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Electron-Transfer-Induced Dimerization of β-Alkylstyrenes and the Structures of the Resulting 1,4-Dilithiobutanes[1]

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Upon reaction with lithium β-alkylstyrenes undergo dimerization of the resulting radical anions with the formation of 2,3-dialkyl-1,4-dilithio-1,4-diphenyl butanes **1**–**8**. The structure and the dynamic behavior of these dilithium organyls are investigated by cryoscopic measurements and ^{1}H-, ^{13}C-, and ^{6}Li-NMR spectroscopy at different temperatures. The butane chain adopts a cisoid conformation; the two benzyl subunits chelate one lithium cation while the other is solvent-separated from the hydrocarbon frame. Depending on the size of the alkyl substituents and the reaction temperature, the dimerization of the radical anions with the formation of two stereogenic centers can proceed diastereoselectively.

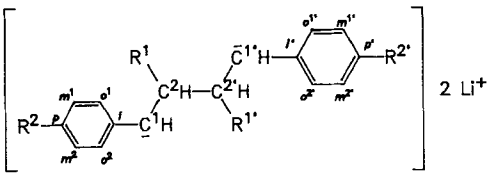
1. Introduction

The importance of organolithium compounds as reactive intermediates in organic synthesis makes a comprehensive understanding of their structures highly desirable. Crucial features are the mode of charge distribution in the organic moiety, the ion-pair structure, and the state of aggregation. Concerning the role of the lithium nuclei, electrostatic interactions are generally most important, but some multicenter covalent character can also be present. The structures of di- and polylithiated hydrocarbon species are particularly complex. Thus, 1,4-dilithium organyls tend to form structures in which the carbanionic centers are doubly bridged by the lithium cations[3,4]. Typical examples are *o,o'*-dilithiobiphenyl[5] and α,α'-dilithioxylenes[6] which have been studied both theoretically and experimentally. In the latter case the bridged structures can be symmetric or asymmetric, depending on the nature of the substituents at the α,α'-carbon centers[7]. Doubly lithium-bridged structures are also found in compounds which allow an increased conformational mobility of the hydrocarbon units such as in 1,4-dilithio-*cis*-butene[4] and 1,4-dilithio-1,4-diphenyl-*cis*-butene[8]. Even 1,4-dilithiobutane is predicted by MNDO calculations to favor 1,4 bridging[9].

Our interest is centered on a new class of 1,4-dilithiobutane systems, the 2,3-dialkyl-1,4-dilithio-1,4-diphenyl-butanes.

These species are similar to the 1,4-dilithiobutane parent case in that there is no restriction to conformational mobility within the chain.

Scheme 1. General structure of the 2,3-dialkyl-1,4-dilithio-1,4-diphenyl-butanes **1**–**8**



Dilithium organyl	R^1, $R^{1'}$	R^2, $R^{2'}$
1	Ethyl	H
2	Propyl	H
3	Butyl	H
4	Hexyl	H
5	2-Ethylhexyl	H
6	Pentadecyl	H
7	Cyclohexyl	H
8	Pentyl	*tert*-Butyl

The synthesis of the title compounds **1**–**8** becomes feasible in a simple manner. β-Alkylstyrenes **9**–**16** are converted into the corresponding radical monoanions by reduction with lithium metal. Reduction is followed by immediate and quantitative dimerization of the radical anions with the formation of two stereogenic centers C-2 and C-2' in a dilithiated species. Thus, in a nonstereoselective process two diastereomers are expected. The mechanism of the dimerization process is unknown, and no spectroscopic studies

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exist which provide information on the configuration and the conformation of the dianionic products.

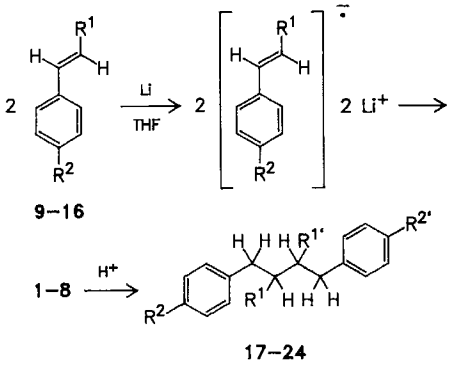
In this paper, we present ^{1}H-, ^{13}C-, and ^{6}Li-NMR-spectroscopic evidence for the structure of compounds **1**–**8**. A crucial question in the structural description of **1**–**8** concerns the possible aggregation in tetrahydrofuran. Therefore, cryoscopic measurements based on an improved experimental set-up have also been applied.

2. Results

2.1. Syntheses

Benzaldehyde is transformed into the corresponding 1-arylalkan-1-ols by a Grignard reaction. Subsequent dehydration leads to the β-alkylstyrenes **9**–**16** whose spectroscopic data are given in the experimental section. The styrene compounds are converted into the corresponding radical monoanions by reduction with lithium in tetrahydrofuran.

Scheme 2. Electron-transfer-induced dimerization of β-alkylstyrenes and protonation of the resulting organodilithium compounds **1**–**8** to **17**–**24**



The electron-transfer reaction leads to immediate dimerization with the formation of the dianions **1**–**8** which are subjected to NMR-spectroscopic analysis.

2.2. NMR Spectroscopy

The coupling of two β-alkylstyrene radical anions can lead to two diastereomers. The existence of both diastereomers is easily proved by an H-H-correlated NMR spectrum which indicates separate signals for these species. According to the ^{1}H- and ^{13}C-NMR spectra the ratio of the diastereomers of the carbanionic species **1**–**8** exactly reflects the ratio of the protonated species **17**–**24** which are obtained upon quenching with methanol. The assignment of the NMR signals to each of the diastereomers of **17**–**24** is discussed below.

The radicals formed by the slow heterogeneous reduction dimerize so rapidly that during an NMR-spectroscopic control of the reaction no signal broadening due to paramagnetic intermediates is observed. The dimerization of β-alkylstyrene radical anions in THF at −78°C leads to a *d,l*:*meso* ratio of the diastereomers **1**–**8** of 2:1. Raising the temperature brings about a decreased diastereoselectivity. Thus, the diastereomeric ratio after coupling at −10°C is only *d,l*:*meso* = 1:1.

Characteristic ^{13}C-NMR chemical shifts of the dilithium organyls **1**–**8** are summarized in Table 1.

Table 1. ^{13}C-NMR chemical shifts of the dilithium organyls **1**–**8** (benzylic region, 50 MHz, [D$_8$]THF, 25°C)

Compound		*i*	*m*^{2}	*m*^{1}	*o*^{2},*o*$^{2'}$	*o*^{1},*o*$^{2'}$	*p*	C-1
1	*d,l*	152.37	129.51	127.86	115.08	107.97	95.94	65.65
	meso	152.92	128.95	127.65	115.68	107.62	96.56	63.98
2	*d,l*	152.09	129.52	127.85	114.87	107.79	95.44	67.45
	meso	152.76	129.52	127.63	115.59	107.65	95.72	64.36
3	*d,l*	152.04	129.55	127.62	114.98	107.72	95.74	67.21
	meso	152.73	129.55	127.62	115.62	107.72	96.42	64.54
4	*d,l*	152.03	129.54	127.82	114.97	107.76	95.69	67.20
	meso	152.70	129.54	127.61	115.59	107.76	96.37	64.57
5	*d,l*	154.07	131.75	129.90	116.92	108.68	98.19	71.71
	meso	154.27	130.69	129.56	117.57	109.31	98.19	66.62
6	*d,l*	152.19	129.64	127.88	115.11	107.76	95.86	(THF)
	meso	152.80	129.64	127.88	115.11	107.76	96.50	64.30
7	*d,l*	152.13	129.66	128.06	114.77	107.90	95.36	64.3
	meso	—	—	—	—	—	—	—
8	*d,l*	150.90	125.87	124.66	116.92	114.69	106.70	64.45
	meso	151.35	126.50	124.64	117.94	115.03	106.70	61.52

The compounds with unbranched chains (**1**–**4**, **6**) show a maximum chemical-shift difference for the *para*-phenyl carbon atoms of $\Delta\delta_C$ = 1.1 and for C-1 of $\Delta\delta_C$ = 1.8. A larger shift range is observed when **5** (R_1 = 2-ethylhexyl) and **7** (R_1 = cyclohexyl) are included (see Table 1).

