Sterically Congested Molecules, 6[1]

Lone Electron Pair Donor Quality of the Imino Function: Increased Front Strain and Electronic Substituent Effects on Sterically Accelerated Nitrogen Inversion in Iminocyclopentanes

Rudolf Knorr*[a], Thi Phung Hoang[a], Johann Mehlstäubl[a], Monika Hintermeyer-Hilpert[a], Hans-Dietrich Lüdemann[b], Elmar Lang[b], Gerhard Sextl[a], Wilfried Rattay[a], and Petra Böhrer[a]

Institut für Organische Chemie der Universität München[a],
Karlstraße 23, W-8000 München 2, Germany

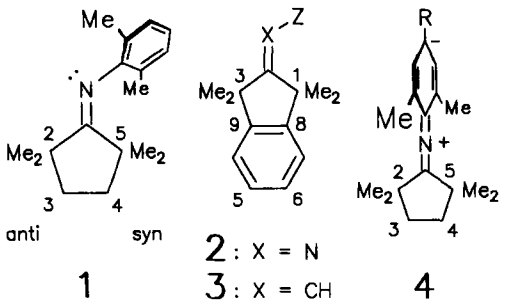
Institut für Biophysik und physikalische Biochemie der Universität Regensburg[b],
Universitätsstraße 31, W-8400 Regensburg, Germany

Received June 9, 1992

Key Words: Imines / Steric acceleration / Substituent constants / Substituent effects

The *p*-substituents of 2,6-dimethyl-*N*-(2,2,5,5-tetramethylcyclopentylidene)anilines are modified without interfering reactions at the CN double bond. The resultant series (**5**–**8**, **10**–**19**) shows a strong (ca. −4.7 kcal/mol) steric acceleration of (*E*/*Z*) diastereotopomerization by front strain along the CN double bond but also the usual electronic substituent dependence, characterized by a Hammett σ_p^- correlation ($\varrho = +2.7$). Conversely, the substituent constant for lithium at the *p*-position of **7** may be estimated. The volume of activation is 1.5(8) cm^3 mol^{-1} for **5**. The π donor quality of the imino group corresponds to ca. 55 (±8)% of p_π character as evaluated by spectral (^{13}C NMR of **5** and **13**, IR of **13**) and reactivity data (of **13**).

The chemistry of imines[2] is dominated by reactions at the C=N bond and (if present) at adjacent CH functions. Therefore, the possible role[3–6] of the imino function as an activating but structurally conserved (i.e., "spectator") substituent does not normally become evident. Whereas the imino double bond in general is prone to hydrolytic or other fission, steric congestion of 2,6-dimethyl-*N*-(2,2,5,5-tetramethylcyclopentylidene)anilines **1** efficiently suppresses such reactivity and may have further energetic, structural, and chemical consequences. Front strain along the C=N bond[7] of **1** is expected to destabilize the ground state energetically and hence to accelerate the *anti*/*syn* stereomutation[8] (diastereotopomerization). The 5,5-dimethyl groups in **1** might shift into closer contact with the opposing aryl moiety, increasing the front strain over that in **2**, because the single bond C-3/C-4 in **1** (1.44–1.50 Å)[7] is longer than the C-8/C-9 bond in **2** (compare 1.382 Å[9] in the isoelectronic olefin **3**, Z = phenyl). Consequently, the (*E*/*Z*)-configurational stability of **1** should be even lower than in the tetramethyl-2-indanylidene series **2**.



Considering the nitrogen lone pair for conjugation[10], one may even imagine a structural change of ground states from **1** (C_s symmetry) to **4** (C_{2v} symmetry) in the case of a very strongly π-accepting *p*-substituent R. For a quantification of the lone-pair donor quality in this sense, we investigate the temperature-dependent symmetry of imines **1** (**5**–**8** and **10**–**19**), their activation parameters of stereomutation (Hammett value), and possible other consequences on reactivity in some preparative reactions.

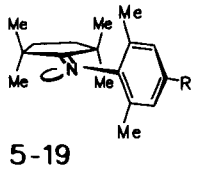
A. Modification of Imines at their *p*-Substituents

The *p*-substituted imines **6** and **19** are easily prepared[11] from **5** because the aromatic ring maintains an orthogonal conformation[7] with respect to the CN double bond, providing for the best possible overlap of the aromatic π system with the imino nitrogen lone pair. Due to steric congestion, the CN double bond of this type of imines appears to be completely inert toward hydrolysis[11], redox reagents[11], or even very strong (organometallic) nucleophiles, thus permitting the transformations described in the sequel (see Schemes 1 and 2 further below).

Metal/halogen exchange (Scheme 1) of *n*-butyllithium with the *p*-bromo derivative **6** proceeds so cleanly that the moderately stable lithium compound **7** may be studied spectroscopically. The half-conversion time at ambient temperature is roughly 2 h in pentane (with *tert*-butyllithium less than 2 min), and **7** slowly deposits from the initially clear solution containing also 1-bromobutane. This colourless precipitate may be washed with cyclopentane and dissolved in ether or THF. It is more convenient to run the lithium/

  0009–2940/93/0101–0217 $ 3.50+.25/0

bromine exchange in ether where the half-conversion time is only 2 min at room temperature; although **7** remains in solution under these conditions and cannot be purified, it persists for some hours despite the presence of 1-bromobutane. The chemical constitution of **7** follows from its NMR spectroscopically determined symmetry and from its carboxylation product **8** which is also formed via the Grignard derivative **9**.



5-19

	R
5	H
6	Br
7	Li
8	CO_2H
9	MgBr
10	$COCH_3$
11	CN
12	NH_2

	R
13	$N_2^+ BF_4^-$
14	OH
15	$O^- K^+$
16	OCH_3
17	$N(CH_3)_2$
18	$NMe_3^+ I^-$
19	NO_2

In pentane solution at room temperature, the ^1H- and ^{13}C-NMR signals of **7** are very broad or even unobservable but narrower in the presence of *n*-butyllithium. The aromatic ^{13}C-NMR shifts (Table 1) and ^1J parameters of **7** in ethereal solvents are quite typical of a phenyllithium derivative[12]. Geminal (^2J = 12.8 Hz) and vicinal CH coupling constants (^3J = 13.5 Hz) with and across the carbanionic *p*-carbon atom are surprisingly large but consistent with known trends[13].

