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# Titanium-catalyzed cycloaddition reactions of phenyl(trimethylsilyl)acetylene to conjugated dienes and 1,3,5-cycloheptatriene. 1-Phenyl-2-(trimethylsilyl)-cyclohexa-1,4-dienes and their aromatization

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**Abstract**

The catalytic system $Et_2AlCl/TiCl_4$ induces Diels–Alder addition of phenyl(trimethylsilyl)acetylene (PTMSA) to 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-pentadiene, and [6+2] addition of PTMSA to 1,3,5-cycloheptatriene. The 1-phenyl-2-(trimethylsilyl)-cyclohexa-1,4-dienes obtained undergo thermolysis, yielding the corresponding *ortho*-(trimethylsilyl)biphenyl derivatives. The cyclohexadienes containing vicinal methyl and trimethylsilyl groups evolve methane at 300°C (the 3-methyl group is released). All other derivatives release hydrogen at only 260°C.

## Introduction

The reaction between non-polar internal alkynes and non-polar dienes generally affords low yields of Diels–Alder adducts without catalyst or when acid catalysts are used [1]. However, good yields of Diels–Alder adducts were attained under mild conditions using low-valent transition-metal complexes as catalyst [2]. Corresponding 1,4-cyclohexadiene derivatives were selectively obtained in the presence of $Fe^0$ complexes [3], a low-valent complex obtained by reducing a (1,4-diaza-1,3-butadiene)$Fe^{II}$ complex [4] or by activating diene systems with $CpFe(Co)_2$ species [5].

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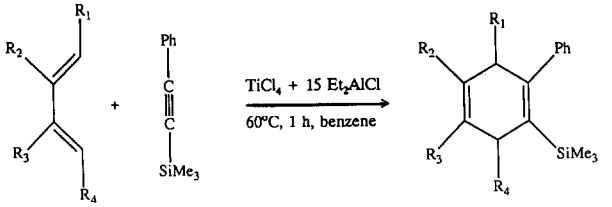



Ia - Ie IIa;IIb,IIb';IIc;IId,IId';IIe,IIe'

a - $R_1,R_2,R_3,R_4$ = H
b - $R_1,R_3,R_4$ = H; $R_2$ = $CH_3$ b' - $R_1,R_2,R_4$ = H; $R_3$ = $CH_3$
c - $R_1,R_4$ = H; $R_2,R_3$ = $CH_3$
d - $R_2,R_3,R_4$ = H; $R_1$ = $CH_3$ d' - $R_1,R_2,R_3$ = H; $R_4$ = $CH_3$
e - $R_2,R_4$ = H; $R_1,R_3$ = $CH_3$ e' - $R_1,R_3$ = H; $R_2,R_4$ = $CH_3$

Scheme 1.

Good yields were also obtained with the $Et_2AlCl/TiCl_4$ system for bis(trimethylsilyl)acetylene (BTMSA), methyl-substituted 1,3-butadienes [6] and 1,3-cyclohexadiene [7]. The same catalyst also induced [6 + 2] addition of BTMSA to 1,3,5-cycloheptatriene (CHT) [8,9] and [2 + 2] addition to norbornadiene followed by a series of electrocyclic reactions affording dihydroindene derivatives [10]. All these reactions could proceed because the presence of the bulky trimethylsilyl (TMS) substituents in BTMSA prevented its competitive titanium-catalyzed cyclotrimerization [11], while the strong interaction of BTMSA with a titanium complex hindered the catalytic homo-oligomerization or polymerization of the dienes or CHT.

Here we report the reactivity of less sterically hindered PTMSA towards a series of methyl-substituted butadiene derivatives and CHT. Analogous to the Diels–Alder adducts of BTMSA, the thermolytic aromatization of 1,4-cyclohexadienes was studied to find an easy entry to *ortho*-(trimethylsilyl)-substituted biphenyls.

## Results and discussion

*Catalysed Diels–Alder addition of PTMSA to conjugated dienes*

The [4 + 2] addition of PTMSA and conjugated dienes (**Ia–Ie**) catalyzed by the $Et_2AlCl/TiCl_4$ (Al/Ti = 4–20) system afforded a series of 1-phenyl-2-(trimethylsilyl)cyclohexa-1,4-dienes (**IIa–IIe,IIe'**) (Scheme 1) in good yields and with high selectivity (Table 1). Turnover numbers, PTMSA/Ti, were close to 125 for all the reactions discussed. 2,4-Hexadienes and 2,4-dimethyl-1,3-pentadiene were unreactive. This allows us to make the generalization that 1,3-butadienes substituted at both ends or doubly substituted at one end should not react with PTMSA using this catalyst. All the compounds obtained (unknown until now) were characterized by mass, IR and $^1H$ and $^{13}C$ NMR spectroscopy.