When comparing *d,l* with *meso* diastereomers of **1**–**8** the resonances of the phenyl units in the latter are generally shifted to lower field and those of the benzyl centers to higher field. Obviously, the degree of π-charge delocalization in the *meso* isomers is smaller than that in the *d,l* isomers. In all cases the resonances of C-*ipso*, of one C-*ortho*, and of C-*para* are deshielded, while C-1 is shielded. Independent information on the charge delocalization should, in principle, be available from the free energy of activation of the rotation of the phenyl ring about the neighboring single bond; this energy can be approximated from the coalescence of the signals of the *ortho* and *meta* protons, respectively, in the high-temperature ^{1}H-NMR spectra. The data, however, lie between 65–70 kJ/mol and fail to exhibit a significant difference between corresponding diastereomers.

Upon cooling the ^{1}H- and ^{13}C-NMR spectra of **1**–**8** exhibit a remarkable dynamic behavior. While the number and the multiplicity of the signals of the *d,l* diastereomers remain constant, particular signals of the *meso* isomer split into two (intensity ratio 1:1) below a characteristic coalescence point. These signals are due to carbon atoms of the 1,4-diphenylbutane frame and the four neighboring carbon atoms of the alkyl substituents. The activation barrier of this process, which is identified below as a rotation about the central C-2–C-2′ bond, can be estimated (see Table 2) from the coalescence temperature and the shift difference in the slow-exchange domain.

Apart from the temperature-dependent line-shape effects most of the ^{13}C-NMR signals are liable to temperature-dependent shifts which can readily be attributed to changes of the ion-pair structures (see below).

Table 2. Free energy of activation of the rotation about the C-2–C-2′ bond in the *meso* isomers of **1–8**

Compound	ΔG^{+} (^{1}H) [kJ/mol]	ΔG^{+}(^{13}C) [kJ/mol]
1	49.7 (245 K)	48.1 (231 K)
2	48.1 (250 K)	49.2 (231–256 K)
3	49.6 (241 K)	>49.2 (253 K)
4	51.6 (253 K)	50.3 (231–257 K)
5	52.9 (269 K)	–
6	52.6 (257 K)	52.7 (244 K)
7	–	–
8	52.4 (257 K)	52.4 (253 K)

In order to obtain further information on ion-pairing effects a series of temperature-dependent ^{6}Li-NMR spectra have been recorded for **1–8** (see Figure 1 as well as Table 3). At low temperatures the lithium atoms of all dilithium organyls except **7** are observable in three different sites whose signals (1, 2, and 3) merge into one average signal at higher temperature.

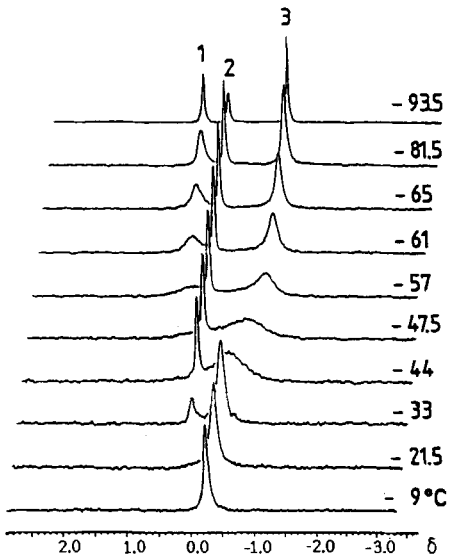


Figure 1. ^{6}Li-NMR spectrum of **5** (29.45 MHz, [D$_8$]THF, external standard 0.1 M LiCl/THF)

Table 3. ^{6}Li-NMR chemical shifts of **1–8** (29.45 MHz, −50°C, [D$_8$]THF, external standard (0.1 M LiCl/THF)

Signal	**1**	**2**	**3**	**4**	**5**	**6**	7	**8**
1	0.31	0.29	0.33	0.36	0.60	0.30	0.49	0.38
2	0.08	0.07	0.10	0.12	0.20	0.11	–	0.11
3	−0.83	−0.83	−0.74	−0.74	−0.72	−0.78	−0.74	−0.76

Surprisingly enough, compound **7** produces two ^{6}Li-NMR signals although its ^{13}C- and ^{1}H-NMR spectra leave no doubt as to the symmetry of the carbon frame.

Since **17–24**, the protonation products of **1–8**, have not been described in the literature, an attempt has been made to coordinate the chiral shift reagent tris[3-(trifluoroacetyl)-*d*-camphorato]europium(III) [Eu(FACAM)$_3$] with the help of (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octadiene)-silver(I) (AgFOD) in order to distinguish between the *meso* and *d,l* isomers. The use of different concentrations and temperatures clearly influences the line width of the signals; it does not, however, allow an identification of the different diastereomers.

Table 4. Free energy of activation for the rotation about the C-2–C-2′ bond in the *d,l* isomers

Compound	ΔG^{+} [kJ/mol]	Compound	ΔG^{+} [kJ/mol]
1	51.4 (253 K)	**5**	47.6 (230 K)
2	50.7 (244 K)	**6**	46.1 (244 K)
3	51.2 (247 K)	7	50.5 (244 K)
4	49.3 (238 K)	**8**	50.4 (241 K)

2.3 Cryoscopy

Cryoscopy is a colligative method and provides direct information on the aggregation behavior in solution. For measurements in THF rather concentrated solutions are required as a consequence of the small cryoscopic constant of −1.874 K·kg/mol. Therefore, the isolated purified compounds **1–8** have been used. The procedure for preparing the pure dilithium organyls is described in the experimental section. In order to check the purity of the samples and to determine the amount of residual THF the dianions were quenched with [D$_4$]methanol and examined by ^{1}H-NMR spectroscopy. It became obvious (see Table 5) that in spite of all manipulations such as washing with pentane and drying in high vacuum the samples contained varying amounts of THF.

Table 5. Amount of solvated THF in the dianions **1–8** as determined by ^{1}H-NMR spectroscopy

Compound	THF/Li	Compound	THF/Li
1	1.0/1	**5**	2.0/1
2	0.9/1	**6**	–
3	2.0/1	7	1.9/1
4	1.0/1	**8**	0.6/1

Obviously, the drying in high vacuum leads to a partial desolvation, thus producing a 1:1 ratio of lithium and THF. To cover the coordination sphere two cations apparently require two or four solvent molecules. Interestingly, the two solids **3** (R^1 = butyl) and **7** (R^1 = cyclohexyl) carry two molecules THF per lithium atom while the other compounds with another THF:Li ratio are highly viscous oils. The results of the cryoscopic measurements are summarized in Table 6 whereby *n* is the calculated mean degree of aggregation of several independent measurements.

Table 6. Cryoscopically determined degrees of aggregation n

Compound	Solvent	Concentration [mol/kg]	ΔT [K]	n_i	n
3	THF	0.03845	−0.090	0.80	0.95
		0.03977	−0.091	0.82	
		0.08892	−0.157	1.06	
7	THF	0.04236	−0.097	0.82	0.86
		0.05013	−0.109	0.82	
		0.0922	−0.188	0.90	
8	THF	0.05339	−0.091	1.10	1.09
		0.05491	−0.091	1.13	
		0.09232	−0.165	1.05	
5	cyclohexane	0.059	−1.282	2.1	1.88
		0.108	−1.566	1.7	
		0.150	−1.306	1.8	
		0.185	−1.714	1.9	

3. Discussion

3.1 Lack of Aggregation

Two findings are crucial for the structural assignment of the dilithium organyls **1**–**7** in THF:

1. In the ^{6}Li-NMR spectra of **7** (R^1 = cyclohexyl) two signals appear although according to the ^{1}H- and ^{13}C-NMR spectra a single stereoisomer with C_2 symmetry is present.

