and isopropyl alcohol) or in nonhydroxylic solvents (acetonitrile, cyclohexane, dioxane, and tetrahydrofuran) was irradiated (after the solution was thoroughly purged with N_2 for 30 min) in a quartz tube with a low-pressure mercury arc lamp to approximately 20% conversion. After the irradiation, the solvent was distilled off, and the products were separated and purified by preparative TLC (silica gel, hexane). Generally it was not possible to separate thiiranes **2** from thioesters **3**. Only in the case of **1a** could thiirane **2a** and thioester **3a** be separated by repeated column chromatography. In the case of the other thioketenes (**1b** and **1c**) the spectra of the mixture were recorded. Products formed; their yields are shown in Schemes I and II, and the spectral data of the products are provided in Table I. Analytical data for **2–5**, where they could be obtained pure, are provided below.

Anal. Calcd for $C_{11}H_{22}SO$ (**2a**): C, 65.31; H, 10.96. Found: C, 64.98; H, 10.27. Anal. Calcd for $C_{11}H_{22}SO$ (**3a**): C, 65.31; H, 10.96. Found: C, 65.54; H, 11.02. Anal. Calcd for $C_{20}H_{38}O_2$ (**4a**): C, 77.36; H, 12.33. Found: C, 77.78; H, 12.05. Anal. Calcd for $C_{22}H_{38}O_2$ (**4b**): C, 78.99; H, 11.45. Found: C, 78.12; H, 11.61. Anal. Calcd for $C_{16}H_{24}S$ (**5a**): C, 77.38; H, 9.74. Found: C, 77.64; H, 9.64. Anal. Calcd for $C_{17}H_{24}O_2$ (**5b**): C, 78.42; H, 9.29. Found: C, 77.98; H, 9.56. Anal. Calcd for $C_{15}H_{22}O_2$ (**5c**): C, 76.88; H, 9.46. Found: C, 77.02; H, 9.38.

Photolysis of Thioketenes in Benzene. A solution of thioketene **1a** or **1b** (0.1 M) in benzene was irradiated under above conditions to 10% conversion. The workup, separation, and characterization of products were done in an analogous manner. Products and their yields are given in Schemes I and II. Spectral data are provided in Table I.

Control Experiment. Solutions of thioketenes **1a** and **1b** (0.02 M) in methanol, benzene, and acetonitrile were kept in dark at room temperature (30 °C). After 4 days the solutions were checked spectrophotometrically (monitored at 570 nm). Practically no change in the OD was observed, indicating that products **2–5** were derived from light-induced reaction of thioketenes and not by thermal means. Even refluxing in the above solvents for 6 h did not show any change.

Selective Excitation and Sensitization Studies: Selective Excitation to S_1. Solutions of **1a** and **1b** (0.02 M) in solvents (methanol, ethanol, acetonitrile, cyclohexane, dioxane, tetrahydrofuran, and benzene) were degassed and sealed in Pyrex tubes. Irradiation was conducted for about 30 days either with 500-W tungsten lamps or with a 450-W medium-pressure mercury arc lamp with Corning glass filter C.S.-3.70. No reaction could be detected both by UV (OD at 570 nm) and by ^1H NMR. Therefore S_1 is excluded as the reactive state.