The symmetrical dienes **Ia** and **Ic** yielded single adducts **IIa** and **IIc** whose structures were established from $^1H$ and $^{13}C$ NMR spectra. The unsymmetrical dienes **Ib**, **Id** and **Ie** gave rise to mixtures of two positional isomers (Table 1) which

Table 1

Yields of products **IIa–IIf** from the cycloaddition of PTMSA to conjugated dienes **Ia–Ie** and to 1,3,5-cycloheptatriene (**If**)

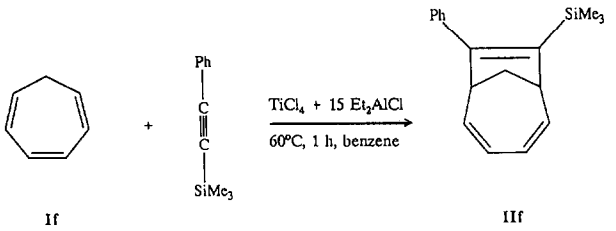
| Diene | Diene/PTMSA (mol) | Yield of crude **II** (%) [a] | Content of **II** (%) [b] | Ratio of isomers [c] |
|---|---|---|---|---|
| **Ia** | 1.40 | 84 | 85 | – |
| **Ib** | 1.30 | 66 | 85 [d] | **b**/**b'** = 60/40 [e] |
| **Ic** | 1.19 | 98 | 73 | – |
| **Id** | 1.43 | 80 | 91 [d] | **d**/**d'** = 17/83 |
| **Ie** | 1.19 | 94 | 87 [d] | **e**/**e'** = 16/84 |
| **If** | 2.01 | 60 | 90 | – |

[a] Liquid products, after first liquid column chromatography (contain some PTMSA) and evaporation of solvents, related to complete conversion of PTMSA to **II**. [b] By GC, individual impurities, except PTMSA, were present in amounts lower than 3% and their structures were not determined. [c] By GC and NMR. [d] Total of two isomers. [e] Assignment of isomers was not made.

could not be separated by chromatographic methods. Two positional isomers **IId** and **IId'** were, however, distinguished by long-range ($^1H$,$^{13}C$) COSY NMR experiments (experimental settings: $J = 5$ and 10 Hz), because the methyl (Me) groups on the 1,4-cyclohexadiene ring gave well separated signals (0.99 and 0.78 ppm). Both TMS and the Me group of the major component exhibited a cross-peak to the same quaternary carbon atom in ($^1H$,$^{13}C$) COSY optimized for distinction of small coupling constants; the structure **IId'** was therefore assigned to this component. Analogous experiments to distinguish between **IIb** and **IIb'**, and **IIe** and **IIe'** failed because of small differences in the chemical shifts of the corresponding methyl groups. Despite this, distinction between the major and minor positional isomers could be made for **IIe** and **IIe'** because the chemical shifts of the methyl groups at C-3 and C-6 were known from **IId** and **IId'**; the major isomer is **IIe'**. Such an approach failed with **IIb** and **IIb'** where the chemical shift difference between the Me groups of both isomers was too small.

The mass spectra of all compounds were dominated by $(M-HSiMe_3)^+$ and $(SiMe_3)^+$ ions. Surprisingly the $(M-CH_3)^+$ ions were present in low abundance. At variance with what was reported for the analogous adducts of BTMSA [6], no retro Diels–Alder fragmentation was detected in the mass spectra. The IR spectra of all adducts **II** exhibited strong bands of TMS groups in the regions 1245–1255 $cm^{-1}$ and 847–857 $cm^{-1}$. The C–H stretching and bending vibrations of the Ph group and Me groups on the cyclohexadiene ring and TMS groups, as well as the overtone bands of the Ph group, were observed in the regions 1300–2000 $cm^{-1}$ and 2800–3100 $cm^{-1}$. The pure adducts or mixtures of two positional isomers were distinguished by bands in the fingerprint region 400–1260 $cm^{-1}$, but no assignment was attempted.

The abundance of **IId** and **IId'** isomers (Table 1) is rather surprising as the sterically more hindered **IId'** with vicinal TMS and Me groups strongly prevails. It shows that kinetic rather than thermodynamic aspects play the main role in this titanium-catalyzed cycloaddition reaction. This probably reflects the fact that the reaction is not a concerted process and that in a transition complex the more reactive, unsubstituted double bond of butadiene and the less hindered, phenyl-substituted carbon atom of PTMSA are preferably involved in bonding interac-




If IIf

Scheme 2.

tions. Apparently the same situation accounts for the prevailing formation of **IIe'** whereas only negligible steric reasons may participate in the formation of **IIb** and **IIb'** isomers.

*Catalyzed [6 + 2] addition of PTMSA to CHT*

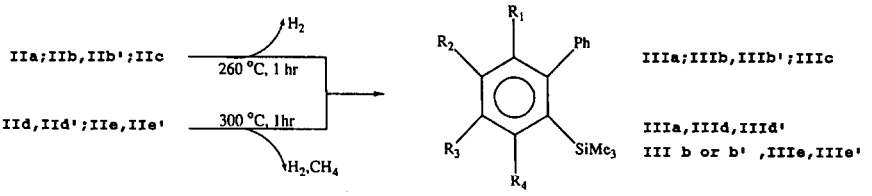
The $Et_2AlCl/TiCl_4$ system also catalyzed a highly selective [6 + 2] addition of CHT to PTMSA (Scheme 2). This reaction afforded 7-phenyl-8-(trimethylsilyl)bicyclo[4.2.1]-nona-2,4,7-triene (**IIf**) in high yield (Table 1) and with turnover number 125. According to the orbital symmetry rules of Woodward and Hoffmann [12], the thermal [6 + 2] addition is a forbidden reaction and is therefore accompanied by a high activation barrier. However, the rule does not hold if a transition-metal atom is present in a transient reaction intermediate [13].