2. In the other dilithium organyls the second diastereomer gives rise to only one more signal in the ^{6}Li-NMR spectra although, according to the low-temperature ^{1}H- and ^{13}C-NMR spectra, its preferred conformation is asymmetric.

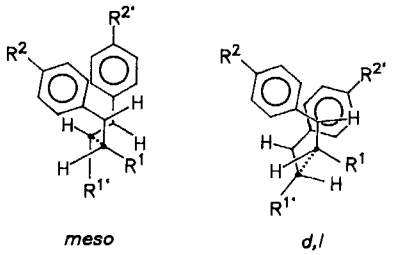
It might be tempting to ascribe these spectroscopic features to the formation of aggregates. The mean degree of aggregation n for **3**, **7**, and **8** in THF, however, clearly indicates the sole existence of monomers (Table 6). Apparently, the formation of aggregates can only be expected for solvents of significantly lower polarity than THF. In order to confirm this expectation cryoscopic measurements on the dilithium derivative **5** (R^1 = 2-ethylhexyl) have also been carried out in cyclohexane. By using the known cryoscopic constant for cyclohexane (−20.2 K·kg/mol), we determined the mean degree of aggregation as 1.9. Thereby, the assumption was made that the THF molecules were still associated with the cation and were not present as free particles.

3.2 Configuration at C-2 and C-2′

In compound **8** the coupling constants $^1J_{CH}$ of the benzylic carbon atoms show a smaller value for the signals of the *meso* isomer (125.9 Hz) than for the signal of the *d,l* isomer (138.5 Hz) at −40°C. With the help of the Muller-Pritchard relation[10] the degree of hybridization – when neglecting charge-induced effects – can be approximated to $sp^{2.97}$ (*meso*) and $sp^{2.61}$ (*d,l*).

In spite of the pronounced degree of sp^3 character neither carbon-lithium nor hydrogen-lithium couplings could be detected. A change in intensity due to a heteronuclear NOE between the hydrocarbon protons and ^{6}Li was not detectable either and has been reported in the literature only for a few covalent organolithium compounds. Protonation at C-1 and C-2 of **1**–**8** forming **17**–**24** should not lead to a change in the diastereomeric ratio compared with the dilithium organyls. Indeed, the *meso/d,l* ratio in the carbanions is exactly reflected in the protonation products. It follows that the carbanionic centers C-1 and C-1′ in **1**–**8** do not cause chirality which is in accord with the experience obtained for other benzyllithium systems[11]. The description of **1**–**8** can, therefore, be restricted to the configuration at C-2/C-2′. Closely related to this is the question as to the diastereoselectivity in the dimerization of β-alkylated styrene radical monoanions. With the aid of models the steric interactions during the radical coupling can be qualitatively understood. If one assumes a typically planar structure[12] for the styrene radical monoanion the dimerization can be accounted for as shown in Scheme 3.

Scheme 3. Stereochemically most favorable arrangement of the β-substituted styrene radical monoanions during the coupling reaction



In the formation of *d,l* isomers an arrangement with minimal interaction is approached in which the two phenyl rings point to one and the two alkyl groups to the other side of the molecule. An analogous conformation seems to be the most favorable one for the generation of the *meso* isomer. However, stronger steric interactions are present than in the formation of the *d,l* isomer.

In compound **7** (R^1 = cyclohexyl) no conformation can be found in which the sterically demanding alkyl substituents of the *meso* isomer do not disturb each other. In fact, as mentioned previously, during the reaction of β-cyclohexylstyrene with lithium only one of the diastereomers of **7** is formed which can thus readily be attributed to the *d,l* isomer. The identification of the diastereomers in the other dilithium organyls is then simply accomplished by a comparison of the chemical shifts. The *d,l* isomer is always the major product, and the extent of the charge delocalization seems to be somewhat more pronounced than in the sterically more hindered *meso* isomers.

3.3 Conformation

Upon cooling the samples **1**–**6** and **8** the ^{1}H- and ^{13}C-NMR signals of the *meso* isomers broaden and subsequently split into two signals of equal intensity. This behavior can be explained by a slow rotation about the C-2–C-2′ bond. In the slow-exchange domain the observation of two sharp resonances points towards a conformation with two nonequivalent molecular halves. The free energy of activation

of this process can be approximated to about 50 kJ/mol (Table 2); it rises with increasing size of the alkyl substituent.

The ^{1}H- and ^{13}C-NMR spectra of the *d,l* isomers fail to show signal splittings. This finding, however, does not necessarily prove the absence of dynamic processes. A glance at the conformers shown in Scheme 4 reveals that, in contrast to the *meso* isomer, the two halves of the molecules are equivalent (C_2 axis), and a rotation about the C-2 – C-2′ bond does not cause a change in the magnetic environment. The close proximity of the benzyl units (shown in Scheme 4) leads to the question as to whether the lithium counterions tend to decrease the conformational mobility of the compounds.

An interpretation of the ^{6}Li-NMR spectra (see Table 3) contributes to a solution of the problem. At low temperature three different chemical environments for the lithium atoms in **1**–**6** and **8** are detectable whose signals (1, 2, and 3) coalesce to an average signal at higher temperatures. In contrast to the ^{6}Li-NMR spectra of **1**–**6** and **8** that of **7** (R^1 = cyclohexyl, 100% *d,l*) shows two signals in spite of the C_2 symmetry of the hydrocarbon moiety (see above). Corresponding signals are found in the diastereomeric mixtures of **1**–**6** and **8** and are thus attributed to the *d,l* forms. The chemical shift difference of the signals 1 and 3 amounts to ca. 1.2 ppm in each case.

A change of the ^{6}Li-NMR chemical shifts has been determined for several organolithium compounds during the conversion of the ion-pair equilibrium from a solvent-separated to a contact-ion pair in the first solvation shell of the cation[13,14]. An additional hint is given by the invariability of the chemical shift of signal 3 with respect to a variation of the alkyl substituent R^1. This points towards the fact that in the *d,l* isomers one cation is in close contact with the anion while the other is separated by a solvent shell.

In a similar configuration for the *meso* isomers one would expect the ^{6}Li-NMR signal of the contact ion at lower field while the resonance of the solvent-separated counterion should not experience a significant shift compared with the *d,l* isomers. The interpretation of the relative signal intensities supports this interpretation. The two signals at low field reflect the known *meso*/*d,l* ratio and possess the same total intensity as the high-field signal which can thereby be easily attributed to the solvent-separated lithium ions from the *meso* and the *d,l* isomers.

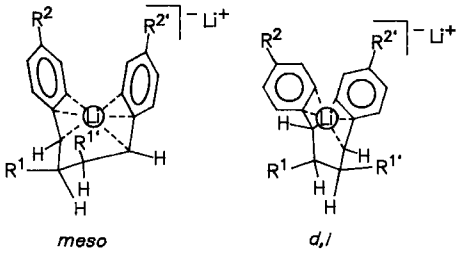
When measuring the ^{6}Li-NMR spectra a longer relaxation time T_1 is noticed for the solvent-separated cation than for the "contact cation". These observations further support the above structural assignment since according to the literature no fast quadrupol relaxation is observable for ^{6}Li nuclei[15,16]. In lithiumorganic compounds one must expect spin-lattice relaxation times of up to 125 s and in completely solvated cations of up to 1000 s[17].

The number of the THF molecules being attached to lithium ions (see Table 5) can now be interpreted again. The highest solvent/substrate ratio amounts to 4 molecules THF per dilithium compound and is found for **3**, **5** and **7**. In the other compounds a partial desolvation due to evaporation under high vacuum is observed. The solvent-separated lithium ion requires four THF molecules to cover its coordination sphere. The second lithium cation could then be surrounded by the two negatively charged benzyl units to saturate completely its coordination sphere.