As expected if the aromatic π electron density is somewhat increased by the imino function, reductive metalation of the bromide **6** is rather difficult: Metallic lithium reacts poorly, and magnesium requires boiling THF solvent for productive formation of the Grignard compound **9** which precipitates at room temperature. The *p*-aminobenzoic acid derivative **8** formed from **9** is not zwitterionic in $CDCl_3$ solution (^{13}C-NMR criterion) and is used for preparation[14] of the *p*-acetyl

Scheme 1

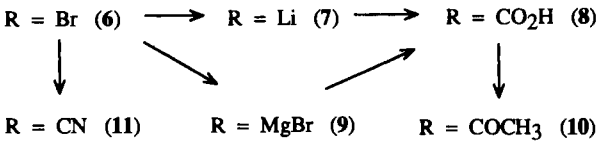


Table 1. ^{13}C- and some ^1H-NMR chemical shifts (δ) of the imines

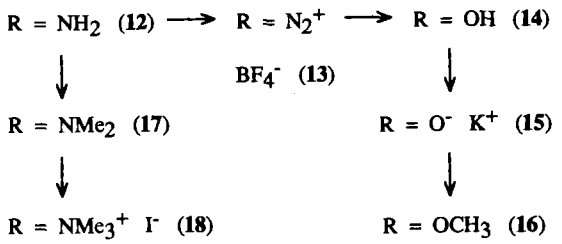
Cpd. :	**7**	**7**	**8**	**10**	**11**	**13**	**14**	**19**
R =	^6Li	Li	CO_2H	$COCH_3$	CN	$N_2^+ BF_4^-$	OH	NO_2
Solvent	Ether	THF	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$[a]	$(Cl_2CD)_2$	$CDCl_3$
Temp. [°C]	+6	+24	-75	-77	-65	-80	+33	-84
2-CH_3	28.4	-	27.8	27.8	27.7	26.1	27.7	27.7
5-CH_3	25.7	-	24.9	24.9	24.9	26.1	25.3	25.0
o-CH_3	19.0	18.9	18.6	18.7	18.4	18.9	18.5	18.8
C-1	183.8	183.7	188.5[b]	188.1	188.6	188.2	190.4	188.8
C-2	44.3	-	45.2	45.1	45.2	46.2	45.2	45.6
C-3	36.7	36.7	35.5	35.4	35.4	36.7	35.8	35.4
C-4	40.2	40.2	38.8	38.6	38.6	36.7	39.2	38.5
C-5	46.2	-	45.7	45.6	45.2	46.2	45.2	45.6
ipso-C	147.3	-	152.6	152.5	151.8	160.3	140.2	154.2
ortho-C	121.8	120.0	125.3	125.0	125.9	127.7	126.8	125.6
meta-C	141.9	144.1	129.6	128.7	131.3	131.5	115.1	123.3
para-C	164.9[c]	174.2	122.1	130.3	120.5	97.9	151.3	141.4
para-R	-	-	173.1	199.1[d]	104.0	-	-	-
2-CH_3	-	1.28[e]	-	1.28[f]	1.23	1.13	1.28[g]	1.29
5-CH_3	-	0.95[e]	-	0.94[f]	0.89	1.13	0.88[g]	0.98
o-CH_3	-	1.98[e]	-	2.12[f]	2.04	2.15	1.83[g]	2.17
CH_2-3,4	-	1.63[e]	-	1.73[f]	1.67, 1.71	1.81	1.70[g]	1.77
arom. *H*	-	7.42[e]	-	7.75[f]	7.23	8.16	6.03[g]	7.94

[a] With CH_2Cl_2 (1:2). – [b] 187.2 at +23°C. – [c] Unresolved broadening below −70°C. – [d] CH_3 at δ = 27.0. – [e] At −9°C in $[D_8]$THF. – [f] At −85°C. – [g] In CCl_4 at −27°C.

compound **10** because the Friedel-Crafts acetylation of **5** had failed[11]. Cyanation[15] of **6** is also very sluggish but generates the nitrile **11** cleanly.

In a second series of transformations (Scheme 2), the diazonium compound **13** is prepared from the primary amine[11] **12** by the usual aqueous nitrosation. The *anti* and *syn* positions of this cation remain NMR-isochronous down to −80°C, simulating the C_{2v} symmetry of **4** (R = N_2^+). However, its chemical shift values (Table 1) differ greatly from those expected for a diazoquinone imine. In particular, the *p*-C atom carrying the diazonium function is observed at δ = 97.9, i.e. between the values for benzenediazonium (ca. 115.6[16–18]) and 4-(dimethylamino)benzenediazonium (ca. 88.8[17–19]), indicating that the π donor quality of the imino substituent approaches 66% of that of the *p*-dimethylamino group at low temperature. The characteristic IR absorption of **13** at 2223 or 2205 cm^{-1} is midway (48–61%) between those of benzenediazonium tetrafluoroborate (2290 cm^{-1})[20,21] and of 4-(diethylamino)benzenediazonium (2151 cm^{-1})[21].

Scheme 2



Although this yellow diazonium compound **13** is thermally rather stable, it is very sensitive to light and also inclined to undergo radical reactions: When subjected to the recommended[22] Sandmeyer cyanation conditions, it yields the nitrile **11** together with the parent compound **5** which is difficult to separate. However, the thermal decomposition of **13** in dilute acid yields the phenol **14** cleanly and has been studied in more detail under conditions taken from literature standards[23,24]. The half-conversion time of **13** in 0.1 N H_2SO_4 is no less than 8 min even at +78.5°C. The Arrhenius activation energy 29.1 (±1.2) kcal/mol again points to a π donor quality which corresponds to 48% of the range between the benzenediazonium (ca. 26.6 kcal/mol)[23,24] and 4-(dimethylamino)benzenediazonium (32.0 kcal/mol)[24] tetrafluoroborates. Our UV measurements reveal strictly first-order kinetics with activation parameters $\Delta H^{\neq}$ = 28.4 (±1.2) kcal/mol and $\Delta S^{\neq}$ = +8.7 (±3.4) e.u. for this hydroxy-dediazoniation reaction[25].

The ensuing phenol derivative **14** is sufficiently basic to form a hydrochloride but rather weakly acidic, such that extraction from ether into alkaline water is inefficient. In single crystals[7], **14** acts as a hydrogen-bond donor and acceptor in a peculiar fashion. The yellow potassium salt **15** is soluble in THF and in hot aqueous 2 N KOH solution, forming the anisole derivative **16** on methylation. Dimethyl sulfate methylates the primary amino function of **12** (Scheme 2) to give **17** in moderate yield. The conditions of exhaustive methylation have been chosen[26] for precipitation of the quaternary ammonium salt, but the desired product **18** remains in solution and is accompanied by another unidentified salt.

B. Steric and Electronic Substituent Effects on (*E,Z*) Stereomutation

The *anti/syn* interconversion shown in **20/21** causes coalescences of NMR absorptions for the corresponding positions and has been measured for the prototype **5** by ^{1}H- and ^{13}C-NMR spectroscopy at various magnetic field strengths and concentrations. The rate constants of this diastereotopomerization are obtained by lineshape analysis[27]; they define a common temperature dependence in $CDCl_3$ (^{13}C) and in anisole (^{1}H), as shown in Figure 1, and are essentially the same as in [D_8]THF with or without metallic lithium and naphthalene (which have been added to check for radical-anion catalysis). A slight retardation (ca. 1.5-fold) is noticed in [D_8]THF containing LiBr which may coordinate to the lone electron pair. Formation of hydrogen bonds is not important because the rate constants in methanol, benzene, and CCl_4 are almost equal to those in 1,2-dibromo-1,1,2,2-tetrafluoroethane (by ^{1}H and ^{13}C NMR).