$^1H$ NMR spectra of **IIf** exhibited signals due to a conjugated diene system flanked by two methines that in turn were connected through a methylene group to form a seven-membered ring. Many protons showed a multitude of long-range couplings typical for a rigid bicyclic system. The absence of any resolved coupling, except for the *geminal* one, was used for the assignment of H-9(*endo*). All the expected carbon signals with appropriate distribution of chemical shifts and multiplicity were observed in the $^{13}C$ NMR spectra. The phenyl and trimethylsilyl group and tetrasubstituted double bond were found in addition to the abovementioned system. This double bond, bearing both phenyl and TMS groups, forms a bridge between the two methines. The deduced structure of **IIf** is similar to that of the BTMSA–CHT adduct [9]. No assignment of the orientation of the substituents at the double bond with respect to the rest of the molecule was attempted. The compound is probably an equimolar mixture of two diastereoisomers indistinguishable by NMR spectroscopy.

The most abundant ions in the mass spectrum are the $(SiMe_3)^+$ and $(M - SiMe_3H)^+$ ions and the main features of its IR spectrum are analogous to the spectra of the Diels–Alder adducts **IIa–IIe,e'**.

*Thermolyses of the Diels–Alder adducts IIa–IIe,IIe'*

Compounds **IIa**, **IIb**, **IIb'** and **IIc** underwent a rather easy dehydrogenation at 260°C which gave the biphenyl derivatives **IIIa**, **IIIb**, **IIIb'** and **IIIc** in nearly theoretical yields (Scheme 3, Table 2). The gas evolved was, according to MS analyses, pure hydrogen. In this series, only **IIIa** was previously prepared by a coupling reaction of 2-chlorobiphenyl and $Me_3SiCl$ and was characterized by its IR spectrum [14]. The adducts **IId**, **IId'** and **IIe**, **IIe'** containing one methyl substituent at the saturated carbon atom in the cyclohexadiene ring were more stable towards




Scheme 3.

heating. Their aromatization was completed only after heating at 300°C for 1 h. The MS analysis of evolved gases revealed that methane was produced together with hydrogen. The comparison of the ratios of positional isomers before and after the thermolysis and the presence of known compounds **IIIa** and **IIIb** or **IIIb'** in the products showed that mainly the methyl group *vicinal* to the TMS group was released (*cf.* Tables 1 and 2). By analogy with the transformation of **IId'** to **IIIa**, the aromatic hydrocarbon obtained from **IIe'** should be **IIIb**. However, this was not proven since structures of **IIIb** and **IIIb'** were not unequivocally assigned to their NMR spectra. The structures of all the other aromatic hydrocarbons were established by $^1H$, $^{13}C$ and 2D NMR experiments. The mass spectra of the biphenyl derivatives are dominated by the $(M - CH_2 - CH_3)^+$ ions and also the $(M - CH_3)^+$ ions are very abundant; the $(SiMe_3)^+$ ions are low in abundance in the mass spectra of the biphenyls, while in the spectra of their 1,4-cyclohexadiene precursors they were the main fragmentation ions.

The elimination of methane competing with the elimination of hydrogen from 1-phenyl-2-(trimethylsilyl)-3-methylcyclohexa-1,4-diene was not previously observed at the thermolysis of 1,2-bis(trimethylsilyl)-3-methylcyclohexa-1,4-diene [6]. Hence, the methane elimination cannot be accounted for only by the steric effect of the TMS group forcing the *vicinal* Me group to occupy the *endo*-position in an excited *cis* configuration of the molecule. The explanation of this phenomenon is, however, beyond the scope of this work.

*The catalytic system*

The interaction of the catalytic system with PTMSA was analogous to that found for BTMSA [6]. Reaction of $TiCl_4$ with $Et_2AlCl$ at Al/Ti = 10–20, was completed after 10 min at 60°C, giving rise to heterogeneous systems containing precipitated $TiCl_3$. However, after addition of PTMSA at ambient temperature the

Table 2

Thermolyses of 1,4-cyclohexadienes **IIa–IIe,IIe'** to give *ortho*-(trimethylsilyl)biphenyls (**III**) [a]

| II | T (°C) | Yields of III (%) [b] | Content of III (%) [c] | Ratio of products [d] | Gas evolved [e] |
|---|---|---|---|---|---|
| **a** | 260 | 92 | 86 | – | $H_2$ |
| **b,b'** | 260 | 90 | 92 [f] | 60/40 | $H_2$ |
| **c** | 260 | 93 | 75 | – | $H_2$ |
| **d,d'** | 300 | 94 | 95 [f] | **d/d'/a** = 19/49/32 | $H_2$, $CH_4$ |
| **e,e'** | 300 | 91 | 85 [f] | **e/e'/b** or **b'** = 18/54/28 | $H_2$, $CH_4$ |

[a] Crude products **II** (*cf.* Table 1) were thermolyzed for 1 h. [b] All volatiles were distilled *in vacuo* up to 100°C. [c] By GC. [d] By GC and NMR. [e] By MS. [f] Total of products.

mixture slowly turned into a homogeneous dark brown solution. At 60°C, the homogeneous solution was obtained after 20 min.

At variance with the BTMSA containing systems, which produced a green solution characterized by an absorption band at 620 nm [6], these systems showed a continuous absorption decreasing in intensity from 300 to ~2000 nm with weak shoulders at 530 and 790 nm. ESR spectra of the homogeneous, PTMSA-containing system showed a weak signal at $g = 1.9690$ with $\Delta H = 1.4$ mT, an intensity corresponding to less than 5% of the overall titanium content. The visual appearance of the system and its spectroscopic characteristics did not change during and after the reaction with dienes when the catalyst was largely deactivated. This indicates that a soluble complex containing titanium and PTMSA (or its oligomer) which exerts the visible spectrum, is not the catalytic species. The catalytic species is thus probably present in a small amount not detected by UV–vis spectroscopy.

