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CONFORMAT~~IO~~NS AND ROTATIONAL BARRIERS OF 2-SUBSTITUTED 1,3-DIPHENYLALLYL ANIONS

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Summary: The conformations and the rotational barriers of the 2-substituted 1,3-diphenylallylanions 1b-g (Tab.2) have been determined. Increasing size of the substituents leads to more exo,endo- and endo,endo-conformers at the cost of the exo,exo-species. This trend is connected with decreasing $\Delta G^{\ddagger}$-values of the rotational barriers; the barriers are essentially not affected by ion pair effects, which is in contrast to the parent "allyl anion".

As shown by the rotational barriers of allyllithium and allylpotassium in tetrahydrofuran (THF) ($E_A = 10.5 \pm 2$ kcal/mole [1] and $\Delta G^{\ddagger}(60^{o}C) \approx 17$ kcal/mole [2], respectively,) it seems impossible to determine the rotational barrier of the parent "allyl anion" experimentally in solution because of the paramount gegenion effects [3]. However, since the lithium salt of the more delocalized 1,3-diphenylallyl anion (1a) is a solvent separated ion pair in THF [4], and since such ion pairs correspond as closely as possible to carbanions [5], we selected the 2-substituted 1,3-diphenylallyl anions 1b-g (Tab.2) for an investigation of the rotational barriers and the conformations as a function of different substituents R at C^2.

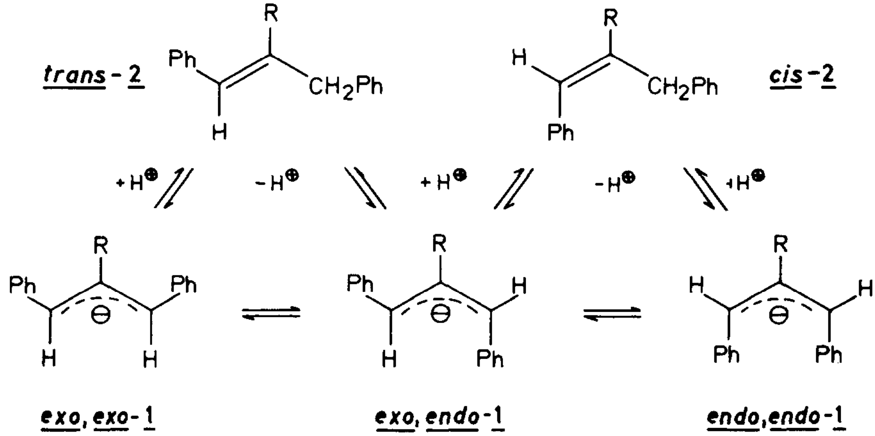
1b-g have been prepared from the olefins 2b-g in THF with lithium cyclohexylisopropylamide (LCIA), n-butyllithium (n-BuLi) and/or n-butyllithium/tetramethylethylene diamine (n-BuLi/TMEDA). Tab.1 summarizes the ^{1}H-nmr data of the cis- and trans-isomers of 2a-g.

		trans		cis	
2	R	vinyl-H	allyl-H	vinyl-H	allyl-H
a[6]:	H	6.40	3.50	6.50	3.62
b[4d,7]:	CH_3	6.30	3.33	6.44	3.60
c[8]:	CN	6.80	3.50	7.40	3.80
d:	C_2H_5	6.23	3.46	6.46	3.60
e[4d,9]:	C_6H_5	6.32	3.70	—	4.05
f:	$CH(CH_3)_2$	5.98	3.43	6.52	3.64
g[4d]:	$C(CH_3)_3$	6.20	3.50	6.72	3.70

Tab.1: ^{1}H-nmr data (δ-values) of the olefins 2a-g in CCl_4.

Scheme I gives the relationships of the *trans*- and *cis*-olefins **2** with the *exo*,*exo*-, *exo*,*endo*- and *endo*,*endo*-anions **1**[10].

Scheme I



Conformations:

By means of ^{1}H-nmr spectroscopy and protonation to give the corresponding *cis*- and/or *trans*-olefins **2b**-**g**[11] the conformations of the 1,3-diphenylallyl anions **1b**-**g** have been revealed. The results are listed in Tab.2.

