Stereoelectronic effect in the capture reaction of the 1,2-dimesityl-2-phenylvinyl radical

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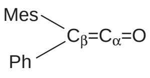
The reduction of (*E*)-1,2-dimesityl-2-phenylvinyl bromide (***E*-4-Br**) to the corresponding ethene (**4-H**) under radical conditions (Bu_3SnH–AIBN–benzene–*hv*) proceeds with predominant inversion of configuration to give an ***E*-4-H**/***Z*-4-H** ratio of ≥9 : 1. This suggests that the intermediate 1,2-dimesityl-2-phenylvinyl radical (**3**) is captured preferentially from the mesityl face. The reason for this is clarified by theoretical calculations which show that in the conformation of **3** the β-mesityl ring is close to perpendicular to (78.2°) and the β-phenyl ring is nearly coplanar (12.0°) to the plane of the double bond (at BLYP/6-31G*). The calculated transition state energy for hydrogen transfer from the model hydrogen donor SiH_4 is 5.7 kcal mol^{-1} lower from the mesityl than from the phenyl face.

Comparison with the analogous ketene MesC(Ph)=C=O and the vinyl cation MesC(Ph)=C^+–Mes systems shows the same preference for reaction from the formally bulkier, but in fact easier to approach mesityl face, which is likewise governed by steric effects.

Introduction

We had investigated previously the ground state geometry and the stereochemistry of nucleophilic addition to C_α of two linear systems having a β-mesityl-β-phenylvinyl moiety, *i.e.*, the ketene **1** and the vinyl cation **2**.[1] The ground state geometry is determined by a stereoelectronic effect, *i.e.*, by competition between the Ar–C=C conjugation of the two aryl groups *vs.* their mutual steric interaction. For steric reasons, two β-aryl rings, one being the bulky mesityl (Mes), cannot be mutually in the C=C bond plane. Since the Mes–C=C conjugation energy exceeds by only 0.3 kcal mol^{-1} the Ph–C=C conjugation energy,[1] the electronic preference for a Mes–C=C *vs.* Ph–C=C planarity appears to be very small. Consequently, in the preferred conformation of both **1** and **2** the β-Ph is almost completely conjugated, whereas the β-Mes ring is almost perpendicular to the C=C bond. The energy differences between these stable conformers and the unstable higher energy conformations with planar Mes and perpendicular Ph are 12.0 and 7.3 kcal mol^{-1} for **1** and **2**, respectively. Since nucleophiles attack the sp hybridized C_α in the molecular plane, and the face of the perpendicular Mes seems sterically more accessible, attack from the *formally* bulkier Mes side seems plausible. This was corroborated both experimentally and by MO calculations.[1]



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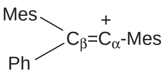

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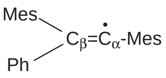


3

Mes = Mesityl =
2,4,6-$Me_3C_6H_2$

Identical arguments to those given above suggest that in the most stable conformation of the corresponding radical **3** the Ph will be in the double bond plane and the Mes perpendicular to it. Previous calculations[2a,b] and experiments[2c] have suggested a linear =$C^•$–Ar geometry for an α-arylvinyl radical. Capture of a linear radical should be in-plane from both faces, and there are many precedents that the stereochemistry of the capture (and hence of the products) depends strongly on the bulk of the two β-groups.[3] The question arises whether the conformation of **3** resembles those of **1** and **2**, and if so whether the capture should again be preferentially from the mesityl substituted face giving a product having *trans* mesityl rings.

In order to investigate this question we reduced 1,2-dimesityl-2-phenylvinyl bromide under radical forming conditions, *i.e.*, with Bu_3SnH–AIBN, and determined the composition of the reduction products. The structure of radical **3** and of simple model transition states for hydrogen transfer to it were determined by calculations.

Results

(*Z*)-1,2-Dimesityl-2-phenylvinyl chloride, ***Z*-4-Cl** was prepared according to the literature[4] and assigned as the *Z*-isomer by its X-ray diffraction. Reflux of phosphoryl bromide with the enol *Z*-MesC(Ph)=C(OH)Mes[5] in the presence of *N*,*N*-diethylaniline in CCl_4 for 2.5 h gave (*E*)-1,2-dimesityl-2-phenylvinyl bromide (***E*-4-Br**).[6]

Hydrodehalogenation, *i.e.*, reduction of ***E*-4-Br** to **4-H** which was conducted under known radical conditions (Bu_3SnH–AIBN–no O_2–*hv* at 350 nm) at rt, is fast: after 15 min (with 3.3 molar excess of Bu_3SnH) it was already complete and GC-MS showed that two hydrodebromination products were formed in a 95 : 5 ratio. At reaction times of 30 and 150 min, these products were formed in 93 : 7 and 90 : 10 ratios, respectively. Consequently, the ratio changes only slightly with time from the initial 95 : 5 ratio. No other product was detected.