A soluble complex resulting from interaction of the catalyst and PTMSA was isolated by evaporating all volatiles at 60°C *in vacuo* and by washing the residue with hexane. Ethylaluminium compounds and traces of PTMSA were found in the washings. The remaining viscous brown oil partly solidified on walls which indicated that its molecular weight was not uniform. Both the oil and solid were readily soluble in toluene. The colour of the solution did not change when toluene was replaced by tetrahydrofuran indicating that the complex was coordinatively saturated. However, the product contained oligomers bound to titanium or free yellow oligomers of PTMSA which could not be washed out from the residue because they were insoluble in hexane (see below). The presence of these oligomers precluded further investigation of the titanium complex.

Thus, the nature of the active species can only be subject to speculation. The interaction of (arene)$Ti^{II}$ complexes or Ziegler–Natta systems with diphenylacetylene (DPA), which is more reactive than PTMSA and cyclooligomerizes easily, is better understood. In such systems, the successive formation of complexes containing TiDPA in ratios 1:1, 1:2 and 1:3 was established and 1:2 and 1:3 complexes were isolated [15,16]. The X-ray single crystal analyses revealed that they were a tetraphenylcyclobutadiene complex, $(Ph_4C_4)Ti(AlBr_4)_2$ [15] and a hexaphenyltitanacycloheptatriene complex, $(Ph_6C_6)$=$TiBr_2$ [16]. In a complex reaction mixture of the present systems, however, no crystalline products were isolated although partial capability of the systems to induce the cyclotrimerization of PTMSA was noticed. After decomposition of the brown titanium-containing compound in air, a yellow benzene soluble extract was isolated. According to MS analyses this extract contained, along with more abundant higher oligomers, a cyclic trimer of PTMSA and another similar compound, although as very minor components. Both these interesting byproducts are the subject of further investigation. The yellow oligomers were insoluble in hexane and were rapidly oxidized in air; their mass spectra indicated that they were probably linear oligomers of PTMSA containing desilylated units.

## Experimental

### *General*

A high-vacuum technique, based on all-sealed glass devices and breakable seals, was used for dosing of catalyst components and substrates, all manipulations and spectroscopic measurements on catalytic mixtures.

*Materials*

PTMSA was prepared by reaction of trimethylsilyl chloride with a Grignard compound obtained by mixing equimolar amounts of ethylmagnesium bromide and phenylacetylene [14]. The dienes, butadiene (**Ia**), isoprene (**Ib**), 2,3-dimethyl-1,3-butadiene (**Ic**), (*E*)-1,3-pentadiene (**Id**), 2-methyl-1,3-pentadiene (**Ie**), 2,4-hexadiene, 2,4-dimethyl-1,3-pentadiene and 1,3,5-cycloheptatriene (**If**) (all Fluka) were dried by standing in $LiAlH_4$, distilled *in vacuo* and stored in solutions containing green "dimeric titanocene". $TiCl_4$ (International Enzymes Ltd.) was distilled *in vacuo* and diluted with benzene to give a 0.1 *M* solution. $Et_2AlCl$ (Fluka) was purified from traces of $EtAlCl_2$ by heating with anhydrous sodium chloride to 180°C; it was then distilled *in vacuo* and diluted with benzene to give a 1.0 *M* solution. PTMSA, the dienes, CHT and the solutions of the catalyst components were distributed *in vacuo* into ampoules equipped with breakable seals and were sealed in.

*Instrumentation*

Chromatographic analyses were carried out on a gas chromatograph Chrom 5 (Laboratorní přistroje, Prague) using 10% SE-30 on a Chromaton N-AW-DMCS column. The mass spectra were recorded on a Hewlett Packard gas chromatograph (5890 series II) equipped with a mass spectrometric detector (5791 A) and a capillary column SPB-1 (Supelco). ESR spectra were recorded on an ERS-220 spectrometer (Academy of Sciences, ZWG, Berlin) in the X-band at room temperature. IR spectra of liquid thin films were recorded on a UR-75 spectrometer (Zeiss, Jena) in the region 400–3500 $cm^{-1}$. The electronic absorption spectra were recorded on a Varian Cary 17 D spectrometer using sealed quartz cuvettes (Hellma; $d = 0.1$ and 1.0 cm) in the region 270–2000 nm. $^1H$, $^{13}C$ NMR and 2D-NMR spectra were measured on a Varian VXR-400 spectrometer (FT mode, 400 MHz for $^1H$, 100 MHz for $^{13}C$). Internal tetramethylsilane or the residual $CHCl_3$ signal were used for reference purposes. Signal multiplicity in the $^{13}C$ NMR spectra was determined by attached proton tests (APT).