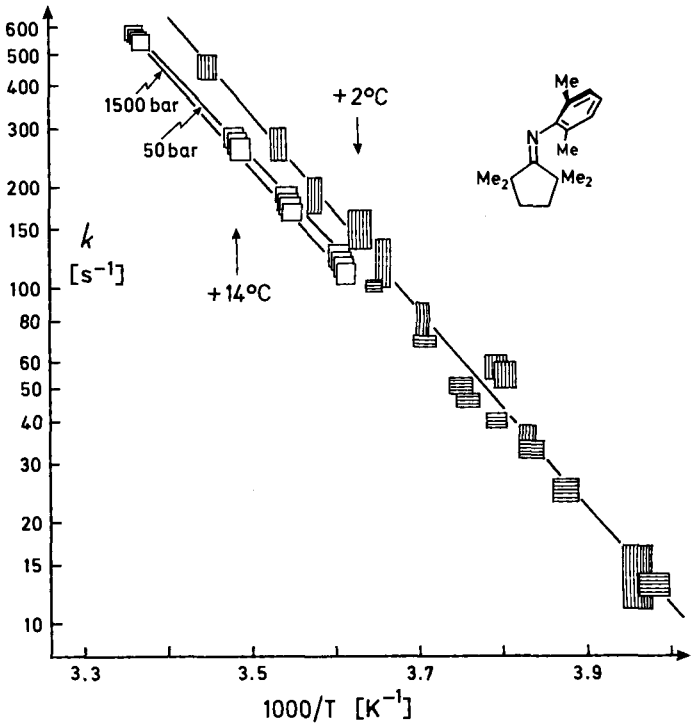
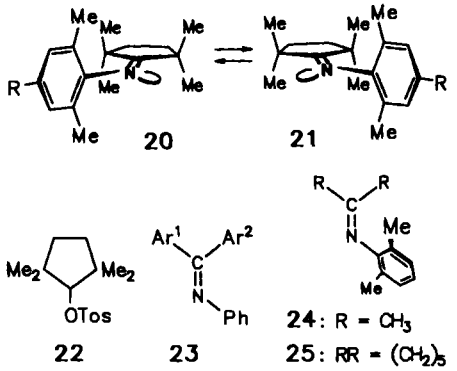


Figure 1. Arrhenius diagram for *anti/syn* stereomutation of **5** in $CDCl_3$ (^{13}C, vertically hatched) und in anisole (^{1}H, horizontally hatched). Rate constants *k* in 1,2-dibromo-1,1,2,2-tetrafluoroethane (^{1}H, open symbols) have been slightly displaced horizontally to reduce overlap

Although independent of concentration, the stereomutation could be a pseudofirst-order process due to latent catalysis by nucleophilic impurities[27]. We have therefore studied the influence of pressure in this second[27] case and have found a similar temperature dependence as above but a very

small retardation (1.3-fold) caused by the solvent 1,2-dibromo-1,1,2,2-tetrafluoroethane (Figure 1). To eliminate individual errors, the isobaric rate values have been interpolated to the common temperature) +14°C (that is, close to coalescence temperature for the calculation of the activation volume $\Delta V^{\neq} = +1.5\ (\pm 0.8)\ cm^3\ mol^{-1}$. This value is substantially more negative than for the related methylimine **2** (Z = CH_3) but still hardly indicative of a bimolecular mechanism[27]; it may point to a small contribution from solvent electrostriction in the transition state formed from **5**, but at least the carbon atom of the CN double bond appears to be excluded from solvation, as suggested by the lack of solvent assistance in the heterolysis of **22**[28,29].



Small decelerations in hydroxylic as compared to hydrocarbon solvents have also been observed for the (*Z*/*E*) isomerization of aldehyde anils in earlier work[30,31]. Reported entropies of activation scatter roughly about $\Delta S^{\neq} = 0$ for such anils[30,31] and for most ketimines. With respect to these two criteria, the sterically congested imine **5** shows normal kinetic behaviour, i.e. a small $\Delta S^{\neq}$ value (Table 2) and vanishing solvent dependence. Hence, it is justified to compare $\Delta G^{\neq} = 13.36(2)$ kcal/mol for the diastereotopomerization of **5** with the value 18.1 kcal/mol[27] for non-congested anils **23**; these are preferred over **24** or **25** as reference compounds for mechanistic reasons explained before[8]. This steric acceleration by −4.7 kcal/mol is larger than that of **2** (*Z* = phenyl) with −2.7 kcal/mol[8], as anticipated. Only part (ca. −0.9 kcal/mol) of the difference (−2.0) is caused by the two *ortho*-CH_3 groups in **5** (or **20**, R = H), as judged from published data on imines of the types **23**[32], **24**[33], **25**[34], and probably also of quinone anils[35,36] and further examples[37].

The conformational unambiguity of the system **20** is one of its merits because less congested anils may change their CN/aryl conformation[10] as a function of the *p*-substituent R. Most authors have reported positive reaction constants ϱ for imine stereomutations[38], but V-shaped Hammett plots have occasionally[37,39] been found and suspected to indicate a substituent-dependent mechanistic change. It is therefore of interest to know the electronic substituent effect on the diastereotopomerization of **20** with the special bonus that all competing bimolecular mechanisms have been excluded.

The activation parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ derived from the rate constants of **20** (**5**–**8**, **10**–**12**, **14**–**19**) are summarized in Table 2. The solvents have practically no influence on rate constants, as shown above, and could be chosen for convenience. All $\Delta G^{\neq}$ values refer to −13.2°C, but their temperature dependence hardly exceeds the error limits due to the small $\Delta S^{\neq}$ values.

Table 2. Enthalpies $\Delta H^{\neq}$ (kcal/mol), entropies $\Delta S^{\neq}$ (cal $mol^{-1}\ K^{-1}$), and free enthalpies of activation $\Delta G^{\neq}$ (kcal/mol) at 260 K, with substituent constants σ_p^- for **5**–**8**, **10**–**12** and **14**–**19**

No.	*p*-R	Solvent	$\Delta H^{\#}$	$\Delta S^{\#}$	$\Delta G^{\#}$	σ_p^-
15	$O^- K^+$	[D8]-THF	16.8 (1.4)	+3 (5)	16.1 (2)	-0.82
14	OH	CCl_4	15.8 (1.4)	+2 (5)	15.2 (2)	-0.37
16	OCH_3	CCl_4	14.8 (5)	0 (2)	14.9 (1)	-0.26
12	NH_2	CCl_4	14.0 (7)	-3 (3)	14.7 (1)	-0.15
17	$N(CH_3)_2$	CCl_4	13.2 (1.0)	-4 (4)	14.2 (1)	-0.12
7	Li	Ether	13.5 (4)	-3 (3)	14.2 (1)	-0.55[a]
5	H	[b]	12.8 (4)	-2 (2)	13.36 (2)	0
6	Br	CCl_4	13.3 (6)	0 (2)	13.33 (1)	+0.25
18	$Me_3N^+ I^-$	$CDCl_3$	10.5 (1)	-6 (2)	12.02 (2)	+0.77
8	CO_2H	$CDCl_3$	11.2 (6)	+1 (3)	10.9 (1)	+0.77
11	CN	$CDCl_3$	10.7 (5)	-1 (2)	10.9 (1)	+1.00
10	$COCH_3$	$CDCl_3$	9.8 (3)	-4 (2)	10.8 (1)	+0.84
19	NO_2	$CDCl_3$[c]	9.1 (4)	-1 (2)	9.3 (2)	+1.27
13	$N_2^+ BF_4^-$	$CDCl_3$[c]	-	-	< 8.6	+3.43

[a] See text. — [b] In anisole (^1H) or in $CDCl_3$ (^{13}C). — [c] Also in CH_2Cl_2.

