(*E,Z*) Equilibria, 12[1]

Differential NMR Shielding by Phenyl, Assigned from Chemical Labelling and (*Z,E*) Equilibration

Rudolf Knorr*, Monika Hintermeyer-Hilpert, and Petra Böhrer

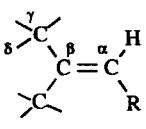
Institut für Organische Chemie der Universität München,
Karlstraße 23, D-8000 München 2, F.R.G.

Received November 8, 1989

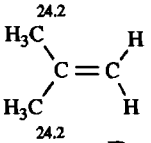
Key Words: Allyl anion / Differential NMR shielding / Schiff's bases / Stereoselective substitution / Isomerization, (*Z,E*)

Unequivocal NMR assignments of the (*E,Z*) isomeric pairs **3** and **8** are possible by (*Z,E*) equilibration. Deprotonation of 2-methyl-1-phenylpropene (**1**) with *n*-BuLi under any conditions gives only a single allyl-metal derivative **2**. Methylation of the latter gives the isomer (Z)-**3**, while deuteriolysis leads to the isotopically labelled derivative **6** of the olefin **1**; this proves the NMR assignments for **1** as well as the *endo* configuration of **2**. The phenyl group gives rise to a differential shielding effect on the γ-carbon nuclei in methyl and methylene groups along a CC double bond (ca. 7 ppm), and this effect is comparable to that along a CN double bond as in **8**. The nitrile function in **5c** is much less effective.

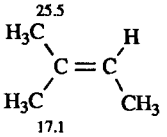
Substituent effects on NMR chemical shifts may be classified topologically as α, β, γ effects, etc., according to the number of chemical bonds separating a particular nucleus from the substituent R, as shown in **A**. For a $^{13}CH_n$ group ($n = 1-3$) connected to one end of a double bond, a strong upfield shift is usually induced by a substituent located at the other end (γ position) in a mutual *cis* arrangement. This phenomenon is akin to the well-known γ-*gauche* effect in saturated systems and has been amply documented[2]. Its magnitude may be seen in a comparison of the δ(^{13}C) values given[2a] in **B** for 2-methylpropene and in **C** for 2-methyl-2-butene. An even larger effect has been observed for the imine **D**[3,4].



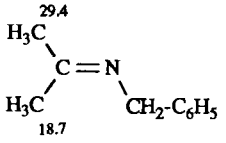
A



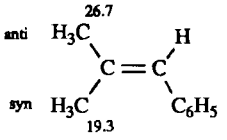
B



C



D



E

However, only very few unequivocal assignments with aryl as a γ substituent have been reported. In particular, the ^{13}C NMR resonances of 2-methyl-1-phenylpropene (**E**) were not detailed in a previous[5] publication, which described the unusual result of almost equal *cis* and *trans* coupling constants $^3J_{CH}$ between the methyl carbon nuclei and the olefinic proton. Unfortunately, almost all of the ^{13}C resonances of **E** were misassigned in a later report[6].

We needed to know the NMR assignments for confirmation of our earlier[7,8] hypothesis that the deprotonation of 2-methyl-1-phenylpropene (**E** or **1**) yields the allyl anion **2** exclusively in the *endo* configuration. The correct δ(^{13}C) values shown in **E** have now been derived by deuteration and methylation of **2** in combination with the empirical prediction[9] of (*E,Z*) equilibrium constants. The latter tool also permits a similar confirmation of the shielding effects due to phenyl as a γ substituent along the CN double bond in **8** for a comparison with **D**.

The differential shielding ($-\Delta_{sa}$) as defined[4] by

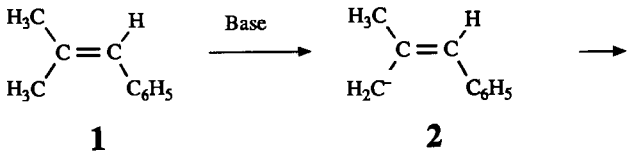
$$\Delta_{sa} = \delta^{syn} - \delta^{anti}$$

and induced by phenyl in **E** is seen to be comparable to that caused by the methyl substituent in **C**. However, the parallelism of chemical shift changes by alkyl and aryl substituents R does not extend to compounds with quaternary γ-carbon atoms in **A**. Such cases, where phenyl as the γ substituent R may induce both *syn* and *anti* deshielding, will be reserved for a later publication.

