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BISNORCARADIENE* - SYNTHESIS AND REACTIONS - THE FIRST STABLE BISNORCARADIENE **

Karl-Heinz Pauly and Heinz Dürr*

Fachbereich 14 - Organische Chemie der
Universität des Saarlandes - D 6600 Saarbrücken

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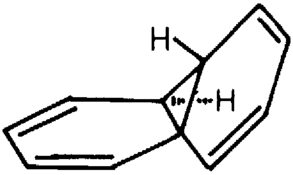
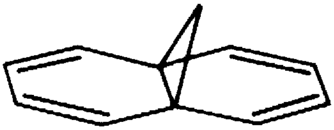
Bisnorcaradienes*are very interesting molecules as far as bonding and structure-reactivity relationship are concerned. In principle two cyclohexadiene rings can be bonded to a cyclopropane ring in two different modes leading to the bisnorcaradienes 1 or 2. (The circumstatial systematic name for 1 is from now on substituted by the term "bisnorcaradiene").



1



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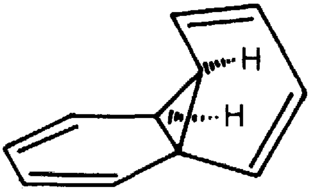

2'

The third alternative of a trans fused cyclohexadiene ring would be the extremely strained molecule 2'. Whereas 2 can be synthesized by the classical procedure of Vogel 1); 1 has been postulated as intermediate in the photolysis of spironorcaradienes 3 2) as well as in thermal reactions 3,4). However only recently we were able to prove really the existence of the 2.5-diphenyl substituted 1a in solution by nmr spectroscopy at low temperature 5).

In this communication we report on: a) the synthesis of substituted bisnorcaradienes in solution as well as the isolation of the first stable derivative of 1, dibenzo-bisnorcaradiene (1e); b) the thermal stability of derivatives of 1 and their photochemical reactions are also discussed.

Photolysis of spiro-norcaradienes 3 (in equilibrium with their valence isomers 4) with uv light of wavelength $\lambda > 300$ nm led to the benzocycloheptatrienes 5 - 7 2,6). Monochromatic light ($\lambda = 300$ nm from a monochromator or Hg high pressure lamp/K_2CrO_4-filter; -50°C in the case of 3a,b; 25°C for