Since the compounds in Table 2 have been arranged by decreasing $\Delta G^{\neq}$ values, the dominant role of π-electronic substituent effects becomes immediately evident. Whereas attempted correlations of $\Delta G^{\neq}$ with most sets of Hammett-type substituent constants give non-linear dependencies, the use of resonance parameters[5b] R^- or of σ_R^- provides acceptable linearity (not illustrated here); but this would be stained by an apparent displacement of the parent compound **5** toward more positive σ values by 0.1–0.2 units. However, "R^- values for π donor substituents are questionable"[5c] as demonstrated, for example, by the hardly credible sequence of absolute values for OH > O^- > OCH_3[5b]. Thus, we prefer the correlation shown in Figure 2 with σ_p^- constants[5b] which are mechanistically unseparated and hence comprise some blend of resonance and "inductive" effects. The reaction constant ϱ(260 K) = +2.7(4) computed from the slope (= $-2.3\ RT\varrho$ with $r = 0.983$) of this plot equals that which we have recalculated from the original data[40] of quinone anils; hence, the steric congestion has not changed the electronic substituent dependence despite accelerations due to a decrease of $\Delta G^{\neq}$ by more than 8–9 kcal/mol. However, the parent compound **5** (H in Figure 2) now appears displaced too much to the negative side of the correlation line, such that σ_p^- has overvalued the non-resonance effects, as may also be suspected for the bromide **6** having a similar $\Delta G^{\neq}$ value as **5**. In fact, a better correlation (broken line in Figure 2) could have been obtained by subtracting (horizontal arrows) from each σ_p^- constant one half of the corresponding σ_I value[5d]. Thereupon, *p*-bromine (in **6**) as well as *p*-trimethylammonio (**18**) fit also much better.

Acceleration by a cyano substituent (in **11**) is comparable with those by carbonyl functions (**8**, **10**) and is stronger than

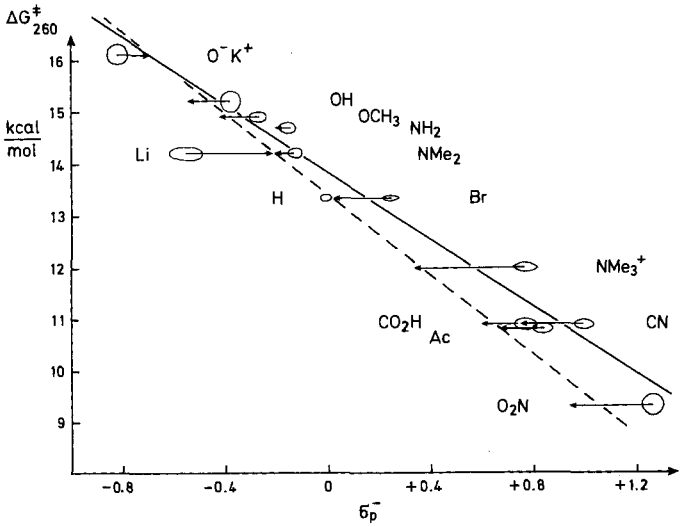


Figure 2. Hammett plot of $\Delta G^{\neq}$ (kcal/mol) versus substituent constants σ_p^-, giving $\varrho = +2.7$ at -13.2°C, and possible correction (arrows) by subtraction of $\sigma_I/2$

that by the ammonium group (in **18**). Such behaviour is typically indicative of π acceptor efficiency and restricts the importance of contributions by other mechanisms. The cyano group acts as a charge acceptor in both the resonance and inductive fashions[41–43], but one of these appears to be somewhat overestimated in the current σ_p^- parameter[5b] because the corrected value does not fit so well to the broken line. By both of these correlation lines, a $\Delta G^{\neq}$ value of ca. 3 kcal/mol is predicted (not measured) for diazonium as the strongest π acceptor.

Lithium as the *p*-substituent in **7** has not been included in these correlations because its substituent constant is apparently unknown[44]. If an "inductive" correction by one half of $\sigma_I' = -0.71$ (for Li in ether[45]) is applied in reverse of the subtraction suggested above, the σ_p^- constant would become ca. -0.55 (and has been used in Figure 2). This number compares well with a Grignard parameter -0.44[5e] and explains why lithium decelerates the (*E*,*Z*) stereomutation relative to **5**, acting as weakly as dimethylamino (in **17**) and much less than the O^- substituent in **15**.

A final significant result is the correlative fit of the *p*-nitro group (in **19**). For this strong π acceptor[41–43] with appreciable "inductive" suction[43] we find no indication from Figure 2 of a mechanistic change[37,39]. Therefore, the peculiar $\Delta G^{\neq}$ enhancement noticed earlier[8] for the nitro-imine **2** (Z = NO_2) has vanished in the phenylogue **19**; this confirms the interpreation[8] that resonance is disfavoured in **2** by causing charge repulsion.

C. Conclusion

The orthogonal arrangement of the aryl and imino systems shown in **20** for the angular ground state, as confirmed in the crystal structure[7] of **14**, provides for optimal conjugation[10,11] between the lone electron pair at sp^2 nitrogen and the aromatic π system. The π donor quality caused by this interaction corresponds to ca. 55 (±8)% p_π character, as measured by NMR of **5**[11] and **13**, by IR of **13**, and by the thermolability of **13**. It makes the properties of the angular imino function somewhat better than "hardly understandable"[4] because residual resonance has now been quantified. This analysis should carry over to the lone electron pair at pyramidalized carbon atoms like in cyclopropyl anions[43]. Although the statement[43] that cyano "stabilizes a negative charge mostly inductively" may be partially justified (because of residual resonance) for that special system with substituents directly attached to the reaction center, it does not appear to be valid for phenylogous systems and hence cannot be generalized.

π Donor quality is also the reason for the pronounced electronic substituent dependence of (*E*/*Z*) diastereotopomerization. The Hammett correlation agrees with some earlier reports[38,40,46] and is improved if the usual substituent constants σ_p^- are corrected by $-\sigma_I/2$. It reveals the dominant role of resonance in a transition state whose structure **4** remains to be proved. Despite its strongly electropositive character, lithium as a *p*-substituent is therefore only as effective as *p*-dimethylamino. A strong steric acceleration (by -4.7 kcal/mol) is superposed over the whole $\Delta G^{\neq}$ pattern.