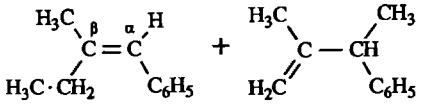
A. *syn*-Stereoselective Methylation of 1 and NMR Assignments by Product Equilibration

The configurational assignment[8] of 2-methyl-1-phenylallyllithium (**2**-Li) in tetrahydrofuran (THF) solution had been based on the tentative order of ^{1}H-NMR methyl shifts in the deuterated 2-methyl-1-phenylpropene **1** (**6** in Section **B**). Definite evidence of the *endo* configuration shown for **2** has now been obtained by methylations in THF with dimethyl sulfate or methyl iodide (the latter in the presence of potassium *tert*-butylate), which yielded exclusively (*Z*)-2-methyl-1-phenyl-1-butene (*Z*-**3**) and 2-methyl-3-phenyl-1-butene (**4**) in 1:9 and 1:3 ratios, respectively, without any trace of (*E*)-**3** according to ^{1}H and ^{13}C NMR analyses of the product mixtures.

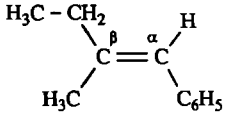
  0009–2940/90/0505–1137 $ 02.50/0



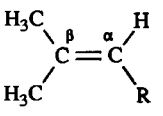
1 2



(Z)-3 4



(E)-3



5a - d

5	R
a	C_6H_5
b	$C(CH_3)_3$
c	CN
d	CO_2H

The configurational assignment of (*Z*)-**3** follows from its stereoisomerization to the thermodynamically more favoured (*E*)-**3**, because a (*Z*:*E*) equilibrium ratio of 25:75 can be predicted[9] from empirical substituent parameters[10]. Since the methylation product mixtures from **2** were not well-suited for equilibration studies, we used the independently prepared[11] pure isomers **3** in equilibration experiments, with thiophenol as a catalyst[12]. An equilibrium ratio of *Z*:*E* = 30:70 was found from both directions. All of the non-aromatic NMR resonances of (*Z*)- and (*E*)-**3** are thus unequivocally assigned and have been collected in Table 1, which shows that the phenyl substituent causes upfield shifts Δ_{sa} along the double bond for C-γ and H-ε nuclei of methyl or ethyl groups in *syn* position relative to the *anti* position, but not for C-δ and H-δ nuclei. A coupling constant $^3J_{CH}$ = 8 Hz between C-γ of methyl and the olefinic proton was discernible only for (*E*)-**3**.

^{1}H-NMR data from other sources[6,13,14] for (*Z*)-**3** or (*E*)-**3** proved to be insufficiently precise or even misleading in comparisons with those of Table 1. This situation contrasts with the beneficially large differential upfield ^{13}C-NMR shifts (Δ_{sa}) of CH_2-γ (−7.9 ppm) or CH_3-γ (−5.8 ppm) groups of **3** for the *syn* vs. *anti* positions.

Klein and co-workers[15] have obtained **3** and **4** in 22:78 ratios by the action of methyl bromide on **2**-Li in hexane, diethyl ether, or THF solutions. The same product ratio was observed in the presence of potassium cations in THF, concurring with our value using methyl iodide, whereas a 43:57 ratio was found in hexane[15]. However, partial twofold deprotonation had occurred here, in the presence of 1,2-bis(dimethylamino)ethane (TMEDA). Although the authors[15] did not specify the configuration of **3** and although their ^{1}H-NMR data do not allow a posterior assignment, our similar experimental conditions indicate that they had likewise prepared (albeit from 2-methyl-3-phenyl-1-propene) the (*Z*) isomer of **3** exclusively. We have also confirmed their observation that (*Z*)-**3** cannot be lithiated further by *n*-butyllithium with TMEDA in THF.

Table 1. ^{13}C- and ^{1}H-NMR chemical shifts and absolute values of coupling constants ^nJ(XY) [Hz] in $CDCl_3$ at ambient temperature. Coding of nuclei is according to $H^{\varepsilon}C^{\delta}-H^{\delta}C^{\gamma}-C^{\beta}=X^{\alpha}-C_6H_5$, and *syn* or *anti* designation with respect to C_6H_5