*Cycloaddition of PTMSA to conjugated dienes and CHT*

The reaction ampoule was charged subsequently with benzene solutions of $TiCl_4$ (0.1 *M*, 1 ml) and $Et_2AlCl$ (1.0 *M*, 1.5 ml), PTMSA (12.8 mmol, 2.5 ml) and with the dienes or CHT (Table 1) by opening the breakable seals in an all-glass evacuated device. After mixing the $Et_2AlCl$ and $TiCl_4$ solutions, the reaction mixture turned into a brown suspension. Adding the acetylene and heating for 10 min at 60°C resulted in a brown homogeneous mixture. The diene was then added and the mixture was heated to 60°C for 2 h in a thermostatted water bath. After cooling to ambient temperature, the ampoule was opened to air and the reaction mixture was chromatographed on a silica gel (L 100/160) column (length 7 cm) with hexane as eluent. Products of the catalyst decomposition and higher oligomers of PTMSA were trapped in the column. Removal of the solvent under reduced pressure gave the crude product as a yellow liquid. The composition of the products was measured by GC. The product yields and composition are given in Table 1. Crude products were further purified by column liquid chromatography over silica gel with hexane as eluent. The single products or mixtures of products with very similar retention times were obtained as colourless liquids after evapora-

tion of hexane. They were characterized by mass spectra, IR spectra in the region 400–1255 $cm^{-1}$ and $^1H$,$^{13}C$ NMR spectra. 2D NMR experiments such as $^1H$,$^1H$ COSY, $^1H$,$^{13}C$ COSY and long-range $^1H$,$^{13}C$ COSY were used to establish the structure of the components. A yellow product was eluted from the column with benzene and the solvent was evaporated at reduced pressure.

*Thermolysis of the 1,4-cyclohexadiene derivatives*

Approximately 1 g of crude **II** was charged into a 50 ml ampoule equipped with a breakable seal and was degassed on a vacuum line. After sealing off, the ampoule was heated for 1 h at the temperature given in Table 2. The ampoule was then opened in a vacuum under cooling to −78°C. A sample of the evolved gases was sealed off in a side ampoule for the MS measurement (Table 2). The liquid product was then distilled *in vacuo* into a trap cooled with liquid nitrogen to give about 95% yield of crude **III**. Its composition was determined by GC. Usually, the crude **III** contained less impurities than crude **II** because some of them polymerized out during heating. The products were further purified by liquid column chromatography and characterized by the same methods as **II**.

*Spectroscopical characteristics*

The isomeric products from unsymmetrical dienes, when distinguished by GC–MS or NMR spectra are denoted as major (ma) and minor (mi).

*1-Phenyl-2-(trimethylsilyl)cyclohexa-1,4-diene (**IIa**).* MS *m/z* (%): 228 ($M^{+\cdot}$,1.8), 213 (5.5), 180 (1.1), 159 (9.2), 154 (100), 129 (7.0), 115 (7.4), 102 (3.4), 73 (46.0), 59 (11.0). IR (neat): 1253s, 1173m, 1100m, 1073m, 1020s, 973m, 927s, 913s, 900s, 840s, 767s, 733s, 706s, 673m, 613m, 540m $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 25°C): $\delta$ −0.225 (s, 9H, $SiMe_3$); 2.873 (s, 4H, $CH_2$); 5.802 (m, 2H, olef); 7.126 (m, 2H, *o*-Ph); 7.223–7.318 (m, 3H, *p*-Ph + *m*-Ph). $^{13}C$ NMR ($CDCl_3$, 25°C): $\delta$ −0.38q (3C); 30.02 (t); 34.39 (t); 124.06 (d); 124.67 (d); 126.63 (d); 127.96 (d, 2C); 128.06 (d, 2C); 130.50 (s); 145.85 (s); 145.91 (s).

*1-Phenyl-2-(trimethylsilyl)-5-methylcyclohexa-1,4-diene (**IIb**) and 1-phenyl-2-(trimethylsilyl)-4-methylcyclohexa-1,4-diene (**IIb'**).* MS *m/z* (%): 242 ($M^{+\cdot}$, 10.4), 227 (10.0), 209 (10.6), 195 (4.0), 168 (100), 159 (17.0), 153 (14.6), 128 (6.2), 115 (8.4), 91 (10.8), 73 (99.0), 59 (50.6), 45 (42.0). IR (neat): 1253s, 1100s, 1090s, 1073s, 1057s, 1033s, 1013s, 973w, 913m, 873m, 833s, 783w, 757s, 700s, 653m, 547m, 470m $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 25°C): $\delta$ −0.215 (s, 9H, $SiMe_3$, ma); 0.001 (s, 9H, $SiMe_3$, mi); 1.684 (s, $CH_3$, mi); 1.731 (s, $CH_3$, ma); 2.735–2.811 (m, $CH_2$); 2.858–2.929 (m, $CH_2$); 5.484 (m, CH, ma); 5.520 (m, CH, mi); 7.106–7.367 (Ph). $^{13}C$ NMR ($CDCl_3$, 25°C): $\delta$ −0.37 (q, 3C, ma); −0.34 (q, 3C, mi); 22.85 (q, mi); 23.11 (q, ma); 31.42 (t, mi); 34.98 (t, ma); 35.84 (t, ma); 39.34 (t, mi); 118.44 (d, ma); 118.78 (d, mi); 126.60 (d, ma); 126.63 (d, mi); 127.62 (d, 2C, mi); 127.93 (d, 2C, ma); 127.99 (d, 2C, mi); 128.14 (d, 2C, ma); 130.34 (s, ma); 131.45 (s, ma); 145.76 (s, ma); 145.94 (s, ma) (singlet signals for the minor component were not observed).