A similar outcome on a somewhat larger scale enabled a quantitative separation of the major product on a preparative TLC plate. The isolated product showed an *m*/*z* of 340 and a

Table 1 Bond lengths, angles and dihedral angles for ***E*-4-H**

Bond/Å		Angle/°		Dihedral angle/°	
C(1)–C(2)	1.337(3)	C(1)–C(2)–C(3)	118.1(2)	H(1) C(1) C(18)/ C(3) C(2) C(12)[a]	0.5
C(1)–C(18)	1.493(3)	C(1)–C(2)–C(12)	123.4(2)	α-ring/H(1) C(1) C(18)	64.0
C(2)–C(3)	1.501(3)	C(2)–C(1)–C(18)	129.1(4)	β-Mes ring/C(3) C(2) C(12)	64.4
C(2)–C(12)	1.484(3)	C(3)–C(2)–C(12)	117.6(2)	Ph ring/C(12) C(2) C(3)	38.2
18 C–C (ring)	1.366(5)–1.402(3)	36 other C–C–C	117.5(2)–122.8(2)		
6 C–Me	1.507(4)–1.516(4)				

[a] Double bond twist angle.

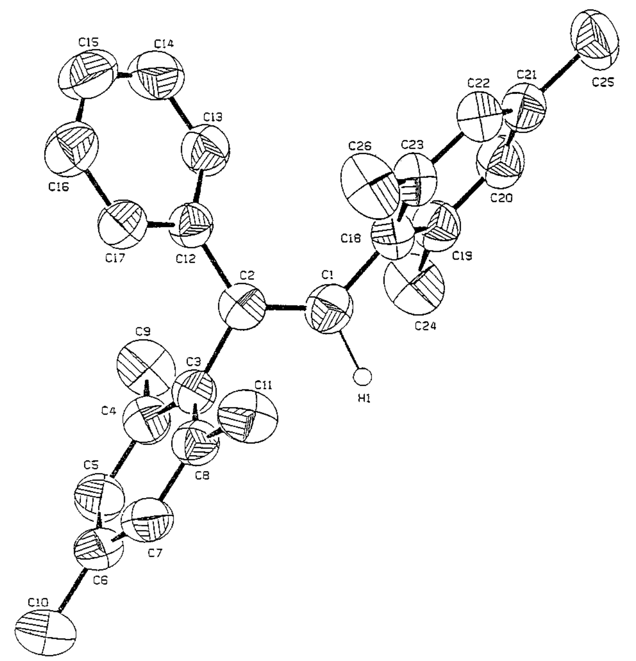
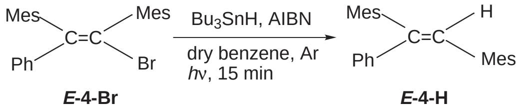


Fig. 1 ORTEP drawing of ***E*-4-H**.

^1H NMR vinylic signal at δ 6.5 ppm and its X-ray diffraction showed that it has two *trans* mesityl rings, *i.e.*, it is ***E*-4-H** (eqn. (1)). The ORTEP drawing is given in Fig. 1, bond lengths, angles and dihedral angles are given in Table 1.†



(1)

The double bond of ***E*-4-H** is nearly planar. Bond lengths and angles are normal for this type of compound with the C(2)–C(1)–C(18) angle of 129.1° being the widest. The Ar–C=C torsional angles are 64° (α-Mes), 64.4° (β-Mes) and 38.2° (β-Ph).

The amount of the other isomer formed in the reduction reaction of eqn. (1) (presumably ***Z*-4-H**) was too small for isolation. Support for its assignment as ***Z*-4-H** comes from its ^1H NMR analysis which is however complicated by overlap of signals (see Experimental section).