Sensitization Studies. Triplet sensitization was carried out only in benzene and methanol. Benzil (53 kcal/mol), Michler's ketone (62 kcal/mol), benzophenone (69 kcal/mol), xanthone (74 kcal/mol), and acetone (79 kcal/mol) were used as sensitizers. In a typical experiment, a solution of thioketene **1a** or **1b** (100 mg, 0.03 M) and sensitizer (0.01 M) in methanol and benzene (40 mL) was irradiated after bubbling with nitrogen for 30 min (Rayonet RPR 3000-Å low-pressure mercury arc lamps). Under analogous conditions 10 mL of acetone and 100 mg of thioketene in 40 mL of methanol and benzene was irradiated. Under these conditions only the sensitizer is excited. A blank solution was also irradiated in an identical manner. After 24 h these solutions were analyzed spectrophotometrically and by ^1H NMR. No reaction could be detected both in the blank solution and in the solution containing the sensitizers benzil, Michler's ketone, and benzophenone. Partial reaction was detected in the case of xanthone and acetone as sensitizers. Under these conditions in methanol only **2** and **4** were formed in low yields (~10%) while **3** was not formed. In benzene **4** and **5** were obtained in low yields (~10%). In brief, acetone- and xanthone-sensitized reactions were very slow, the product yields were low, and moreover, **3** was not formed in methanol. Therefore it was concluded that the reaction is not a triplet process.

Preparation of Thio Esters 3a and 3b.[7] A solution of thioketene **1** (200 mg) in 25 mL of dry methanol containing a drop of sulfuric acid was refluxed for 1 h. The reaction mixture was passed through anhydrous sodium sulfate to remove acid and evaporated. The thio ester thus obtained (yield 90%) was purified on preparative TLC. The spectral data are summarized in Table I.

Raney Nickel Desulfurization of 2a. To a solution of 150 mg of **2a** in 25 mL of petroleum ether (40–60 °C) was added excess of Raney nickel (1 g), and the mixture was refluxed for 12 h. After the reaction, the catalyst was removed by filtering through Whatman No. 1 filter paper and the solvent evaporated. The colorless liquid was purified by TLC (silica gel, hexane) to give 70 mg (yield 50%) of a volatile product identified to be 2,2-di-*tert*-butylethyl methyl ether on the basis of its spectral properties: mass spectrum (70 eV), 172, 116, 101, 57 mass units; ^1H NMR (CCl_4) δ 1.0 (s, 18 H), 2.2 (t, 1 H), 3.2 (s, 3 H), 3.35 (d, 2 H); IR (neat) 2970, 1470, 1380, 1230 cm^{-1}.

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Registry No. **1a**, 16797-75-4; **1b**, 54440-00-5; **1c**, 54439-99-5; **1d**, 57738-75-7; **2a**, 88181-00-4; **2b**, 98687-81-1; **2c**, 98687-82-2; **2d**, 98687-84-4; **2e**, 98687-85-5; **2f**, 98687-86-6; **2g**, 98687-92-4; **3a**, 16797-77-6; **3b**, 16797-70-9; **3c**, 98687-93-5; **3d**, 98687-87-7; **3e**, 98687-88-8; **3f**, 98687-89-9; **3g**, 98687-94-6; **4a**, 29679-00-3; **4b**, 98687-83-3; **5a**, 88181-01-5; **5b**, 98687-90-2; **5c**, 98687-95-7; **14**, 98687-91-3.

6,6-Dimethyl-2,4-diphenylcyclohexadienyl Anion and the Failure of Carbanion Homoaromaticity

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The title carbanion was generated by methyllithium deprotonation of 6,6-dimethyl-2,4-diphenyl-1,4-cyclohexadiene in tetrahydrofuran. Attempted generation of the identical carbanion using potassium (methylsulfinyl)methide in Me_2SO led to cyclopropanation only via isomerization to the 1,3-diene followed by addition/elimination of (methylsulfinyl)methide anion. Except for modest changes in carbon chemical shifts, the title compound exhibits little thermodynamic driving force toward ring closure or homoaromaticity. The NMR spectra at all temperatures were consistent with a planar nonaromatic anion, again failing to establish the existence of homoaromaticity in such carbanions.