In the preferred conformation (see Scheme 4) the unsolvated cations fit easily between the two benzylic subunits in the *d,l* as well as in the *meso* diastereomers. The intramolecular chelation of the lithium ion by the two benzyl units makes the dianion less attractive for the second cation which then prefers the competing solvent as coordination partner.

The structural suggestions shown in Scheme 4 are in congruence with the demand for a symmetric conformation of the *d,l* and an asymmetric one of the *meso* isomer. They offer a plausible explanation for the chemical shifts of the lithium signals and their intensities.

Scheme 4. Suggested structure for the diastereomers at low temperature



The sequence of ^{6}Li-NMR spectra of **5** in Figure 1 provides an insight into the temperature-dependent behavior of the compound which cannot be derived from the ^{13}C- and ^{1}H-NMR spectra.

At −93.5 °C the frozen conformations of the *d,l* and *meso* isomer are both present. The signals at low field represent, according to their intensities, the intramolecularly chelated lithium atoms of both diastereomers. The signals of the two solvent-separated cations are located at the high-field end. Upon warming a coalescence of the two signals 1 and 3 is observed. In the *d,l* diastereomer the two lithium atoms slowly become indistinguishable. The solvent-separated cation of the *meso* isomer is also involved in the exchange.

At ca. −50 °C the coalescence point is reached. With the corresponding frequency difference the free energy of activation for the underlying process can be estimated as ca. 47 kJ/mol. The removal of the cation from the sphere of the two benzyl units is caused by the beginning rotation about the central molecular axis C-2 – C-2′. For a rapid rotation the cations become equivalent and the signals coalesce.

On the other hand, the low-field signal in the *meso* form is still sharp up to −43 °C. An analogous estimation of the free energy of activation gives 51.9 kJ/mol. This value lies 1 kJ/mol below that one calculated from the ^{1}H-NMR spectra. In view of the simplified evaluation one may safely assume that the dynamic process in both experiments is the same (see Table 4).

Superimposed on the rotation and intramolecular exchange of both lithium atoms is the intermolecular exchange between *d,l* and *meso* isomers which at higher temperatures leads to a singlet signal.

Thus, an interpretation of the dynamic phenomena in the ^{6}Li-NMR spectrum provides information on the C-2–C-2′ rotation in the *d,l* diastereomers which due to symmetry reasons could not be gained by ^{1}H- and ^{13}C-NMR spectroscopy.

4. Conclusion

The combined use of ^{1}H-, ^{13}C-, and ^{6}Li-NMR spectroscopy at various temperatures and of cryoscopic measurements as well as the examination of the protonation reactions of **1**–**8** to **17**–**24** provide a consistent picture of the structure of 2,3-dialkyl-1,4-dilithio-1,4-diphenylbutanes **1**–**8** in solution. Corresponding to the stereoselectivity in the dimerization reaction of lithiated β-alkylstyrenes the title compounds nearly quantitatively form two diastereomers in varying amounts. The two benzylic carbon atoms in the molecule do not cause any chirality. In THF as solvent the dilithium compounds **1**–**8** are present in monomeric form as [LiR] [Li(THF)$_4$] species (R is the organic rest of compound **1**–**8**). The butane framework exists in a cisoid arrangement with a minimized interaction of the alkyl substituents. The two negatively charged benzyl units chelate one lithium cation while the other is solvent-separated from the organic moiety. The beginning of the rotation about the central C-2–C-2′ bond breaks up this unusual structure, and the two cations become equivalent.

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Experimental

For reactions and measurements under inert gas as well as for the storage of the lithium organyls argon was used. Traces of oxygen, carbon dioxide and moisture were removed from the gas by using a series of absorption towers. Anhydrous THF was obtained by refluxing over a sodium/potassium alloy for several days followed by distillation from lithium aluminium hydride under argon. All other solvents were dried and freed from oxygen according to standard literature procedures.

NMR-Spectroscopic Data and Elemental Analyses: The NMR spectra were measured with a Bruker AM 400 spectrometer and a 10-mm ^{1}H/^{13}C dual-probe head, a Bruker AC 200 with a 5-mm ^{1}H/^{13}C dual-probe head and 10-mm broad-band probe head, as well as a Bruker WH 90 with a 5-mm ^{1}H-selective probe head. Each time the probe head was exchanged or after a longer waiting time the temperature calibration was checked and, if necessary, corrected with the help of a methanol and ethylene glycol thermometer. The ^{1}H- and ^{13}C-NMR resonances were referenced to TMS and the ^{6}Li-NMR resonances to a 0.1 M LiCl solution in THF.

Scheme 5. Assignment of NMR signals

= *n*-Alkyl: $-C^3-C^m-C^{n+2}$

[m = 0 (for n = 2), 4...(n+1) (for n > 2); n = 2...6,15]

R^1 = 2-Ethylhexyl: $-C^3-C^{4...7}-C^8$ with C^9-C^{10} branch

R^1 = Cyclohexyl: 

Syntheses of the 2,3-Dialkyl-1,4-dilithio-1,4-diphenylbutane Systems (**1**–**8**): The 2,3-dialkyl-1,4-dilithio-1,4-diphenylbutane systems **1**–**8** were obtained either by reduction of the corresponding β-alkylstyrenes **9**–**16** in [D$_8$]THF with ^{6}Li in a sealed NMR tube or by contact with ^{7}Li in a flask with gas inlet in non deuterated THF. In the latter case β-alkylstyrenes (0.05 M) were dissolved in 150 ml of dry, degassed THF, and the solution was added through a septum to a 250-ml flask containing 1.1 equivalents of lithium pieces. Upon vigorous stirring at −20°C the solution turned orange-red during a period of 5 min. The reaction mixture was kept at −20°C for 3–4 h, followed by removal of the solvent under vacuum. The remaining highly viscous residue was washed 3–5 times with dried and degassed pentane. The addition and removal of the solvent was performed with the help of a 50-ml syringe. – With increasing chain length of the alkyl substituent R^1 the solubility of the dilithium organyls increases in *n*-pentane, thus the washing had to be carried out while cooling. Compound **6** (R^1 = pentadecyl) remained in solution even near the freezing point of *n*-pentane and could not be purified according to the above technique. After the last washing procedure the compound was held at room temperature at 10^{-2} mbar, and any residual solvent was removed at 10^{-4} mbar for 2 h. In a glove box the residue was transferred into the cryoscopy apparatus and into an NMR tube, respectively.

Experimental Data of Products **1**–**8**

1: ^{1}H-NMR (200 MHz, [D$_8$]THF, −42°C): *d,l*: δ = 6.04, 5.84 (2 × t, 4H, *meta*); 5.55, 5.36 (2 × d, 4H, *ortho*); 4.66 (t, 2H, *para*); 2.22 (m, 2H, 1-H); 1.0–1.9 (m, 6H, aliphatic); 0.77 (t, 6H, 4-H); *meso*: δ = 6.04, 5.84 (2 × t, 4H, *meta*); 5.55, 5.34 (2 × d, 4H, *ortho*); 4.68 (t, 2H, para); 2.04 (m, 2H, 1-H); 1.0–1.9 (m, 6H, aliphatic); 0.90 (t, 6H, 4-H). – ^{13}C-NMR (50 MHz, [D$_8$]THF, −67°C): *d,l*: δ = 151.8 (*ipso*); 129.5, 127.9 (*meta*); 115.0, 107.6 (*ortho*); 95.8 (*para*); 65.1 (C-1); 45.2 (C-2); 25.4 (C-3); 10.2 (C-4); *meso*: δ = 152.4 (*ipso*); 130.0, 127.6 (*meta*); 115.4, 107.6 (*ortho*); 96.2, 96.4 (*para*); 64.7, 62.8 (C-1); 43.4, 43.0 (C-2); under THF (C-3); 13.0, 15.5 (C-4). – ^{6}Li-NMR (29.4 MHz, [D$_8$]THF, −60°C): *d,l*: δ = 0.31; −0.83; *meso*: δ = 0.08; −0.83.