Attempted reduction of ***Z*-4-Cl** under a variety of conditions, such as Bu_3SnH–AIBN–*hν*–17 h or $LiAlH_4$–THF[7] did not give a significant amount of the hydrodechlorination product or isomerization to ***E*-4-Cl**. The reactions were apparently much slower than with ***E*-4-Br** since nearly all ***Z*-4-Cl** was recovered unchanged. However, the only minute additional signal in the GC-MS analysis of the reaction mixture appears at the same position as ***E*-4-H**. Reduction of ***Z*-4-Cl** with excess Na–THF gave a product with a mass spectrum showing *m*/*z* 342 (M), 209 (100%, M − $MesCH_2$) and 133 ($MesCH_2^+$) which we tentatively ascribe to the full reduction product, 1,2-dimesityl-1-phenylethane $MesCH(Ph)CH_2Mes$ (**5**) in analogy to the reduction of MesC(Ph)=C=O to both 2-mesityl-2-phenylethenol and 2-mesityl-2-phenylethanol.[8]

Calculations

Ab initio (HF/3-21G)[9] and nonlocal BLYP density functional theory[10] calculations were carried out for radical **3** and for a pair of hydrogen transfer transition states (TSs) leading to **4-H**, using the GAUSSIAN94 program.[11] Literature calculations show that at C_α an α-aryl substituted radical is linear whereas an α-alkyl substituted radical is bent.[2a,b] Radical **3** is calculated to be only slightly bent (164.6°) at BLYP/3-21G and is nearly linear at a higher BLYP/6-31G*[12] level. This structure in which the C=C_α–Mes bond angle is 174.4° with *cis* Mes/Ph rings, and the Mes–C_β=C and Ph–C_β=C torsional angles are 78.2° and 12.0°, respectively, is shown in Fig. 2a. Thus, the β-Mes ring is nearly perpendicular to and the β-Ph ring is close to planar with the double bond plane. This conformer of **3** is 8.8 kcal mol^{-1} more stable than the conformation (not a minimum on the potential energy surface) in which torsional angles at the β-Mes and β-Ph rings are *arbitrarily* fixed at 0.0° and 90.0°, respectively (Fig. 2b). The C_β–C_α–C_{ipso} angle of 174.4° is slightly smaller than the same angle in cation **2** which is 177.7°, in line with the expected stronger π(C=C)–π(α-Mes) conjugation in the cation than in the radical.

From the Mulliken charges and spin distribution of **3** (Fig. 2) the spin density is mostly localized at C_α and the α-Mes. The planar β-aryl group (Ph at **3**, or Mes in its unstable conformation) is more positively charged than the perpendicular β-aryl ring, suggesting a more efficient charge transfer from the planar ring into the electron deficient C_α. The perpendicular aryl group (Mes in **3** and Ph in the unstable conformation) has more spin density than the planar aryl, in line with a through-space overlap between the perpendicular aryl and the spin center at C_α.

In order to find out whether the hydrogen transfer to radical **3** occurs from the Mes side to give ***E*-4-H** or from the Ph side to give ***Z*-4-H**, a pair of transition structures were optimized for the reactions of **3** and SiH_4, which was used rather than Bu_3SnH in order to simplify the calculations. With this large reaction system the calculations were necessarily carried out at a smaller basis set (3-21G) at the BLYP density functional theory.

The reaction of SiH_4 with the smaller radical PhC(H)=C$^\bullet$Ph was first examined in order to test the suitability of the BLYP/3-21G level to describe steric effects in radical reactions. The transition state is shown in Fig. 3a. The calculated *E*-TS is 1.4 kcal mol^{-1} less stable than the *Z*-TS, reflecting qualitatively the steric repulsion between the Ph and SiH_4. The calculated transition structures for the reaction of **3** with SiH_4 (Fig. 3b) were verified as the expected TSs by having one imaginary frequency corresponding to the reaction coordinate for the hydrogen atom transfer motion. The *E*-TS was found to be 5.7 kcal mol^{-1} more stable than the *Z*-TS. This is consistent with the

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† CCDC no. 188/166. A stereoview of ***E*-4-H** is available as supplementary data from BLDSC (SUPPL. NO. 57576, pp. 3) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http:www.rsc.org/authors).