Unconventional forms of aromaticity—e.g., spiroaromaticity, Y-aromaticity, homoaromaticity, antiaromaticity—have been significant in testing theoretical concepts against the demands of experiment. Of the

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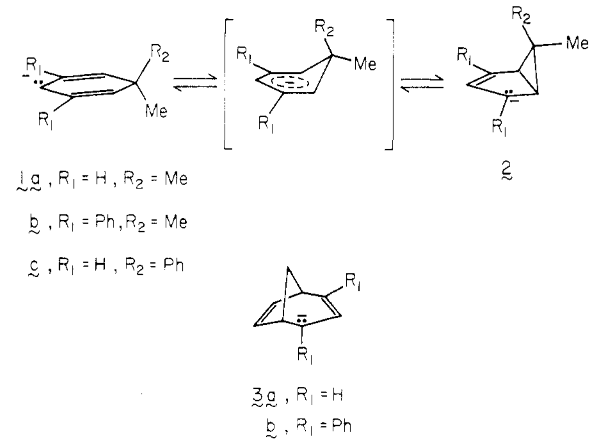

Figure 1. Candidates for homoaromaticity.

various classes of molecules, carbanions have been most reluctant to confirm simple theoretical models. In seeking to expand the concept of aromaticity to carbanions, we have generated a Y-aromatic carbanion[2] as well as an antiaromatic carbanion.[3] Our approach has been to generate resonance stabilized carbanions, which, following the pioneering work of Bordwell and coworkers,[4] in dimethyl sulfoxide (Me_2SO) are relatively unemcumbered by counterion effects and thus can more nearly approximate molecular orbital calculations based upon the gas phase.

No firm evidence exists yet for a homoaromatic carbanion. For the simplest model anion, cyclohexadienyl anion, partial ring closure would lead to a sextet of electrons within a five-orbital cycle and would minimally satisfy the primary criteria for aromaticity. Despite extensive efforts, no indication of such homoaromaticity has been gained for either cyclohexadienyl anion or its minimally substituted dimethyl derivative **1a**,[5a,b] although the methylphenyl derivative **1c** is postulated to undergo an allowed ring closure to bicyclic derivative **2c** during the course of further rearrangement,[5c] and certain ferrocene analogues have been synthesized.[6] The interpretation of ^{13}C NMR chemical shifts for the leading candidate for a bishomoaromatic anion,[7a] bicyclooctadienyl anion **3a**, has been challenged.[7b] Calculations indicate that electron-repulsion terms dominate any potential aromatic stabilization in such systems,[7c] and the conclusion has been drawn that "homoaromatic stabilization is not expected to be an important phenomenon in anions."[7c] Calculations aside, a minimal requirement in valence bond terms for the observation of aromaticity is that two resonance contributors have comparable energies, a criterion not satisfied by anion **3**. Clearly 1,3-cyclohexadienyl anion **1a** pays a price in ring strain of ca. 27 kcal upon closure to bicyclo[3.1.0]hex-2-enyl anion **2a**. Moreover, the pK_a difference between propene and pentadiene will also add to this thermodynamic cost. Considering the potentially homoaromatic anion as a "negative transition state"[8] for interconverting the two structures, the difference in heats of formation will lead to a dominance of the planar form **1a** and the nonobservation of aromatic properties. Thus a true test will only occur if the bicyclic form **2** is comparable in energy to the monocyclic form **1**. Our approach was to stabilize the bicyclic anion by phenyl substitution at the formal sites of negative charge. Such substitution would have the role of allowing its formation in the non-ion-pairing solvent Me_2SO, thus providing a more rigorous test of homoaromaticity (see Figure 1).

In studies on 1,3-diphenylallyl anions,[9] we have observed that substitution at a node in the HOMO has only a minimal effect on the conjugate acid pK_a or other physical properties such the NMR spectrum. Thus for cyclohexadienyl anion **1b**, nodes exist in the HOMO at C-2 and C-4, and phenyl substitution at those positions would have relatively little effect while the comparable substitution in **2b** would have a profound effect. That effect may most closely be approximated by considering the corresponding pK_a's. 2,4-Diphenyl-6,6-dimethylcyclohex-2-ene is comparable to 1,3-diphenylpropene ($pK_a = 29$), while 6,6-dimethylcyclohex-2-ene is comparable to propene ($pK_a \simeq 42$). Thus the stabilization by phenyl is ca. 2.3 RT ΔpK_a, or 20 kcal, which nearly compensates for the strain introduced by cyclopropane formation, 27 kcal. This approach is complementary to that of Trimitsis and Zimmerman[7b] on anion 3, which by analogously stabilizing the *planar* form still did not remove the apparent "bishomoaromatic" chemical shift effects. We now report generation of the title anion, provide some details its unusual substitution chemistry, and comment on its apparent lack of aromaticity.