2: ^{1}H-NMR (200 MHz, [D$_8$]THF, −42°C): *d,l*: δ = 6.03, 5.85 (2 × t, 4H, *meta*); 5.52, 5.35 (2 × d, 4H, *ortho*); 4.63 (t, 2H, *para*); 2.20 (m, 2H, 1-H); 1.8–0.9 (m, 8H, aliphatic); 0.84 (t, 6H, 5-H); *meso*: δ = 6.06, 5.88 (2 × t, 4H, *meta*); 5.56, 5.33 (2 × d, 4H, *ortho*); 4.70 (t, 2H, *para*); 2.1, 2.3 (m, 2H, 1-H); 1.8–0.9 (m, 8H, aliphatic); 0.84 (t, 6H, 5-H). – ^{13}C-NMR (50 MHz, [D$_8$]THF, −67°C): *d,l*: δ = 151.6 (*ipso*); 129.8, 127.8 (*meta*); 114.7, 107.9 (*ortho*); 95.6 (*para*); under THF (C-1); 41.6 (C-2); 37.1 (C-3); 19.2 (C-4); 16.5 (C-5); *meso*: δ = 152.1; 152.4 (*ipso*); 129.5, 129.5, 127.6, 127.6 (*meta*); 115.3, 115.3, 107.9, 107.9 (*ortho*); 95.9, 96.5 (*para*); 63.0, 65.6 (C-1); 39.2, 41.9 (C-2); 34.6, 37.0 (C-3); 23.3, 23.8 (C-4); 16.3, 16.3 (C-5). – ^{6}Li-NMR (29.4 MHz, [D$_8$]THF, −50°C) *d,l*: δ = 0.29; −0.83; *meso*: δ = 0.07; −0.83.

3: ^{1}H-NMR (200 MHz, [D$_8$]THF, −45°C): *d,l*: δ = 6.03, 5.84 (2 × t, 4H, *meta*); 5.52, 5.34 (2 × d, 4H, *ortho*); 4.63 (t, 2H, *para*); 2.21 (m, 2H, 1-H); 1.83 (m, 2H, 2-H); 1.0–1.6 (m, 12H, aliphatic); 0.84 (t, 6H, 6-H); *meso*: δ = 6.03, 5.88 (2 × t, 4H, *meta*); 5.56, 5.32 (2 × d, 4H, *ortho*); 4.79 (t, 2H, *para*); 2.31, 2.09 (m, 2H, 1-H); 1.92 (m, 2H, 2-H); 1.0–1.6 (m, 12H, aliphatic); 0.86 (t, 6H, 6-H). – ^{13}C-NMR (50 MHz, [D$_8$]THF, −45°C): *d,l*: δ = 151.7 (*ipso*); 129.6, 127.8 (*meta*); 114.9, 107.6 (*ortho*); 95.6 (*para*); 66.7 (C-3); 41.3 (C-2); 35.5 (C-3); 28.3 (C-4); 25.6 (C-5); 15.6 (C-6); *meso*: δ = 152.2, 152.4 (*ipso*); 129.6, 129.6, 127.6, 127.6 (*meta*); 115.4, 115.4, 107.6, 107.6 (*ortho*); 96.0, 96.3 (*para*); 63.2, 65.8 (C-1); 39.9, 42.1 (C-2); 33.1, 33.1 (C-3); 32.7, 32.7 (C-4); under THF (C-5); 15.4, 15.4 (C-6). – ^{6}Li-

NMR (29.4 MHz, [D$_8$]THF, −50°C): *d,l*: δ = 0.33; −0.74; *meso*: δ = 0.10; −0.74.

4: ^{1}H-NMR (200 MHz, [D$_8$]THF, −58°C): *d,l*: δ = 6.03, 5.84 (2 × t, 4H, *meta*); 5.52, 5.34 (2 × d, 4H, *ortho*); 4.67 (t, 2H, *para*); 2.22 (m, 2H, 1-H); 0.9−2.1 (m, 22H, aliphatic); 0.85 (t, 6H, 8-H); *meso*: δ = 6.03, 5.84 (2 × t, 4H, *meta*); 5.55, 5.28 (2 × d, 4H, *ortho*); 4.67 (t, 2H, *para*); 2.35 (m, 2H, 1-H); 0.9−2.1 (m, 22H, aliphatic); 0.85 (t, 6H, 8-H). − ^{13}C-NMR (50 MHz, [D$_8$]THF, −58°C): *d,l*: δ = 151.5 (*ipso*); 129.6, 127.8 (*meta*); 114.9, 107.5 (*ortho*); 95.6 (*para*); 65.8 (C-1); 40.9 (C-2); 34.1 (C-3); 34.0 (C-4); 32.7 (C-5); 24.4 (C-7); 15.18 (C-8); *meso*: δ = 152.1, 152.3 (*ipso*); 129.6, 129.6, 127.8, 127.8 (*meta*); 115.1, 115.2, 107.5, 107.5 (*ortho*); 95.9, 96.4 (*para*); 63.1, 63.1 (C-1); 39.8, 42.1 (C-2); 33.3, 31.4, 32.69, 30.05 under THF (aliphatic); 15.2, 15.2 (C-6). − ^{6}Li-NMR (29.4 MHz, [D$_8$]THF, −50°C): *d,l*: δ = 0.36; −0.74; *meso*: δ = 0.12; −0.74.

5: ^{1}H-NMR (200 MHz, [D$_8$]THF, −50°C): *d,l*: δ = 6.00, 5.81 (2 × t, 4H, *meta*); 5.46, 5.38 (2 × d, 4H, *ortho*); 4.55 (t, 2H, *para*); 2.31 (d, 2H, 1-H, ^3J = 7.3 Hz); 0.7−2.1 (m, 36H, aliphatic); *meso*: δ = 6.10, 6.06, 5.85, 5.90 (4 × t, 4H, *meta*); 5.53, 5.53, 5.38, 5.30 (4 × d, 4H, *ortho*); 4.69, 4.72 (2 × t, 2H, *para*); 2.36, 2.42 (m, 2H, 1-H); 0.7−2.1 (m, 36H, aliphatic). − ^{13}C-NMR (50 MHz, [D$_8$]THF, −65°C): *d,l*: δ = 151.8 (*ipso*); 129.9, 127.9 (*meta*); 114.1, 107.3 (*ortho*); 95.0 (*para*); 70.6 (C-1); 44.8 (C-2); 11.0−39.0 (aliphatic); *meso*: δ = 151.9 (*ipso*); 129.5, 127.9 (*meta*); 115.4, 107.5 (*ortho*); 96.2 (*para*); 63.0, 65.4 (C-1); 43.7 (C-2); 11.0−39.0 (aliphatic). − ^{6}Li-NMR (29.4 MHz, [D$_8$]THF, −50°C): *d,l*: δ = 0.60; −0.72; *meso*: δ = 0.20; −0.72.