Nucleus	δ or *J*	1	(*Z*)-3	(*E*)-3	(*Z*)-8	(*E*)-8
C^{δ}	δ		12.8	12.8	11.2	10.1
	^1J(CH)		125 q	125 q	128 q	127 q
	^nJ(CH)		4.5 t	3.5 t	4 t	4 t
C^{γ}	δ	19.3	25.6	17.7	26.8	18.8
syn	^1J(CH)	126 q	123 t	125 q	128 t	128 q
	^3J(CH)	8.4; 4.2 dq	m	8; 4 dt	m	2.2 t
C^{γ}	δ	26.7	23.5	33.5	24.9	34.1
anti	^1J(CH)	126 q	124 q	125 t	128 q	126 t
	^3J(CH)	7.5; 4.5 dq	m	m	3 t	m
C^{β}	δ	135.1	141.1[a]	140.9	172.7	171.7
	^nJ(CH)	6.5 > quint	m	m		5 q
C^{α}	δ	125.4	125.0	123.9		
	^1J(CH)	ca. 151 dm	152 dm	152 dm		
C-*o*	δ	128.8	128.6[b]	129.0	(118.9)	118.9
	^1J(CH)	158 d	160 d	158 d		160 d
	^3J(CH)	6 q	5 q	5 q		m
C-*m*	δ	128.0	128.2[b]	128.2	(128.3)	128.3
	^1J(CH)	158 d	159 d	159 d		161 d
	^3J(CH)	6 d	6 d	6 d		8 d
C-*p*	δ	125.8	125.9	125.9	(122.3)	122.3
	^1J(CH)	160 d	160 d	160 d		161 d
	^3J(CH)	7 t	7 t	7 t		7.5 t
C-*i*	δ	138.8	138.8[a]	139.0	150.6	151.2
	^3J(CH)	m	m	ca. 6 t		8 t
H^{ε}	δ		1.10	1.13	0.97[c]	1.13[c]
	^3J(HH)		7.5 t	7.2 t	7.5 t	7.5 t
H^{δ}	δ	1.82[c,d]	2.26	1.88	2.03[c]	1.65[c]
syn	^nJ(HH)	1.2[c,d] d	7.5 q	1.6 d	q	s
H^{δ}	δ	1.88[c,d]	1.90	2.21	2.03[c]	2.32[c]
anti	^nJ(HH)	1.3[c,d] d	1.5 d	7.2 q	s	7.5 q
H^{β}	δ	6.23	6.23	6.23		
	^4J(HH)	1.3[c]	m	m		
C_6H_5	δ	7.14	7.19	7.20		6.54; 7.05

[a,b] Chemical shifts carrying equal labels may be interchanged. — [c] In CCl_4. — [d] Ref.[17].

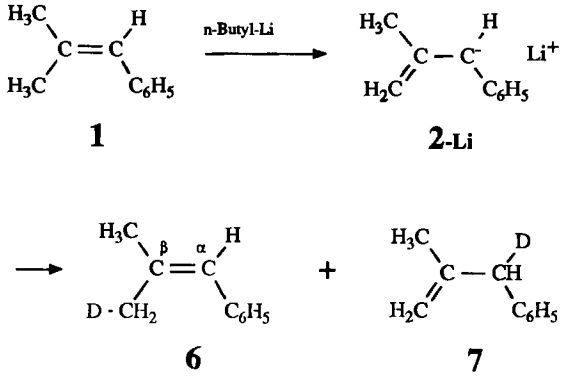
The exclusive formation of (*Z*)-**3** under various conditions thus leaves little doubt concerning the *endo* configuration of the "allyl anion" **2**. We have convinced ourselves by direct spectroscopic observation that the same stereochemically unique intermediate **2**-Li is formed not only in THF[7,8] (and as the potassium salt[16] in ammonia) but also from **1** by *n*-butyllithium in hexane with TMEDA or in THF with tris(dimethylamino)phosphane oxide (HMPA, at −50°C). Since **2**-Li is protonated by diisopropylamine or 2,2,6,6-tetramethylpiperidine, it is more basic than LDA and LiTMP; these bases did not accelerate the deprotonation of **1** by *n*-butyllithium to give again the same anion **2**. Deprotonation in pure hexane occurred too sluggishly; rough estimates of the half-lifes of the reactions revealed a considerable acceleration with increasing donor character of the cosolvents (see Experimental). However, the *endo* configuration of **2** does *not* prove its direct formation from **1** by *syn* deprotonation.

B. *syn*-Stereoselective Monodeprotonation of 1

The NMR assignment of diastereotopic methyl groups in isobutene derivatives **5** can be a non-trivial task[17,18]; it has been described as "by no means conclusive"[17] for **1** (**5a**) because of the almost coincident ^{1}H-NMR absorptions in different solvents[6,17,19] and the barely diagnostic ^4J interproton coupling constants (compare the data[17] in Table 1 with $^4J = -1.41$ and -1.53 Hz[19] for **1** in CS_2). According to their moderate nuclear Overhauser effects on the olefinic proton, the *anti* methyl protons of **5a** (**1**) resonate at lower[20] but those of **5b** at higher[21] magnetic field.

A straightforward solution to this problem can now be offered in the case of **1**, since the configuration of the allyl anion derivative **2** is known from Section A. It is only necessary to analyse the mixture of deuteriolysis products **6** and **7** of **2**, obtainable in a 3:1 ratio either with deuterium oxide[8] or with CH_3OD in THF/hexane.