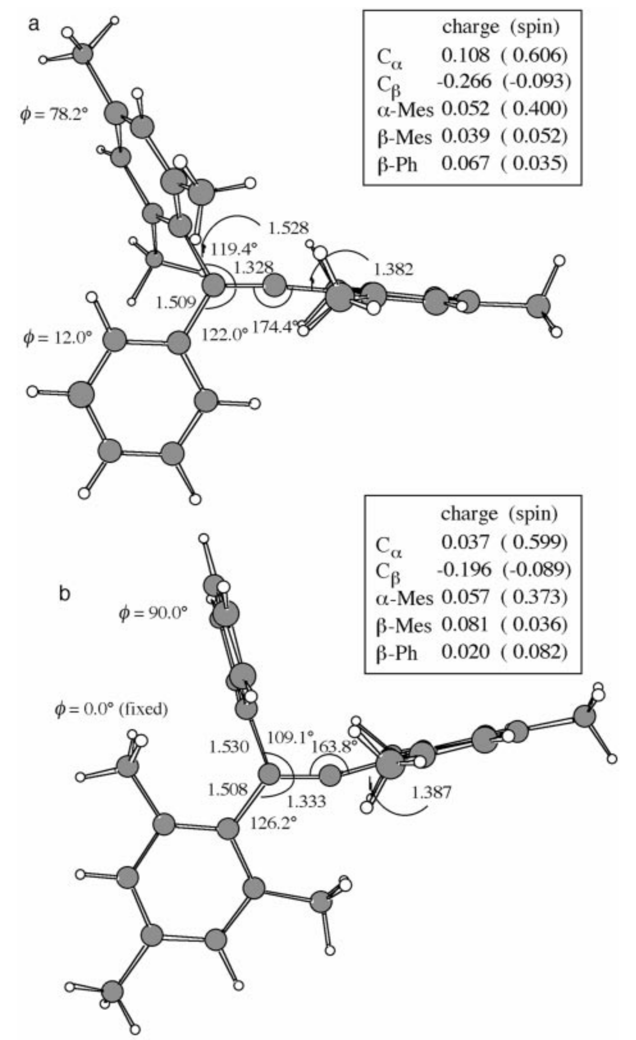

Fig. 2 Optimized structure of **3** at BLYP/6-31G*. (a) Low energy conformation; (b) Conformation with the mesityl ring constrained to be coplanar with the C=C plane. Numbers given in the boxes are Mulliken populations. Spin densities are given in parentheses.

preferred formation of stereoisomer ***E*-4-H** in the reaction, but the calculated energy difference is higher than the experimentally found difference.

Discussion

The calculated ground state structures of the 1,2-dimesityl-2-phenylvinyl ketene **1** and the related cation **2**, revealed nearly orthogonal β-aryl groups, with the β-phenyl ring being in, and the β-mesityl ring nearly perpendicular to the $C{=}C(C_{ipso})_2$ plane and a C_α-substituent (=O in **1** and Mes in **2**) nearly linear with the C_α–C_β bond. In both cases, the nucleophile approaches C_α from the less hindered mesityl side, giving a product with a mesityl group *cis* to the nucleophile moiety. We expected a similar conformation for radical **3** and hence that hydrogen transfer should take place from the β-mesityl face. Both expectations are now corroborated by calculations and an experiment.

Stereochemistry of the vinyl radical 3

With **1** and **2**, only the difference between the β-Mes and β-Ph makes the two faces inequivalent, since the C=C=O and $C{=}C_\alpha$–Mes are linear or nearly so. The situation may differ for **3** if it is bent at C_α. However, our calculations indicate that **3** is nearly linear at C_α, with $\angle C{=}C_\alpha\text{–Mes} = 174.4°$ (at BLYP/6-31G*). When the $C{=}C_\alpha^{\bullet}$–Mes in **3** is constrained to 180° the energy increases by ≤0.1 kcal mol^{-1}, indicating that the non-linearity is within the uncertainty of the calculation. Hence, the stereochemistry can be deduced by studying either ***E*-4-Br** or ***Z*-4-Br** which will presumably give the same linear (at C_α) **3**. This is important since so far we have only been able to synthesize the ***E*-4-Br** isomer.

