or 11	7.72a)	7.67a)	7.74a)
3	6.81	6.83	6.97	13	7.57	7.54a)	7.61
4	7.16	7.10	7.15	14	≅7.27	7.20a)	7.35
5	4.64	4.37	3.58	15	≅7.27	6.92a)	7.09
6	6.66	6.67	b)	16	4.23	4.27	4.16
7 or (8)	6.42a)	6.39a)	b)	17	3.47	3.52	3.38
8 or (7)	6.51a)	6.50a)	b)	CH_2	4.23	3.96	4.33
9	7.44a)	7.43a)	7.41a)	CH_3	1.27	0.91	1.37
10	7.77a)	7.77a)	7.78a)				

a) Calculated values.

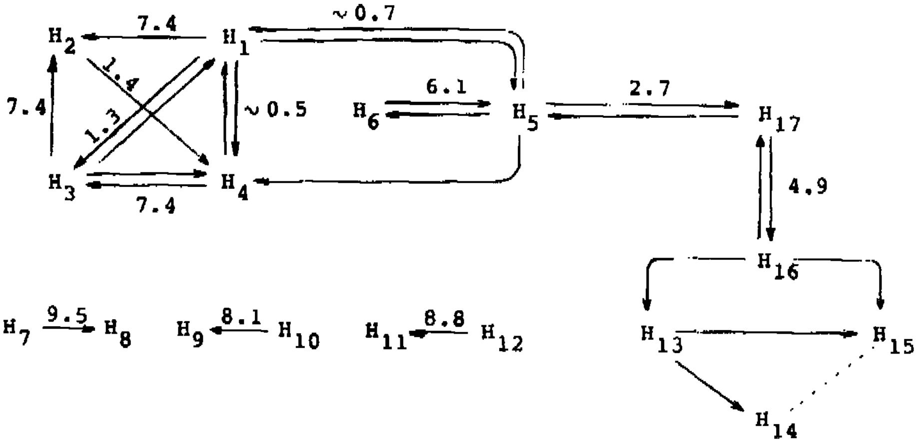
b) 7 H between 0.8 and 3.2 ppm.

Structure of **2a**. The structure of **2a** was assigned by UV., ^1H-INDOR, NOE and catalytic hydrogenation. The INDOR studies are summarised in Fig. 1 and the chemical shifts are collected in Table 1.

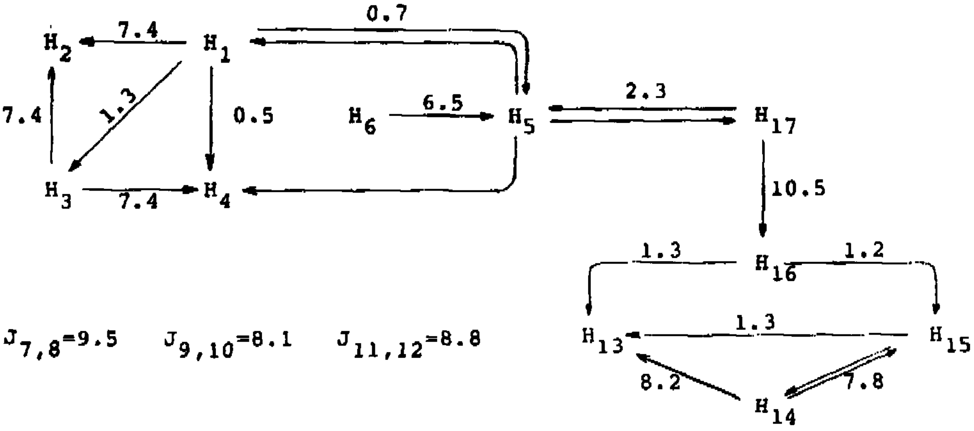
The expected modifications of the ^1H-NMR. spectrum are observed following the catalytic hydrogenation of the two non-benzenoid double bonds of **2a** [H_2, Pd/C, C_6H_6; yield of the 6,6a,7,8-tetrahydro derivative **3a**, 90%; m.p. 199–200°, white needles from CH_3CN; M^+ for *m/e* 430].

Calc. for $C_{31}H_{26}O_2$ (430.5) C 86.5; H 6.1. Found: C 86.6; H 6.2%

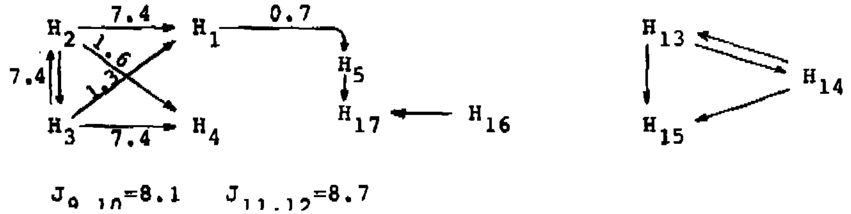
INDOR on **2a** (J).



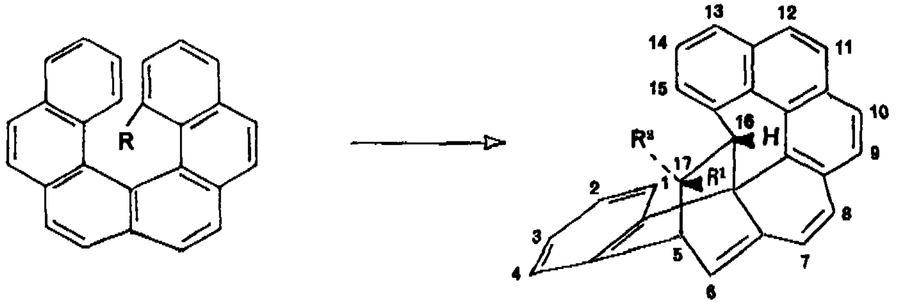
INDOR on **2b** (J).