The high-field shoulder of the methyl absorptions is observed with decreased intensity in **6**, and the corresponding upfield methyl-carbon signal appears as a 1:1:1 triplet with $^1J_{CD} = 19.5$ Hz, thus establishing the differential ^{1}H- and ^{13}C-NMR upfield shifts Δ_{sa} due to the phenyl group. Therefore, the previous authors[6,17,19] have assigned the proton resonances of **1** correctly.



1 **2-Li** **6** **7**

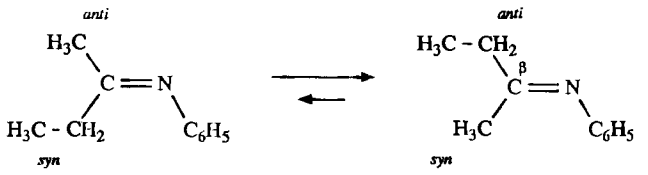
In addition to the $\delta(^{13}C)$ values of the methyl groups (see **E** or Table 1), all of the further carbon absorptions of **1** were identified by their multiplicities in a gated-decoupling experiment, which also revealed the equal magnitude of both $^1J(CH_3)$ couplings and verified the reported[5] values of the ^3J(CH) methyl splittings. The latter are subject to a *syn*-γ effect in such a way that they cannot be used for a reliable assignment[5]. The C-*p* signal with its characteristic dt pattern of proton splitting was easily distinguished from the adjacent C-α absorption with a typically smaller olefinic ^1J(CH) value (Table 1). As an additional confirmation of this, the C-α signal of the previously[8] prepared 1-deuterio-2-methyl-1-phenylpropene appeared as a 1:1:1 triplet.

In order to see if the empirical relation[22] of methyl-^{13}C relaxation times T_1 (*syn*: *anti* ca. 1.6–3.3) holds true also for **1**, we determined this T_1 ratio to be 1.4 in a non-degassed $CDCl_3$ solution of **1**, with similar T_1 values for all other ^{13}C nuclei except for the much more slowly relaxing *ipso* and C-β atoms.

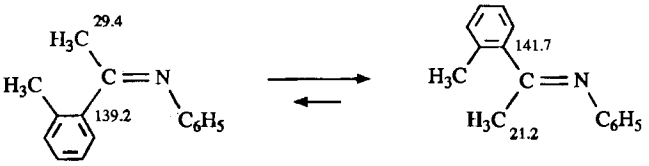
In view of contradictions in their reported[23,24] methyl proton shifts, the spectra of commercial 3-methyl-2-butenenitrile (**5c**) were recorded and the more recent data[24] were verified. Nuclear Overhauser experiments[25] gave no clear difference in ^{1}H-NMR intensity enhancements (ca. 5%). However, we could connect the upfield methyl ^{1}H signal with the upfield methyl carbon absorption[18,24] by selective decoupling; this carbon signal belongs to the *syn*-CH_3 group according to ^3J(CC) coupling constants[18]. The differential γ-shielding $-\Delta_{sa} = 2.5$ ppm due to the cyano substituent thus turned out to be much smaller than that caused by the phenyl group or the carboxy function in **5d**[5], albeit its effect was in the same direction. Again, the ^3J(CH) coupling constants of **5c** were found to be too similar to be of diagnostic value.

C. NMR Assignments in the Anil 8

Five of the eight ^{13}C-NMR resonances of 2-butanone anil[26] (**8**) are clearly doubled, with intensity ratios of approximately 4:1 (corresponding to ^{1}H NMR) for the two components. All of these absorptions can readily be assigned to the *Z* and the *E* isomers of **8**, because 80% of (*E*)-**8** is calculated[9] for the mobile equilibrium. A conclusive distinction between the methyl γ and δ resonances within each isomer makes use of the triplet splitting, which is smaller for ^3J(CH) of CH_3-γ (Table 1) across the imino carbon atom than for ^2J(CH) of CH_3-δ along the CC bond.