6: ^{1}H-NMR (200 MHz, [D$_8$]THF, −42°C): *d,l*: δ = 6.33, 6.05 (2 × t, 4H, *meta*); 5.53, 5.36 (2 × d, 4H, *ortho*); 4.64 (t, 2H, *para*); 2.23 (d, 2H, 1-H); 1.0−2.0 (m, 58H, aliphatic); 0.87 (t, 6H, 17-H); *meso*: δ = 6.33, 6.05; (2 × t, 4H, *meta*); 5.55, 5.34 (2 × d, 4H, *ortho*); 4.66 (t, 2H, *para*); 2.27, 2.12 (m, 2H, 1-H); 1.0−2.0 (m, 58H), aliphatic); 0.87 (t, 6H, 17-H). − ^{13}C-NMR (50 MHz, [D$_8$]THF, −42°C): *d,l*: δ = 151.7 (*ipso*); 129.6, 128.0 (*meta*); 115.2, 107.6 (*ortho*); 95.9 (*para*); under THF (C-1); 41.5 (C-2); 24−35 (aliphatic); 15.0 (C-17); *meso*: δ = 152.2, 152.5 (*ipso*); 129.6, 129.6, 126.8, 126.8 (*meta*); 115.6, 115.6, 107.6, 107.6 (*ortho*); 96.1, 96.5 (*para*); 63.0, 65.8 (C-1); 40.0, 41.5 (C-2); 24−35 (aliphatic); 15.0 (C-17). − ^{6}Li-NMR (29.4 MHz, [D$_8$]THF, −50°C): *d,l*: δ = 0.30; −0.78; *meso*: 0.11; −0.78.

7: ^{1}H-NMR (200 MHz, [D$_8$]THF, −30°C): *d,l*: δ = 5.96, 5.82 (2 × t, 4H, *meta*); 5.50, 5.44 (2 × d, 4H, *ortho*); 4.56 (t, 2H, *para*); 2.34 (d, 2H, 1-H); 0.8−2.0 (m, 24H, aliphatic). − ^{13}C-NMR (50 MHz, [D$_8$]THF, −4°C): *d,l*: δ = 152.2(*ipso*); 129.3, 127.9 (*meta*); 114.3, 108.7 (*ortho*); 94.8 (*para*); 64.7 (C-1); 45.6 (C-2); 45.2 (C-3); 33.7, 28.8, 28.6, 28.4, 26.8 (C-4−C-8). − ^{6}Li-NMR (29.4 MHz, [D$_8$]THF, −50°C): *d,l*: δ = 0.49; −0.74.

8: ^{1}H-NMR (200 MHz, [D$_8$]THF, −58°C): *d,l*: δ = 6.12, 5.94 (2 × t, 4H, *meta*); 5.55, 5.28 (2 × d, 4H, *ortho*); 2.12 (d, 2H, 1-H, ^3J = 7.1 Hz); 0.98 (s, 18H, *tert*-butyl); 0.7−1.9 (m, 20H, aliphatic); 0.88 (t, 6H, 7-H); *meso*: δ = 6.14, 5.97 (2 × t, 4H, *meta*); 5.57, 5.18 (2 × d, 4H, *ortho*); 2.24 (m, 2H, 1-H); 0.98 (s, 18H, *tert*-butyl); 0.7−1.9 (m, 20H, aliphatic); 0.88 (t, 6H, 7-H). − ^{13}C-NMR (50 MHz, [D$_8$]THF, −58°C): *d,l*: δ = 150.4 (*ipso*); 125.9, 124.7 (*meta*); 116.3, 114.6 (*ortho*); 106.3 (*para*); 63.9 (C-1); 41.2 (C-2); 32.9 *tert*-butyl); 22−36 (aliphatic); 15.5 (C-7); *meso*: δ = 150.6, 150.9 (*ipso*); 126.2, 126.4, 124.4, 124.7 (*meta*); 117.6, 116.8, 114.6, 114.6 (*ortho*); 106.5, 106.5 (*para*); 60.6, 63.0 (C-1); 39.5, 42.3 (C-2); 34.9 (*tert*-butyl); 22−36 (aliphatic); 15.5, 15.5 (C-7). − ^{6}Li-NMR (29.4 MHz, [D$_8$]THF, −50°C): *d,l*: δ = 0.38; −0.76; *meso*: δ = 0.11; −0.76.

Deuteration and Protonation of **1**−**8**: For deuteration of the dilithium compounds with [D$_4$]methanol, ca. 20 mg of the compound was placed into an NMR tube which was sealed with Parafilm and quickly treated with the electrophile outside the glove box. − In order to quantitatively determine the ratio of substrate to complexed THF the solutions were analyzed by ^{1}H-NMR spectroscopy without further manipulation. − Protonation was carried out in the same manner by using methanol in a small flask. Excess solvent was removed and the hydrocarbon formed was dissolved in chloroform. After filtration through a short silica-gel column, the solvent was exchanged for [D$_1$]chloroform and the sample examined by NMR spectroscopy.

Experimental Data of Products **17**, **18**, **21**, *and* **23**

17: ^{1}H-NMR (200 MHz, $CDCl_3$, 25°C): δ = 6.8−7.2 (m, 10H, aromatic); 2.67 (^2J = 14 Hz, ^3J = 6 Hz), 2.55 (^2J = 14 Hz) (dd, 4H, 1-H, *d,l/meso*); 0.85−1.55 (m, 6H, aliphatic); 0.68, 0.62 (2 × t, 6H, 4-H, *d,l/meso*).

18: ^{1}H-NMR (200 MHz, $CDCl_3$, 25°C): δ = 6.6−7.1 (m, 10H, aromatic); 2.60 (^2J = 14 Hz, ^3J = 7 Hz), 2.48 (^2J = 14 Hz, ^3J = 7.5 Hz), 2.72 (^2J = 14 Hz, ^3J = 7 Hz), 2.46 (^2J = 14 Hz, ^3J = 8 Hz) (dd, 4H, 1-H, *d,l/meso*); 1.39 (m, 2H, 2-H); 0.8−1.2 (m, 8H, aliphatic); 0.54, 0.48 (t, 6H, 5-H, *d,l/meso*).

21: ^{1}H-NMR (200 MHz, $CDCl_3$, 25°C): δ = 6.8−7.1 (m, 10H, aromatic); 2.1−2.5 (m, 4H, 1-H); 0.6−1.8 (m, 30H, aliphatic); 0.49, 0.40 (2 × t, 3H, 8-H, *d,l/meso*).

23: ^{1}H-NMR (200 MHz, $C_2D_2Cl_4$, 25°C): δ = 6.9−7.2 (m, 10H, aromatic); 2.70 (^2J = 14 Hz, ^3J = 4.7 Hz), 2.52 (^2J = 14 Hz, ^3J = 10 Hz) (dd, 4H, 1-H); 0.8−1.7 (m, 24H, aliphatic). − ^{13}C-NMR (50 MHz, $C_2D_2Cl_4$, 25°C): δ = 142.6 (*ipso*); 128.8 (*meta*); 128.0 (*ortho*). 125.3 (*para*); 34.4 (C-1); 44.0 (C-2); 39.3(C-3); 32.0 (C-4); 27.0 (C-5); 26.7 (C-6); 26.8 (C-7); 29.3 (C-8).

Cryoscopy[18]

Figure 2 shows the instrumentation that was developed and employed during this work. The cryoscopic vessel itself consists of a

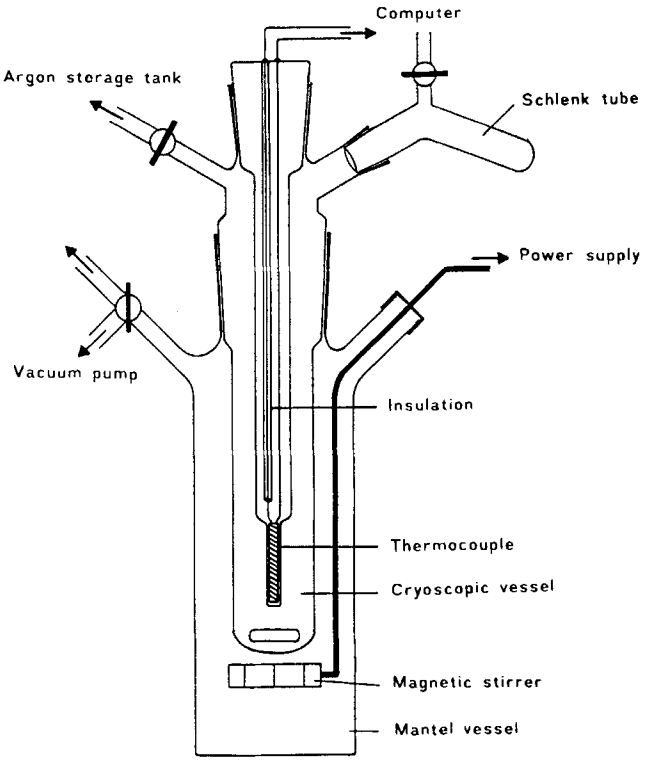

Figure 2. Cryoscopic instrumentation

flask with gas inlet into which a high-precision thermocouple is inserted. A storage tank containing argon is connected to the gas inlet to ensure a safe gas atmosphere above the solution. It was found that fluctuations in pressure, due to the strong compression of the solvent THF at low temperatures, can affect the reproducibility of the data. A second side arm allows the connection to a specially formed Schlenk tube which contains the lithium organyls. For the measurement the cryoscopic vessel is placed in a glass jacket which is dipped into a cooling medium (THF: liq. nitrogen; cyclohexane: cryostate with methanol). The gap between the two vessels contains gaseous nitrogen which allows heat exchange. With the help of a vacuum pump the cooling rate can be controlled.