Although the positive reaction constant ϱ is compatible with polarized transition states **4**, the (*E*,*Z*) topomerization of the unsubstituted compound **5** does not show considerable solvation effects by electrostriction ($\Delta V^{\neq}$) or solvent-dependent rate constants. Hence, stabilization of the nitrogen lone pair by the phenyl group in **4** is not accompanied by an increase of the gross molecular polarity over that of the angular ground state **5** (or **20**).

We thank the *Deutsche Forschungsgemeinschaft*, the *Leibniz-Rechenzentrum der Bayerischen Akademie der Wissenschaften*, and the *Fonds der Chemischen Industrie* for their generous support.

Experimental

The syntheses of **5**, **6**, **12**, and **19** have been described[11] as well as the spectrometric equipment.

2,6-Dimethyl-N-(2,2,5,5-tetramethylcyclopentylidene)aniline (**5**): The ^{1}H-NMR spectrum of 170 mg (0.7 mmol) of **5**[11] in 0.40 ml of dry [D_8]THF was indistinguishable from that in $CDCl_3$ solution and did not change in the presence of lithium metal (10 mg) nor after the subsequent addition of naphthalene (10 mg). An unidentified, non-basic product was partially formed in this dark green solution during several d. – Lineshape analysis at normal pressure: ^{13}C NMR ($CDCl_3$), Δδ = 2.86 (2,5-CH_3), 3.38 (CH_2-3,4), 0.92 (C-2,5); ^{1}H NMR (anisole), Δδ = 0.410 (2,5-CH_3). – Pressure dependence by ^{1}H-NMR lineshapes with 20 mg of **5** in 1.0 g of 1,2-dibromo-1,1,2,2-tetrafluoroethane as described[8] at 50, 500, 1000, and 1500 bar (Figure 1) between +4 and +24°C.

4-Bromo-2,6-dimethyl-N-(2,2,5,5-tetramethylcyclopentylidene)aniline (**6**)[11]: ^{1}H-NMR lineshapes (CCl_4): Δδ = 0.317 (2,5-CH_3).

4-^{6}Lithio-2,6-dimethyl-N-(2,2,5,5-tetramethylcyclopentylidene)aniline (**7**) *in Ether:* A 12-mm NMR test tube containing 400 mg (1.24 mmol) of **6**[11] in 2.0 ml of dry ether and 1 droplet of TMS was cooled under argon to −70°C, and 0.70 ml of [^{6}Li]-*n*-butyllithium (1.90 M in pentane, 91.1% ^{6}Li) was added. The exothermic reaction was controlled by intermittent cooling during warming up. From a similar but smaller run, 56% of **8** was secured after carboxylation. – ^{1}H NMR (pentane): δ = 7.40 (s, *m*-H). – ^{1}H NMR (ether, +30°C): δ = 1.27 (broadened s, 2- and 5-CH_3), 1.95 (s, 2 *o*-

CH_3), 7.42 (s, *m*-H). – ^{1}H NMR ([D$_8$]THF): Table 1; $\Delta\delta$ (2,5-CH_3) = 0.33, T_c = +17(3)°C at 60 MHz, $\Delta G^{\neq}$ = 14.8(2) kcal/mol. – ^{13}C NMR (THF): Table 1; $\Delta\delta$ = 3.5 (CH_2-3,4), T_c = ca. +30(3)°C at 25.15 MHz, $\Delta G^{\neq}$ = 14.6(2) kcal/mol. – ^{13}C NMR (ether at +27°C): δ = 27.1 (2- and 5-CH_3), ca. 38.5 (CH_2-3,4), 45.5 (m, C-2,5), 121.7 (m, *o*-C), 141.9 (ddq, ^1J = 146, ^3J = 13.5, ^3J = 5 Hz, *m*-C), 146.9 (m, *ipso*-C), 165.8 (sharp t, ^2J = 12.8 Hz, *p*-C), 183.6 (m, C-1); lineshape analysis: $\Delta\delta$ = 2.70 (2,5-CH_3), 3.54 (CH_2-3,4), 1.87 (C-2,5) down to −95°C.

3,5-Dimethyl-4-[(2,2,5,5-tetramethylcyclopentylidene)amino]-benzoic acid (**8**): 2.00 g (6.1 mmol) of the *p*-bromo imine **6**[11] in 5 ml of dry THF was slowly added from a dropping funnel under argon to 170 mg (7.0 mmol) of Mg turnings (activated by a small iodine crystal) in 10 ml of boiling THF. After 2 additional h at reflux, the clear solution with little residual Mg was cooled under argon whereupon a copious precipitate of **9** deposited. Carboxylation with a large excess of dry, solid carbon dioxide and distribution between 2 N NaOH and ether gave 550 mg (37%) of the *p*-protonation product **5** from the ethereal layers. The alkaline phase was acidified and extracted with ether; the extract was washed, dried with Na_2SO_4, and the solvent evaporated to yield 890 mg (51%) of the colourless acid **8**, m.p. 233–234°C. – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (v br), 2954, 2871, 2603, 1676, 1599, 1300, 1235, 1207. – ^{1}H NMR ($CDCl_3$, +32°C): δ = 1.10 (s, 4 CH_3), 1.70 (s, 2 CH_2), 2.08 (s, 2 *o*-CH_3), 7.65 (s, 2 arom. H), ca. 9.3 (br, CO_2H). – ^{13}C NMR ($CDCl_3$): Table 1; lineshape analysis: $\Delta\delta$ = 2.86 (2,5-CH_3), 0.48 (C-2,5) down to −75°C.

$C_{18}H_{25}NO_2$ (287.4) Calcd. C 75.23 H 8.77 N 4.87
Found C 75.39 H 8.90 N 4.61

4-Acetyl-2,6-dimethyl-N-(2,2,5,5-tetramethylcyclopentylidene)aniline (**10**): A suspension of 500 mg (1.74 mmol) of **9** in 10 ml of dry ether was stirred under argon and cooled in an ice bath. The precipitate dissolved upon dropwise addition of 2.20 ml of methyllithium (1.6 M in ether) with evolution of methane. The orange-coloured solution was kept at room temp. for 2 d and poured into 30 ml of ice-cooled 2 N HCl. The combined ethereal extracts were shaken with aqueous sodium carbonate, washed neutral, dried with Na_2SO_4, and evaporated to leave 400 mg (80%) of solid **10**; pale yellow, short needles with m.p. 96–97°C (from ligroin). – IR (KBr): $\tilde{\nu}$ = 2958 cm^{-1}, 2870, 1695, 1670, 1595, 1304, 1189. – ^{1}H NMR ($CDCl_3$): δ = 1.10 (s, 4 CH_3), 1.71 (s, 2 CH_2), 2.10 (s, 2 *o*-CH_3), 2.53 (s, Acetyl), 7.57 (s, 2 *m*-H); lineshape anlysis: $\Delta\delta$ = 0.350 (2,5-CH_3) down to −85°C. – ^{13}C NMR ($CDCl_3$): Table 1; lineshape analysis: $\Delta\delta$ = 2.90 (2,5-CH_3), 3.26 (CH_2-3,4), 0.50 (C-2,5) down to −77.4°C.