(Z)-8 **(E)-8**



(Z)-9 **(E)-9**

All differential γ-shifts Δ_{sa} of **8** are smaller than that of acetone *N*-benzylimine (**D**). The first extensive collection[4] of ^{13}C-NMR shifts of imines contains no examples with *N*-aryl groups or *tertiary* γ-carbon atoms and concedes that resonances differing by less than two ppm might be reversely assigned. Indeed, the *syn*-methyl carbon nucleus of 3-pentanone *N*-benzylimine was first reported to resonate at higher[4] but later found at lower[27] magnetic field than the diastereotopic *anti* carbon. Whereas the ^{13}C-NMR shifts of (*E*)- and (*Z*)-**8** agree well with those of 2-butanone *N*-alkylimines[4], including the (*E*) isomer of the *N*-methylimine[2b,28], the values reported for the (*Z*) isomer of the latter must be

considered to be erroneous. A conclusive assignment was given[29] for the (*Z,E*) pair **9** using $^2J(^{15}N,^{13}C)$ coupling constants rather than the equilibrium ratio of 1:2 which is quite unexpected, as pointed out by the authors. The calculated *Z*:*E* ratio (ca. 5:1) would have given the wrong assignment in this special case because the λ^d parameter[9] of a 2-tolyl group poses a special problem. Nevertheless, the differential shielding for methyl in **9** is seen to be compatible with that of **8** but much smaller for the *ipso* (δ) carbon atoms (lacking hydrogen), as previously postulated for benzophenone imines[30], 1,1-diarylalkenes[31,32] or the azobenzenes[33,34].

D. Conclusion

The method of assignment by (*E,Z*) equilibration can be recommended as long as reliable substituent parameters[9] λ^d are known; it has been used before[3,4,27] without explicit prediction of equilibria. It enabled us to derive secure differential deshielding values Δ_{sa} induced by a phenyl group on γ, δ, and ε nuclei along CC and CN double bonds. For the δ positions, Δ_{sa} is zero in **3** and +1.1 ppm in **8**; this latter is the same as that found along the saturated bonds in the rigid 2-phenyladamantane moiety[35]. The varying sign of Δ_{sa} for the δ carbon in this skeleton had led to the conclusion[35] that a secure assignment requires deuteration or two-dimensional NMR techniques.

We thank Prof. *Manfred Schlosser* for his kind help, and the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for their generous support.

Experimental

The previously[8] described equipment and experimental techniques were used. ^{13}C-NMR spectra were recorded on Bruker WP-80-DS and Varian XL-100 spectrometers and are described herein with multiplicities from off-resonance or gated decoupling. Selective $^{13}C\{^1H\}$ decoupling was performed using the recommended[5] settings.

2-Methyl-1-phenylpropene (**1**): Preparation and purification as published[8]. – Crude values of ^{13}C NMR relaxation times ($CDCl_3$): T_1 = 8.2 s (*syn*-CH_3), 6.0 (*anti*-CH_3), 8.7 (C-α), 4.8 (C-*para*), 8.5 (C-*meta*), 7.8 (C-*ortho*), 41 (C-β), 53 (C-*ipso*).

1-Deuterio-2-methyl-1-phenylpropene[8]: ^{13}C NMR (pure): δ = 125.5 (t, $^1J_{CD}$ = 23.2 Hz, CD-α), 125.8 (residual CH-α), 134.6 (C-β), further shifts as for **1** (Table 1).

2-Methyl-1-phenylallyllithium (**2**-Li). – a) *In Hexane/TMEDA:* A ^1H NMR tube was charged at −70°C under a stream of N_2 with 1.50 ml (2.3 mmol) of *n*-butyllithium, 0.320 ml (2.1 mmol) of TMEDA, 0.040 ml of TMS and 0.280 ml (2.1 mmol) of 2-methyl-1-phenylpropene (**1**). The tube was quickly warmed up and was closed with a tight stopper; spectra were taken immediately at ca. 27°C. The starting material **1** and the base disappeared and a single allyl anion **2** developped with a first half-life of ca. 25 min, but a small amount of the dianion[15] might have been formed. – ^1H NMR (hexane): δ = 3.13 (broad, 3-H, *exo*), 3.50 (sharper, 3-H, *endo*), 3.96 (d, ^4J = 1.2 Hz, 1-H), 6.21 (m, *p*-H), 6.79 (d, *o*- and *m*-H), in supplementation of the published data[15]; see also Figure 2 in ref.[8].

The deep red solution containing a little precipitate was poured into 1.00 ml of CH_3OD and worked up to give 0.260 g (92%) of a ca. 3:1 mixture of **6** and **7**, both with almost full monodeuteration.

b) *In Hexane/THF/TMEDA:* In a similar run with equal volumes of THF and hexane the first half-life was less than 10 min. – ^1H NMR (hexane/THF, 1:1): δ = 3.03 (broad, 3-H, *exo*), ca. 3.48 (3-H, *endo*), 3.92 (1-H), 6.08 (m, *p*-H), 6.73 (d, *o*- and *m*-H); see above. Decolourization by dimethyl sulfate at −78°C required several seconds and produced a mixture of (*Z*)-**3** and **4**.