The calculated ground state conformation of **3** (at BLYP/6-31G*) indicates that the mesityl ring is nearly orthogonal (78.2°) to and the Ph ring is nearly (12.0°) in the $C{=}C(C_{ipso})_2$ plane (Fig. 2a). These values and the linearity of the $C{=}C_\alpha$–X moiety are somewhat lower than for **1** and **2**. If the difference between the lowest energy conformation and the arbitrary non-minimum "opposite" conformation (perpendicular Ph/planar Mes) reflects the preference for the sterically less strained conformation, the 8.8 kcal mol^{-1} difference is between the corresponding values of 12.0 and 7.3 kcal mol^{-1} for **1** and **2**, respectively.[1] The compromise of electronic/steric effect discussed above, and the lack of direct conjugation of the π-β-aryl with the sp-C_α orbitals are responsible for the close values for **2** and **3**.

Stereochemistry of the hydrogen transfer to 3

Ground state arguments therefore suggest that reactions involving the in-plane p orbital of **3** will be preferentially from the direction of the less hindered β-mesityl substituted face than from the phenyl-substituted face. We assume that preferential shielding from the phenyl side by the Bu_3SnBr formed in the generation of **3** which may increase the probability of attack from the Mes side, is not affecting the stereochemistry because no stereochemical effect on the *E*/*Z* composition of the dehydrohalogenated product had been previously observed on changing the hydrogen donor reagent.[2c]

The **major** hydrodebromination product is ***E*-4-H**, the product of capture from the β-mesityl face. The minor product is an isomer (according to its MS), presumably ***Z*-4-H**, but its small amount precluded additional identification. It is formed in the 5–10% range and the reason for this range may be due either to a large error in the determination of this product, or to isomerization at a longer reaction time. A BLYP/3-21G (MM3) calculation shows that ***E*-4-H** is more stable than ***Z*-4-H** by 0.72 (1.75) kcal mol^{-1}.

Consequently, this mechanism which involves **3** as an intermediate is consistent with the favored conditions for generation of **3**, with the ground state arguments and the transition state calculations and its stereochemical outcome is analogous with that for **1** and **2**. We prefer it over other mechanisms (*e.g.*, addition–isomerization–elimination) which initiate by the presumably difficult $Bu_3Sn^{\bullet}$ addition to the crowded double bond and involve several further assumptions.

If the small signal observed in reduction of ***Z*-4-Cl** is tentatively ascribed to ***E*-4-H** this can support with caution the near-linearity of the $C{=}C_\alpha^{\bullet}$–Mes moiety of **3** since ***Z*-4-Cl** and ***E*-4-Br** have different geometry. Moreover, in this case at the transition state for the hydrogen transfer, the Bu_3SnX moiety (X = Cl, Br) formed by abstraction of X from the vinyl halide is sufficiently remote from C_α that any bulk difference of Cl and Br is not manifested.

Comparison with reactions of 1 and 2

Since ketene **1** reacts with MesMgBr to give 75–81% reaction from the β-mesityl face, and cation **2** reacts with AcO^- exclusively from the same face, the reaction of **3** appears more stereoselective than that of **1** and less stereoselective than that of **2**, in line with the notion that "the stereoselectivity of acyclic radicals is close to or often lower than that of cations".[13] However, the different bulk of the reagents (MesMgBr with **1**, AcO^- with **2**, Bu_3SnH with **3**) should be also considered. Interestingly, a 95 : 5 stereoselectivity in hydrogen atom delivery to an α-phenylvinyl radical from the less hindered side was recently observed.[14]

The calculated energy difference between the two transition states for H transfer from SiH_4 to **3** from both sides of 5.7 kcal