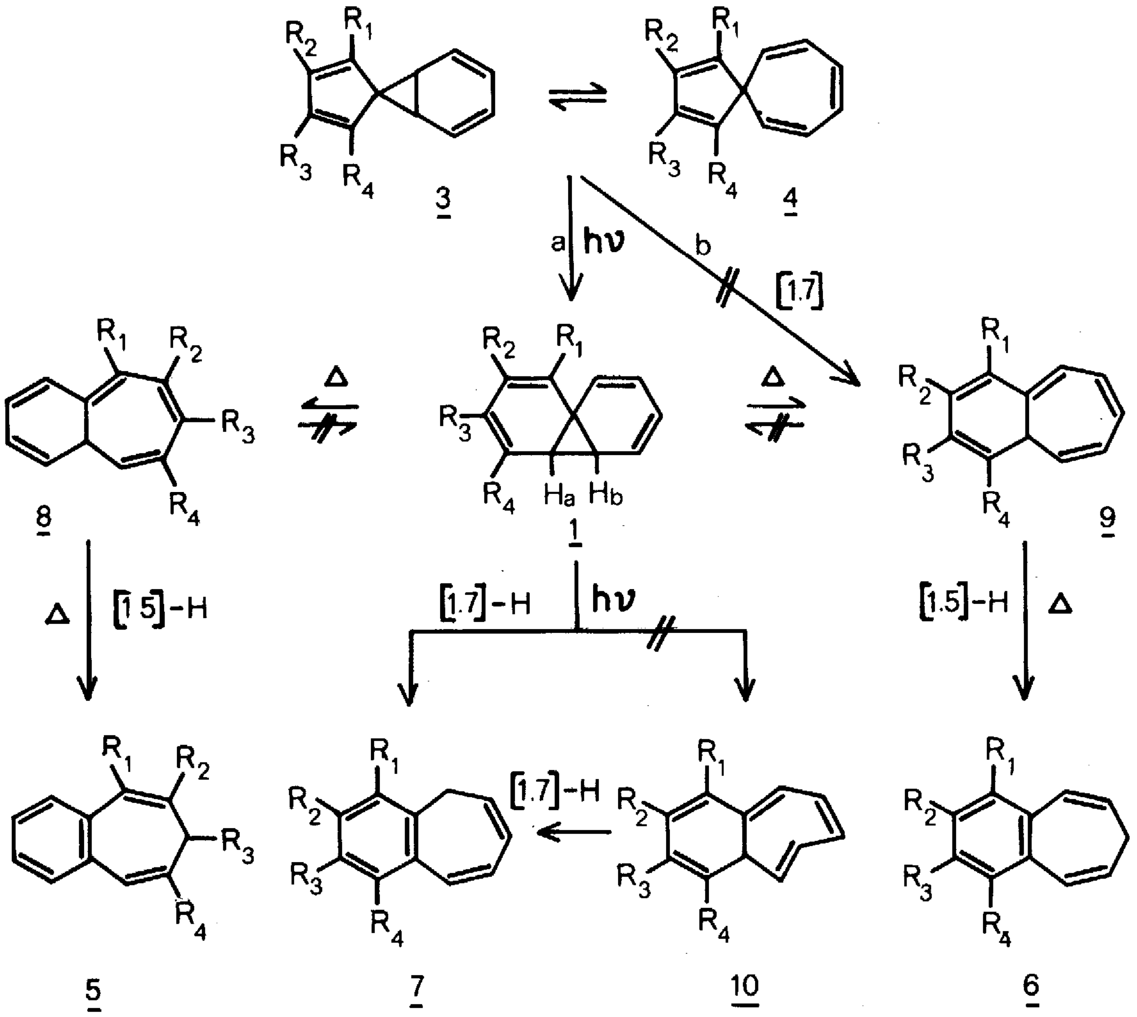

Table 1

1	R1	R2	R3	R4	chem. shift Ha	Hb[δ, ppm]	Yield [%]
a[5)]	Ph	H	H	Ph	2,90	4,67	> 90
b	Cl	Cl	Cl	Cl	2,87	4,89	> 90
c*)	Benzo		Ph	Ph	3,43	4,21	> 90
c'	Ph	Ph	Benzo		2,92	5,21	> 90
d	Benzo		H	H	3,22-3,51	4,93	> 60
e	Benzo		Benzo		2,98	5,15	15-20

*) ratio 1c/1c'= 3:1

3c-e, 0.2% etheral solution) on the other hand afforded among little side products mainly bisnorcaradienes 1a-e.

The structure of 1 was established mainly by ^{1}H-nmr spectroscopy (selected data see table 1). 1e is the first stable bisnorcaradiene having the following analytical and spectroscopic data: mp 104°; uv, λ_{max} 357($\varepsilon \approx 8000$); ^{1}H-nmr ($CDCl_3$, δ in ppm): 7.2-8.2(m, 8 arom. H); 6.8-7.0 (m, 3 olefinic H); 6.3 (m, 1H, at C-8); 5.15 (dd, J=5.8/9.0 cps, 1H at C-7); 2.98 (d, J=5.8 cps 1H at C-6); ir(KBr): 3200, 3000, 1580, 1500, 760, 725 cm^{-1}; mass spectrum m/e 242 (M^+, 100%).

From the two possible pathways leading to 1a-e: a) a di-π-methane rearrangement and b) a [1.7]-sigmatropic shift to 9 followed by ring closure to 1 [2)] we favor alternative a). The insensitivity of the nmr-spectra of 1 to temperature changes [5)] between -90 and -20°C argues strongly for the formation of only 1 or 1' and against an equilibrium of the valence isomers 1 or 1' and 8 or 9. Formation of 1c and 1c' in the ratio of 3:1 demonstrates also that this di-π-methane rearrangement is regiospecific. A theoretically possible antara-antara[5.5]-sigmatropic rearrangement could not be observed.

Thermolyses of the bisnorcaradienes 1a-e gave, via a disrotatory ring opening followed by a [1.5]-sigmatropic shift, the benzocycloheptatrienes 5-6. A kinetic study of this reaction by means of UV-spectroscopy (in iso-octane) affords the activation parameters collected in table 2.

Table 2: Activation parameters of the thermolyses of 1

1	ratio 5/6	$\Delta E_a^{\#}$ a)	$\Delta H^{\#}$ a)	$\Delta G^{\#}$a)	$\Delta S^{\#}$b)	$t_{1/2}$ 25°C[min]
a	25/75	15.8	15.2	21.5	-21	16
b	75/27	16.1	15.5	21.3	-19	7,9
c	only 6	15.9	15.3	24.4	-30	$15.4 \cdot 10^2$
d		20.2	19.6	24.6	-16.6	$20.5 \cdot 10^2$
e		-	-	-	-	stable

a) kcal/mole b) e.u.

Whereas in 1c, 1d and 1e annelation with one or two aromatic rings stabilizes the bisnorcaradiene-system considerably, chlorine substitution destabilizes 1 obviously. It is not completely clear, if the -I or the +M-effect (-I > +M) is responsible for this fact.

The photochemical behaviour of the bisnorcaradienes 1 was studied. Irradiation of 3 $\rightleftharpoons$ 4 at room temperature (λ=300 nm, $CDCl_3$ or ether) gave directly 5 and 6 (via 1 as intermediate). However irradiating 1 at -50° (where 1 is a stable compound) with 380 nm light (or K_2CrO_4 or Pyrex-filter additionally in the case of 1b) provided mainly 5H-benzocycloheptatrienes 7 as photoproducts and very small amounts of the benzonorcaradiene, which is due to irradiation of 7.

Since a photochemical ring opening of the norcaradiene bond should be conrotatory leading to a strained trans-cycloheptatriene system 10, a direct [1.7]-sigmatropic H-shift of 1 to 7 seems to be a more likely pathway for the formation of 7.

The isolation of a stable bisnorcaradiene of type 1 renders this system more liable to reactivity studies. Such studies, e.g. addition of electrophiles, dienophiles etc., photochemical mechanistic studies as well as an X-ray analysis are currently under way.

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*) The systematic name is Tricyclo[5.4.0.0 ^{1,6}]undeca-2,4,8,10-tetraene

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