c) *In the Presence of Amides:* Lithium diisopropylamide (0.7 mmol) in 0.40 ml of [D_8]THF did not react with 0.22 mmol of **1**. After addition of 1 mmol of *n*-butyllithium in 0.5 ml of hexane, deprotonation occurred with a first half-life of ca. 30 min: ^1H NMR similar to that in b). The final addition of diisopropylamine or of 2,2,6,6-tetramethylpiperidine regenerated **1**.

d) *In [D_8]THF with HMPA:* A single anion **2** was also formed at −50°C from **1** with *n*-butyllithium in hexane/[D_8]THF (3:1) in the presence of one equivalent of HMPA. The educt was consumed with a first half-life of 10 min. – ^1H NMR (hexane/[D_8]THF, at −19°C): δ = 1.68 (s, CH_3), 2.96 (broad, 3-H, *exo*), 3.34 (d, ^2J = 3 Hz, 3-H, *endo*), 3.70 (unresolved, 1-H), 5.58 (m, *p*-H), 6.40 (d, *o*- and *m*-H); compare above.

(Z)-2-Methyl-1-phenyl-1-butene (*Z*-**3**) *and 2-Methyl-3-phenyl-1-butene* (**4**). – a) *With n-Butyllithium/TMEDA:* A three-necked flask (250 ml) fitted with a condenser (N_2 bubbler), internal thermometer, magnetic stirring bar, and a pressure-equalizing dropping funnel was charged under N_2 with 6.60 g (50 mmol) of **1** and 10.0 ml (66 mmol) of TMEDA in 110 ml of absol. THF. The stirred mixture was kept below +20°C during the addition (70 min) of 65 mmol of *n*-butyllithium in hexane. Although an orange-red powder deposited from the dark-red solution on cooling, stirring remained possible down to −20°C when 10.0 ml (105 mmol) of dimethyl sulfate were slowly added from a second dropping funnel. The solution became colourless after addition of the calculated amount (47 ml) of dimethyl sulfate, an excess of which caused the slow formation of a heavy, colourless precipitate. The mixture was stirred for 30 min at room temperature, diluted with 200 ml of water and extracted three times with ether. The ethereal layers were thoroughly washed with 2 N HCl, thereafter with dist. water, and dried. The crude residue after evaporation contained **4** and (*Z*)-**3** in a 9:1 ratio by ^1H NMR. A first distillation, giving a total yield of 90% (6.46 g), was followed by fractionation in a split-tube distillation column.

4: B.p. 77.5–78°C/15 Torr (Lit.[15] no b.p.). – ^1H NMR (CCl_4): δ = 1.35 (d, ^3J = 7.2 Hz, 4-CH_3), 1.57 (d, ^4J = 0.9 Hz, 2-CH_3), 3.31 (broad q, ^3J = 7 Hz, 3-H), 4.82 (broad s, olefin. 1-CH_2, resolved only at 200 MHz), 7.13 (s, C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 20.0 (q, 2-CH_3), 21.3 (q, C-4), 46.5 (d, C-3), 109.7 (t, C-1), 125.9 (d, C-*p*), 127.2 and 128.1 (2 d, C-*m* and C-*o*), 144.9 (s, C-*i*), 148.9 (s, C-2).

(*Z*)-**3**: B.p. 87–88°C/15 Torr) Lit. 100°C/30 Torr[14]; for an unspecified isomer 98–100°C/23 Torr[36]). – ^1H and ^{13}C NMR: Table 1.

b) *By Inverse Addition to n-Butyllithium in the Presence of KOtBu:* In a similar run, 60 mmol of *n*-butyllithium was added at −78°C to 3.40 g (30 mmol) of potassium *tert*-butylate (instead of TMEDA) in 80 ml of absol. THF. Dropwise addition of 4.00 g (30 mmol) of **1** in 20 ml of absol. THF at −30°C led to a yellow precipitate in a dark-red solution, which was stirred at room temperature for 2.5 h and recooled to −35°C. Methyl iodide (5.00 ml, 80 mmol) was added dropwise and the yellow solution stirred for 30 min at ambient temperature prior to workup as above. The

crude material obtained in 78% yield (3.45 g) contained **4** and only (*Z*)-**3** (by ^{13}C NMR) in a 3:1 ratio by ^1H NMR, but no product[15] of dimethylation.