*1-Phenyl-2-(trimethylsilyl)-4,5-dimethylcyclohexa-1,4-diene (**IIc**).* MS *m/z* (%): 256 ($M^{+\cdot}$, 3.7), 241 (4.4), 223 (3.3), 209 (2.6), 182 (100), 167 (22.2), 152 (7.4), 115 (5.6), 105 (4.8), 73 (40.7), 59 (13.0). IR (neat): 1248s, 1142w, 1127w, 1093w, 1068w, 1030w, 1003w, 967m, 935w, 901m, 867m, 837s, 760s, 703s, 637m, 553w $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 25°C): $\delta$ −0.194 (s, 9H, $SiMe_3$); 1.665 (s, $CH_3$); 1.722 (s, $CH_3$); 2.833 (m, 4H, $CH_2$); 7.146 (m, 2H, *o*-Ph); 7.229–7.325 (m, 3H, *m*-Ph + *p*-Ph). $^{13}C$

NMR ($CDCl_3$, 25°C): $\delta$ −0.31 (q, 3C); 18.11 (q); 18.12 (q); 37.51 (t); 41.53 (t); 123.07 (s); 123.36 (s); 126.62 (d); 127.92 (d, 2C); 128.14 (d, 2C); 130.85 (s); 145.80 (s); 146.48 (s).

*1-Phenyl-2-(trimethylsilyl)-6-methylcyclohexa-1,4-diene (**IId**, mi) and 1-phenyl-2-(trimethylsilyl)-3-methylcyclohexa-1,4-diene (**IId'**, ma).* MS *m/z* (%): 242 ($M^{+\cdot}$, 1.9), 227 (5.6), 209 (4.5), 195 (5.6), 168 (100), 153 (11.2), 135 (5.2), 115 (7.5), 81 (7.1), 73 (54.0), 45 (10.8). IR (neat); 1153s, 1181m, 1139m, 1075m, 1063m, 1037m, 1023m, 1003m, 971w, 947m, 847s,br, 767s, 733s, 708s, 693s, 647m, 613m, 568w, 537w, 517w, 465m $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 25°C): $\delta$ −0.403 (s, 9H, $SiMe_3$, mi); −0.343 (s, 9H, $SiMe_3$, ma); 0.784 (d, $CH_3$, 6.9, mi); 0.993 (d, $CH_3$, 6.9, ma); 2.630 (m, 1H, $CH_2$, mi); 2.685 (m, 1H, $CH_2$, ma); 2.748 (m, 1H, $CH_2$, ma); 2.804 (m, 1H, $CH_2$, mi); 2.845–2.900 (m, $CH_3CH$), 5.573–5.639 (m, CH, olef); 5.644–5.492 (m, CH, olef); 6.937 (m, 2H, *o*-Ph, mi); 6.991 (m, 2H, *o*-Ph, ma); 7.073–7.167 (m, *m*-Ph + *p*-Ph). $^{13}C$ NMR ($CDCl_3$, 25°C): $\delta$ −0.30 (q, 3C, mi); 0.92 (q, 3C, ma); 20.98 (q, mi); 23.19 (q, ma); 30.15 (t, mi); 34.12 (d, ma); 34.80 (t, ma); 36.55 (d, mi); 122.63 (d, ma); 123.52 (d, mi); 126.50 (d, mi); 126.78 (d, ma); 127.67 (d, 2C, mi); 127.92 (d, 2C, ma); 128.49 (d, 2C, ma); 130.79 (d, mi); 131.78 (d, ma); 136.87 (s, ma); 145.75 (s, ma); 146.79 (s, ma).

*1-Phenyl-2-(trimethylsilyl)-4,6-dimethylcyclohexa-1,4-diene (**IIe**, mi) and 1-phenyl-2-(trimethylsilyl)-3,5-dimethylcyclohexa-1,4-diene (**IIe'**, ma).* MS *m/z* (%): 256 ($M^{+\cdot}$, 1.9), 241 (5.2), 223 (2.6), 209 (5.6), 182 (100), 167 (22.3), 135 (7.8), 105 (7.4), 91 (5.9), 73 (96.7), 59 (22.3), 45 (18.2). IR (neat): 1253s, br, 1157m, 1076m, 1057m, 1026m, 992m, 973s, 928m, 895m, 847s, br, 767s, 733s, 708s, 693s, 657m, 613m, 568w, 567w, 517w, 465m $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 25°C): $\delta$ 0.000 (s, 9H, $SiMe_3$, mi); 0.047 (s, 9H, $SiMe_3$, ma); 1.133 (d, $CH_3$, alif, 6.9, mi); 1.355 (d, $CH_3$, alif, 6.9, ma); 1.937 (m, $CH_3$, olef, ma); 1.971 (m, $CH_3$, olef, mi); 2.954 (d, m, 1H, $CH_2$, 6.7, mi); 3.002 (d, m, 1H, $CH_2$, 6.6, mi); 3.021 (d, m, 1H, $CH_2$, 5.0, ma); 3.076 (d, m, 1H, $CH_2$, 5.1, ma); 3.143 (m, $CH_3CH$, mi); 3.268 (m, $CH_3CH$, ma); 5.622 (m, CH, olef, mi); 5.728 (CH, olef, ma); 7.311 (m, 2H, *o*-Ph, mi); 7.386 (m, 2H, *o*-Ph, ma); 7.415–7.549 (m, *m*-Ph + *p*-Ph). $^{13}C$ NMR ($CDCl_3$, 25°C): $\delta$ −0.26 (q, 3C, mi); 0.96 (q, 3C, ma); 21.15 (q, mi); 22.64 (q, ma); 23.02 (q, mi); 23.36 (q, ma); 35.11 (t, mi); 35.55 (d, ma); 37.89 (d, mi); 39.67 (t, ma); 125.31 (d, mi); 126.02 (d, ma); 126.47 (d, mi); 126.78 (d, ma); 127.64 (d, 2C, mi); 127.93 (d, 2C, ma); 128.50 (d, 2C, ma); 129.65 (s, ma); 136.47 (s, ma); 145.68 (s, ma); 146.73 (s, ma).