Results

Synthesis of Reactants. 6,6-Dimethyl-2,4-diphenyl-1,3-cyclohexadiene (**4**) was synthesized by an adaptation of the procedure of Zhou and Huang.[10] Thus dimedone trimethylsilyl ether was treated with phenyllithium, and the resulting 5,5-dimethyl-3-phenylcyclohex-2-enone was treated again with phenyllithium. Acid-catalyzed elimination of the enol yielded diene **4** in overall 32% yield. 6,6-Dimethyl-1,4-diphenyl-1,4-cyclohexadiene (**5**) was obtained by a cold methanol quench of the anion derived by treatment of diene **4** with KH/[18-crown-6] in tetrahydrofuran at −78 °C.

Generation of Diphenylcyclohexadienyl Anion 1b. Our initial efforts concentrated on 1,3-cyclohexadiene **4**, the anion precursor most readily available. Treatment of a Me_2SO solution of this substrate with potassium methylsulfinylmethide ("dimsyl") led to formation of a deep violet solution which decolorized upon standing. Isolation of the products by silica gel column chromatography revealed the presence of a new hydrocarbon **6** as well as four diasteromers whose molecular weight (338) and NMR spectra allowed us to assign their structures as Me_2SO adducts **7**. An exact mass molecular formula determination for hydrocarbon **6** ($C_{21}H_{22}$) indicated the addition of a methylene group to diene **4**. The proton NMR spectrum contained a three-proton ABC pattern of an ABCX system

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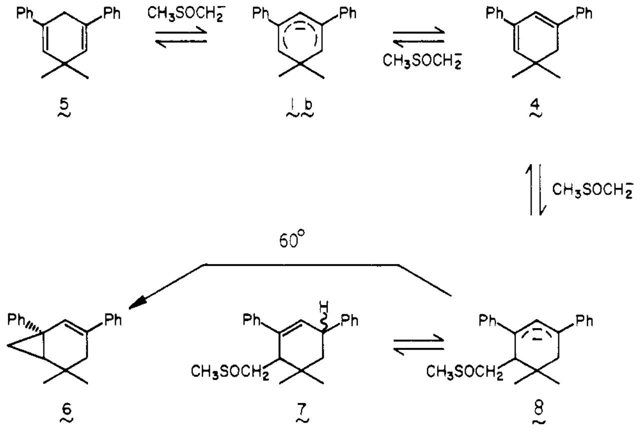

Figure 2. Reaction pathways of cyclohexadienyl anion 1.

in the cyclopropyl region as well as a geminal two-proton AB portion of an ABX-like pattern at 2.19 and 2.10 ppm coupled to a single remaining downfield vinyl proton at 6.45 ppm, with additional coupling to a single cyclopropyl proton. Moreover, the methyl peaks had become nonequivalent. On this basis, we conclude that hydrocarbon **6** is 5,5-dimethyl-1,3-diphenylbicyclo[4.1.0]hept-2-ene. Although the 3-heptene isomer cannot be eliminated on spectroscopic grounds, we exclude it on chemical grounds (vide infra). When the four diastereomeric sulfoxides were again subjected to the reaction conditions with additional base, a red-violet solution containing two distinct species by NMR was observed. The proton and chemical shifts of the anionic species so produced were indicative of conjugate adducts of dimsyl anion to hydrocarbon **4**. When heated to 60 °C., these two species disappeared and hydrocarbon **6** was formed exlusively (see Figure 2). Finally, an attempt to generate anion **1b** by deprotonation of the unconjugated cyclohexadiene **5** yielded the identical sulfoxide adducts **7** and homologated hydrocarbon **6**.