INDOR on **3a** (J).



The UV. spectrum (Fig. 2) of **3a** is akin to the spectrum of phenanthrene.



1 R = CHO

2a $R^1 = CO_2Et$ $R^2 = H$
2b $R^1 = H$ $R^2 = CO_2Et$
3a 6,6a,7,8-Tetrahydro derivative of **2a**

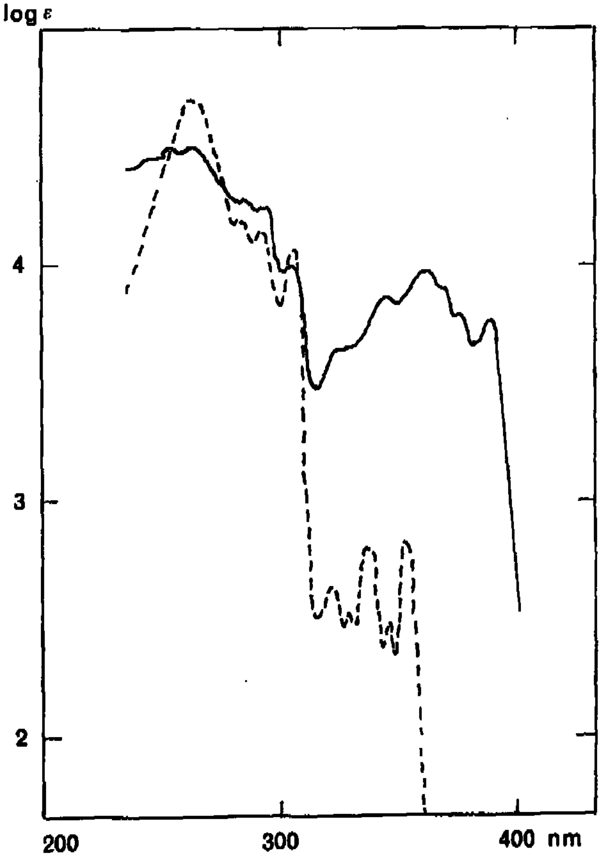


Fig. 2. *UV. spectra of* **2a** (——) *and* **3a** (– – –)

The *configuration* at C(17) in **2a** was assigned on account of the $J_{16,17}$ and of NOE experiments. The relatively small $J_{16,17}$ (4.9 Hz) is characteristic of a *trans* configuration [3]. Examination of a space-filling model shows that in the *trans* stereoisomer, H(15) and H(17) are in close proximity. This was confirmed by the fact that irradiation of H(15) gave an 11% increase of the integrated area of H(17) in **2a**, using H(5) as an internal reference.

An X-ray diffraction study carried out by *Van Meerssche et al.* [2] fully confirmed the structure and the configuration provisionally assigned to **2a**.

Structure of **2b**. Present UV. and ^{1}H-NMR. evidences strongly suggest that **2b** is the *cis* epimer of **2a** (inverted configuration at the chiral center C(17)). The δ(ppm) in **2b** are very similar to the δ(ppm) in **2a** ($\Delta < 5$ Hz; $\Delta = \delta(\mathbf{2a}) - \delta(\mathbf{2b})$) but for the ester radical ($-CH_2CH_3$) and for H(5) and H(15): ΔCH_2 0.27 ppm, ΔCH_3 0.36 ppm, Δ(H(5)) 0.27 ppm and Δ(H(15)) 0.35 ppm. Furthermore, the J's are of the same order in **2b** and **2a**, with the exception of the $J_{16,17}$: **2b** 10.5 Hz (*cis*); **2a** 4.9 Hz (*trans*) [3]. No NOE was observed between H(15) and H(17) in **2b**. The ^{1}H-NMR. results are fully compatible with structure **2b**.

On the other hand, the presence of a four spin system containing three aliphatic and one olefinic protons connected to a four spin aromatic system by long-range couplings ($J_{1,5}$ and $J_{4,5}$) seems to exclude alternative structures.

The ease of formation of the thermal cycloaddition products involving a (formal) phenanthrene system is probably due to the following favourable factors: the close proximity of the reacting carbon atoms in the intermediate β-(1-hexahelicyl)acrylic esters, a $\Delta S^{\ne}$ term much smaller, in absolute value, than the $\Delta S^{\ne}$ term of bimolecular *Diels-Alder* reactions and the departure from planarity of the aromatic system.

We now plan to carry out the cycloaddition reaction and the acid catalysed rearrangement [1], starting from optically active 1-formyl- and 1-hydroxymethyl[6]-helicene, respectively.

Experiments designed to determine the minimum requisite to observe 1,4 cycloadditions to a helicene skeleton are also under consideration.

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REFERENCES

[1] *R. H. Martin, J. Jespers & N. Defay*, Tetrahedron Letters, in the press.

[2] *M. Van Meerssche* et al., private communication.

[3] *C. K. Fay, J. B. Grutzner, L. F. Johnson, S. Sternhell & P. W. Westerman*, J. org. Chemistry *38*, 3125 (1973).