$C_{19}H_{27}NO$ (285.4) Calcd. C 79.95 H 9.54 N 4.91
Found C 80.25 H 9.49 N 5.41

3,5-Dimethyl-4-[(2,2,5,5-tetramethylcyclopentylidene)amino]-benzonitrile (**11**): Sodium cyanide (490 mg, 10 mmol) and copper cyanide (890 mg, 9.9 mmol) were preheated[15] in 5 ml of dry dimethylformamide for 10 min at 95°C. Then 1.06 g (3.3 mmol) of the *p*-bromide **6** was added and the inhomogeneous mixture heated under argon at 160°C for at least 5 d. After distribution between 80 ml of ether and 30 ml of water, washing, drying of the ethereal layer, and evaporation the residue crystallized exothermically to give a very hard mass which contained only **11** and a trace of unreacted **6**. It was dissolved in 5 ml of hexane, the solution filtered and concentrated to 1 ml for crystallization of **6** at −20°C. The other liquor afforded 136 mg (15%) of the almost colourless nitrile **11**; m.p. 110.5–111.5°C from hexane at −40°C, b.p. 130–180°C (bath-temp.)/0.05 mbar. – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2870, 2219 (CN), 1676, 1600, 1461, 1033. – ^{1}H NMR (CCl_4): δ = 1.07 (s, 4 CH_3), 1.67 (s, 2 CH_2), 1.99 (s, 2 *o*-CH_3), 7.11 (s, 2 *m*-H). – ^{1}H and ^{13}C NMR ($CDCl_3$): Table 1. Lineshape analysis: $\Delta\delta$ = 0.340 (2,5-CH_3 protons) down to −74°C.

$C_{18}H_{24}N_2$ (268.4) Calcd. C 80.55 H 9.01 N 10.44
Found C 80.55 H 9.02 N 10.18

3,5-Dimethyl-4-[(2,2,5,5-tetramethylcyclopentylidene)amino]aniline (**12**): ^{1}H NMR (CCl_4 at −23°C): δ = 0.91 (s, 5-CH_3), 1.22 (s, 2-CH_3), 1.64 (s, CH_2-3,4), 1.91 (s, 2 *o*-CH_3), 3.54 (s, NH_2), 6.21 (s, 2 arom. H); lineshape analysis: $\Delta\delta$ = 0.318 (2,5-CH_3).

3,5-Dimethyl-4-[(2,2,5,5-tetramethylcyclopentylidene)amino]benzenediazonium Tetrafluoroborate (**13**): The hot solution of 3.00 g (11.6 mmol) of the primary amine **12**[11] in 17 ml of 2 N HCl was chilled in ice. On dropwise addition of 950 mg (13.8 mmol) of sodium nitrite in 30 ml of water within 20 min, the stirred suspension dissolved. After a positive nitrite test 7.5 ml (32 mmol) of aqueous hydrogen tetrafluoroborate (31%) was added to produce a voluminous precipitate which was filtered by suction after 1 h, washed with water and ether, and dried in vacuo with protection from light (3.54 g, 83%). It was dissolved in 40 ml of CH_2Cl_2 and reprecipitated by 200 ml of ether to yield 3.41 g (82%) of bright-yellow, spear-shaped crystals of **13** which turn dark blue on exposure to light; m.p. 122–123°C (with gas evolution). – IR (KBr): $\tilde{\nu}$ = 2965 cm^{-1}, 2870, 2223 (N_2^+), 1730 (CN), 1575, 1105, 1083, 1027. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2205 cm^{-1} (N_2^+), 1718 (CN), 1570, 1102, 1060, 1023. – UV (CH_2Cl_2): λ_{max} (lg ε) = 256 nm (2.292), 388 (3.993). – UV (water or 0.1 N H_2SO_4): λ_{max} (lg ε) = 243 nm (3.689), 364 (4.212), changing to the spectrum of phenol **14** after 4 min in sunlight. – ^{1}H NMR (CH_2Cl_2 or CH_3OH, +28°C): As in Table 1. – ^{13}C NMR ($CDCl_3$, +35°C): Deviations up to ±0.5 ppm from Table 1.

$C_{17}H_{24}BF_4N_3$ (357.2) Calcd. C 57.16 H 6.77 N 11.76
Found C 57.28 H 6.91 N 11.63

3,5-Dimethyl-4-[(2,2,5,5-tetramethylcyclopentylidene)amino]-phenol (**14**)

a) *By Thermolysis:* A suspension of the diazonium tetrafluoroborate **13** (1.79 g, 5.0 mmol) in 50 ml of 0.1 N H_2SO_4 was magnetically stirred and heated at 95–105°C for rapid dissolution and evolution of nitrogen (121 ml, 95%). The clear solution was cooled and its pH adjusted to 6–7 with KOH solution. The colourless suspension was shaken with ether (3 × 100 ml), and the combined extracts were washed and dried with Na_2SO_4. The crude material (1.0 g, 77%) obtained by evaporation of the ether was recrystallized from cyclohexane: Colourless platelets or fine needles, 0.77 g (59%), m.p. 167–169°C.

b) *By Photolysis:* 200 ml of 0.1 N H_2SO_4 was required to dissolve 360 mg (1.01 mmol) of **13** completely. The yellow solution was exposed to diffuse light for several d (or to a 100-W bulb for ca. 1 h) at ambient temp. until bleached. Workup as above gave 260 mg (99%) of pure **14**. – IR (KBr): $\tilde{\nu}$ = 3350 cm^{-1} (br, OH), 2960, 2865, 1676, 1666, 1459, 1306, 1200. – UV (cyclohexane): λ_{max} (lg ε) = 236 nm (3.925), 297 (3.468). – UV (0.1 N H_2SO_4): λ_{max} (lg ε) = 272 nm (3.067), 300 (sh, 2.759). – ^{1}H NMR (CCl_4): Table 1; lineshape analysis: $\Delta\delta$ = 0.400 (2,5-CH_3) down to −27°C. – ^{13}C NMR (Cl_2CD-$CDCl_2$): Table 1.

$C_{17}H_{25}NO$ (259.4) Calcd. C 78.72 H 9.71 N 5.40
Found C 78.75 H 9.75 N 5.40

Rate Constants for Hydroxy-dediazoniation of **13**: Degassed dilute sulfuric acid (0.1 N) was preheated in the cuvette of a photometer (Zeiss PMQ II) until the internal temperature (controlled by thermocouple) was constant. A more concentrated stock solution of **13** in the same solvent (light-protected) was quickly added for initial concentrations adjusted to give suitable extinction values (variation

up to five-fold). After mixing and several min of thermal equilibration, extinctions were read at λ_{max} = 364 nm where the product **14** does not absorb, leading to first-order plots over at least two half-lives. A control experiment with a sample permanently exposed to the photometer beam revealed only 2% loss during 19 h at room temp. — Rate constants 10^5 k (s^{-1}): 6.1(1) at 54.0(2)°C, 27.3(6) at 65.0(2)°C, 34.3(7) at 68.5°C, and (for two concentrations) 138(4) and 141(4) at +78.5(2)°C.