In order to more carefully elucidate the sequence of events leading to hydrocarbon **6**, extensive deuterium labeling studies were performed using dimsyl potassium solutions generated from Me_2SO-d_6 on hydrocarbons **4**, **5**, and nondeuterated sulfoxides **7**. Thus we were able to construct Figure 2 to account for formation of all observed products.

Attempts to generate anion **1b** as its lithium derivative by treatment of **4** with *n*-butyllithium were similarly diverted by conjugate addition. However, addition of *n*-butyllithium or methyl lithium to tetrahydrofuran solutions of hydrocarbon **5** were successful, producing clean solutions of the desired cyclohexadienyllithium which were stable with an excess of base at room temperature or below.

NMR Studies of 6,6-Dimethyl-2,4-diphenyl-2,4-cyclohexadienyllithium (2b-Li). At room temperature, **2b**-Li exhibited a simple proton NMR spectrum consistent with a planar cyclohexadienyl structure. Proton NMR analysis as low as −105 °C did not indicate any loss of equivalency of the two methyl groups, although all the proton absorbances did exhibit a temperature-dependent chemical shift. These results are summarized in Table I. The carbon NMR spectra (Table II) were similarly straightforward, and indicated C_2 symmetry throughout the temperature range from −88 to 25 °C. For comparison purposes, NMR data for *trans,trans*-1,3-diphenyl-2-propenyl anion (**9**) are included as well.[9b]

Discussion

Cyclopropanation of Dienes 3 and 4. Our deuterium labeling studies indicate that cyclopropanation of diene **5** occurs by prior tautomerization to diene **4**. Thus the key mechanistic issue concerns formation of cyclopropane **6** from diene **4**. Cyclopropanation of hydrocarbons by dimsyl anion, although uncommon, has been observed in a few specialized cases.[11] In most cases where the terminus of the olefin contains a proton, 1,2-elimination occurs to yield a methylene group which tautomerizes to methyl.[12] Our results, then, indicate the intervention of the E_1cB mechanism. Moreover, for most E_1cB mechanisms, formation of the carbanion is rate-limiting and the intermediate is not observed. Due to stabilization of the carbanion by two phenyl groups, our carbanionic intermediate is not only observable but persistent, requiring somewhat elevated temperatures for elimination, with a half-life of of ca. 10 min at 60 °C.

Table I. Proton Chemical Shifts for 6,6-Dimethyl-2,4-diphenylcyclohexadienyl Anion

temp, °C	H_1	H_3	H_o	H_m	H_p	CH_3	ref
+22.9	3.81	4.93	7.54	7.15	7.06	0.90	THF-d_7
−19.6	3.72	4.69	7.43	7.13	7.04	0.90	3.58 ppm
−34.1	3.72	4.61	7.51	7.13	7.03	0.90	
−59.9	3.77	4.50	7.61	7.12	6.98	0.91	
−79.8	3.72	4.48	7.60	7.11	6.97	0.89	
−105.5	3.66	4.52	7.60	7.12	6.99	0.89	