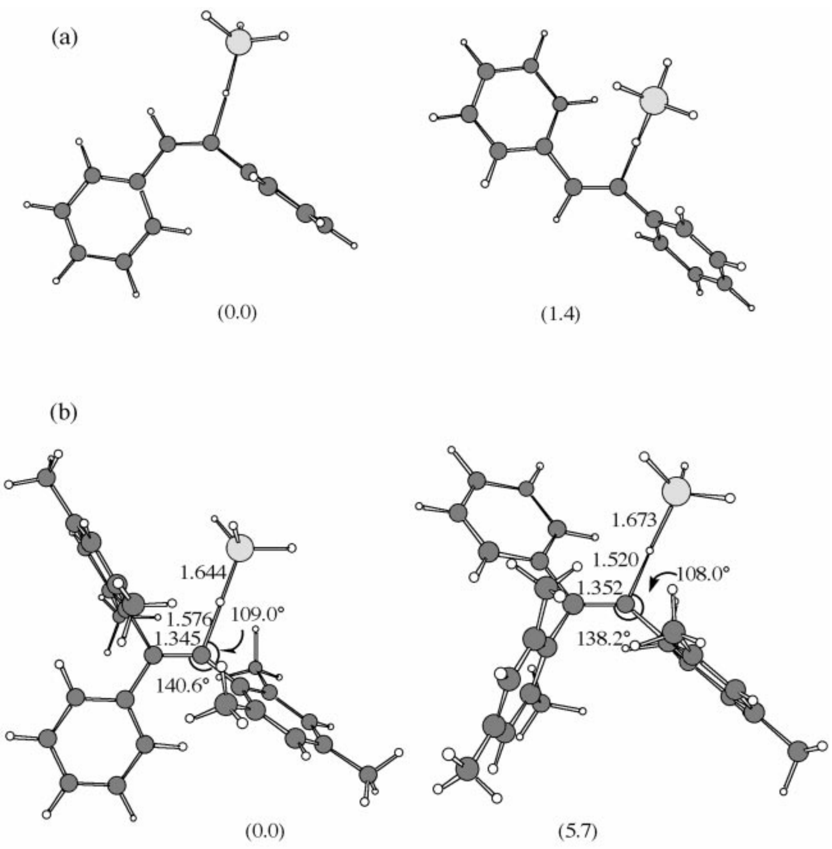

Fig. 3 Transition structures for the two radical abstraction reactions calculated at BLYP/3-21G. (a) H_3SiH + $PhCH{=}C^{\bullet}{-}Ph$; (b) H_3SiH + **3**. Relative energies in kcal mol^{-1} are given in parentheses.

mol^{-1}, *i.e.* of 4 orders of magnitude in favor of reaction from the Mes over the Ph face, gives a 1000-fold higher selectivity than the observed value, assuming that the minor reduction product is ***Z*-4-H**. We do not know if this is due to the method or to the use of a different H-donor than that experimentally studied or to the unlikely possibility of a misassignment of the minor reduction product as ***Z*-4-H**.

The HF/3-21G calculations gave a lower energy transition state by 1.5 kcal mol^{-1} for addition of MeLi to **1** from the mesityl face.[1] The agreement with experiment is much better than for **3**. However, this may be fortuitous, since the two calculation methods differ, and MeLi served as a model for the bulkier MesMgBr in the addition to **1**.

The calculated transition structure for the reduction of **3** is less advanced for the more stable transition state leading to ***E*-4-H** (Fig. 3b). This result supports the finding that the transition state for related reactions often comes earlier for the faster reaction.

In conclusion, in an in-plane attack of a nucleophilic reagent or a hydrogen donor on the sp-hybridized C_α of the MesC(Ph)=CR system with CR = C=O (**1**), C^+–Mes (**2**) and $C^{\bullet}$–Mes (**3**), the reagent approaches from the face of the **formally** larger mesityl ring, which is the least hindered side since the mesityl ring is perpendicular to the double bond, while the phenyl ring is coplanar with it.

Experimental

(*E*)-1,2-Dimesityl-2-phenylvinyl bromide (*E*-4-Br)

A solution containing (*Z*)-1,2-dimesityl-2-phenylethenol (180 mg, 0.50 mmol), $POBr_3$ (1.32 g, 4.6 mmol) and $PhNEt_2$ (0.8 mL) in CCl_4 (2.5 mL) was refluxed for 2.5 h. The mixture was cooled, stirred for 2 min after addition of ice (6 g), extracted with CCl_4 (20 mL), washed with water until neutral and dried (Na_2SO_4). Removal of the solvent left a colorless liquid (0.66 g) which was mostly $PhNEt_2$. Chromatography on silica gel using 19 : 1 petroleum ether–AcOEt as eluent afforded a liquid (0.21 g, 99%) from which a solid precipitated on standing overnight. Washing with AcOEt gave pure colorless crystals of (*E*)-1,2-dimesityl-2-phenylvinyl bromide (***E*-4-Br**) (83 mg, 39%) mp 180–181 °C. IR (nujol): 1614, 1719, 2933 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.24–2.34 (18H, 3s, 1 + 2 + 3 Me), 6.82–7.06 (9H, s + m, Ar-H); MS (CI) (relative abundance, assignment): 420, 418 (20, 22%, M), 339 (100%, M − Br), 219 (35%, M − HBr − Mes); HRMS: 420.1207 and 418.1258 (calcd. for $C_{26}H_{27}{}^{81}Br$ and $C_{26}H_{27}{}^{79}Br$ 420.1277 and 418.1297), 339.2134 (calcd. for $C_{26}H_{27}$ 339.2114), 219.1230 (calcd. for $C_{17}H_{15}$ 219.1175). Anal. Calcd. for $C_{26}H_{27}Br$: C, 74.46; H, 6.49; Br, 19.05. Found: C, 74.78; H, 6.69; Br, 18.55%.