(E,Z) Equilibration[12] *of 2-Methyl-1-phenyl-1-butene* (**3**): In two separate experiments, 40 mg of the spectroscopically pure[11] (*Z*) or (*E*) isomers and 0.009 ml of thiophenol were dissolved in 0.45 ml of benzene and 0.05 ml of TMS. NMR tubes containing these solutions were kept at room temperature in diffuse daylight and the reaction followed by ^1H NMR spectroscopy. Isomerization of the (*Z*) isomer was immediately apparent, yielding a final (*E*:*Z*) ratio of 70:30 and a ^1H NMR spectrum which was superimposable on the equilibrium spectrum obtained from the (*E*) isomer after 49 h. A similar run in $CDCl_3$ solution proved to be extremely sluggish.

^1H NMR (benzene): δ = 0.92 and 0.98 [2 t, ^3J = 7 Hz, 4-CH_3 of (*Z*)- and (*E*)-**3**, resp.], 1.71 (d, ^4J = 1.5 Hz, 2-CH_3), 2.02 and 2.15 [2 q, ^3J ca. 7 Hz, CH_2 of (*E*)- and (*Z*)-**3**, resp.], 6.24 (m, olefin. H). — ^1H and ^{13}C NMR in $CDCl_3$: See Table 1.

3-Methyl-2-butenenitrile (**5c**): ^1H NMR ($CDCl_3$): δ = 1.93 (d, ^4J = 1.6 Hz, *syn*-CH_3), 2.05 (d, ^4J = 1.2 Hz, *anti*-CH_3), 5.09 (sept, ^4J = 1.4 Hz, olefin. 2-H). — ^{13}C NMR ($CDCl_3$): δ = 22.5 (qdq, ^1J = 128 Hz, ^3J(olefin. H) = 8 Hz, ^3J = 4 Hz, *syn*-CH_3), 25.0 (qdq, ^1J = 128 Hz, ^3J(olefin. H) = 6 Hz, ^3J = 4 Hz, *anti*-CH_3), 95.6 (d, sept, ^1J = 173 Hz, ^3J = 6 Hz, C-2), 116.9 (broad s, CN), 161.5 (> quint, d, ^2J = 6.5 and 3 Hz, C-3).

3-Deuterio-2-methyl-1-phenylpropene (**6**) *and 3-Deuterio-2-methyl-3-phenylpropene* (**7**): *n*-Butyllithium (150 mmol) in 115 ml of hexane and TMEDA (22.3 ml, 148 mmol) in 60 ml of absol. THF were mixed at −70 °C under N_2. A solution of **1** (15.0 g, 114 mmol) in 60 ml of absol. THF was added dropwise at 25 °C, and stirring was continued for 3 h. After cooling to −30 °C, CH_3OD (8.00 ml, 194 mmol) was quickly introduced and the decolourized solution worked up as described for **3**, **4** to give 12.82 g (85%) of **6** and **7** after distillation[8].

^1H NMR (CCl_4)[8]: 26% of **7** with 40% D in position 3; 74% of **6** with 27% D in *syn*-CH_3, position 3.

6: ^{13}C NMR (pure, with C_6D_6): δ = 19.0 (*syn*-CH_2D, $^1J_{CD}$ = 19.5 Hz), 19.3 (residual *syn*-CH_3), 26.7 (q, *anti*-CH_3), 126.0 (C-α and -*p*), 128.2 (d, C-*m*), 129.0 (d, C-*o*), 134.7 (s, C-β), 139.0 (s, C-*i*).

7: ^{13}C NMR (pure, with C_6D_6): δ = 21.9 (q, 2-CH_3), 44.6 (CHD, position 3, $^1J_{CD}$ = 19.5 Hz), 44.9 (residual 3-CH_2), 112.1 (t, olefin. 1-CH_2), 126.2 (d, C-*p*), 128.4 (d, C-*o* and -*m*), 139.8 (s, C-*i*), 144.9 (s, olefin. C-2).

N-(1-Methylpropylidene)benzenamine (**8**): See compound **6a** in ref.[26].

CAS Registry Numbers

1: 768-49-0 / **2**-Li: 66639-74-5 / (*Z*)-**3**: 13384-54-8 / (*E*)-**3**: 7302-03-6 / **4**: 53172-83-1 / **5c**: 4786-24-7 / **6**: 125520-65-2 / **7**: 77028-63-8 / (*Z*)-**8**: 75250-70-3 / (*E*)-**8**: 72037-54-8 / 1-deuterio-2-methyl-1-phenylpropene: 78631-73-9