*7-Phenyl-8-(trimethylsilyl)bicyclo[4,2,1]nona-2,4,7-triene (**IIf**).* MS *m/z* (%): 266 ($M^{+\cdot}$, 7.7), 233 (1.9), 192 (31.5), 159 (17.3), 115 (15.0), 92 (63.5), 73 (100). IR (neat): 1253s,br, 1073s, 1028s, 1004s, 995s, 963m, 921s, 907s, 875s, 863s, 843s,br, 787s, 760s, 713s,br, 661s, 635s, 620m, 580m, 548w, 487s, 440m $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 25°C): $\delta$ −0.087 (s, 9H, $SiMe_3$); 1.641 (d, 1H, H-9 *endo*, 11.4); 2.304 (ddddd, 1H, H-9 *exo*, 11.4, 7.0, 6.6, 1.3, 1.2); 3.276 (dd, 1H, H-6, 7.3, 6.6); 3.513 (dd, 1H, H-1, 7.2, 7.0); 5.832 (ddd, 1H, H-4, 12.0, 7.2, 1.5); 5.859 (ddd, 1H, H-3, 12.0, 7.2, 1.5); 5.975 (ddddd, 1H, H-2, 12.0, 7.2, 2.1, 1.5, 1.2); 6.187 (ddddd, 1H, H-5, 12.0, 7.2, 2.1, 1.5, 1.3); 7.179–7.258 *m*, 5H, Ph). $^{13}C$ NMR ($CDCl_3$, 25°C): $\delta$ 0.59 (q, 3C, $SiMe_3$); 31.63 (t, C-9); 49.21 (d, C-6); 51.61 (d, C-1); 123.61 (d, C-4); 124.68 (d, C-3); 127.87 (d, *p*-Ph); 127.64 (*d*,2C, *m*-Ph); 129.07 (d, 2C, *o*-Ph); 135.18 (s, Ph); 137.98 (d, C-2); 138.98 (d, C-5); 147.22 (s, 2C, C-7 + C-8).

*1-Phenyl-2-(trimethylsilyl)benzene (**IIIa**).* MS *m/z* (%): 226 ($M^{+\cdot}$, 7.4), 211 (70.4), 195 (100), 180 (7.4), 165 (42.6), 152 (14.8), 129 (4.8), 115 (4.4), 98 (4.6), 73

(7.0), 53 (5.9). IR (neat): 1254s, 1127m, 1090m, 1073m, 1045w, 1033w, 1011m, 917w, 843s,sh, 767s,sh, 757s, 734s, 708s, 627m,sh, 557w, 540w, 463m $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 25°C): $\delta$ 0.028 (s, 9H, SiMe3); 7.245–7.415 (m, 8H, arom); 7.651 (m, 1H, arom). $^{13}C$ NMR ($CDCl_3$, 25°C): $\delta$ 0.56 (q, 3C); 126.27 (d); 127.02 (d); 127.65 (d, 2C); 128.46 (d); 129.39 (d, 2C); 129.46 (d); 134.62 (d); 138.49 (s); 144.50 (s); 149.24 (s).

*1-Phenyl-2-(trimethylsilyl)-5-methylbenzene (**IIIb**) and 1-phenyl-2-(trimethylsilyl)-4-methylbenzene (**IIIb'**).* MS *m/z* (%): major component: 240 ($M^{+\cdot}$, 24.0), 225 90.9), 209 (100), 195 (9.1), 179 (20.2), 165 (29.3), 152 (10.7), 139 (4.0), 104 (16.6), 91 (6.3), 73 (22.2), 59 (14.1), 43 (22.4); minor component: 240 ($M^{+\cdot}$, 18.1), 225 (93.4), 209 (100), 195 (10.0), 179 (20.1), 165 (29.9), 152 (10.0), 139 (3.6), 104 (17.1), 91 (6.0), 73 (18.1), 59 (14.3), 43 (20.1). IR (neat): 1255s, 1221w, 1183w, 1147m, 1093m, 1073m, 1012m, 921m, 887s, 845s, 767s, 737m, 710s, 653w, 630m, 560m, 548m, 473m $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 25°C): $\delta$ 0.205 (s, 9H, $SiMe_3$, mi); 0.213 (s, 9H, $SiMe_3$, ma); 2.585 (s, $CH_3$, mi); 2.621 (s, $CH_3$, ma); 7.280–7.745 (m, arom). $^{13}C$ NMR ($CDCl_3$, 25°C): $\delta$ 0.60 (q); 21.27 (q); 126.89 (d, ma); 126.96 (d, mi); 127.11 (d, mi); 127.63 (d, 2C, ma); 129.22 (d, ma); 129.35 (d, ma); 129.48 (d, 2C, mi); 129.52 (d, 2C, ma); 130.42 (d, mi); 134.76 (d, mi); 135.32 (d, ma); 135.59 (s, ma); 138.30 (s, ma); 144.44 (s, ma); 146.46 (s, ma).