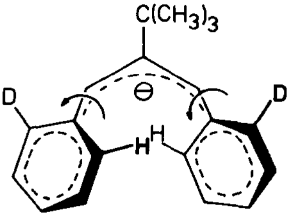
1	R	*exo*,*exo*	$\Delta G^{\ddagger}_{273°C}$ $\rightleftharpoons$	*exo*,*endo*	$\Delta G^{\ddagger}_{273°C}$ $\rightleftharpoons$	*endo*,*endo*
a[6]:	H	92	$\xleftarrow{17.0}$	8		—
b[7]:	CH_3	8	$\xleftarrow{14.2}$	92		—
c[8]:	CN	4.5	$\xleftarrow{16.4}$	91	$\xrightarrow{16.4}$	4.5
d:	C_2H_5	15	$\xleftarrow{13.8}$	68	$\xrightarrow{13.8}$	17
e:	C_6H_5	—		56	$\xrightarrow{14.3}$	44
f:	$CH(CH_3)_2$	—		38	$\xrightarrow{12.5}$	62
g[7]:	$C(CH_3)_3$	—		—		100

Tab.2: Populations of *exo*,*exo*-, *exo*,*endo*- and *endo*,*endo*-conformers of anions **1a**-**g** (Li-salts in THF at temperatures between -46 and -20°C [12]) and $\Delta G^{\ddagger}_{273°C}$-values (exp.error ±0.2-0.4 kcal/mole) for the transformations shown.

With hydrogen at C^2 (**1a**)[6], the *exo*,*exo*-conformation is the most stable one. Introduction of small substituents like methyl or cyano (**1b**[7] and **1c**[8], respectively), however, causes the *exo*,*endo*-anion to be more stable. With an ethyl substituent (**1d**) significant amounts of the *endo*,*endo*-anion are detectable. The *exo*,*exo*-conformer disappears with phenyl (**1e**)[9] and isopropyl (**1f**) at C^2, and only the *endo*,*endo*-anion is present in the case of R=t-butyl (**1g**)[7]. Thus, the interaction(s) of the group R at C^2 with the *exo*-phenyl substituent(s) essentially determines the position of the equilibrium.

The large proportion of the *endo*,*endo*-conformers in the case of **1e**-**g** seems surprising at a first glance. However, the slow phenyl rotation on the ^{1}H-nmr time scale at low temperatures[13] reveals how the expected steric congestion is avoided. At 30°C, e.g. 1g displays 4 H-meta at δ=6.50-7.00 and 4 H-ortho + 2 H-para at 5.80-6.15; at -57°C one observes 4 H-meta + 2 H-ortho at 6.30-7.00, 2 H-para at 5.80-6.15 and, most importantly, 2 H-ortho at 4.70-5.00. This strong upfield shift of 2 H-ortho (unambiguously demonstrated by means of deuterium labeling experiments, e.g. with $1g\text{-}D_2$) is in accord with both a cyclophane type conformation of the two phenyl rings [14] and an expansion of the normal sp^2 angles in the allyl moiety of 1g [15], as indicated below. A comparable shift is observed in the ^{1}H-nmr spectra of 1e and f.

$1g\text{-}D_2$



Rotational Barriers:

From the temperature-dependant ^{1}H-nmr spectra of 1b-f we determined the barriers of rotation around the allyl anion bonds by means of line shape analyses with the computer program DNMR 2 [16]. The decreasing $\Delta G^{\ddagger}_{273°C}$-values on going from 1a (17.0 kcal/mole) to 1f (12.5 kcal/mole) (Tab.2) strongly suggest an increasing destabilization of the ground state conformations as the reason for this trend. The less crowded transition states, undoubtedly, are more similar in energy.

Ion pair effects do not play a significant role: addition of 4.5 equiv. HMPA to 1a in THF raises $\Delta G^{\ddagger}$ by 0.9 kcal/mole; no change is observed, if HMPA is added to the THF-solution of 1b; $\Delta G^{\ddagger}$ in the case of the Li-salt of 1c in THF is identical to the $\Delta G^{\ddagger}$-values of the Li-, Na- and K-salts of 1c in dimethylsulfoxid [8]; preparation of 1f with n-BuLi/TMEDA or with t-BuLi leads to the same line shapes. Thus, while the ground states of 1a-f correspond to solvent separated ion pairs [4], one may have some contact ion pair character in the benzyl anion type transition states with only little or no effect on the rotational barriers [17]. These results, therefore, provide a close approximation to the situation in the unperturbed carbanions, which, among others, is of interest for a comparison with the rotational barriers of the corresponding radicals and cations [18].

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10) Instead of the (E,Z)-nomenclature we prefer here the exo/endo- and cis/-trans-denotations as shown in Scheme I. This allows to survey the stereochemical effects of the different substituents R more easily.

11) Some experimental details are given, e.g., in Lit. 6 and 8.

12) The error caused by the different temperatures at which the equilibria have been measured is within the experimental error (±4%).

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16) We are very grateful to Professor G.Binsch and Dr. D.Stephenson, Universität München, for the program DNMR 2 and their help.

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