4-Hydroxy-2,6-dimethyl-N-(2,2,5,5-tetramethylcyclopentylidene)anilinium Chloride (**14** Hydrochloride): From a solution of 31 mg (0.12 mmol) of the phenol **14** in a mixture of 0.4 ml of methanol, 0.2 ml of 2 N HCl, and 0.03 ml of conc. HCl slowly deposited large, transparent, colourless parallelepipeds of **14** hydrochloride. These were quickly washed with very little methanol (readily soluble) and recrystallized from methanol/2 N HCl (1:1); decomp. above 230°C, structure confirmed by X-ray analysis. — ^{1}H NMR ([D$_6$]DMSO/[D$_6$]acetone, 5:1): δ = 1.07 (s, 5-CH$_3$), 1.54 (s, 2-CH$_3$), 1.73 (s, 1 CH$_2$), 1.94 (s, 2 *o*-CH$_3$), 6.63 (s, 2 *m*-H).

$C_{17}H_{26}ClNO$ (295.9) Calcd. C 69.02 H 8.86 N 4.73
Found C 68.96 H 8.99 N 4.69

Potassium 3,5-Dimethyl-4-[(2,2,5,5-tetramethylcyclopentylidene)amino]phenoxide (**15**): Potassium hydride (45 mg) was placed in a dried 5-mm NMR test tube, washed oil-free with dry benzene (5 × 1 ml) under N_2, and covered with 0.3 ml of [D$_8$]THF. Brisk hydrogen evolution was noticed after the addition of the phenol **14** (45 mg) to give a bright-yellow, clear solution. — ^{1}H NMR ([D$_8$]THF at −26°C or +24°C): δ = 0.97 (s, 5-CH$_3$), 1.24 (s, 2-CH$_3$), 1.60 (s, CH$_2$-3,4), 1.93 (s, 2 *o*-CH$_3$); lineshape analysis: Δδ = 0.167 (2,5-CH$_3$).

4-Methoxy-2,6-dimethyl-N-(2,2,5,5-tetramethylcyclopentylidene)aniline (**16**): 550 mg (2.12 mmol) of the phenol **14** was heated in 15 ml of aqueous 2 N KOH on a steam-bath until dissolved (5 min). Without further heating, 1.0 ml (10.5 mmol) of dimethyl sulfate was slowly added during 20 min and the exothermic reaction completed on the hot steam-bath for 15 min. The combined ether extracts were shaken exhaustively with 2 N KOH (7 × 25 ml) to remove residual **14**, then washed neutral and dried with calcium chloride. After evaporation of the solvent the crude residue (440 mg, 72%) distilled at 130−152°C (bath temp.)/0.12 Torr and solidified to afford 360 mg (62%) of almost colourless blocks of **16** with m.p. 57−58°C. — IR (KBr): $\tilde{\nu}$ = 2958 cm^{-1}, 2875, 1675 (CN), 1466, 1317, 1204, 1152, 1064, 853. — UV (cyclohexane): λ_{max} (lg ε) = 238 nm (4.037), 297 (3.482). — ^{1}H NMR (CCl_4 at −26°C): δ = 0.90 (s, 5-CH$_3$), 1.24 (s, 2-CH$_3$), 1.65 (s, CH$_2$-3,4), 1.97 (s, 2 *o*-CH$_3$), 3.68 (s, OCH$_3$), 6.40 (s, 2 *m*-H); lineshape analysis: Δδ = 0.340 (2,5-CH$_3$).

$C_{18}H_{27}NO$ (273.4) Calcd. C 79.07 H 9.95 N 5.12
Found C 78.90 H 9.86 N 5.28

4-(Dimethylamino)-2,6-dimethyl-N-(2,2,5,5-tetramethylcyclopentylidene)aniline (**17**): Dimethyl sulfate (1.90 ml, 20 mmol) and 2.15 g (8.3 mmol) of the amine **12**[11] in 30 ml of toluene were stirred for 2 h at room temp. The clear solution got milky and slightly warm on dropwise addition of 2.2 ml (19 mmol) of aqueous (35%) sodium hydroxide. After further stirring overnight, residual dimethyl sulfate was destroyed with 60 ml of aqueous (25%) ammonia solution (1 h at room temp.). The emulsion was diluted with 30 ml of water, extracted with ether (5 × 50 ml), and the combined extracts were washed and dried with Na_2SO_4. Distillation at 145−154°C (bath temp.)/0.07 Torr afforded 840 mg (35%) of a yellow oil which solidified to colourless blocks with m.p. 56−57°C. — IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1}, 2865, 1675 (CN), 1487, 1461. — UV (cyclohexane): λ_{max} (lg ε) = 256 nm (4.193), 315 (3.512). — ^{1}H NMR (CCl_4 at −27°C): δ = 0.92 (s, 5-CH$_3$), 1.25 (s, 2-CH$_3$), 1.64 (s, CH$_2$-3,4), 1.95 (s, 2 *o*-CH$_3$), 2.80 (s, dimethylamino), 6.25 (s, 2 arom. H); lineshape analysis: Δδ = 0.327 (2,5-CH$_3$).

$C_{19}H_{30}N_2$ (286.5) Calcd. C 79.66 H 10.56 N 9.78
Found C 79.47 H 10.71 N 9.79

N,N,N,3,5-Pentamethyl-4-[(2,2,5,5-tetramethylcyclopentylidene)amino]anilinium Iodide (**18**): An unknown, colourless byproduct deposited during 2 d at room temp. on treatment of 820 mg (2.86 mmol) of the dimethylamino compound **17** in 30 ml of acetone[26] with 0.35 ml (5.6 mmol) of methyl iodide. The whole mixture was concentrated and the remainder leached out with chloroform on a filter funnel. The filtrate was again evaporated and the residue recrystallized from 4 ml of 2-propanol to give 210 mg (17%) of almost colourless platelets with m.p. 199−202°C (decomp.). — IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1}, 2864, 1682 (CN), 1460. — UV ($CHCl_3$): λ_{max} (lg ε) = 248 nm (4.291), 290 (sh, 3.291), 363 (2.436). — ^{1}H NMR ($CDCl_3$, −55°C): δ = 0.92 (s, 5-CH$_3$), 1.27 (s, 2-CH$_3$), 1.73 (s, CH$_2$-3,4), 2.16 (s, 2 *o*-CH$_3$), 3.90 (s, NMe$_3^+$), 7.51 (s, 2 arom. H); lineshape analysis: Δδ = 0.355 (2,5-CH$_3$) down to −65°C.

$C_{20}H_{33}IN_2$ (428.4) Calcd. C 56.07 H 7.76 N 6.54
Found C 56.12 H 7.85 N 6.13

2,6-Dimethyl-4-nitro-N-(2,2,5,5-tetramethylcyclopentylidene)aniline (**19**)[11]: ^{1}H and ^{13}C NMR ($CDCl_3$): Table 1. Lineshape analysis: Δδ = 0.305 (2,5-CH$_3$ protons), 2.66 (2,5-^{13}CH$_3$), 3.15 (^{13}CH$_2$-3,4).