*1-Phenyl-2-(trimethylsilyl)-4,5-dimethylbenzene (**IIIc**).* MS *m/z* (%): 254 ($M^{+\cdot}$, 29.3), 239 (96.3), 223 (100), 209 (14.4), 179 (22.2), 165 (22.6), 152 (6.7), 115 (4.4), 104 (5.6), 73 (7.8), 59 (15.2). IR (neat): 1253s, 1182w, 1167m, 1097s, 1079m, 1037m, 1027m, 1006w, 995w, 947s, 925m, 893s, 853s,br, 773s, 757s, 740s, 712s, 657s, 653s, 751s, 478s, 450m $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 25°C): $\delta$ 0.000 (s, 9H, $SiMe_3$); 2.266 (s, 4-$CH_3$); 2.311 (s, 5-$CH_3$); 7.037 (s, 6-CH, arom); 7.264–7.356 (m, Ph); 7.374 (s, 3-CH, arom). $^{13}C$ NMR ($CDCl_3$, 25°C): $\delta$ 0.67 (q, 3C); 19.46 (q, 4-$CH_3$); 19.56 (q, 5-$CH_3$); 126.84 (d, *p*-Ph); 127.61 (d, 2C, *m*-Ph); 129.48 (d, 2C, *o*-Ph); 131.05 (d, 6-CH); 134.41 (s, Ph); 135.36 (s, C-4); 136.08 (d, C-3); 136.98 (s, C-5); 144.48 (s, C-2); 147.00 (s, C-1).

*1-Phenyl-2-(trimethylsilyl)-6-methylbenzene (**IIId**, mi) and 1-phenyl-2-(trimethylsilyl)-3-methylbenzene (**IIId'**, ma).* MS *m/z* (%): major component: 240 ($M^{+\cdot}$, 10.0), 225 (87.6), 209 (100), 195 (7.3), 179 (19.5), 165 (42.6), 152 (16.8), 139 (7.3), 115 (7.8), 77 (3.9), 73 (14.6), 43 (9.7), minor component: 240 ($M^{+\cdot}$, 8.3), 225 (100), 209 (87.9), 195 (10.3), 179 (16.6), 165 (35.3), 152 (8.1), 130 (3.0), 115 (5.1), 77 (3.0), 73 (6.1), 59 (9.7), 43 (8.1). IR (neat): 1257s, 1195w, 1152m, 1127m, 1090m, 1075m, 1055m, 1030m, 1012m, 969m, 920m, 880s, 853s,br, 797s, 770s,br, 737s, 710s, 653m, 627m, 583m, 556m, 533m,br, 463m $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 25°C): $\delta$ 0.064 (s, 9H, $SiMe_3$, mi); 0.076 (s, 9H, $SiMe_3$, ma); 2.084 (s, $CH_3$, mi); 2.621 (s, $CH_3$, ma); 7.101 (dm, C-4, 7.5, ma); 7.214–7.549 (m, arom); 7.645–7.711 (m, arom). $^{13}C$ NMR ($CDCl_3$, 25°C): $\delta$ 0.49 (q, 3C, mi); 2.35 (q, 3C, ma); 20.90 (q, mi); 24.48 (q, ma); 126.64 (d); 126.84 (d); 126.91 (d); 127.69 (d, 2C, Ph, ma); 127.80 (d); 128.00 (d); 129.01 (d, ma); 129.48 (d, 2C, ma); 129.89 (d); 130.52 (d, mi); 131.93 (d); 135.63 (s, mi); 136.83 (s, ma); 141.25 (s, mi); 142.67 (s, mi); 144.57 (s, ma); 145.72 (s, ma); 148.16 (s, mi); 150.03 (s, ma). Signals due to **IIIa** were also present in the spectrum.

*1-Phenyl-2-(trimethylsilyl)-4,6-dimethylbenzene (**IIIe**, mi) and 1-phenyl-2-(trimethylsilyl)-3,5-dimethylbenzene (**IIIe'**, ma).* MS *m/z* (%): major component: 254 ($M^{+\cdot}$, 19.2), 239 (100), 223 (79.0), 209 (14.2), 129 (24.9), 165 (29.5), 139 (3.2), 115 (5.3), 91 (3.5), 73 (12.1), 59 (18.1), 43 (8.9); minor component: 254 ($M^{+\cdot}$, 15.0), 239

(92.8), 223 (100), 209 (10.0), 179 (23.0), 165 (31.1), 152 (7.0), 115 (6.0), 105 (3.0), 73 (16.0), 59 (11.6). IR (neat): 1113w, 1092m, 1073m, 1060m, 1031m, 917m, 880m, 860m, 843s,br, 770s, 734m, 708s, 652m, 632w, 593m, 567w, 543m, 473m $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 25°C): $\delta$ 0.053 (s, 9H, $SiMe_3$, ma); 0.061 (s, 9H, $SiMe_3$, mi); 2.053 (s, $CH_3$, mi); 2.372 (s, $CH_3$, ma); 2.441 (s, $CH_3$, mi); 2.586 (s, $CH_3$, ma); 6.942 (m, H-3, arom, ma); 7.068 (m, H-5, arom, ma); 7.140–7.426 (m, arom). $^{13}C$ NMR ($CDCl_3$, 25°C): $\delta$ 0.63 (q, 3C, mi); 2.41 (q, 3C, ma); 20.80 (q, mi); 20.92 (q, ma); 21.22 (q, mi); 24.36 (q, ma); 126.78 (d); 127.66 (d, 2C, ma); 127.78 (d); 128.67 (d); 129.44 (d, 2C, ma); 130.03 (d); 130.13 (d); 131.37 (d); 132.60; 133.28 (s); 134.76 (d); 137.76 (s); 138.29 (s); 144.64 (s); 145.77 (s); 150.18 (s). **IIIb** or **IIIb'** is also present in the mixture.

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