Hydrodebromination of *E*-4-Br

In a representative experiment a mixture of ***E*-4-Br** (7 mg, 16.7 mmol), Bu_3SnH (15 µL, 56.6 mmol), and AIBN (3 mg, 18.3 mmol) in dry benzene (250 µL) degassed with argon before use was irradiated in a small Pyrex flask at rt with a Rayonet RPR-100 photochemical reactor fitted with 16 “350” nm lamps. After 2.5 h of irradiation the reaction was complete (by GC-MS) and two isomeric dehydrobromination products (with *m*/*z* 340) had formed in a 1 : 9 ratio. In a similar experiment ***E*-4-Br** was absent after 15 min and the same products were formed in a 5 : 95 ratio.

The ^1H NMR analysis of the reduction mixture is complicated by signal overlap and the small percentage of ***Z*-4-H** but it nevertheless supports the GC-MS analysis with some assumptions. Judging from the published δ(=CH) assignments of related structure An(Ph)C=CHAn (An = *p*-anisyl) (δ = 6.6 for *E*- and 6.8 for *Z*-)[15] we can ascribe the relevant signal at δ 6.45 of our reduction mixture to the prevailing *E* isomer of **4-H**. The δ(=CH) of the minor *Z* isomer, consistently at lower fields, would be masked by the Ar-H signals at 6.8–7.1 ppm.

Another model is Mes(Ph)C=C(OAc)Mes, where the Mes-H signals are at δ 6.68 in the *E*-isomer (*cis* Mes groups) and at 6.8–6.9 for the *Z*-isomer.[1] If similar relative positions apply for **4-H**, the two signals at 6.72 and 6.74, when compared with the above δ(=CH) signal of ***E*-4-H** at 6.45 ppm, would account for a 5–10% contamination from the 4 Mes-H hydrogens of ***Z*-4-H**, thus corroborating the ***E*-4-H** : ***Z*-4-H** 95 : 5 ratio from GC-MS.

The reaction was repeated on a 3-fold higher scale. After 30 min irradiation the solution was concentrated under a nitrogen stream and chromatographed on a preparative TLC silica gel plate. Elution with 9 : 1 toluene–$CHCl_3$ gave a band which was rechromatographed using $CHCl_3$ eluent, giving a waxy compound (7 mg) showing *m*/*z* 340 and a ^{1}H NMR vinylic signal at δ 6.5. This was analyzed by X-ray diffraction.

***E*-4-H**: $C_{26}H_{28}$; space group: $P\bar{1}$; $a = 11.438(3)$ Å, $b = 11.467(2)$ Å, $c = 8.844(2)$ Å, $\alpha = 104.68(1)°$; $\beta = 104.87(2)°$; $\gamma = 67.71(2)°$; $V = 1021.3(6)$ Å^3; $Z = 2$, $\rho_{\text{calcd.}} = 1.11$ g cm^{-3}; μ(Cu-Kα) = 4.32 cm^{-1}; no. of unique reflections: 2986, no. of reflections with $I \geq 3\sigma_I$: 2121, $R = 0.061$, $R_w = 0.095$.

Attempted reduction of *Z*-4-Cl

In an attempted similar reduction of ***Z*-4-Cl**, it was almost completely recovered after 17 h irradiation or on reaction with $LiAlH_4$–THF. Reduction of ***Z*-4-Cl** with a 100-fold excess of Na–THF at rt for 8 h, gave only hydrocarbon **5** according to GC/MS analysis: *m*/*z* 342 (2, M$^+$), 209 (100, M − CH_2Mes), 194 (12, M − MesCH_2 − Me), 179 (24, M − MesCH_2 − 2Me), 165 (10, M − MesCH_2CH_2 − 2Me), 133 (42, MesCH_2^+). Reaction for 1 or 5 h with a 10-fold excess of Na gave mainly **5** and a minor amount of ***E*-4-H**. No attempt to isolate **5** was made.

Acknowledgements

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