[1] Part 5: R. Knorr, T. P. Hoang, H. Nöth, G. Linti, *Organometallics* **1992**, *11*, 2669−2673.
[2] *The chemistry of Functional Groups* (Ed.: S. Patai), Interscience Publ., London: [2a] Vol. 7, **1970**. — [2b] Suppl. A, vol. 2, **1989**.
[3] J. J. Ryan, A. A. Humffray, *J. Chem. Soc. B* **1966**, 842−845.
[4] O. Exner, J. Lakomý, *Collect. Czech. Chem. Commun.* **1970**, *35*, 1371−1386.
[5] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165 to 195. — [5a] Table I, entries 65, 252, 452, 471. — [5b] Table V. — [5c] p. 188. — [5d] Table I. — [5e] Table IV.
[6] M. Charton in ref.[2b], p. 239−298.
[7] R. Knorr, K. Polborn, *J. Chem. Soc., Perkin Trans. 2*, **1991**, 1505−1508.
[8] R. Knorr, K. Ferchland, J. Mehlstäubl, T. P. Hoang, P. Böhrer, H.-D. Lüdemann, E. Lang, *Chem. Ber.* **1992**, *125*, 2041−2049.
[9] K. Polborn, R. Knorr, P. Böhrer, *Acta Crystallogr., Sect. C*, **1992**, *48*, 490−492.
[10] V. I. Minkin, Yu. A. Zdhanov, E. A. Medyantzewa, Yu. A. Ostroumov, *Tetrahedron* **1967**, *23*, 3651−3666.
[11] R. Knorr, M. Hintermeyer-Hilpert, J. Mehlstäubl, T. P. Hoang, B. Neuner, P. Böhrer, *Chem. Ber.* **1993**, *126*, 211−215, preceding paper.
[12] J. P. C. M. van Dongen, H. W. D. van Dijkman, M. J. A. de Bie, *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 29−32.
[13] H.-O. Kalinowski, S. Berger, S. Braun, *^{13}C-NMR-Spektroskopie*, G. Thieme Verlag, Stuttgart and New York, **1984**, chapter 4.
[14] M. J. Jorgenson, *Org. React.* **1970**, *18*, 1−97.
[15] H. O. House, W. F. Fischer, *J. Org. Chem.* **1969**, *34*, 3626−3627.
[16] G. A. Olah, J. L. Grant, *J. Am. Chem. Soc.* **1975**, *97*, 1546−1548.
[17] M. Gruner, D. Pfeiffer, H. G. O. Becker, R. Radeglia, J. Epperlein, *J. Prakt. Chem.* **1985**, *327*, 63−79.
[18] R. M. Elofson, N. Cyr, J. K. Laidler, K. F. Schulz, F. F. Gadallah, *Can. J. Chem.* **1984**, *62*, 92−95.
[19] R. Radeglia, K. Jackowski, H.-J. Jessen, *Z. Chem.* **1975**, *15*, 311−312.
[20] M. Aroney, R. J. W. LeFèvre, R. L. Werner, *J. Chem. Soc.* **1955**, 276.
[21] K. B. Whetsel, G. F. Hawkins, F. E. Johnson, *J. Am. Chem. Soc.* **1956**, *78*, 3360−3363.
[22] H. T. Clarke, R. R. Read, *Org. Synth. Coll. Vol. I*, **1951**, 514 to 516.
[23] D. F. DeTar, A. R. Ballentine, *J. Am. Chem. Soc.* **1956**, *78*, 3916−3920.
[24] D. Schulte-Frohlinde, H. Blume, *Z. Phys. Chem. (Frankfurt)* **1968**, *59*, 299−315, and earlier references cited therein.
[25] Review: H. Zollinger, *Angew. Chem.* **1978**, *90*, 151−160, 402; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 141.

[26] H. Z. Sommer, L. L. Jackson, *J. Org. Chem.* **1970**, *35*, 1558–1562.
[27] See ref.[8] for details and citations.
[28] D. E. Horn, A. P. Krapcho, B. J. Grenon, *J. Org. Chem.* **1979**, *44*, 454–456.
[29] T. W. Bentley, B. Irrgang, H. Mayr, P. v. R. Schleyer, *J. Org. Chem.* **1988**, *53*, 3492–3498.
[30] K. Giebel, B. Staudinger, K. H. Grellmann, H. Wendt, *Ber. Bunsenges. Phys. Chem.* **1972**, *76*, 1246–1251.
[31] U. Berns, G. Heinrich, H. Güsten, *Z. Naturforsch., Teil B*, **1976**, *31*, 953–959.
[32] R. Knorr, A. Schnegg, *Chem. Ber.* **1979**, *112*, 3515–3519.
[33] D. Wurmb-Gerlich, F. Vögtle, A. Mannschreck, H. A. Staab, *Liebigs Ann. Chem.* **1967**, *708*, 36–50.
[34] M. Yoshida, M. Kobayashi, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3471–3472.
[35] H. Kessler, *Angew. Chem.* **1967**, *79*, 997; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 977.
[36] J. M. Klerks, G. van Koten, K. Vrieze, P. Seignette, *J. Organomet. Chem.* **1981**, *219*, 9–20.
[37] W. G. Herkstroeter, *J. Am. Chem. Soc.* **1973**, *95*, 8686–8691.
[38] See ref.[37,39] for literature collections.
[39] G. E. Hall, W. J. Middleton, J. D. Roberts, *J. Am. Chem. Soc.* **1971**, *93*, 4778–4781.
[40] A. Rieker, H. Kessler, *Tetrahedron* **1967**, *23*, 3723–3732; H. Kessler, D. Leibfritz, *Tetrahedron* **1970**, *26*, 1805–1820.
[41] Recent evidence has been collected in refs.[42,43]
[42] M. D. Brickhouse, R. R. Squires, *J. Am. Chem. Soc.* **1988**, *110*, 2706–2714.
[43] H.-U. Wagner, G. Boche, *Z. Naturforsch., Teil B*, **1982**, *37*, 1339–1343.
[44] $\sigma_R = \pm 0.14$ (!) is quoted for Li in phenyllithium by A. R. Katritzky, R. D. Topsom, *Chem. Rev.* **1977**, *77*, 639–660.
[45] R. Knorr, *Tetrahedron* **1981**, *37*, 929–937.
[46] D. Y. Curtin, E. J. Grubbs, C. G. McCarty, *J. Am. Chem. Soc.* **1966**, *88*, 2775–2786.

[245/92]

CAS Registry Numbers

5: 142294-73-3 / **6**: 143142-53-4 / **7**: 143142-56-7 / **8**: 143142-57-8 / **10**: 143142-58-9 / **11**: 143142-59-0 / **12**: 143142-54-5 / **13**: 143142-61-4 / **14**: 137588-81-9 / **14** · HCl: 143142-66-9 / **15**: 143142-62-5 / **16**: 143142-63-6 / **17**: 143142-64-7 / **18**: 143142-65-8 / **19**: 143142-55-6