An efficient mixing of the solution is crucial for the quality of the cooling curve. The magnetic stirrer must move fast enough to avoid formation of a temperature gradient but has to be slow enough so that no gas bubbles are pulled into the solution. To fulfill these demands an eight-pole electromagnet has been constructed which fits into the outer vessel and produces an alternating field of adjustable frequency from 1 to 100 Hz. The main body of the electromagnet is a soft iron core which ends in eight vertical spikes each carrying one coil. Each opposite pair of coils forms one magnet. A pulse generator and eight power supply units trigger one pair after the other with a defined frequency. – The freezing-point lowering of THF in a 0.01 – 0.2 M solution is in the order of $10^{-1}-10^{-2}$°C. Thus, an exact evaluation of the cooling curve requires a data acquisition system. The temperature-measuring device (S1220 Company System Technique, Sweden) is connected to a platinum resistance probe PT 100 (Burster Präzisionsmeßtechnik, Gensbach). Every 0.5 s the temperature is sampled by a computer and then stored. Data collection is continued typically for 15 – 20 min and contains 2000 – 3000 temperature values. The computer calculates the straight-line equation of the cooling branch and the plateau of the cooling curve by using a linear regression. The intersection of both lines gives the melting point. – A typical experiment is described for 2,3-dibutyl-1,4-dilithio-1,4-diphenylbutane (**3**). – Dried and purified THF was distilled under argon into the cryoscopic vessel. The exact amount of 69.835 g was determined by differential weighing. In a stream of argon the Schlenk tube containing 1.7229 g of purified and pentane-washed compound **3** including coordinatively bound THF was fitted to the vessel. – In the carefully sealed apparatus with pressure equilibration the melting point of the pure THF was determined to be −108.532°C by averaging 3 successive measurements. Compound **3** was washed out of the Schlenk tube by tilting the entire apparatus. After complete dissolution of the dianion **3** further measurements followed resulting in a new average melting point of −108.623°C. Thus, the melting point depression ΔT amounts to −0.091°C. Substituting this into the known equation

$$n = c \cdot E_k/\Delta T$$

gives the degree of aggregation as $n = 0.82$. Since the actual measurement of the compound and the calibration without compound were carried out under identical conditions errors due to the electrical resistance of the probe, the slight argon overpressure and Joule's heat due to stirring can be eliminated. – At a concentration c of ca. 2.8 mmol of compound **3** in 70 ml of THF the weighing uncertainty of 0.001 g of THF and 0.0001 g of the compound cause a maximal error of 0.1% in the calculation of c. An unknown amount of complexed THF in the purified substrate would cause a much greater uncertainty. To minimize this error a small amount was taken from the sample and treated with [D_4]methanol. With the help of ^{1}H-NMR spectroscopy the molar amount of THF was determined and a quality control was performed. Even after drying compound **3** contained 4 equivalents of THF. Taking into account the molar mass of **3** · 4 THF, the actual amount used was calculated as 0.9252 g (2.770 mmol). The concentration can vary by about 2%, however, if one assumes solvent-separated ion pairs (**3** · 4 THF + 4 THF yields **3** · 8 THF) or completely desolvated ions (**3** · 4 THF yields **3** + 4 THF). Several independent measurements at similar concentrations showed that the error limits in the determination of the degree of aggregation must be extended to 10 – 20%. This value is attributed especially to the systematic errors in the temperature measurements. Repeated measurements and averaging are therefore indispensable. – On the assumption that the cryoscopic constant has a negligible uncertainty the measurement of **3** yields a value of 0.03967 mol/kg for c and −0.091 K for ΔT with the uncertainty $c_{err} = 0.00056$ mol/kg and $\Delta T_{err} = 0.01$ K according to the error propagation rule. This leads to an error in aggregation of $n_{err} = 0.09 = 11\%$.

General Procedure for the Synthesis of 1-Arylalkan-1-ols: In a 6-l glass reaction vessel with cooling jacket, drain, valve, and anchor mixer 254 g (10.5 mol) of magnesium turnings and 3.2 l of dry diethyl ether were suspended; 0.5 mol of the appropriate bromoalkane was added. The addition of 3 ml of iodomethane initiated the reaction. As soon as the reaction has started, further 9 mol of the bromoalkane was added with intensive cooling by means of a cooling jacket while the solvent refluxed. After the addition was complete, the reaction mixture was stirred at 40°C for 1 h. After cooling to 10°C, benzaldehyde (1008 g, 9.5 mol) was added over a period of 2 h. The reaction mixture was stirred at 35°C for another 1 h and then washed once with a solution of ammonium chloride (640 g, 12 mol in 2 l of water) and twice with 1 l of water. The solvent was removed and the residue distilled off at 0.02 mbar.

Synthesis of 1-Arylalk-1-enes from 1-Arylalkan-1-ols: The 1-arylalkan-1-ols (5 mol) were placed in a 2-l round-bottom flask equipped with a Dean-Stark trap and a thermometer; 10 g of dry phenyl phosphate was added as dehydration catalyst. To remove the water formed during the reaction, *n*-octane was added. The amount of *n*-octane was controlled such that the temperature in the round-bottom flask remained between 195 to 200°C. Dehydration started immediately. After a further 5 h, 5 g of dry phenyl phosphate was added, and the mixture was heated for another 5 h. The total amount of water removed was between 75 to 95% of the theoretical yield, depending on the type of compound. Isolation and purification were accomplished by fractional distillation over a seven-plate column. Yields of pure products varied between 70 and 90%.

Variation of the General Procedure: An alternative method for obtaining 1-arylalk-1-enes was also employed. Herein, after addition of the benzaldehyde the reaction mixture was stirred at 350°C for 1 h and acetic acid anhydride (13.3 mol) was added. The mixture was stirred for 1 h, then 1 l of water was added carefully. The organic layer was extracted twice with 1 l of water and washed with 1.5 M sodium hydrogen carbonate solution. The organic layer was dried with sodium hydrogen carbonate and concentrated. The progress of the reaction could be monitored by measuring the amount of acetic acid formed. It was stopped as soon as no more acetic acid was distilled. The 1-arylalk-1-enes were purified by vacuum distillation at 0.02 mbar.

Experimental Data of Products **9** – **16**

9: ^{1}H-NMR (200 MHz, [D_8]THF, 25°C): δ = 7.1 – 7.4 (m, 5H, aromatic); 6.40 (d, 1H, 1-H, ^3J = 16 Hz); 6.29 (dt, 1H, 2-H; ^3J = 6 Hz); 2.22 (dq, 2H, CH_2, ^3J = 7.4 Hz); 1.09 (t, 3H, CH_3). – ^{13}C-NMR (50 MHz, [D_8]THF, 25°C): δ = 138.9 (*ipso*); 129.1 (*meta*);

126.7 (*ortho*); 127.5 (*para*); 132.8 (C-1); 130.1 (C-2); 26.9 (C-3); 14.1 (C-4).