Anion 2b and the Failure of Homoaromaticity. Although our original objective of generating **2b** in dimethyl sulfoxide was thwarted by its reaction with solvent, our ability to generate its lithium salt in tetrahydrofuran allow us to draw some conclusions about the anion independent of counterion effects. First, the temperature-dependent proton chemical shifts indicate that at low temperatures solvent-separated ion pairs are being formed. The fact that any asymmetry induced by lithium involvement does not show up in inequivalency of the methyl groups is also consistent with that conclusion. Second, the degeneracy of the methyl groups indicates that to the extent that homoaromaticity participates, it does not result in partial bond formation with ring puckering toward structure **2b** within the limits of the NMR experiment. Although this observation does not exclude rapid interconversion between two puckered conformers, the chemical shift of the quaternary carbon also legislates against any partial bond formation. That is, the chemical shift of the methylene carbon for cyclohexadienyl anion based upon the empirical π electron density–chemical shift correlation and assuming homoaromaticity is predicted to be 63.3 ppm as compared to the observed 30.8 ppm for the corresponding carbon atom in anion **1a**.[13] Similarly, the predicted shift for diphenyl anion **1b** is 51.8 ppm as opposed to the observed 34.3 ppm. Finally, the carbon chemical shifts do not indicate any significant delocalization of charge density either to atoms 2 and 4 or their associated phenyl rings (see Table I).

To a certain extent, we remain where we started. Clearly structure **2b** has not been stabilized enough to overcome a substantial ring strain effect. Moreover, the difference between bicyclo[3.1.0]hexenyl anion **2a** and the isoelectronic bicyclo[5.1.0]octadienyl cation, which *is* homoaromatic, is that in the latter case the cyclopropylcarbinyl cation is stabilized by a HOMO–LUMO interaction while in the former the cyclopropylcarbinyl anion is destabilized by a HOMO-HOMO interaction. Thus any attempt to make the bicyclic anion of comparable energy to the mo-

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Table II. Carbon Chemical Shifts for Allyl Anions 1, 3, and 9

anion	C_1	C_2	C_3	C_4	C_5	C_6	C_i	C_o	C_m	C_p	CH_3
1a	91.7	127.9	71.8	127.9	91.7	30.8					31.4
1b	87.4	136.7	79.4	136.7	87.4	34.3	145.1	127.0	127.8	125.6	31.5
3b	41.7	94.3	115.7	94.3	41.7	37.6					
9		90.3	129.0	90.3			146.9	118.5	128.9	112.1	

nocyclic isomer must contend not only with ring strain effects but also this substantial electronic effect. We note that in an analogous neutral case, electron-withdrawing groups on a cyclopropane ring stabilize the ring-closed form.[14] We anticipate an analogous effect for cyclohexadienyl anions similarly substituted, and any rigorous test of homoaromaticity still awaits this or similar modifications which will make the two valence isomers of comparable energy.

Experimental Section

6,6-Dimethyl-2,4-diphenylcyclohexa-1,3-diene (4). Phenyl-5,5-dimethylcyclohex-2-enone was prepared by a modification of the method of Woods[15] using dimedone trimethylsilyl ether rather than dimedone ethyl ether. The product (bp 105–110 °C (0.03 torr); lit.[15] bp 110–135 °C, (0.1 torr) was collected to yield 10.7 g (49%) of 3-phenyl-5,5-cyclohex-2-enone as a colorless liquid which solidified in the receiver (mp 51–52.5 °C; lit.[15] mp 54–54.5 °C). ^{1}H NMR ($CDCl_3$) δ 7.45 (m, 5 H), 6.42 (m, 1 H, 2.63 (m, 2 H), 1.13 (s, 6 H).

Similarly, treatment of 3-phenyl-5,5-dimethylcyclohex-2-enone at −78 °C with phenylithium in ether/hexane followed by acidic work up gave 6,6-dimethyl-2,4-diphenylcyclohexa-1,3-diene in 67% yield as a colorless crystalline solid, mp 50.5–51.5 °C (lit.[15] mp 55 °C). The product was indefinitely stable if stored as a solid under argon. ^{1}H NMR ($CDCl_3$) δ 7.40 (m, 10 H), 6.70 (m, 1 H), 5.90 (m, 1 H), 2.57 (m, 2 H), 1.17 (s, 6 H). MS (70 eV), 260.