[1] Part 11, see H. Dietrich, W. Mahdi, R. Knorr, *J. Am. Chem. Soc.* **108** (1986) 2462.
[2] H.-O. Kalinowski, S. Berger, S. Braun, *^{13}C-NMR-Spektroskopie*, G. Thieme Verlag, Stuttgart and New York 1984. — [2a] Table 3.18. — [2b] Table 3.46.
[3] R. R. Fraser, J. Banville, K. L. Dhawan, *J. Am. Chem. Soc.* **100** (1978) 7999. See footnote 15 therein.
[4] R. R. Fraser, J. Banville, F. Akiyama, N. Chuaqui-Offermanns, *Can. J. Chem.* **59** (1981) 705.
[5] U. Vögeli, W. v. Philipsborn, *Org. Magn. Reson.* 7 (1975) 617.
[6] L. Hevesi, J. B. Nagy, A. Krief, E. G. Derouane, *Org. Magn. Reson.* **10** (1977) 14.
[7] R. Knorr, E. Lattke, *Tetrahedron Lett.* **1977**, 4659.
[8] R. Knorr, E. Lattke, *Chem. Ber.* **114** (1981) 2116.
[9] R. Knorr, *Chem. Ber.* **113** (1980) 2441.
[10] We chose λ^d = 3 for C_6H_5, but (*E*)-**3** is the preferred isomer with any other possible[9] phenyl value.
[11] We thank Prof. *M. Schlosser* for having repeated the syntheses of (*Z*)- and (*E*)-**3** and for providing ^{13}C NMR spectra with permission to publish their parameters; see M. Schlosser, K.-F. Christmann, *Synthesis* **1969**, 38.
[12] Prof. M. Schlosser has pointed out to us that this very useful method of equilibration without double-bond migration was described earlier, although under more forcing conditions: C. Moussebois, J. Dale, *J. Chem. Soc. C*, **1966**, 260.
[13] W. Dauben, G. Lodder, J. D. Robbins, *Nouv. J. Chim.* **1** (1977) 243 (on p. 252).
[14] J. G. Duboudin, B. Jousseaume, A. Saux, *J. Organomet. Chem.* **162** (1978) 209 (on p. 212 and 220).
[15] J. Klein, A. Medlik-Balan, A. Y. Meyer, M. Chorev, *Tetrahedron* **32** (1976) 1839.
[16] G. J. Heiszwolf, H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas* **86** (1967) 1345.
[17] H. Rottendorf, S. Sternhell, J. R. Wilmshurst, *Aust. J. Chem.* **18** (1965) 1759.
[18] J. W. Jaroszewski, M. G. Ettlinger, *J. Org. Chem.* **48** (1983) 883.
[19] E. R. Curry, D. J. Sardella, *J. Am. Chem. Soc.* **96** (1974) 1822.
[20] Ref.[6], on p. 16.
[21] D. H. Hunter, R. W. Mair, *Can. J. Chem.* **47** (1969) 2361.
[22] A. Okubo, H. Kawai, T. Matsunaga, T. Chuman, S. Yamazaki, S. Toda, *Tetrahedron Lett.* **21** (1980) 4095.
[23] J. M. Jackman, G. Y. Sarkis, *Bull. Chem. Soc. Jpn.* **42** (1969) 1179.
[24] D. A. C. Compton, W. F. Murphy, H. H. Mantsch, *Spectrochim. Acta, Part A*, **37** (1981) 453 [*Chem. Abstr.* **95** (1981) 202760v].
[25] We thank Dr. *Thi Phung Hoang* for irradiation experiments on all three ^1H-NMR absorptions.
[26] R. Knorr, A. Weiß, P. Löw, E. Räpple, *Chem. Ber.* **113** (1980) 2462.
[27] J. K. Smith, D. E. Bergbreiter, M. Newcomb, *J. Org. Chem.* **46** (1981) 3157.
[28] N. Naulet, M. L. Filleux, G. J. Martin, J. Pornet, *Org. Magn. Reson.* **7** (1975) 326.
[29] G. W. Buchanan, B. A. Dawson, *Org. Magn. Reson.* **13** (1980) 293.
[30] J. M. Ruxer, A. Solladié-Cavallo, G. Solladié, D. Olliero, *Org. Magn. Reson.* **10** (1977) 105.
[31] T. W. Proulx, W. B. Smith, *J. Magn. Reson.* **23** (1976) 477.
[32] A. Nourmamode, R. Lapouyade, B. Barbe, M. Pétraud, *Bull. Soc. Chim. Fr.* **1981** II, 207.
[33] A. Lyčka, *Collect. Czech. Chem. Commun.* **47** (1982) 1112.
[34] S. Simova, E. Fanghänel, R. Radeglia, *Org. Magn. Reson.* **21** (1983) 163.
[35] H. Duddeck, M. Kaiser, D. Rosenbaum, *Tetrahedron Lett.* **27** (1986) 473, and references cited therein.
[36] M. Tiffeneau, J. Levy, *Bull. Soc. Chim. Fr.* **33** (1923) 759 (on p. 769).

[368/89]