$C_{10}H_{12}$ (132.20) Calcd. C 90.44 H 9.03
Found C 90.75 H 9.15

10: ^{1}H-NMR (200 MHz, [D$_8$]THF, 25°C): δ = 7.1–7.4 (m, 5H, aromatic); 6.40 (d, 1H, 1-H, ^3J = 15.9 Hz); 6.24 (dt, 1H, 2-H, ^3J = 6.7 Hz); 2.19 (dt, 2H, 3-H); 1.59 (m, 2H, 4-H); 0.97 (t, 3H, 5-H). – ^{13}C-NMR (50 MHz, [D$_8$]THF, 25°C): δ = 138.9 (*ipso*); 129.1 (*meta*); 126.7 (*ortho*); 127.5 (*para*); 131.2 (C-1); 131.1 (C-2); 36.0 (C-3); 23.5 (C-4); 14.1 (C-5).

$C_{11}H_{14}$ (146.2) Calcd. C 90.35 H 9.65
Found C 90.01 H 9.65

11: ^{1}H-NMR (200 MHz, [D$_8$]THF, 25°C): δ = 7.0–7.4 (m, 5H, aromatic); 6.39 (d, 1H, 1-H, ^3J = 16 Hz); 6.23 (dt, 1H, 2-H, ^3J = 6.5 Hz); 2.21 (dt, 2H, 3-H, ^3J = 6.7 Hz); 1.2–1.6 (m, 4H, aliphatic); 0.94 (t, 3H, 6-H). – ^{13}C-NMR (50 MHz, [D$_8$]THF, 25°C): δ = 138.9 (*ipso*); 129.1 (*meta*); 126.7 (*ortho*); 127.4 (*para*); 131.3 (C-1); 131.0 (C-2); 33.6 (C-3); 32.5 (C-4); 23.1 (C-5); 14.3 (C-6).

$C_{12}H_{16}$ (160.3) Calcd. C 89.94 H 10.06
Found C 89.75 H 9.94

12: ^{1}H-NMR (200 MHz, [D$_8$]THF, 25°C): δ = 7.1–7.4 (m, 5H, aromatic); 6.39 (d, 1H, 1-H, ^3J = 15.9 Hz); 6.25 (dt, 1H, 2-H, ^3J = 6.5 Hz); 2.20 (dt, 2H, 3-H, ^3J = 6.8 Hz); 1.2–1.6 (m, 8H, aliphatic); 0.91 (t, 3H, 8-H). – ^{13}C-NMR (50 MHz, [D$_8$]THF, 25°C): δ = 138.9 (*ipso*); 129.1 (*meta*); 126.7 (*ortho*); 127.4 (*para*); 131.1 (C-1); 130.9 (C-2); 33.9 (C-3); 32.7 (C-4); 30.6 (C-5).

$C_{14}H_{20}$ (188.3) Calcd. C 89.30 H 10.70
Found C 89.16 H 10.51

13: ^{1}H-NMR (200 MHz, [D$_8$]THF, 25°C): δ = 7.1–7.4 (m, 5H, aromatic); 6.39 (d, 1H, 1-H, ^3J = 16 Hz); 6.22 (dt, 1H, 2-H, ^3J = 6.0 Hz); 2.22 (dt, 2H, 3-H, ^3J = 5.2 Hz); 1.2–1.5 (m, 9H, aliphatic); 0.93 (t, 6H, 2 × methyl). – ^{13}C-NMR (50 MHz, [D$_8$]THF, 25°C): δ = 138.2 (*ipso*); 128.6 (*meta*); 126.1 (*ortho*); 126.8 (*para*); 131.1 (C-1); 129.8 (C-2); 39.7, 37.1, 33.0, 29.3, 26.1, 23.3 (aliphatic); 14.3 (C-8); 11.2 (C-10).

$C_{16}H_{24}$ (216.4) Calcd. C 88.82 H 11.18
Found C 88.55 H 11.46

14: ^{1}H-NMR (200 MHz, [D$_8$]THF, 25°C): δ = 7.1–7.4 (m, 5H, aromatic); 6.38 (d, 1H, 1-H, ^3J = 16 Hz); 6.23 (dt, 1H, 2-H, ^3J = 6.5 Hz); 2.20 (dt, 2H, 3-H, ^3J = 6.9 Hz); 1.1–1.6 (m, 26H, aliphatic); 0.89 (t, 3H, 17-H).

$C_{23}H_{38}$ (314.6) Calcd. C 87.82 H 12.18
Found C 87.68 H 12.32

15: ^{1}H-NMR (200 MHz, [D$_8$]THF, 25°C): δ = 7.0–7.4 (m, 5H, aromatic); 6.36 (d, 1H, 1-H, ^3J = 16 Hz); 6.18 (dd, 1H, 2-H, ^3J = 6.5 Hz); 2.13 (m, 1H, 3-H); 1.0–2.0 (m, 10H, aliphatic). – ^{13}C-NMR (50 MHz, [D$_8$]THF, 25°C): δ = 139.1 (*ipso*); 129.0 (*meta*); 126.7 (*ortho*); 127.4 (*para*); 137.0 (C-1); 128.6 (C-2); 42.2 (C-3); 33.9 (C-4, C-8); 26.9 (C-5, C-7); 27.1 (C-6).

$C_{14}H_{18}$ (186.3) Calcd. C 90.26 H 9.74
Found C 90.48 H 9.62

16: ^{1}H-NMR (200 MHz, [D$_8$]THF, 25°C): δ = 7.2–7.4 (m, 4H, aromatic); 6.36 (d, 1H, 1-H, ^3J = 15.9 Hz); 6.19 (dt, 1H, 2-H, ^3J = 6.7 Hz); 2.20 (dt, 2H, 3-H, ^3J = 6.5 Hz); 1.2–1.6 (m, 6H, aliphatic); 1.30 (s, 9H, *tert*-butyl); 0.95 (t, 3H, 7-H). – ^{13}C-NMR (50 MHz, [D$_8$]THF, 25°C): δ = 136.2 (*ipso*); 125.9 (*meta*); 126.5 (*ortho*); 150.3 (*para*); 130.8 (C-1); 130.5 (C-2); 33.9 (C-3); 32.4 (C-4); 30.1 (C-5); 25.3 (C-6); 23.4 (C-7); 35.1 (*tert*-butyl); 31.7 (*tert*-butyl, methyl).

$C_{17}H_{26}$ (230.4) Calcd. C 88.63 H 11.37
Found C 88.51 H 11.18

CAS Registry Numbers

1: 135887-54-6 / **2**: 135887-55-7 / **3**: 135887-56-8 / **4**: 135887-57-9 / **5**: 135887-58-0 / **6**: 135887-59-1 / **7**: 135887-60-4 / **8**: 135887-61-5 / **9**: 1005-64-7 / **10**: 16002-93-0 / **11**: 6111-82-6 / **12**: 28665-60-3 / **13**: 123494-37-1 / **14**: 135887-62-6 / **15**: 18869-27-7 / **16**: 123494-42-8 / *d,l*-**17**: 135887-63-7 / *meso*-**17**: 135887-71-7 / *d,l*-**18**: 135887-64-8 / *meso*-**18**: 135887-72-8 / *d,l*-**19**: 135887-65-9 / *meso*-**19**: 135887-73-9 / *d,l*-**20**: 135887-66-0 / *meso*-**20**: 135887-74-0 / **21**: 135887-67-1 / *d,l*-**22**: 135887-68-2 / *meso*-**22**: 135887-75-1 / *d,l*-**23**: 135887-69-3 / *d,l*-**24**: 135887-70-6 / *meso*-**24**: 135887-76-2

[1] Dedicated to Professor *Leopold Horner* on the occasion of his 80th birthday.
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