6,6-Dimethyl-1,4-diphenyl-1,4-cyclohexadiene (5). Potassium hydride (4.00 g), 6,6-dimethyl-2,4-cyclohexa-1,3-diene (4, 1.04 g), and [18-crown-6] (2.00 g) in 15 mL of tetrahydrofuran were stirred at ambient temperature for 43 h. The mixture was quenched at −78 °C with 1:3 methanol/ether followed by neutralization with dilute hydrochloric acid and ether extraction. Silica gel column chromatography of the organic extract afforded 212 mg (20%) of almost pure 1,4-diene 5, along with 58.6 mg (5.6%) of recovered starting material and 350 mg (34%) of a dimeric product. Recrystallization from MeOH afforded colorless crystals, mp 82–83 °C. ^{1}H NMR ($CDCl_3$): δ 7.43 (m, 10 H), 6.00 (t, J = 1.7 Hz, 2 H), 3.40 (t, J = 1.7 Hz, 2 H), 1.23 (s, 6 H); MS (70 eV), 260. Anal. Calcd for $C_{20}H_{20}$: 260.1565. Found: 260.1454

5,5-Dimethyl-1,3-diphenylbicyclo[4.1.0]hept-2-ene. (a) Reaction at Room Temperature. Dimsylpotassium (17.0 mL, 0.480 M in Me_2SO, 8.16 mmol) was added to 5.5-dimethyl-2,4-diphenyl-1,3-cyclohexadiene (1.00 g, 3.85 mmol) in 90 mL of Me_2SO. After 5.5 h the deep-violet reaction mixture was poured to 200 mL of dilute (2.5%) sulfuric acid. Extraction with pentane/hexane (ca. 200 mL) drying with $MgSO_4$, and filtration followed acid quenching. The filtrate was cooled to −10 °C to afford two pairs of diastereoisomeric dimethylsulfoxide adducts 7 as colorless crystals, mp 140–150 °C (233 mg, 18%). ^{1}H NMR ($CDCl_3$) δ 7.30 (m, 10 H), 6.00, 5.83 (m, m, 1 H, 3.57 (m, 1 H, 3.23–2.50 (m, 3 H), 2.28, 2.21 (s, s, 3 H), 2.00–1.50 (m, 2 H), 1.20–1.10 (d, d, 6 H). MS, m/e at 338 (0.8), 322 (1), 274 (100), 259 (35), 231 (55), 218 (71). The mother liquor was concentrated in vacuo yielding a yellow oil (1.00 g). ^{1}H NMR examination showed a mixture of adducts 7, bicyclic product 6 and unreacted substrate 4. The mixture was allowed to stand in the air for 2 days to oxidize substrate 4 to high-polarity products. Column chromatography on silica gel (hexane) afforded 402 mg of yellow oil which was a 2:1 mixture of 6 and 4. A second exposure to air, followed by preparative TLC on silica gel (hexane) yielded 237 mg (22.5%) of 6 as a colorless oil. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.23 (m, 10 H), 6.45 (d, J = 2.7 Hz, 1 H, 2.19 (d of d, J = 16.5 Hz, 1.8 Hz, 1 H), 2.10 (br, d of d, J = 16.5 Hz, J = 2.7 Hz, 1 H), 1.29 (m, J = 1.8 Hz, 3 H), 1.23 (s, 3 H), 1.11 (s, 3 H). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 146.1, 142.2, 131.7, 129.5, 128.4, 128.2, 127.8, 126.4, 125.9, 125.2, 37.9, 35.9, 30.0, 28.3, 28.1, 27.4, 18.2. Anal. Calcd for $C_{21}H_{22}$: 274.1722. Found: 274.1667. MS: (M + 1):M:M − 1, 22:100:17; 274 (28), 259 (19), 231 (52), 218 (67), 205 (100).

(b) Reaction at 60 °C. A mixture of dimsylpotassium (5.5 mL, 0.333 M in Me_2SO, 1.83 mmol) and diene 4 (157 mg, 0.604 mmol) in 10 mL of Me_2SO was kept at 60 °C for 4.5 h and then poured onto 20 mL of dilute (4%) sulfuric acid at 0 °C. Extraction with pentane and usual work up afforded crude 6 as a yellow oil. Column chromatography an silica gel (hexane) afforded 139 mg (84%) of bicycloheptene 6 as a colorless oil.

Formation of 5,5-Dimethyl-1,3-diphenylbicyclo[4.1.0]hept-2-ene: Deuterium Incorporation in Me_2SO-d_6. Reactions were carried out in sealed 5-mm NMR tubes and directly monitored by ^{1}H NMR (90 MHz). (a) 1,3-Cyclohexadiene 4 (56.0 mg, 0.215 mmol) was dissolved in 0.4 mL of 0.6 M dimsylpotassium in Me_2SO-d_6. The ^{1}H NMR spectrum after 1 h at room temperature indicated the presence of anion 8 and the bicyclic product 6 in a 2.5:1 ratio, and traces of the unreacted substrate 4. After 15 min at 60 °C the ratio was 1:4. The reaction was complete after 45 min and no further change, including H/D exchange, was detected. The seal was broken and the reaction mixture was poured into 10 mL of dilute (3%) sulfuric acid. Extraction with pentane, washing with water, and concentration of the dried extract in vacuo afforded 57.5 mg of yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.23 (m, 10 H), 6.45 (d, 0.5 H), 2.15 (m, 1 H), 1.23, 1.11 (s, s, 6.6 H). MS (70 eV), 281 (10), 280 (45), 279 (52), 278 (35), 277 (30), 276 (100), 275 (19). (b) 1,4-Cyclohexadiene 5 (9.70 mg, 0.0373 mmol) was dissolved in 0.3 mL of Me_2SO-d_6. Dimsylpotassium (0.25 mL, 1.2 M in Me_2SO-d_6) was added and after 15 min at room temperature the ^{1}H NMR spectrum indicated anion 8 and traces of product 6. After 50 min at 60 °C the reaction was complete, yielding deuterated product 6. Extraction with pentane, washing with water, and concentration of the dried extract in vacuo afforded 10.0 mg of 6 as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.23 (m, 10 H), 6.45 (m, 0.25 H), 2.15 (m, 0.9 H), 1.23, 1.11 (s, s, 6.5 H). (c) Adduct 7 (36.0 mg, 0.107 mmol) was dissolved in 0.35 mL of 1.2 M dimsylpotassium in Me_2SO-d_6. After 45 min at room temperature anion 8 and traces of product 6 were observable. The reaction mixture was warmed to 60 °C and gradual disappearance of anion 8 and formation of product 6 was observed. After 45 min at 60 °C the reaction was complete. Extraction with pentane, washing with water, and concentration of the dried extract in vacuo work up afforded 25.2 mg (86%) of 6 as an yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.23 (m, 10 H), 6.45 (d, 1 H), 2.15 (m, 1.6 H), 1.29, 1.23, 1.11 (m, s, s, 7.8 H); MS, m/e at 277 (25), 276 (100), 275 (88), 274 (67), 273 (13).

6,6-Dimethyl-2,4-diphenylcyclohexadienyllithium in THF-d_8: NMR Studies. A 0.45–2.0-mL solution of 0.1–0.7 mmol of MeLi in THF-d_8 added to 6.5–65 mg (0.025–0.25 mmol) of 6,6-dimethyl-2,4-diphenyl-1.4-cyclohexadiene was sealed in vacuo in an NMR tube and examined by ^{1}H NMR. The gradual disappearance of substrate and a decrease in intensity of the MeLi absorption was observed. After 20 h at room temperature the reaction was complete, and the ^{1}H NMR spectrum of the deep-violet solution indicated the presence of anion **1b**, MeLi (1:1–2.5), and THF-d_7, as well as traces of methane and residual diethyl ether. The tubes were stored at −78 °C.

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